filtration of the (mostly) insoluble Pb(II) salts, evaporation of the solvent, and chromatography of the residue on a flash column. A mixture of petroleum ether–ethyl acetate in varying proportions was used as eluant, and only for the last few fractions, which contain **9a**, a 10% mixture of methanol in ethyl acetate was used.

The product was further purified by recrystallization from ethyl acetate–petroleum ether and was assigned as the *N*-acylimine **9a**: mp 119–20 °C; IR (Nujol) 1613, 1570, 1328, 1319, 1298, 1138, 902, 767, 752, 713 cm^{-1}; MS (70 eV) *m/z* 292 (M^+, 1), 173 (15), 119 (29), 77 (100); ^1H NMR ($CDCl_3$) δ 2.34 (s, 3 H, Me-4), 2.41 (s, 3 H, Me-5), 7.22–7.54 (m, 6 H, H-3′, H-4′, H-5′, H-3″, H-4″, H-5″), 7.57–7.80 (m, 2 H, H-2′, H-6′), 7.93–8.12 (m, 2 H, H-2″, H-6″). Anal. Calcd for $C_{17}H_{16}N_4O$: C, 69.84; H, 5.52; N, 19.17. Found: C, 70.00; H, 5.73; N, 18.84.

According to the general procedure described earlier all *N*-acylimines **9** were prepared. In some cases bisazoethylenes **2** in very small yields (<3%) were obtained in the early fractions. Yields reported in Table I are after isolation and recrystallization from ethyl acetate–petroleum ether.

9b: mp 100–1 °C; IR (Nujol) 1601, 1515, 1324, 1298, 1138, 1069, 903, 847, 829, 715 cm^{-1}; MS (70 eV) *m/z* 306 (M^+, 9), 187 (47), 91 (100); ^1H NMR ($CDCl_3$) δ 2.35 (s, 6 H, Me-4, Me-4′), 2.42 (s, 3 H, Me-5), 7.05–7.48 (m, 5 H, H-3′, H-5′, H-3″, H-4″, H-5″), 7.61 (d, *J* = 10.6 Hz, 2 H, H-2′, H-6′), 7.91–8.17 (m, 2 H, H-2″, H-6″). Anal. Calcd for $C_{18}H_{18}N_4O$: C, 70.56; H, 5.92; N, 18.29. Found: C, 70.64; H, 6.03; N, 18.38.

9c: mp 95–6 °C; IR (Nujol) 1608, 1570, 1518, 1324, 1299, 1266, 1031, 904, 846, 721 cm^{-1}; MS (70 eV) *m/z* 322 (M^+, 1), 203 (34), 119 (55), 64 (100); ^1H NMR ($CDCl_3$) δ 2.33 (s, 3 H, Me-4), 2.41 (s, 3 H, Me-5), 3.78 (s, 3 H, CH_3O), 6.91 (d, *J* = 8.7 Hz, 2 H, H-3′, H-5′), 7.37–7.45 (m, 3 H, H-3″, H-4″, H-5″), 7.58 (d, *J* = 8.7 Hz, 2 H, H-2′, H-6′), 7.91–8.13 (m, 2 H, H-2″, H-6″). Anal. Calcd for $C_{18}H_{18}N_4O_2$: C, 67.06; H, 5.63; N, 17.38. Found: C, 67.18; H, 5.78; N, 17.44.

9d: mp 129–31 °C; IR (Nujol) 1610, 1568, 1490, 1322, 1297, 1138, 1092, 850, 828, 715 cm^{-1}; MS (70 eV) *m/z* 328 and 326 (M^+, 1 and 3), 209 and 207 (27 and 75), 127 and 125 (34 and 100), 119 (95); ^1H NMR ($CDCl_3$) δ 2.30 (s, 3 H, Me-4), 2.35 (s, 3 H, Me-5), 7.20–7.47 (m, 3 H, H-3″, H-4″, H-5″), 7.36 (d, *J* = 8.8 Hz, 2 H, H-3′, H-5′), 7.68 (d, *J* = 8.8 Hz, 2 H, H-2′, H-6′), 7.90–8.17 (m, 2 H, H-2″, H-6″). Anal. Calcd for $C_{17}H_{15}N_4OCl$: C, 62.48; H, 4.63; N, 17.15. Found: C, 62.47; H, 4.82; N, 17.23.

9e: mp 133–4 °C; IR (Nujol) 1601, 1569, 1520, 1317, 1288, 1138, 962, 908, 860, 722 cm^{-1}; MS (70 eV) *m/z* 337 (M^+, 3), 218 (32), 119 (36), 105 (100); ^1H NMR ($CDCl_3$) δ 2.40 (s, 3 H, Me-4), 2.48 (s, 3 H, Me-5), 7.21–7.56 (m, 3 H, H-3″, H-4″, H-5″), 7.90–8.13 (m, 4 H, H-2′, H-6′, H-2″, H-6″), 8.34 (d, *J* = 8.6 Hz, 2 H, H-3′, H-5′). Anal. Calcd for $C_{17}H_{15}N_5O_3$: C, 60.53; H, 4.48; N, 20.76. Found: C, 60.51, H, 4.68; N, 20.87.

Irradiation of 22 in the Presence of 21b. A solution of 300 mg (2 mmol) of **22** and 50 mg (0.25 mmol) of **21b** in 2 mL of methylene chloride was irradiated in a quartz vessel, using a 250-W medium-pressure mercury arc at 20 °C. When the nitrogen evolution subsided (ca. 0.5 h) the resulting orange-brown solution was chromatographed. Apart from the unreacted **22** (111 mg), **23** (157 mg, 57%, based on the amount of consumed **22**) and **9d** (7 mg, 9%, based on the amount of starting **21b**) were obtained.

Thermolysis of 9a in DMSO. A solution of 292 mg (1 mmol) of **9a** in 2 mL of DMSO was refluxed for 35 min. From the mixture, after chromatography, 133 mg (77%) of **21a** and 83 mg (78%) of **23** were obtained.

Photolysis of 9a in DMSO. A stirred solution of 292 mg (1 mmol) of **9a** in 2 mL of DMSO was irradiated with an immersed 125-W medium-pressure mercury arc for 10 h. From the resulting brown solution the solvent was removed in vacuo and from the oily residue, after chromatography, 135 mg (78%) of **21a**, 34 mg (27%) of **27**, 54 mg (45%) of **26**, and 54 mg (28%) of **25** were obtained.

Acknowledgment. We are indebted to Dr. P. D. Akrivos for performing the MNDO calculations.

Registry No. **7a**, 31400-24-5; **7b**, 138815-25-5; **7c**, 138815-26-6; **7d**, 138815-27-7; **7e**, 138815-28-8; **9a**, 138815-29-9; **9b**, 138815-30-2; **9c**, 138815-31-3; **9d**, 138815-32-4; **9e**, 138815-33-5; **12**, 55590-53-9; **21a**, 58737-90-9; **21b**, 90799-28-3; **22**, 582-61-6; **23**, 102-07-8; **25**, 31280-33-8; **26**, 55-21-0; **27**, 1575-94-6; phenylhydrazine, 100-63-0; *p*-tolylhydrazine, 539-44-6; *p*-anisylhydrazine, 3471-32-7; (*p*-chlorophenyl)hydrazine, 1073-69-4; (*p*-nitrophenyl)hydrazine, 100-16-3; lead tetraacetate, 546-67-8; benzoylnitrene, 50401-20-2.

Supplementary Material Available: X-ray crystallographic data for **9a** and tables of atomic coordinates, atomic thermal parameters, bond lengths, and bond angles (5 pages). Ordering information is given on any current masthead page.

Acid-Induced Ring Opening of α-[Bis(methylthio)methylene]alkyl Cyclopropyl Ketones: A Novel Route to Substituted Cyclopentanones through Carbocationic Cyclizations

Balaram Patro, Biswajit Deb, Hiriyakkanavar Ila,* and Hiriyakkanavar Junjappa*

Department of Chemistry, North-Eastern Hill University, Shillong - 793 003, Meghalaya, India

Received August 15, 1990

α-[Bis(methylthio)methylene]alkyl 2-styrylcyclopropyl ketones **10a–d,f** and their higher enyl analogues **10e,g** undergo acid-induced ring opening and carbocationic cyclizations to afford substituted cyclopentanone derivatives. The structures of these products depend on the reaction conditions and the nature of the substituent in the aryl ring. The methodology has been extended to the synthesis of 11-oxosteroid precursors **22** and **25**.

Introduction

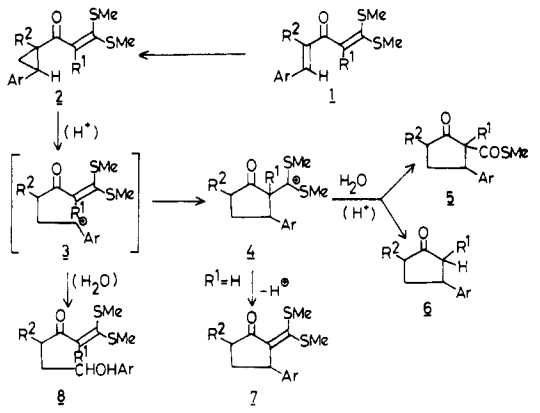
Cyclopentanone chemistry enjoys current interest due to its widespread occurrence in many natural products.[1] Their synthesis by classical reactions such as Dieckmann cyclization, Friedel–Crafts acylation, and aldol condensation etc. have limitations.[1a] Thus, the most common classical approach involving the cyclization of an enolate anion of γ-halo ketones or the corresponding β-keto esters leads to the corresponding alkylidenetetrahydrofurans instead of cyclopentanones owing to stereoelectronic factors.[1a] However, some ingenious efforts have been made to convert these alkylidenetetrahydrofurans to the desired cyclopentanones under the influence of Pd(0)-assisted rearrangements.[1a,2] Interestingly, no efforts seem to have

(1) Reviews: (a) Trost, B. M. *Chem. Soc. Rev.* **1982**, *11*, 141. (b) Ramaiah, M. *Synthesis* **1984**, 529.

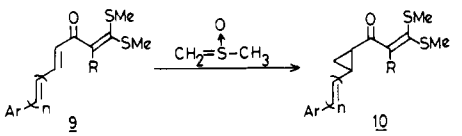
(2) (a) Trost, B. M.; Jungheim, L. N. *J. Am. Chem. Soc.* **1980**, *102*, 7910. (b) Trost, B. M.; Runge, T. A. *Ibid.* **1981**, *103*, 7550. (c) Trost, B. M.; Runge, T. A. *Ibid.* **1981**, *103*, 7559.

0022-3263/92/1957-2257$03.00/0

Scheme I

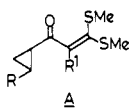


Scheme II



9, 10a, Ar = C_6H_5; R = H; n = 1
b, Ar = C_6H_5; R = Me; n = 1
c, Ar = 4-$MeOC_6H_4$; R = Me; n = 1
d, Ar = 3,4-$(MeO)_2C_6H_3$; R = H; n = 1
e, Ar = C_6H_5; R = H; n = 2
f, Ar = 4-$MeOC_6H_4$; R = H; n = 1
g, Ar = 4-$MeOC_6H_4$; R = H; n = 2

been made to examine the role of masked β-keto ester functionality in such cyclizations. The acid-mediated cyclizations of cyclopropyl ketone A having the α-oxoketene dithioacetal functionality as a masked β-keto ester[3] could provide a route to cyclopentanones. The acid-assisted ring



A

opening of cyclopropyl ketones has long been a subject of synthetic and mechanistic interest.[4,5] The carbocation generated in the presence of a suitable acid catalyst is often intercepted either by an external nucleophile or by intramolecular participation of a neighboring aryl or olefinic double bond.[6,7]

In our preliminary paper,[8a] we had described our successful results on these studies to afford the corresponding cyclopentanones in good yields (Scheme I). The key intermediate 4 formed via trapping of carbocation 3 by the mercapto double bond was proposed for the formation of thioester 5, ketone 6 (H_3PO_4/HCO_2H), and thioacetal 7 ($SnCl_4/C_6H_6$).[8b,9] The isolation of open-chain carbinol 8 (Ar = 4-$MeOC_6H_4$) could prove the intermediacy of carbocation 3 in support of a stepwise mechanism for the transformation.[8b] Thus, the ketene dithioacetal moiety in 2 not only serves as an efficient cationic cyclization terminator[10] but also retains the original α-oxoketene dithioacetal functionality in the product cyclopentanones. However, the cyclopentanone ring formation was successful

Scheme III

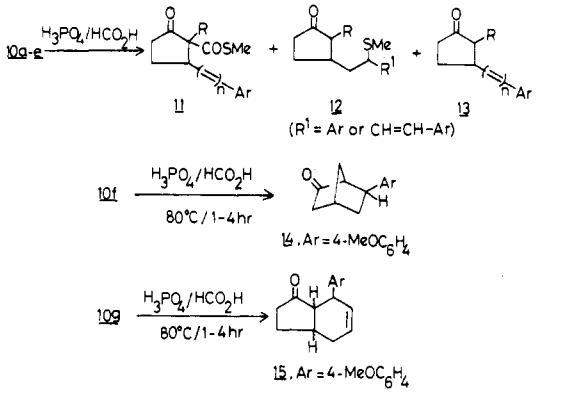


Table I. Cyclization of 10a–g in H_3PO_4/HCO_2H (Scheme III)

starting material	reactn condns		product(s) and yields (%)				
	temp (°C)	time (h)	11	12	13	14	15
10a	20	2	77				
	80	1		81			
	80	4			67		
10b	20	4	71				
	80	1	60				
	80	48			65		
10c	20	30		68			
	80	1		72			
	80	4[a]		48	30		
10d	20	15		63			
	80	1		78			
	80	4		80			
	80	48[a]					
10e	20	4	76				
	80	1		56			
	80	4		50	32		
	80	48			48		
10f	20	40[b]					
	80	1				60	
	80	4				56	
10g	80	1					62
	80	4					56

[a] Longer reaction time leads to tar. [b] No definite products could be obtained.

(3) Reviews: (a) Junjappa, H.; Ila, H.; Asokan, C. V. *Tetrahedron* **1990**, *46*, 5423. (b) Dieter, R. K. *Tetrahedron* **1986**, *42*, 3029. (c) Kolb, M. *Synthesis* **1990**, 171. (d) Yokoyama, M.; Togo, H.; Kondo, S. *Sulfur Rep.* **1990**, *10*, 23.

(4) Reviews: (a) Wong, H. N. C.; Hon, M.-Y.; Tse, C.-W.; Yip, Y.-C.; Tanko, J.; Hundlicky, T. *Chem. Rev.* **1989**, *89*, 165. (b) Wenkert, E. *Acc. Chem. Res.* **1980**, *13*, 27. (c) Meijere, A. de *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 809.

(5) (a) Murphy, W. S.; Wattanasin, S. J. *Chem. Soc., Perkin Trans. 1* **1982**, 1029 and references cited therein. (b) Corey, E. J.; Balanson, R. D. *Tetrahedron Lett.* **1973**, 3153. (c) Grieco, P. A.; Finkelhor, R. S. *Ibid.* **1974**, 527.

(6) (a) Stork, G.; Gregson, M. *J. Am. Chem. Soc.* **1969**, *91*, 2373. (b) Stork, G.; Marx, M. *Ibid.* **1969**, *91*, 2371. (c) Stork, G.; Grieco, P. A. *Ibid.* **1969**, *91*, 2407.

(7) (a) Murphy, W. S.; Wattanasin, S. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2920. (b) Murphy, W. S.; Wattanasin, S. *Ibid.* **1982**, 271. (c) Hantawong, K.; Murphy, W. S.; Russell, N.; Boyd, D. R. *Tetrahedron Lett.* **1984**, *25*, 999.

(8) (a) Deb, B.; Asokan, C. V.; Ila, H.; Junjappa, H. *Tetrahedron Lett.* **1988**, *29*, 2111. (b) Deb, B.; Ila, H.; Junjappa, H. *J. Chem. Res. Synop.* **1990**, 356; *J. Chem. Res., Miniprint* **1990**, 2728.

(9) The cation 4 does not appear to exist in equilibrium with α-oxoketene dithioacetal 7 in H_3PO_4/HCO_2H since 7 (Ar = 4-$MeOC_6H_4$) remained unchanged when stirred with H_3PO_4/HCO_2H at room temperature (8 h), while under heating intractable mixture of products were obtained.

(10) Unconjugated ketene dithioacetals have been used as terminators in cationic cyclizations for synthesis of five-membered pyrrolizidine, indolizidine, and quinolizidine alkaloids: (a) Chamberlin, A. R.; Nguyen, H. D.; Chung, J. Y. L. *J. Org. Chem.* **1984**, *49*, 1682. (b) Chamberlan, A. R.; Chung, J. Y. L. *Tetrahedron Lett.* **1982**, *23*, 2619. (c) Chamberlin, A. R.; Chung, J. Y. L. *J. Am. Chem. Soc.* **1983**, *105*, 3653. For use of ketene dithioacetal as initiator in cationic cyclizations, see: (a) Brinkmeyer, R. S. *Tetrahedron Lett.* **1979**, 207. (b) Mizyuk, V. L.; Semenovsky, A. V. *Ibid.* **1978**, 3603. (c) Andersen, N. H.; Yamamoto, Y.; Denniston, A. D. *Ibid.* **1975**, 4547. (d) Rigby, J. H.; Kotnis, A. S. *Ibid.* **1987**, *28*, 4943. (e) Rigby, J. H.; Kotnis, A.; Kramer, J. *Ibid.* **1983**, *24*, 2939. For a review, see also ref 3c.

only with cyclopropyl ketones carrying substituents capable of stabilizing the developing benzyl carbocation **3**. This limitation became a constraint on this methodology for side-chain elaboration at the 3-position of the product cyclopentanones. It was therefore considered of interest to explore further structural changes so that the overall transformation results in the formation of cyclopentanones. The cyclopropyl ketones **10** (Scheme II) were considered suitable precursors to meet these requirements. The resulting 3-styrylcyclopentanones could be of further interest since they can be utilized as potential synthons for 11-oxosteroids.[2b,c,11]

Results

Preparation of Cyclopropyl Ketones 10a–g (Scheme II). The required α-(5-aryl-2,4-pentadienoyl)- (**9a–d,f**) and α-(7-aryl-2,4,6-heptatrienoyl)ketene dithioacetals (**9e,g**) were prepared as reported earlier.[12] The regio- and chemoselective cyclopropanation of **9a–g** was achieved by treating them with dimethyloxosulfonium methylide in the presence of a phase-transfer catalyst[13] in 89–97% overall yields. The structures of **10a–g** were fully confirmed by their analytical and spectral data.

Cyclization of 10 in H_3PO_4 (80%)/HCO_2H (98%) (1:3) (Scheme III). The results are summarized in Table I.

From 10a. At room temperature, a product characterized as the thioester **11a** (77%) was isolated. The ring stereochemistry in **11a** was assigned as trans with respect to styryl and methylthiocarbonyl groups on the basis of chemical shift values for methine protons and their coupling constants. Thus, the H-1 methine proton in **11a** appears as a doublet at δ 3.25 with J = 12 Hz in accordance with the reported values[2b,c] in similar compounds. The downfield shift of the H-5 methine proton in **11a** (δ 3.31–3.67) due to the deshielding effect of the *cis*-methyl(thiocarbonyl) group is also in conformity with similar compounds reported earlier.[2b,c] At 80 °C (1 h), the isolated product was identified as the thiomethylated ketone **12a** (81%). The structure of **12a** was confirmed by its analytical and spectral data. At 80 °C (4 h), elimination of the methylmercapto group in **12a** occurred to afford the corresponding 3-styrylcyclopentanone **13a** (67%).

From 10b. At room temperature, **10b** gave **11b** (71%). From ^{1}H NMR data, **11b** was shown to have the same stereochemistry as **11a**. Demethylthiocarbonylation of **11b** was found to be slow and required prolonged heating (48 h) to afford **13b** (65%).

From 10c. At room temperature, **10c** required 30 h for ring closure to give **12c** (68%) (formation of **11c** could not be detected in the reaction mixture). At 80 °C (1 h), **12c** was obtained in improved yield (72%). On continued heating (4 h) at the same temperature, a mixture of **12c** and **13c** was obtained; any further heating did not improve the yield of **13c**, but tars were formed.

From 10d. Under similar reaction conditions, **10d** gave only **12d** at various temperatures and times. On prolonged heating (48 h), only tars were obtained.

From 10e. At room temperature, **11e** was obtained (76%). It was a mixture of cis and trans (1:4) ring-substituted isomers as observed by its ^{1}H NMR spectrum. At 80 °C (1 h), **12e** was isolated (56%); after 4 h, a mixture of **12e** (50%) and **13e** (32%) was obtained; and after 48 h, **13e** could be isolated in 48% yield.

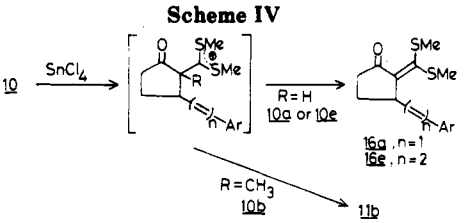
From 10f. At room temperature **10f** did not yield any of the desired products. At 80 °C (1–4 h), the isolated product was characterized as 6-*exo*-(4-methoxyphenyl)-2-oxobicyclo[2.2.1]heptane (**14**) (60%). The exo stereochemistry in **14** was assigned on the basis of the observed A_2B_2 pattern of aromatic protons and the triplet at δ 2.98 for the benzylic protons in its ^{1}H NMR spectrum, which is in accordance with the earlier observations reported[14] for exo-substituted norbornane compounds.

From 10g. At room temperature, **10g** afforded a complex product mixture. At 80 °C (1–4 h), a product characterized as bicyclic ketone **15** (62%) was isolated.[15] The compound was analyzed for $C_{16}H_{18}O_2$, and its mass spectrum exhibited a molecular ion peak at m/z 242 (100%) along with prominent peaks at m/z 82 (50%), 134 (46%), and 160 (36%). The characteristic carbonyl frequency at 1743 cm^{-1} was observed in its IR spectrum, while its ^{1}H and ^{13}C NMR data were in conformity with the assigned structure (Experimental Section).

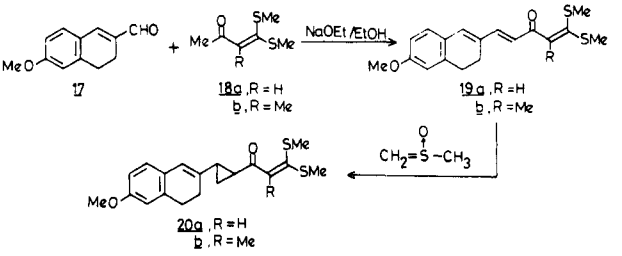
It is interesting to note that from all the ketones **10** where R = H, no compounds analogous to **7** could be isolated under these reaction conditions (H_3PO_4/HCO_2H) containing H_2O in the acid/solvent system.

Cyclization of 10 in the Presence of $SnCl_4$ in C_6H_6 or CH_2Cl_2 (Scheme IV). It is well-known that the re-

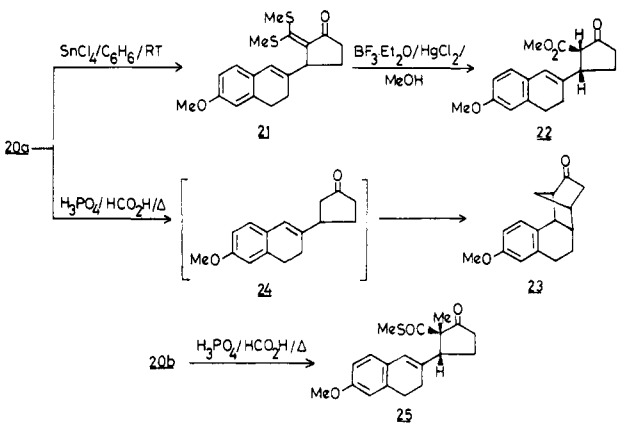
Scheme IV



Scheme V



Scheme VI



(11) Posner, G. H.; Chapdelaine, M. J.; Lentz, C. M. *J. Org. Chem.* **1979**, *44*, 3661.
(12) (a) Thuillier, A.; Vialle, J. *Bull. Soc. Chim. Fr.* **1962**, 2182. (b) Asokan, C. V.; Ila, H.; Junjappa, H. *Synthesis* **1985**, 163.
(13) Merz, A.; Mark, G. *Angew Chem., Int. Ed. Engl.* **1973**, *12*, 845.
(14) Flautt, T. J.; Erman, W. F. *J. Am. Chem. Soc.* **1963**, *85*, 3212.
(15) The ^{1}H NMR spectrum of initially isolated product showed it to be a mixture of more than one isomeric olefinic compound from which **15** could be obtained as the pure major product.

actions initiated by Lewis acid catalysis need precise and specific conditions (nature of the acid, temperature, reaction time, and solvent). In this paper, we describe only three procedures which allow preparation of specific compounds. Thus, cyclopropyl ketones **10a** and **10e** afforded the products **16a** (74%) and **16e** (71%), respectively, on treatment with $SnCl_4$ in C_6H_6 or CH_2Cl_2 at room temperature. On the other hand, **10b** (R = CH_3) in the absence of an α-proton gave the thioester **11b** (69%) under identical conditions.

Synthesis of 11-Oxosteroid Precursors. As an application of these new cyclizations, the synthesis of 11-oxosteroid precursors was investigated[2b,c,11] (Schemes V and VI).

Preparation of Starting Cyclopropyl Ketones 20a and 20b. The starting cyclopropyl ketones **20a,b** were synthesized as shown in Scheme V. The ene aldehyde **17** was condensed with α-acetyl ketene dithioacetals **18a** and **18b** to afford the corresponding dienoylketene dithioacetals **19a** and **19b**, respectively, in high yields. Subsequent cyclopropanation as described earlier gave the desired cyclopropyl ketones **20a** and **20b** in 93% and 81% yields, respectively.

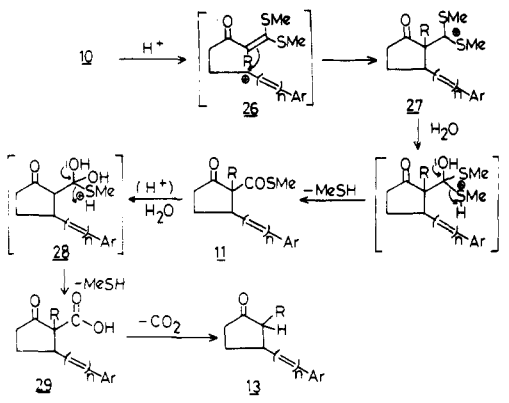
Cyclization of 20a (Scheme VI). β-Keto ester **22** could be obtained in 78% overall yield by treating **20a** initially with $SnCl_4$ in benzene at room temperature. The resulting α-oxoketene dithioacetal **21** on subsequent methanolysis (BF_3·Et_2O/$HgCl_2$/MeOH) gave the expected cyclopentanone **22** which was found to be a single trans-substituted isomer. The assignment of ring stereochemistry was based on its ^1H NMR spectral data which were in accordance with the corresponding 6-bromo analogue reported by Trost and co-workers.[2b,c] However, the cyclopropyl ketone **20a** when cyclized in H_3PO_4/HCO_2H yielded a product characterized as bicyclic ketone **23** (cyclopentanone **24**, the precursor of **23** was not detected). The mass spectrum of **23** exhibited a molecular ion peak at m/z 242, while its IR spectrum showed a characteristic cyclopentanone carbonyl peak at 1750 cm^{-1}. The structure of **23** was further supported by its ^1H NMR spectrum which showed absence of any olefinic proton while the benzylic methine proton appeared as a broad doublet (J = 6.5 Hz) at δ 2.85 partially merged with methylene protons.

Cyclization of 20b (Scheme VI). Ketone **20b** in H_3PO_4/HCO_2H afforded the expected thioester **25** (83%) which was found to be a single stereoisomer. The ^1H NMR spectrum of **25** exhibited sharp singlets for methyl, methylthio, methoxy, and olefinic protons at δ 1.20, 2.32, 3.77, and 6.22, respectively. The trans stereochemistry of the cyclopentanone ring was confirmed from the low-field chemical shift for the H-5 methine proton which appeared at δ 3.65 as a broad triplet merged with the methoxy signal. Its low-field shift is primarily due to the deshielding effect of the *cis*-methylthiocarbonyl group and is in conformity with the reported values for similar compounds.[2b,c]

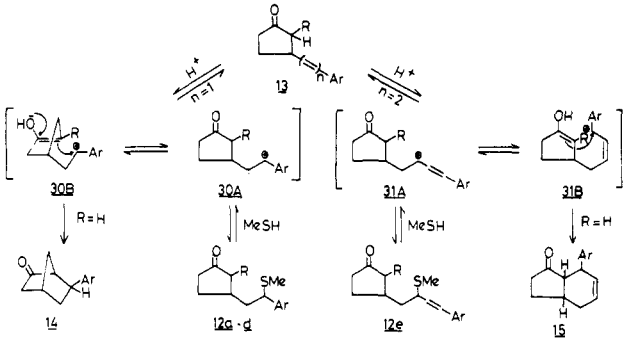
Discussion

The formation of compounds **11**, **13**, and **16** from the cyclopropyl ketones **10** can be rationalized by the mechanism shown in Scheme VII analogous to Scheme I. However, the presence of an ethylenic double bond in **13** leads to the formation of secondary products **12**, **14**, and **15** (Scheme VIII). Thus, the ketone **10** undergoes initial ring opening to form acyclic carbocation **26** followed by ring closure to afford cyclic bis(methylthio)methyl cation **27**. Subsequent hydrolytic cleavage of cation **27** affords the corresponding thioester **11** which on dethiocarbonylation at higher temperatures yields the corresponding 3-styrylcyclopentanone **13**. The conversion of

Scheme VII



Scheme VIII



11 to **13** probably proceeds through β-keto acids **29**, which, however, could not be isolated even under mild conditions. In the presence of stannic chloride in CH_2Cl_2, cation **27** (R = H) can undergo deprotonation to afford the corresponding α-oxoketene dithioacetals **16** (Scheme IV). Rapid protonation of the styryl double bond in **13** leads to stable benzylic (or phenylallylic) carbocations **30** or **31** which are trapped by MeSH to afford thiomethylated ketones **12** (Scheme VIII). In most of the cases, **12** underwent dethiomethylation on prolonged heating to afford the desired cyclopentanone **13**. On the other hand, the more stable carbocations **30** and **31** (Ar = 4-$MeOC_6H_4$) underwent intramolecular trapping by an enolic double bond to afford bicyclic ketones **14** and **15**, respectively[5b,c,6c,16] (Scheme VIII).

The formation of products **22**, **23**, and **25** from ketones **20a,b** (Scheme VI) can also be rationalized by a similar mechanism.

In summary, we have shown that conjugation of either one or two double bonds with the phenyl group in cyclopropyl ketones **10** facilitates the formation of the cyclopentanone ring under acid-induced cyclization. Cyclopropyl ketones **10a,b,e** having an unsubstituted phenyl group afforded the corresponding thioesters (**11a,b,e**) or 3-styrylcyclopentanones derivatives (**13a,b,e**) in moderate to good yields along with thiomethylated ketones (**12a,e**). However, under varying reaction conditions, methoxy-substituted ketone **10c** yielded **13c** in poor yield along with **12c** as a major product, while the corresponding dimethoxy ketone **10d** did not yield either **11d** or **13d**, and only **12d** was formed in all the conditions studied. Similarly, the 4-methoxyphenyl-substituted ketones **10f** and **10g** resulted in the corresponding bicyclic ketones **14** and **15** exclusively. The methodology was successfully extended to the synthesis of 11-oxostereoid precursors **22** and **25**.

(16) Murphy, W. S.; Culhane, A.; Juo, R.-R. *J. Chem. Soc., Perkin Trans. 1* **1989**, 2123 and references cited therein.

Experimental Section

Melting points were determined on a capillary apparatus and are uncorrected. ^1H NMR spectra (δ) were recorded at 90 MHz. J values are given in Hz. The α-oxoketene dithioacetals **9a–g** were prepared according to known procedures,[12] while trimethylsulfoxonium iodide was prepared by Corey's method.[17]

Synthesis of Cyclopropyl Ketones 10a–g and 20a,b. General Procedure. A suspension of the appropriate α-oxoketene dithioacetal (10 mmol), trimethylsulfoxonium iodide (13 mmol), tetrabutylammonium iodide (15 mmol) in aqueous NaOH (50%, 70 mL) and CH_2Cl_2 (70 mL) was magnetically stirred at 50 °C for 7 h. The organic layer was separated, concentrated, and diluted with EtOAc to precipitate tetrabutylammonium iodide which was filtered off. The filtrate was evaporated to give crude cyclopropyl ketones which were purified by column chromatography over silica gel using EtOAc/hexane (1:20) as eluent.

1-[[Bis(methylthio)methylene]acetyl]-2-styrylcyclopropane (10a): colorless crystals ($CHCl_3$); yield 2.81 g (97%); mp 116–117 °C; IR (KBr) 1640, 1495 cm^{-1}; ^1H NMR ($CDCl_3$) 0.85–1.20 (m, 1 H, CH_2), 1.46–1.71 (m, 1 H, CH_2), 1.85–2.33 (m, 2 H, COCH and ArCH=CHCH), 2.42 (s, 6 H, SCH_3), 5.75 (dd, J = 16, 8, 1 H, =CH), 6.54 (s, 1 H, =CH), 6.49 (d, J = 16, 1 H, =CH), 7.0–7.41 (m, 5 H, ArH); MS m/z 290 (M$^+$, 8), 275 (36). Anal. Calcd for $C_{16}H_{18}OS_2$: C, 66.17; H, 6.25. Found: C, 66.29; H, 6.38.

1-[2-[Bis(methylthio)methylene]propanoyl]-2-styrylcyclopropane (10b): colorless oil; yield 2.83 g (93%); IR (neat) 1665, 1428 cm^{-1}; ^1H NMR (CCl_4) 0.98–1.31 (m, 1 H, CH_2), 1.38–1.71 (m, 1 H, CH_2), 1.93–2.33 (m, 2 H, COCH and ArCH=CHCH), 2.07 (s, 3 H, CH_3), 2.19 (s, 3 H, SCH_3), 2.25 (s, 3 H, SCH_3), 5.74 (dd, J = 16.8, 1 H, =CH), 6.47 (d, J = 16, 1 H, =CH), 6.98–7.34 (m, 5 H, ArH); MS m/z 304 (M$^+$, 3), 288 (85). Anal. Calcd for $C_{17}H_{20}OS_2$: C, 67.06; H, 6.62. Found: C, 67.19; H, 6.79.

1-[2-[Bis(methylthio)methylene]propanoyl]-2-(4-methoxystyryl)cyclopropane (10c): colorless oil; yield 2.88 g (86%); IR (neat) 1690 cm^{-1}; ^1H NMR (CCl_4) 0.93–1.20 (m, 1 H, CH_2), 1.35–1.70 (m, 1 H, CH_2), 1.90–2.30 (m, 2 H, COCH and ArCH=CHCH), 2.04 (s, 3 H, CH_3), 2.16 (s, 3 H, SCH_3), 2.25 (s, 3 H, SCH_3), 3.66 (s, 3 H, OCH_3), 5.66 (dd, J = 16, 8, 1 H, =CH), 6.48 (d, J = 16, 1 H, =CH), 6.70 (d, J = 9, 2 H, ArH), 7.10 (d, J = 9, 2 H, ArH). Anal. Calcd for $C_{18}H_{22}O_2S_2$: C, 64.63; H, 6.63. Found: C, 64.81; H, 6.78.

1-[[Bis(methylthio)methylene]acetyl]-2-(3,4-dimethoxystyryl)cyclopropane (10d): colorless crystals ($CHCl_3$); yield 2.91 g (83%); mp 116–117 °C; IR (KBr) 1632, 1490 cm^{-1}; ^1H NMR ($CDCl_3$) 0.79–1.38 (m, 1 H, CH_2), 1.48–1.80 (m, 1 H, CH_2), 1.87–2.36 (m, 2 H, COCH and ArCH=CHCH), 2.46 (brs, 6 H, SCH_3), 3.88 (brs, 6 H, OCH_3), 5.68 (dd, J = 16, 8, 1 H, =CH), 6.21 (s, 1 H, =CH), 6.46 (d, J = 16, 1 H, =CH), 6.67–6.94 (m, 3 H, ArH); MS m/z 350 (M$^+$, 11), 335 (38), 303 (25). Anal. Calcd for $C_{18}H_{22}O_3S_2$: C, 61.68; H, 6.33. Found: C, 61.82; H, 6.21.

1-[[Bis(methylthio)methylene]acetyl]-2-(4-phenyl-1,3-butadienyl)cyclopropane (10e): colorless crystals ($CHCl_3$); yield 2.56 g (81%); mp 123–124 °C; IR (KBr) 1633, 1490 cm^{-1}; ^1H NMR ($CDCl_3$) 0.85–1.10 (m, 1 H, CH_2), 1.45–1.70 (m, 1 H, CH_2), 1.78–2.23 (m, 2 H, COCH and Ar(CH=CH)$_2$CH), 2.44 (s, 6 H, SCH_3), 5.37 (dd, J = 16, 9, 1 H, =CH), 6.14 (s, 1 H, =CH), 6.27–6.84 (m, 2 H, =CH), 7.10–7.40 (m, 6 H, ArH and =CH); MS m/z 316 (M$^+$, 10), 301 (26). Anal. Calcd for $C_{18}H_{20}OS_2$: C, 68.31; H, 6.37. Found: C, 68.46; H, 6.53.

1-[[Bis(methylthio)methylene]acetyl]-2-(4-methoxystyryl)cyclopropane (10f): colorless crystals ($CHCl_3$); yield 2.78 g (87%); mp 108–109 °C; IR (KBr) 1625, 1495 cm^{-1}; ^1H NMR ($CDCl_3$) 0.94–1.18 (m, 1 H, CH_2), 1.47–1.73 (m, 1 H, CH_2), 1.83–2.30 (m, 2 H, COCH and ArCH=CHCH), 2.46 (s, 6 H, SCH_3), 3.77 (s, 3 H, OCH_3), 5.64 (dd, J = 16, 8, 1 H, =CH), 6.18 (s, 1 H, =CH), 6.47 (d, J = 16, 1 H, =CH), 6.80 (d, J = 9, 2 H, ArH), 7.22 (d, J = 9, 2 H, ArH); MS m/z 320 (M$^+$, 12), 305 (24). Anal. Calcd for $C_{17}H_{20}O_2S_2$: C, 63.71; H, 6.29. Found: C, 63.86; H, 6.42.

1-[[Bis(methylthio)methylene]acetyl]-2-[4-(4-methoxyphenyl)-1,3-butadienyl]cyclopropane (10g): colorless crystals ($CHCl_3$); yield 2.88 g (83%); mp 103–104 °C; IR (KBr) 1615, 1470 cm^{-1}; ^1H NMR ($CDCl_3$) 0.74–1.16 (m, 1 H, CH_2), 1.38–1.72 (m, 1 H, CH_2), 1.81–2.20 (m, 2 H, COCH and Ar(CH=CH)$_2$CH), 2.42 (s, 6 H, SCH_3), 3.76 (s, 3 H, OCH_3), 5.38 (dd, J = 16, 9, 1 H, =CH), 6.18 (s, 1 H, =CH), 6.27–6.63 (m, 3 H, =CH), 6.83 (d, J = 9, 2 H, ArH), 7.31 (d, J = 9, 2 H, ArH); MS m/z 346 (M$^+$, 3), 331 (9). Anal. Calcd for $C_{19}H_{22}O_2S_2$: C, 65.86; H, 6.40. Found: C, 65.98; H, 6.56.

1-[[Bis(methylthio)methylene]acetyl]-2-(3,4-dihydro-6-methoxynaphth-2-yl)cyclopropane (20a): colorless crystals ($CHCl_3$); yield 3.22 g (93%); mp 94–95 °C; IR (KBr) 1660, 1620 cm^{-1}; ^1H NMR ($CDCl_3$) 0.77–1.24 (m, 1 H, cyclopropyl CH_2), 1.29–1.53 (m, 1 H, cyclopropyl CH_2), 1.74–2.50 (m, 4 H, cyclopropyl CH and ring CH_2), 2.38 (s, 3 H, SCH_3), 2.43 (s, 3 H, SCH_3), 2.70 (t, J = 6, 2 H, ring CH_2), 3.70 (s, 3 H, OCH_3), 6.06 (s, 1 H, =CH), 6.15 (s, 1 H, =CH), 6.36–6.63 (m, 2 H, ArH), 6.79 (d, J = 9, 1 H, ArH); MS m/z 346 (M$^+$, 21), 331 (30), 299 (21). Anal. Calcd for $C_{19}H_{22}O_2S_2$: C, 65.86; H, 6.40. Found: C, 65.98; H, 6.55.

1-[2-[Bis(methylthio)methylene]propanoyl]-2-(3,4-dihydro-6-methoxynaphth-2-yl)cyclopropane (20b): colorless crystals ($CHCl_3$); yield 2.92 g (81%); mp 67–68 °C; IR (KBr) 1665 cm^{-1}; ^1H NMR (CCl_4) 1.09–1.36 (m, 1 H, cyclopropyl CH_2), 1.38–1.67 (m, 1 H, cyclopropyl CH_2), 1.96–2.37 (m, 4 H, cyclopropyl CH and ring CH_2), 2.08 (s, 3 H, CH_3), 2.20 (s, 3 H, SCH_3), 2.29 (s, 3 H, SCH_3), 2.71 (m, 2 H, ring CH_2), 3.70 (s, 3 H, OCH_3), 6.16 (s, 1 H, =CH), 6.40–6.67 (m, 2 H, ArH), 6.85 (d, J = 9, 1 H, ArH); MS m/z 360 (M$^+$, 11), 345 (41), 313 (15). Anal. Calcd for $C_{20}H_{24}O_2S_2$: C, 66.63; H, 6.71. Found: C, 66.52; H, 6.48.

Cyclization of Cyclopropyl Ketones (10a–g) in the Presence of Phosphoric Acid/Formic Acid (H_3PO_4/HCO_2H). General Procedure. A solution of **10** (10 mmol) in HCO_2H (98%, 30 mL) and H_3PO_4 (85%, 10 mL) was either stirred at rt or heated at 80 °C for the time given in Table I (monitored by TLC). The reaction mixture was poured over saturated $NaHCO_3$ solution (300 mL) and extracted with $CHCl_3$ (2 × 200 mL). The organic layer was washed with water (2 × 200 mL), dried (Na_2SO_4), and evaporated to give viscous residues which were subjected to column chromatography using EtOAc/hexane (1:20) as eluent to afford pure products.

Cyclization of 10a afforded products **11a** (20 °C, 2 h, 2.01 g, 77%), **12a** (80 °C, 1 h, 1.89 g, 81%), and **13a** (80 °C, 4 h, 1.24 g, 67%), respectively (Table I).

***S*-Methyl *trans*-5-styryl-2-oxocyclopentane-*r*-1-thiocarboxylate (11a)**: colorless crystals ($CHCl_3$); mp 110–111 °C; R_f 0.56 in C_6H_6/EtOAc (20:1); IR (KBr) 1750, 1678, 1630 cm^{-1}; ^1H NMR ($CDCl_3$) 1.64–2.58 (m, 4 H, CH_2), 2.33 (s, 3 H, SCH_3), 3.25 (d, J = 12, 1 H, H-1), 3.31–3.67 (m, 1 H, H-5), 6.12 (dd, J = 16, 7, 1 H, =CH), 6.52 (d, J = 16, 1 H, =CH), 7.18–7.49 (m, 5 H, ArH); MS m/z 260 (M$^+$, 7), 213 (20), 185 (67). Anal. Calcd for $C_{15}H_{16}O_2S$: C, 69.20; H, 6.20. Found: C, 69.34; H, 6.32.

3-[2-(Methylthio)-2-phenylethyl]cyclopentanone (12a): pale yellow viscous oil; R_f 0.40 in C_6H_6; IR (neat) 1740 cm^{-1}; ^1H NMR (CCl_4) 1.17–2.58 (m, 9 H, CH and CH_2), 1.76 (s, 3 H, SCH_3), 3.62 (brt, J = 7, 1 H, ArCH), 7.03–7.39 (m, 5 H, ArH); MS m/z 234 (M$^+$, 33), 187 (85). Anal. Calcd for $C_{14}H_{18}OS$: C, 71.75; H, 7.74. Found: C, 71.93; 7.86.

3-Styrylcyclopentanone (13a): colorless viscous oil; R_f 0.62 in C_6H_6/EtOAc (20:1); IR (neat) 1743 cm^{-1}; ^1H NMR (CCl_4) 1.17–3.07 (m, 6 H, CH_2), 2.68–3.15 (m, 1 H, H-3), 6.14 (dd, J = 16, 7, 1 H, =CH), 6.41 (d, J = 16, 1 H, =CH), 7.02–7.40 (m, 5 H, ArH); MS m/z 186 (M$^+$, 68), 129 (71). Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 84.08; 7.76.

Cyclization of 10b yielded products **11b** (20 °C, 4 h, 1.95 g, 71%; 80 °C, 1 h, 1.64 g, 60%) and **13b** (80 °C, 48 h, 1.3 g, 65%) (Table I).

***S*-Methyl *trans*-1-methyl-5-styryl-2-oxocyclopentane-*r*-1-thiocarboxylate (11b)**: pale yellow oil; R_f 0.60 in C_6H_6/EtOAc (20:1); IR (neat) 1740, 1660 cm^{-1}; ^1H NMR (CCl_4) 1.40 (s, 3 H, CH_3), 1.51–2.52 (brm, 4 H, CH_2), 2.32 (s, 3 H, SCH_3), 3.39–3.85 (m, 1 H, CH), 6.03 (dd, J = 16, 8, 1 H, =CH), 6.46 (d, J = 16, 1 H, =CH), 7.03–7.52 (m, 5 H, ArH); MS m/z 274 (M$^+$, 3), 227 (16), 192 (74). Anal. Calcd for $C_{16}H_{18}O_2S$: C, 70.04; H, 6.61. Found: C, 70.28; H, 6.46.

2-Methyl-3-styrylcyclopentanone (13b): pale yellow viscous oil; R_f 0.63 in C_6H_6/EtOAc (20:1); IR (neat) 1742 cm^{-1}; ^1H NMR (CCl_4) 1.05 (d, J = 7, 3 H, CH_3), 1.36–2.70 (m, 5 H, CH, CH_2), 2.71–3.25 (m, 1 H, H-3), 6.21 (dd, J = 18, 6.5, 1 H, =CH), 6.63 (d, J = 18, 1 H, =CH), 7.48 (brs, 5 H, ArH); MS m/z 200 (50).

(17) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 3782.

Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 84.23; H, 8.30.

Cyclization of 10c yielded product **12c** (20 °C, 30 h, 1.89 g, 68%; 80 °C, 1 h, 2.01 g, 72%) or a mixture of **12c** (1.11 g, 48%) and **13c** (80 °C, 4 h, 0.69 g, 30%).

2-Methyl-3-[2-(methylthio)-2-(4-methoxyphenyl)ethyl]-cyclopentanone (12c): yellow viscous oil; R_f 0.56 in C_6H_6/EtOAc (20:1); IR (neat) 1748 cm^{-1}; ^1H NMR (CCl_4) 0.93 (d, J = 7, 3 H, CH_3), 1.87 (s, 3 H, SCH_3), 1.15–2.48 (m, 8 H, CH, CH_2), 3.65 (t, J = 7, 1 H, CHSMe), 3.80 (s, 3 H, OCH_3), 6.81 (d, J = 9, 2 H, ArH), 7.21 (d, J = 9, 2 H, ArH). Anal. Calcd for $C_{16}H_{22}O_2S$: C, 69.02; H, 7.97. Found: C, 69.23; H, 8.30.

2-Methyl-3-(4-methoxystyryl)cyclopentanone (13c): pale viscous oil; R_f 0.60 in C_6H_6/EtOAc (20:1); IR (neat) 1750 cm^{-1}; ^1H NMR (CCl_4) 0.9 (d, J = 7, 3 H, CH_3), 1.40–2.59 (m, 5 H, CH, CH_2), 2.60–3.31 (brm, 1 H, CH), 3.70 (s, 3 H, OCH_3), 5.61 (dd, J = 18, 7, 1 H, =CH), 6.32 (d, J = 18, 1 H, =CH), 6.68 (d, J = 9, 2 H, ArH), 7.20 (d, J = 9, 2 H, ArH). Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.51; H, 8.06.

Cyclization of 10d yielded only **12d** under various conditions (20 °C, 15 h, 1.85 g, 63%; 80 °C, 1 h, 2.3 g, 78%; 80 °C, 4 h, 2.35 g, 80%).

3-[2-(Methylthio)-2-(3,4-dimethoxyphenyl)ethyl]cyclopentanone (12d): pale yellow viscous oil; R_f 0.40 in C_6H_6/EtOAc (20:1); IR (neat) 1743 cm^{-1}; ^1H NMR (CCl_4) 1.19–2.37 (m, 9 H, CH and CH_2), 1.78 (s, 3 H, SCH_3), 3.60 (brt, J = 7, 1 H, ArCH), 3.76 (s, 3 H, OCH_3), 3.80 (s, 3 H, OCH_3), 6.60–6.89 (m, 3 H, ArH); MS m/z 294 (M^+, 17), 247 (74), 151 (100). Anal. Calcd for $C_{16}H_{22}O_3S$: C, 65.27; H, 7.53. Found: C, 65.46; H, 7.65.

Cyclization of 10e yielded products **11e** (20 °C, 4 h, 2.18 g, 76%), **12e** (80 °C, 1 h, 1.45 g, 56%), **13e** (80 °C, 48 h, 1.01 g, 48%), or a mixture of **12e** (1.30 g, 50%) and **13e** (0.68 g, 32%) (80 °C, 4 h).

***S*-Methyl 5-(4-phenyl-1,3-butadienyl)-2-oxocyclopentane-*r*-1-thiocarboxylate (11e)**: (cis/trans (1:4)) pale yellow viscous semisolid; R_f 0.50 in C_6H_6/EtOAc (20:1); IR (KBr) 1750, 1675 cm^{-1}; ^1H NMR ($CDCl_3$) 1.14–2.51 (m, 4 H, CH_2), 2.28 (s, 0.6 H, SCH_3), 2.33 (s, 2.4 H, SCH_3), 2.60–2.89 (m, 0.4 H, H_a, H_b of Z isomer), 3.14 (d, J = 12, 0.8 H, H-1), 3.13–3.65 (m, 0.8 H, H_b), 5.69 (dd, J = 16, 7, 1 H, =CH), 6.00–6.83 (m, 3 H, =CH), 7.03–7.44 (m, 5 H, ArH); MS m/z 286 (M^+, 40), 239 (20), 211 (100). Anal. Calcd for $C_{17}H_{18}O_2S$: C, 71.30; H, 6.33. Found: C, 71.52; H, 6.47.

3-[2-(Methylthio)-4-phenylbut-3-enyl]cyclopentanone (12e): pale yellow viscous liquid; R_f 0.62 in C_6H_6/EtOAc (20:1); IR (neat) 1750 cm^{-1}; ^1H NMR (CCl_4) 0.85–2.57 (m, 9 H, CH, CH_2), 1.87 (s, 3 H, SCH_3), 3.22 (brq, J = 7, 1 H, CHSMe), 5.92 (dd, J = 18, 7, 1 H, =CH), 6.38 (d, J = 18, 1 H, =CH), 6.97–7.52 (brm, 5 H, ArH); MS m/z 260 (M^+, 16), 213 (36), 117 (100). Anal. Calcd for $C_{16}H_{20}OS$: C, 73.80; H, 7.74. Found: C, 73.55; H, 8.01.

3-(4-Phenyl-1,3-butadienyl)cyclopentanone (13e): pale yellow viscous oil; R_f 0.62 in C_6H_6/EtOAc (20:1); IR (neat) 1745 cm^{-1}; ^1H NMR (CCl_4) 1.45–3.33 (m, 7 H, CH, CH_2), 5.71–6.72 (m, 4 H, =CH), 7.25 (brs, 5 H, ArH). Anal. Calcd for $C_{15}H_{16}O$: C, 84.86; H, 7.60. Found: C, 84.63; H, 7.41.

Cyclization of 10f gave only **14** (80 °C, 1 h, 1.29 g, 60%; 80 °C, 4 h, 1.2 g, 56%) (Table I).

***6-exo*-(4-Methoxyphenyl)bicyclo[2.2.1]heptan-2-one (14)**: colorless viscous oil; R_f 0.50 in C_6H_6/EtOAc (20:1); IR (KBr) 1748 cm^{-1}; ^1H NMR (CCl_4) 1.48–2.27 (m, 5 H, CH_2 and H-4), 2.02–2.56 (m, 2 H, CH_2), 2.72 (brs, 1 H, CH-1), 2.98 (t, J = 8, 1 H, ArCH), 3.70 (s, 3 H, OCH_3), 6.69 (d, J = 9, 2 H, ArH), 7.05 (d, J = 9, 2 H, ArH); MS m/z 216 (M^+, 96). Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.74; H, 7.46. Found: C, 77.91; H, 7.63.

Cyclization of 10g gave only **15** (80 °C, 1 h, 1.50 g, 62%; 80 °C, 4 h, 1.35 g, 56%).

7-(4-Methoxyphenyl)-3a,4,7,7a-tetrahydroindan-1-one (15): colorless viscous oil; R_f 0.55 in C_6H_6/EtOAc (20:1); ^1H NMR (250 MHz) ($CDCl_3$) 1.68–2.05 (m, 3 H, CH_2), 2.06–2.38 (m, 4 H, CH, CH_2), 2.56 (brq, 1 H, CH), 3.80 (s, 3 H, OCH_3), 3.82 (m, merged with OCH_3, ArCH), 5.67 (brd, J = 11, 1 H, =CH), 5.81 (ddd, J = 11, 4, 2, 1 H, =CH), 6.83 (d, J = 9, 2 H, ArH), 7.15 (d, J = 9, 2 H, ArH); ^{13}C NMR ($CDCl_3$) δ 25.5, 26.1, 33.4 (CH_2), 29.6, 37.1 (CH), 55.1 (ArCH), 56.4 (OCH_3), 113.8, 128.6 (ArCH), 125.5, 128.1 (=CH), 137.7 (C-1′, aryl), 158.0 (C-4′, aryl), 217.1 (C=O). Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.54; H, 7.56.

Stannic Chloride Induced Cyclization of Cyclopropyl Ketones 10a,b,e. General Procedure. A solution of cyclopropyl ketone (10 mmol) in dry benzene (100 mL) was treated with $SnCl_4$ (1.5 equiv), and the reaction mixture was stirred at rt for 2 h. It was then poured into cold aqueous sodium hydroxide (5%) and extracted with CH_2Cl_2 (3 × 60 mL), and the organic layer was washed with water, dried (Na_2SO_4), and evaporated to afford crude products, which were purified by column chromatography over silica gel using EtOAc/hexane (1:20) as eluent.

Cyclization of 10a. 2-[Bis(methylthio)methylene]-3-styrylcyclopentanone (16a): yellow viscous oil; yield 2.15 g (74%); R_f 0.45 in C_6H_6; IR (neat) 1693 cm^{-1}; ^1H NMR (CCl_4) 1.72–2.63 (m, 4 H, CH_2), 2.38 (s, 3 H, SCH_3), 2.44 (s, 3 H, SCH_3), 3.84–4.08 (brt, J = 7, 1 H, H-3), 6.14–6.50 (m, 2 H, =CH), 7.08–7.45 (m, 5 H, ArH); MS m/z 290 (M^+, 21), 243 (80). Anal. Calcd for $C_{16}H_{18}OS_2$: C, 66.17; H, 6.25. Found: C, 66.31; H, 6.37.

Cyclization of 10b. *S*-Methyl *trans*-1-Methyl-5-styryl-2-oxocyclopentane-*r*-1-thiocarboxylate (11b). According to the general $SnCl_4$-catalyzed cyclization procedure, **10b** yielded **11b** (1.89 g, 69%). The material was spectrally identical with that obtained by H_3PO_4/HCO_2H cyclization of **10b**.

Cyclization of 10e. 2-[Bis(methylthio)methylene]-3-(4-phenyl-1,3-butadienyl)cyclopentanone (16e): pale yellow viscous oil; yield 2.25 g (71%); R_f 0.40 in C_6H_6; IR (neat) 1680 cm^{-1}; ^1H NMR (CCl_4) 1.45–2.51 (m, 4 H, CH_2), 2.39 (s, 3 H, SCH_3), 2.43 (s, 3 H, SCH_3), 3.89 (brt, J = 7, 1 H, H-3), 5.76 (dd, J = 16, 7, 1 H, =CH), 5.90–6.85 (m, 3 H, =CH), 7.08–7.44 (m, 5 H, ArH); MS m/z 301 (M^+ − 15, 26). Anal. Calcd for $C_{18}H_{20}OS_2$: C, 68.31; H, 6.37. Found: C, 68.44; H, 6.46.

Cyclization of 20a. 2-[Bis(methylthio)methylene]-3-(3,4-dihydro-6-methoxynaphthyl)cyclopentanone (21). $SnCl_4$-catalyzed cyclization of **20a** yielded **21** as pale yellow viscous oil: yield 2.84 g (82%); R_f 0.40 in C_6H_6/EtOAc (20:1); IR (neat) 1690 cm^{-1}; ^1H NMR ($CDCl_3$) 1.58–2.61 (m, 6 H, CH_2), 2.38 (s, 3 H, SCH_3), 2.47 (s, 3 H, SCH_3), 2.80 (t, J = 6, 2 H, CH_2), 3.65–3.98 (m, 1 H, CH-5), 3.75 (s, 3 H, OCH_3), 6.0 (s, 1 H, =CH), 6.55–6.78 (m, 2 H, ArH), 6.90 (d, J = 9, 1 H, ArH); MS m/z 331 (M^+ − 15, 26). Anal. Calcd for $C_{19}H_{22}O_2S_2$: C, 65.86; H, 6.40. Found: C, 66.03; H, 6.48.

Boron Trifluoride Etherate Catalyzed Methanolysis of 21. Methyl *trans*-2-(3,4-Dihydro-6-methoxy-2-naphthyl)-5-oxocyclopentane-*r*-1-carboxylate (22). A suspension of **21** (0.4 g, 1 mmol) and $HgCl_2$ (0.3 g, 1.1 mmol) in anhydrous methanol (10 mL) was stirred at rt (10 min) followed by addition of BF_3·Et_2O (1.5 mL). The reaction mixture was refluxed (3 h), cooled, and filtered. The filtrate was poured into saturated $NaHCO_3$ solution (50 mL) followed by extraction with chloroform (3 × 30 mL). The combined extracts were washed with water (50 mL), dried (Na_2SO_4), and evaporated to give a viscous residue which on column chromatography over silica gel (EtOAc/hexane (1:20)) afforded pure ester **22** as a colorless viscous oil: yield 2.34 g (78%); R_f 0.40 in C_6H_6/EtOAc (20:1); IR (neat) 1730, 1760 cm^{-1}; ^1H NMR ($CDCl_3$) 1.5–1.98 (m, 2 H, CH_2), 2.03–2.58 (m, 4 H, CH_2), 2.79 (t, J = 8, 2 H, CH_2), 3.10–3.43 (m, 2 H, CH), 3.71 (s, 3 H, OCH_3), 3.75 (s, 3 H, OCH_3), 6.27 (s, 1 H, =CH), 6.54–6.81 (m, 2 H, ArH), 6.91 (d, J = 9, 1 H, ArH); MS m/z 300 (M^+, 100), 269 (20), 241 (72). Anal. Calcd for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71. Found: C, 71.71; H, 6.63.

8-Methoxy-4a,5,6,10b-tetrahydronaphtho[2,1-*e*]norbornen-2-one (23). In H_3PO_4/HCO_2H (80 °C, 45 min), **20a** gave **23** as a yellow viscous oil: yield 1.50 g (62%); R_f 0.45 in C_6H_6/EtOAc (20:1); IR (neat) 1750, 1610 cm^{-1}; ^1H NMR (CCl_4) 1.18–1.69 (m, 3 H, CH_2), 1.73–2.92 (m, 8 H, CH, CH_2), 2.85 (brd, J = 6.5, ArCH), 3.70 (s, 3 H, OCH_3), 6.44–6.90 (m, 2 H, ArH), 7.11 (d, J = 9, 1 H, ArH); MS m/z 242 (M^+, 100). Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.58; H, 7.65.

Cyclization of 20b. *S*-Methyl *trans*-(3,4-Dihydro-6-methoxy-2-naphthyl)-1-methyl-5-oxocyclopentane-*r*-1-thiocarboxylate (25). In H_3PO_4/HCO_2H (80 °C, 30 min), **20b** gave **25** as colorless crystals ($CHCl_3$/hexane): yield 2.74 g (83%); mp 118–119 °C; R_f 0.50 in C_6H_6/EtOAc (20:1); IR (KBr) 1738, 1660 cm^{-1}; ^1H NMR ($CDCl_3$) 1.20 (s, 3 H, CH_3), 1.41–2.63 (m, 6 H, CH_2), 2.32 (s, 3 H, SCH_3), 2.72 (t, J = 7, 2 H, CH_2), 3.65 (brt, J = 6, 1 H, merged with OCH_3, CH-5), 3.77 (s, 3 H, OCH_3), 6.22 (s, 1 H, =CH), 6.51–6.77 (m, 2 H, ArH), 6.95 (d, J = 9, 1 H, ArH); MS m/z 330 (M^+, 28), 283 (22), 255 (100). Anal. Calcd for $C_{19}H_{22}O_3S$:

C, 69.06; H, 6.71. Found: C, 69.21; H, 6.86.

Acknowledgment. B.D. and B.P. thank CSIR, New Delhi, for Senior and Junior Research Fellowships. Financial assistance from UGC, New Delhi under COSIST programme is also acknowledged. We are grateful to the reviewers for critical comments and suggestions.

Registry No. **9a**, 137612-32-9; **9b**, 139378-05-5; **9c**, 139378-06-6; **9d**, 139378-07-7; **9e**, 137612-35-2; **9f**, 137612-33-0; **9g**, 137612-36-3; **10a**, 139378-08-8; **10b**, 139378-09-9; **10c**, 139378-10-2; **10d**, 139378-11-3; **10e**, 139378-12-4; **10f**, 139378-13-5; **10g**, 139378-14-6; **11a**, 139378-15-7; **11b**, 139378-16-8; *cis*-**11e**, 139407-35-5; *trans*-**11e**, 139492-52-7; **12a**, 139378-17-9; **12c**, 139378-18-0; **12d**, 139378-19-1; **12e**, 139378-20-4; **13a**, 139378-21-5; **13b**, 139378-22-6; **13c**, 139378-23-7; **13e**, 139378-24-8; **14**, 139378-25-9; **15**, 139378-26-0; **16a**, 139378-27-1; **16e**, 139378-28-2; **17**, 52714-10-0; **18a**, 17649-86-4; **18b**, 17649-87-5; **19a**, 139378-29-3; **19b**, 139378-30-6; **20a**, 139378-31-7; **20b**, 139378-32-8; **21**, 139378-33-9; **22**, 139378-34-0; **23**, 139378-35-1; **25**, 139378-36-2.

Bis(2-acetoxyacrylonitrile) and Its Phenylene and Alkylene Bis Homologues. Preparation, Isomerization, and Intramolecular [2 + 2] Photocycloaddition

Akira Oku,* Shin-Ichi Urano, Toshiyuki Nakaji, Ge Qing, and Manabu Abe

Department of Chemistry, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606, Japan

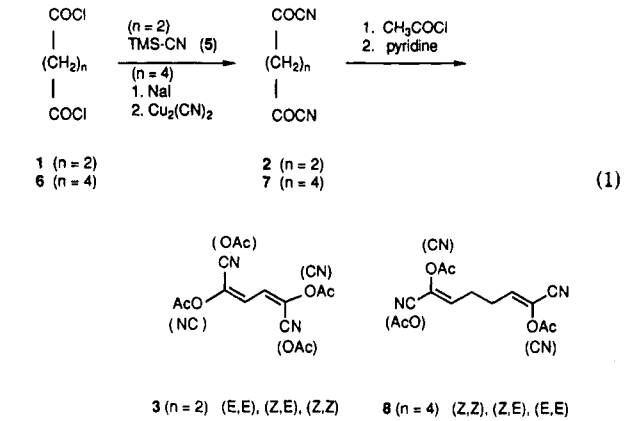
Received March 13, 1990 (Revised Manuscript Received November 22, 1991)

The title compounds, 1,4-diacetoxy-1,4-dicyano-1,3-butadiene (**3**), 1,6-diacetoxy-1,6-dicyano-1,5-hexadiene (**8**), 1,2-bis(2-acetoxy-2-cyanovinyl)benzene (**13**), and 1,4-bis(2-acetoxy-2-cyanovinyl)benzene (**17**) were prepared by acetylation of the corresponding diacyl dicyanides. Dicyanides were prepared from diacyl chlorides by reaction with cyanotrimethylsilane or the NaI–$Cu_2(CN)_2$ reagent. Among the three geometrical isomers of the title compounds, the *Z,Z* diene predominated in **8** whereas *E,E* dienes predominated in conjugated dienes **3**, **13**, and **17**. Conjugated *E,E* dienes underwent photoisomerization to *E,Z* and *Z,Z* isomers much faster than unconjugated diene **8**. Prolonged irradiation on **13** yielded intramolecular [2 + 2] cycloadducts *endo,exo*- and *exo,exo*-5,6-diacetoxy-5,6-dicyano-2,3-benzobicyclo[2.1.1]hex-2-ene (**22**). Photochemistry in the formation of **22** is discussed.

While ketenes have been considered useful compounds in organic synthesis, their instability limits their utility in many ways. Consequently, several synthetic equivalents for ketenes have been developed.[1] One example is 2-acetoxyacrylonitrile, which is useful as a dienophile,[2] Michael acceptor,[3] carbene acceptor,[4] and monomer[5] for polymer synthesis. The few synthetic methods available produce mainly nitriles unsubstituted at the 3-position.[6] However, acylation of the enolates of acyl cyanides[7] enabled us to prepare a number of 3-substituted 2-(acyloxy)acrylonitriles. In the present report syntheses of bis(2-acetoxyacrylonitrile)s bearing either a conjugated or unconjugated diene are described as well as their photochemical isomerization and photochemical intramolecular [2 + 2] cycloaddition reactions.

Results and Discussion

Preparation of Aliphatic Dienes. A synthetic route to 1,4-diacetoxy-1,4-dicyano-1,3-butadiene (**3**) is shown in eq 1. The first attempt to prepare bis(acyl cyanide) **2** by the reaction of succinyl chloride (**1**) with sodium iodide[8] followed by the treatment with cuprous cyanide was unsuccessful and 4,4-dicyano-γ-butyrolactone (**4**) was obtained. The formation of **4** can be explained in analogy to the dimer formation of simple acyl cyanides.[9] However, the use of cyanotrimethylsilane (**5**)[10] was found to successfully give **2** in 63% yield. The reaction of **2** with acetyl chloride and pyridine finally afforded the expected butadiene **3** (63% yield), which consisted only of the *E,E* isomer.[11]



The choice of cyanation reagents is important.[12] When adipyl chloride (**6**) was treated with cyanosilane **5**, tetra-

(1) (a) Corey, E. J.; Welnshenker, N. M.; Schaff, T. K.; Huber, W. *J. Am. Chem. Soc.* **1969**, *91*, 5675. (b) Ranganathan, S.; Ranganathan, D.; Mehrotra, A. K. *Synthesis* **1977**, 289. (c) Bartlett, P. D.; Tate, B. T. *J. Am. Chem. Soc.* **1956**, *78*, 2473.

(2) (a) Evans, D. A.; Scott, W. L.; Truesdale, K. *Tetrahedron Lett.* **1972**, 21. (b) Oku, A.; Hasegawa, H.,; Shimadzu, H.; Nishimura, J.; Harada, T. *J. Org. Chem.* **1981**, *46*, 4152.

(3) Oku, A.; Horiie, N.; Harada, T. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 609.

(4) Oku, A.; Yokoyama, T.; Harada, T. *J. Org. Chem.* **1981**, *48*, 5333.

(5) (a) Ohta, T. *Kogyo Kagaku Zasshi*, **1968**, *71*, 1542. (b) Miyashita, Y.; Shimada, N.; Yamamoto, Y.; Kohjiya, S.; Yamashita, S.; Oku, A. *Chem. Soc. Jpn., 45th Ann. Meeting*, Tokyo (1982), Abstract II, 1J11.

(6) (a) Baker, J. W. *J. Chem. Soc.* **1942**, 520. (b) Johnston, F. U.S. Patent 2395930, 1946.

(7) (a) Oku, A.; Arita, S. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3337. (b) Oku, A.; Nakaohji, S.; Kadono, T.; Imai, H. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2966.

(8) THF was inadequate as the solvent because it underwent a ring-cleavage reaction by the intermediate acyl iodide to give bis(4-iodobutyl) succinate. Oku, A.; Harada, T.; Kita, K. *Tetrahedron Lett.* **1982**, *23*, 681.

(9) Tate, D. E. *J. Am. Chem. Soc.* **1956**, *78*, 5575.

(10) (a) Zubrik, J. W.; Dubar, B. L.; Durst, H. D. *Tetrahedron Lett.* **1975**, 71. (b) Herrman, K.; Simdren, G. *Synthesis* **1979**, 204.

(11) For the NMR spectra see the Experimental Section and for the details of structure determination see the supplementary material pages (S-1) for **3**, (S-2) for **8**, (S-3) for **13**, (S-4) for **17**, (S-5) for **22**, and also from (S-1-1) to (S-5-1) for spectra charts.

(12) Hünig, S.; Schaller, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 36.

0022-3263/92/1957-2263$03.00/0