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.

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

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

Department of Chemistry, North-Eastern Hill University, Shillong – 799 003, 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 carbocyclic 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.1,4 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 alkyldienetetrahydrofurans instead of cyclopentanones owing to stereoelectronic factors.1,4 However, some ingenious efforts have been made to convert these alkyldienetetrahydrofurans to the desired cyclopentanones under the influence of Pd(0)-assisted rearrangements.1,4 Interestingly, no efforts seem to have been made to convert these enolates to any other type of cyclopentanone.

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

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

Department of Chemistry, North-Eastern Hill University, Shillong - 799 003, 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 carbocyclic 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.1,4 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 alkyldienetetrahydrofurans instead of cyclopentanones owing to stereoelectronic factors.1,4 However, some ingenious efforts have been made to convert these alkyldienetetrahydrofurans to the desired cyclopentanones under the influence of Pd(0)-assisted rearrangements.1,4 Interestingly, no efforts seem to have
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 could provide a route to cyclopentanones. The acid-assisted ring opening of cyclopropyl ketones has long been a subject of synthetic and mechanistic interest.\(^5\) 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 ary1 or olefinic double bond.\(^6\)

In our preliminary paper,\(^a\) 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 (\(\text{H}_3\text{PO}_4/\text{HCO}_2\text{H}\)), and thioacetal 7 (\(\text{SnCl}_2/\text{C}_6\text{H}_5\))\(^8\)\(^9\). The isolation of open-chain carbinal 8 (\(\text{Ar} = 4\text{-MeO-C}_6\text{H}_4\)) could prove the intermediacy of carbocation 3 in support of a stepwise mechanism for the transformation.\(^10\) 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 cyclopentane ring formation was successful with the reaction time leading to tar. No definite products could be obtained.

The cation 4 does not appear to exist in equilibrium with α-oxoketene dithioacetal in \(\text{H}_3\text{PO}_4/\text{HCO}_2\text{H}\) since 7 (\(\text{Ar} = 4\text{-MeO-C}_6\text{H}_4\)) remained unchanged when treated with \(\text{H}_3\text{PO}_4/\text{HCO}_2\text{H}\) at room temperature (6 h), while under heating intractable mixture of products were obtained.\(^10\)

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.  

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. The regio- and chemoselective cyclopropagation of 9a–g was achieved by treating them with dimethylsulfoxonium methyldide in the presence of a phase-transfer catalyst in 89–97% overall yields. The structures of 10a–g were fully confirmed by their analytical and spectral data.  

Cyclization of 10 in H₃PO₄ (80%)/HCO₂H (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 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-methylthiocarbonyl group is also in conformity with the earlier observations reported. At 80 °C (1 h), the isolated product was identified as the thiomethylated product 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 15a (67%).  

From 10b. At room temperature, 10b gave 11b (71%). From 'H NMR data, 11b was shown to have the same stereochemistry as 11a. Dimethylthiocarbonylation 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 (65%) (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 observed.  

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 '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 A₂B₂ pattern of aromatic protons and the triplet at δ 2.98 for the benzylic protons in its 'H NMR spectrum, which is in accordance with the earlier observations reported 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. The compound was analyzed for C₇H₆O₂, 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 'H and 13C 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 (H₃PO₄/HCO₂H containing H₂O in the acid/solvent system).  

Cyclization of 10 in the Presence of SnCl₄ in C₆H₆ or CH₂Cl₂ (Scheme IV). It is well-known that the re-
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 10b afforded the products 16a (74%) and 16e (71%), respectively, on treatment with SnCl₄ in C₆H₆ or CH₂Cl₂ at room temperature. On the other hand, 10b (R = CH₃) 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 (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 cyclopropagation 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 SnCl₄ in benzene at room temperature. The resulting α-oxoketene dithioacetal 21 on subsequent methanolation (BF₃·Et₂O/HgCl₂/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. However, the cyclopropyl ketone 20a when cyclized in H₃PO₄/HCO₂H yielded a product characterized as bicyclic ketone 23 (cyclopentanone 24, the precursor of 25 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 H₃PO₄/HCO₂H 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, methyliithio, 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 3.85 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.

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 dethio-carbonylation at higher temperatures yields the corresponding 3-styrylcyclopentanone 13. The conversion of 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 CH₂Cl₂, 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 benzylidene (or phenylallylic) carbocations 30 or 31 which are trapped by MeSH to afford thiomethylated ketones 12 (Scheme VII). 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-MeOC₆H₄) underwent intramolecular trapping by an enolic double bond to afford bicyclic ketones 14 and 15, respectively (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-oxosteroid precursors 22 and 23.

Cyclopropyl Ketones 10a-g and 20a,b. General Procedure. A suspension of the appropriate α-oxo ketone dihydroacetal (10 mmol), trimethylsulfoxonium iodide (13 mmol), and cyclopropane (10a): colorless crystals (CHCl₃); yield 2.83 g (98%); mp 169-170 °C; IR (neat) 1690 cm⁻¹; 'H NMR (CDCl₃) 0.85-1.10 (m, 1 H, CH₃), 1.45-1.70 (m, 1 H, CH₂), 1.78-2.23 (m, 2 H, CH₂); MS m/z 290 (M⁺, 11), 235 (30), 185 (67). Anal. Calcd for C₁₄H₁₈O₃S: C, 71.75; H, 7.92. Found: C, 71.88; H, 7.82.

1-[Bis(methylthio)methylene]acetyl]-2-(3,4-dimethoxystyryl)cyclopropane (10d): colorless crystals (CHCl₃); yield 2.91 g (97%); mp 116-117 °C; IR (KBr) 1640, 1495 cm⁻¹; 'H NMR (CDCl₃) 0.85-0.93 (m, 1 H, CH₃), 1.46-1.73 (m, 1 H, CH₂), 1.85-2.33 (m, 2 H, COCH and ArCH═CH₂CH₂); 2,4,6 (s, 3 H, SCH₃); 5.75 (d, J = 16, 8, 1 H, =CH), 6.54 (d, J = 16, 8, 1 H, =CH), 6.89 (d, J = 9, 2 H, ArH). Anal. Calcd for C₁₉H₂₄O₂S₂: 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 (CHCl₃); yield 3.22 g (93%); mp 169-170 °C; IR (KBr) 1640, 1495 cm⁻¹; 'H NMR (CDCl₃) 0.85-0.93 (m, 1 H, CH₃), 1.46-1.73 (m, 1 H, CH₂), 1.85-2.33 (m, 2 H, COCH and ArCH═CH₂CH₂); 2,4,6 (s, 3 H, SCH₃); 5.75 (d, J = 16, 8, 1 H, =CH), 6.54 (d, J = 16, 8, 1 H, =CH), 6.89 (d, J = 9, 2 H, ArH). Anal. Calcd for C₁₉H₂₄O₂S₂: C, 65.86; H, 6.40. Found: C, 65.98; H, 6.56.

Experimental Section

Melting points were determined on a capillary apparatus and are uncorrected. 'H NMR spectra (δ) were recorded at 90 MHz. J values are given in Hz. The α-oxo ketone dihydroacetals 8a-g were prepared according to known procedures, while trimethylsulfonium iodide was prepared by Corey's method.

1-[Bis(methylthio)methylene]acetyl]-2-(3,4-dihydro-6-methoxynaphth-2-yl)cyclopropane (20a): colorless crystals (CHCl₃); yield 3.22 g (93%); mp 169-170 °C; IR (KBr) 1640, 1495 cm⁻¹; 'H NMR (CDCl₃) 0.85-0.93 (m, 1 H, CH₃), 1.46-1.73 (m, 1 H, CH₂), 1.85-2.33 (m, 2 H, COCH and ArCH═CH₂CH₂); 2,4,6 (s, 3 H, SCH₃); 5.75 (d, J = 16, 8, 1 H, =CH), 6.54 (d, J = 16, 8, 1 H, =CH), 6.89 (d, J = 9, 2 H, ArH). Anal. Calcd for C₁₉H₂₄O₂S₂: C, 65.86; H, 6.40. Found: C, 65.98; H, 6.56.

1-[Bis(methylthio)methylene]acetyl]-2-(3,4-dimethoxystyryl)cyclopropane (10d): colorless crystals (CHCl₃); yield 2.91 g (97%); mp 116-117 °C; IR (KBr) 1640, 1495 cm⁻¹; 'H NMR (CDCl₃) 0.85-0.93 (m, 1 H, CH₃), 1.46-1.73 (m, 1 H, CH₂), 1.85-2.33 (m, 2 H, COCH and ArCH═CH₂CH₂); 2,4,6 (s, 3 H, SCH₃); 5.75 (d, J = 16, 8, 1 H, =CH), 6.54 (d, J = 16, 8, 1 H, =CH), 6.89 (d, J = 9, 2 H, ArH). Anal. Calcd for C₁₉H₂₄O₂S₂: 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 (CHCl₃); yield 3.22 g (93%); mp 169-170 °C; IR (KBr) 1640, 1495 cm⁻¹; 'H NMR (CDCl₃) 0.85-0.93 (m, 1 H, CH₃), 1.46-1.73 (m, 1 H, CH₂), 1.85-2.33 (m, 2 H, COCH and ArCH═CH₂CH₂); 2,4,6 (s, 3 H, SCH₃); 5.75 (d, J = 16, 8, 1 H, =CH), 6.54 (d, J = 16, 8, 1 H, =CH), 6.89 (d, J = 9, 2 H, ArH). Anal. Calcd for C₁₉H₂₄O₂S₂: 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 (CHCl₃); yield 3.22 g (93%); mp 169-170 °C; IR (KBr) 1640, 1495 cm⁻¹; 'H NMR (CDCl₃) 0.85-0.93 (m, 1 H, CH₃), 1.46-1.73 (m, 1 H, CH₂), 1.85-2.33 (m, 2 H, COCH and ArCH═CH₂CH₂); 2,4,6 (s, 3 H, SCH₃); 5.75 (d, J = 16, 8, 1 H, =CH), 6.54 (d, J = 16, 8, 1 H, =CH), 6.89 (d, J = 9, 2 H, ArH). Anal. Calcd for C₁₉H₂₄O₂S₂: 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 (CHCl₃); yield 3.22 g (93%); mp 169-170 °C; IR (KBr) 1640, 1495 cm⁻¹; 'H NMR (CDCl₃) 0.85-0.93 (m, 1 H, CH₃), 1.46-1.73 (m, 1 H, CH₂), 1.85-2.33 (m, 2 H, COCH and ArCH═CH₂CH₂); 2,4,6 (s, 3 H, SCH₃); 5.75 (d, J = 16, 8, 1 H, =CH), 6.54 (d, J = 16, 8, 1 H, =CH), 6.89 (d, J = 9, 2 H, ArH). Anal. Calcd for C₁₉H₂₄O₂S₂: C, 65.86; H, 6.40. Found: C, 65.98; H, 6.56.
Cyclization of 10e yielded product 12e (20 °C, 30 h, 1.89 g, 65%; 80 °C, 1 h, 2.01 g, 72%) or a mixture of 12e (11.1 g, 48%) and 13e (80 °C, 4 h, 0.82 g, 30%).

3-[4-Methoxyphenyl]ethyl)cyclopentanone (12e): yellow viscous oil; Rf 0.56 in C6H5/CH2OAc (201); IR (neat) 1748 cm\(^{-1}\); \(^{1}H\) NMR (CDCl3) 0.93 (d, J = 7, 3 H, CH3), 1.87 (s, 3 H, SCH3), 1.15-2.48 (m, 8 H, CH2 and H-4), 3.70 (s, 3 H, OCH3), 6.81 (d, J = 18, 1 H, Arm), 7.21 (d, J = 9, 2 H, ArH). Anal. Calcd for C16H16O3: C, 79.31; H, 7.49. Found: C, 79.42; 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 SnCl4 (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 CH2Cl2 (3 x 60 mL), and the organic layer was washed with water, dried (Na2SO4), 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-styrylcyclohexanone (16a): yellow viscous oil; yield 2.15 g (74%); Rf 0.45 in C6H5/IR (neat) 1693 cm\(^{-1}\); \(^{1}H\) NMR (CDCl3) 1.45-2.51 (m, 4 H, CH2), 2.38 (s, 3 H, SCH3), 2.43 (s, 3 H, SCH3), 3.89 (brt, J = 7, 1 H, Arm), 5.76 (d, J = 16, 1 H, Arm). MS m/z 290 (M\(^+\)*, 21), 243 (80). Anal. Calcd for C18H18O3S: C, 79.51; H, 7.86. Found: C, 79.51; H, 7.84.

Cyclization of 10b. S-Methyl trans-5-styrylcyclopentanone-1-thiocarbamate (11b). According to the general SnCl4-catalyzed cyclization procedure, 10b yielded 11b (1.91 g, 69%). The material was spectroscopically identical with that obtained by H2PO3/HCO2H cyclization of 10b.

Cyclization of 10c. 2-[Bis(methylthio)methylene]-3-(4-phenyl-1,3-butadienyl)cyclopentanone (16c). 2-

Boron Trifluoride Etherate Catalyzed Methanalysis of 21. 2-Methyl trans-3-(3,4-Dihydro-6-methoxynaphthyl)cyclopentanone (21). SnCl4-catalyzed cyclization of 20a yielded 21 as pale yellow viscous oil: yield 2.84 g (82%); Rf 0.40 in C6H5/CH2OAc (201); IR (neat) 1690 cm\(^{-1}\); \(^{1}H\) NMR (CDCl3) 1.58-2.51 (m, 6 H, CH2), 2.38 (s, 3 H, SCH3), 2.47 (s, 3 H, SCH3), 2.80 (s, J = 2, 2 H, Arm), 3.65-3.99 (m, 20 H, Arm), 4.16-4.89 (m, 3 H, OCH3), 5.15 (s, 3 H, OCH3), 6.05 (s, 1 H, Arm), 6.60-6.83 (m, 3 H, Arm), 7.03-7.44 (m, 5 H, ArH). MS m/z 331 (M\(^+\)*, 15), 26. Anal. Calcd for C21H18O8S: C, 66.63; H, 6.48. Found: C, 66.63; H, 6.48.

For the rest of the text, please refer to the original source.
Y.; Shimada, N.; Yamamoto, Y.; Kohjiya, A.; Mehrotra, Harada, T.

1. The reaction of succinyl chloride (1) with sodium iodides led us to prepare a number of 3-substituted 2-(acyl-

2. chemical isomerization and photochemical intramolecular polymer synthesis. The few synthetic methods available


4. Preparation, Isomerization, and Intramolecular [2 + 2] Photocycloaddition

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

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

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

8. 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 for polymer synthesis. The few synthetic methods available produce mainly nitriles unsubstituted at the 3-position.5 However, acylation of the enolates of acyl cyanides 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.

9. Results and Discussion

10. 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 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 and Its Phenylene and Alkylene Bis (Z,Z)

11. The title compounds, 1,4-diacetoxy-1,6-dicyano-1,5-hexadiene (8), 1,2-bis(2-acycloxy-2-cyanovinyl)benzene (13), and 1,4-bis(2-acycloxy-2-cyanovinyl)benzene (17) were prepared by acylation of the corresponding diacyl dicyanides. Dicyanides were prepared from diacyl chlorides by reaction with cyanotrimethylsilane or the NaI-CN(CN)3 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-benzocyclo[2.1.1]hex-2-ene (22). Photochemistry in the formation of 22 is discussed.

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


14. (11) For the NMR spectra see the Experimental Section and for the details of structure determination see the supplementary material pages (S-1) to (S-2) for 8, (S-3) for 13, (S-4) for 17, (S-5) for 22, and also from (S-1) to (S-6) for spectra charts.