of $AlCl_3$ on **1a–c**(I) at room temperature.[18]

Moreover, the isomerization reactions are strongly dependent on the nature of the X_1 and X_2 substituents and the polarity of the solvent.

With the 1,2-dichloroethane as solvent, the isomerization of **1b** is the quickest reaction ($t_{1/2}$ = 6 min at 60 °C) whereas **1c** is the slowest ($t_{1/2}$ = 180 min at 70 °C).

For compounds **1a–c**, the isomerization always takes place with 1,2-dichloroethane as solvent while it is never observed in hexane. Finally, only compound **1b** undergoes the isomerization reaction in benzene or toluene solution.

The rate constant of the interconversion depends on the polarity of the solvents. For the reaction **1b**(I) → **1b**(II), $t_{1/2}$ = 20 min at 60 °C in the benzene whereas $t_{1/2}$ = 6 min in the dichloroethane at the same temperature. However, in the most polar solvent used (nitrobenzene), compounds **1a–c**(I) do not undergo the expected isomerisations but one ionization reaction takes place which leads to the formation of phosphonium phosphaalkenes **3a–c**. The calculated dipolar moment for the conformation I and II of $HP{=}CHPH_2$ are respectively 0.76 and 1.25 Debye. This result is consistent with the influence of polar solvent on the isomerization reactions I → II.

The fact, that the diphosphapropenes substituted on the phosphorus by the TSi group are thermodynamically stable in the syn conformation II is probably the consequence of the difference in steric bulkiness and of the electronic effect of Tsi group which, in this case, reduces the stabilizing $n_P \rightarrow \pi^*_{P=C}$ interaction.

Conclusion

The 1,3-diphosphapropenes exist in the form of two stable rotamers; their existence predicted by a theoretical study is verified experimentally using ^{31}P NMR method. The structural deformations of these two rotamers are connected to differentiate interactions between the P=C system and the phosphino group. These structural changes manifested through different NMR parameters would result in very different reactivities for these isolated systems.

Acknowledgment. We thank the Direction Chimie Du CNRS for the calculation time dotation on the VP 200 computer of the CIRCE and the GRECO "Basse Coordinence".

---

[18] Gouygou, M.; Tachon, C.; Etemad-Moghadam, G.; Koenig, M. *Tetrahedron Lett.* **1989**, *30*, 7411.

Notes

Bromine-Catalyzed Configuration Isomerization in Bicyclic [3.2.1] Systems

Osman Çakmak, Yavuz Taşkesenligil, and Metin Balci*

Department of Chemistry, Atatürk University, Faculty of Science, Erzurum, Turkey

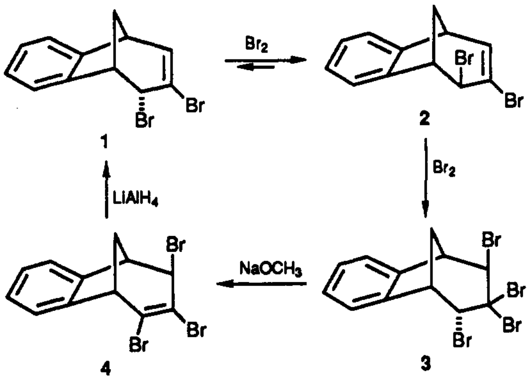
Received March 9, 1990

The study of ground state and photochemical solvolysis and Wagner–Meerwein rearrangements in certain bridge-ring systems containing aromatic groups and nucleofugal groups has been of considerable interest.[1,2] Study of these compounds has shown that there are stereo- and regiochemical requirements for both ionization and subsequent rearrangements. In this paper, we describe a new system where similar rearrangements have been observed. We report also an unusual configurational isomerization of *endo*-2,3-dibromo-6,7-benzobicyclo[3.2.1]octa-3,6-diene (**1**) in the presence of bromine, which provides evidence for radical rearrangement.

Results and Discussion

The starting material **2**[3] was synthesized by addition of dibromocarbene to the readily available benzonorbornadiene,[4] as reported in the literature. The reaction of **2** with bromine[5] under radical conditions provided **3** in a yield of 65% besides six other products.[6] Treatment of **3** with 1 mol of sodium methoxide gave the tribromide **4** (Scheme I). The structure of **4** and the exo position of the bromine was determined by means of ^1H and ^{13}C NMR spectra.[7]

Scheme I



---

[1] (a) Cristol, S. J.; Strom, R. M. *J. Am. Chem. Soc.* **1979**, *102*, 5707. (b) Cristol, S. J.; Dickenson, W. A.; Stanko, M. K. *J. Am. Chem. Soc.* **1983**, *105*, 1218. (c) Cristol, S. J.; Seapy, D. G.; Aelling, O. E. *J. Am. Chem. Soc.* **1983**, *105*, 7345.

[2] Tanida, H.; Tori, K.; Kitahonoki, K. *J. Am. Chem. Soc.* **1967**, *89*, 3012.

[3] Kitahonoki, K.; Takano, Y.; Matsuura, A.; Kotera, K. *Tetrahedron* **1969**, *25*, 335.

[4] Mich, T. F.; Nienhouse, E. J.; Farina, T. E.; Tufariello, J. J. *J. Chem. Educ.* **1968**, *45*, 272.

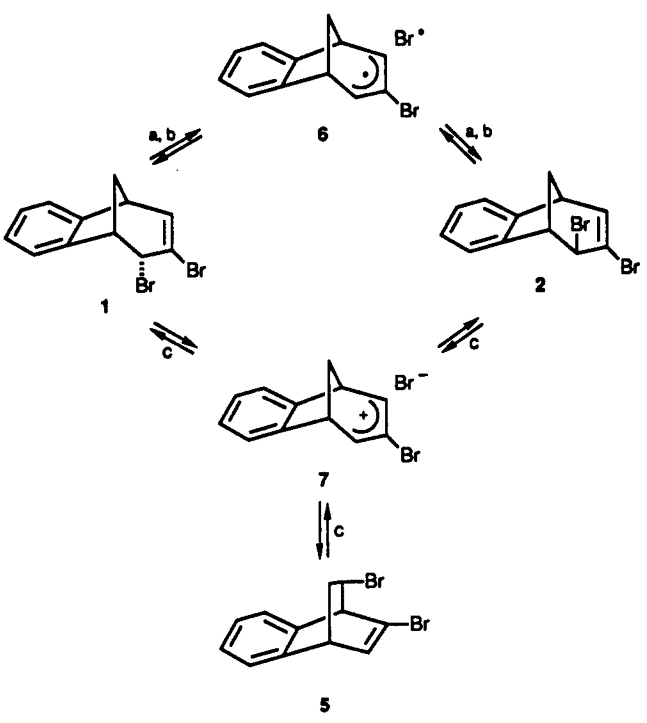
[5] Treatment of **2** with bromine causes at first configuration isomerization in 10 min followed by addition of bromine to give **3** as the major product.

[6] Çakmak, O.; Balci, M. *J. Org. Chem.* **1989**, *54*, 181.

[7] The exo configuration of bromine at C_4 has been established by analysis of the AB system arising from the bridge methylene protons H_{8e} and H_{8i}. The B part of the AB system shows a doublet. There is no further measurable coupling with the adjacent bridge head protons H_1 and H_5 due to nearly 90° dihedral angles between H_{8e} and H_1 and H_5. However, the A part of the AB system is split into triplets of doublets of doublet. The second doublet splitting ($^4J_{48i}$ = 1.5 Hz) originates from the proton on C_4 which is in the endo position. In the case of ^4J in the bicyclic systems one speaks of the M or W arrangement. The bonding arrangement of the coupled protons H_4 and H_{8i} meets M criterion. The fact that there is any coupling between H_{8i} and H_4 is an indication for the exo configuration of the bromine atom at C_4.

0022-3263/91/1956-3442$02.50/0

Scheme II

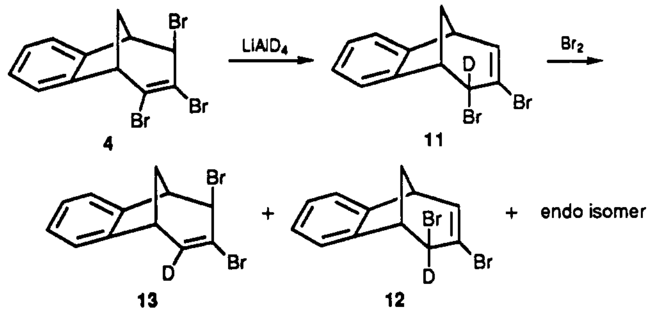


a = *h*ν, b = Δ, c = FeBr$_3$

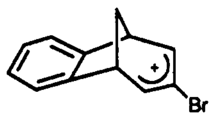
LiAlH$_4$ reduction of 4 furnished the endo bromide 1. The attack of hydride ion occurs stereospecifically at C$_2$ from the exo face of the molecule, the exo bromine at C$_4$ being displaced according to a S$_N$2′ mechanism. Probably, α-substitution sterically retards the normal S$_N$2 mechanism, so that the nucleophile attacks at the γ-carbon rather than at the usual position, and an allylic rearrangement takes place. This mechanism is a stereospecific cis process, involving hydride attack from the same side from which bromide leaves. A similar stereochemical course was observed in cyclohexane systems.[8] The structure of 1 was ascertained by its ^{1}H NMR spectrum, very similar to that of 2, indicating that the two products are stereoisomers. The interesting feature of these ^{1}H NMR spectra is the AB system arising from the bridge protons H_{8e} and H_{8i} in 1 and 2. There is no large chemical shift difference between the resonances of the internal hydrogens H_{8i} ($\Delta\delta$ = 0.1 ppm) in 1 and 2. But H_{8e} in 2 resonates at lower field (δ = 2.6 ppm) compared to the H_{8e} (δ = 2.2 ppm) in 1. This fact can be explained on the basis of strong steric repulsion between H_{8e} in 2 and neighboring bromine in the exo position. It is well known that interactions related to the van der Waals effect cause a paramagnetic contribution to the shielding constants which results in a shift to lower field.[9]

Pure 1 or 2 were each subjected to direct irradiation with a sun lamp (250 W); a mixture of 1 and 2 in which the later predominated (13:87) was formed. A similar product distribution was also observed by heating of pure samples 1 and 2. The same reactions were conducted in the presence of free radical inhibitors like 2,4,6-tri-*tert*-butylphenol and 2,4,6-tri-*tert*-butylnitrosobenzene under the same reaction conditions. In these cases no configuration isomerization was observed which strongly supports a radical mechanism for interconversion of the endo and exo bromides (Scheme II). In both cases, photochemical and thermal reactions, no trace of the [2.2.2] system could be detected.

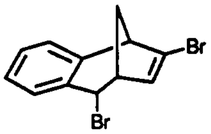
Scheme III



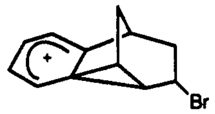
Treatment of endo or exo bromide 1 and 2 with FeBr$_3$ at 100 °C for 2 h gave a mixture of 1, 2, and 5 in a ratio of approximately 16:38:46. A similar product ratio was also obtained by treatment of pure sample of 5 with FeBr$_3$. It would appear that thermodynamic control leads largely, but not entirely, to the bicyclo[2.2.2]octadiene system. These results are completely in agreement with those reported by Cristol and Strom[1a] for the dichloro system. Kinetic control of carbenium ion reactions result largely in exo capture of nucleophile to give 2, with smaller amount of endo capture to give 1. The fact that we did not observe any alkyl-shifted product such as 8, indicates that the lowest lying (in energy) intermediate in this system is the allylic cation 7 and the bridged phenonium ion 9 is a somewhat higher energy species in the equilibration and there are no kinetically significant ions of the type 10 that lead to 8. Probably these are more strained than either of 7 and 9.



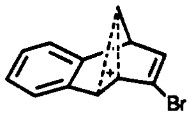
7



8



9



10

A solution of the pure endo bromide 1 in chloroform was treated with bromine in day light for 10 min. The reaction was monitored by ^{1}H NMR spectroscopy. In 10 min the equilibrium mixture consisting from exo and endo dibromides 1 and 2 (14:86) was reached (Scheme I). This ratio is in good agreement with the ratio obtained by direct irradiation or heating. The same equilibrium mixture was also obtained by bromination of the exo dibromide 2 with bromine in 10 min of daylight.

In order to shed light on the reaction mechanism of this conversion and to show whether this configuration isomerization takes place at the C$_2$ carbon atom or it is also accompanied by an allylic rearrangement, we synthesized the deuterated compound 11 by reduction of 4 with LiAlD$_4$. The position and exo configuration of deuterium atom was established on the basis of the ^{1}H NMR spectrum (Scheme III).

Deuterated compound 11 was treated with bromine under the same reaction conditions as reported above. ^{1}H

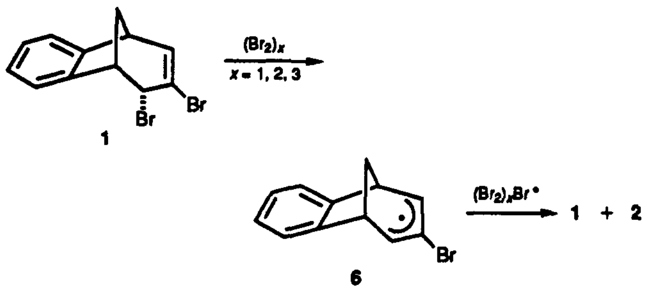
---

[8] Stork, G.; White, W. N. *J. Am. Chem. Soc.* **1956**, *78*, 4609.

[9] (a) Tori, K.; Ueyama, M.; Tsuji, T.; Matsamura, H.; Tanida, H.; Iwamura, H.; Kushida, K.; Nishida, T.; Satoh, S. *Tetrahedron Lett.* **1974**, 327. (b) Davis, S. G.; Whitman, G. H. *J. Chem. Soc., Perkin Trans. 2* **1975**, 861. (c) Cristl, M.; Leininger, H.; Brunn, E. *J. Org. Chem.* **1982**, *47*, 662. (d) Gheorghiu, M. D.; Olteanu, E. *J. Org. Chem.* **1987**, *52*, 5158.

[10] Balci, M.; Çakmak, O.; Harmandar, M. *Tetrahedron Lett.* **1985**, *26*, 5469.

Scheme IV



NMR analysis of the product has revealed the scrambling of deuterium at C_2 and C_4 in a ratio of exactly 1:1. Our results clearly shows that bromine atom at C_2 changes its position in **11**. The fact that deuterium scrambling is exactly 1:1 implies that the formed intermediate must have symmetrical structure from which the products **12** and **13** can be derived. For this conversion we suggest the following mechanism involving the allylic radical **6** (Scheme IV).

According to this mechanism, a $(Br_2)_x$ molecule performs a molecule-induced homolysis of **1** to yield radical pairs **6**, which can explain the scrambling of the deuterium atom. Recombination of the allylic radical and bromine radical gives **1** and **2** in a ratio of 14:86.

Conclusion

Finally, we conclude that bromine catalyses the homolytic cleavage of the carbon–bromine bond and recombination of the radicals formed causes configuration isomerization. On the basis of the above-mentioned reaction mechanism we suggest that all reactions giving cis products by addition of bromine to alkenes (like styrene, indene, etc.) have to be checked on whether cis products are formed as suggested by direct syn collapse or they are formed as secondary products according to the above-mentioned reaction mechanism.

Experimental Section

General Methods. Melting points were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected. Solvents were concentrated at reduced pressure. Infrared spectra were obtained from solution in 0.1-mm cells or KBr pellets for solids on a Perkin-Elmer 337 infrared recording spectrophotometer. The ^1H NMR spectra were recorded on EM 360 Varian, and Brucker WM 400 spectrometers and reported in δ units with TMS as the internal standard. Apparent splittings are given in all cases. Mass spectra were recorded on a Finnigan-MAT MS Model 4000 mass spectrometer at an ionizing voltage 70 eV. Analytical thin-layer chromatography (TLC) was performed on silica gel 60_{254} plates. Column chromatography was done on silica gel (60–200 mesh) from Merck Company.

(1*RS*,2*RS*,4*RS*,5*SR*)-2,3,3,4-Tetrabromo-6,7-benzobicyclo[3.2.1]oct-6-ene (3).[6] To a solution of 2 g (6.37 mmol) of exo dibromide **2** in 60 mL of methylene chloride was added dropwise, with stirring and during 3.5 h, a solution of 1.1 g (6.9 mmol) of bromine in 25 mL of methylene chloride at room temperature. The reaction flask was irradiated during the reaction with a 150-W sunlamp. The reaction mixture was allowed to stir $^1/_2$ h, and the solvent was removed under reduced pressure. The oily residue was crystallized from CH_2Cl_2/petroleum ether (3:1) to give tetrabromide **3** (1970 mg, 65%).

(1*SR*,4*RS*,5*RS*)-2,3,4-Tribromo-6,7-benzobicyclo[3.2.1]octa-2,6-diene (4). To a solution of 4.74 g of **3** (12 mmol) in 70 mL of dry and freshly distilled tetrahydrofuran was added 0.65 g (12 mmol) of sodium methoxide at room temperature while stirring magnetically. The resulting reaction mixture was stirred for 2.5 h at room temperature. The solution was poured into a mixture of petroleum ether (100 mL) and water (100 mL). The layers were separated, and the aqueous phase was extracted with petroleum ether. The combined organic layers were washed with water (2 × 50 mL), dried, and evaporated to give the crude product. The residue was filtered on a short silica gel column (25 g), eluting with petroleum ether, yield 97%. Recrystallization from hexane/chloroform (4:1) afforded colorless crystals: mp 99–100 °C; ^1H NMR (360 MHz, $CDCl_3$, TMS) 7.15–7.30 (m, 4 H, aromatic H), 4.75 (dd, 1 H, J = 4.5 and 1.5 Hz, H_4), 3.85 (d, 1 H, J = 1 Hz), H_1), 3.80 (dd, 1 H, J = 4.5 and 2.0 Hz, H_5), 2.83 (d, 1 H, B part of AB system, J = 11.5 Hz, H_{8e}), 2.4 (ddt, 1 H, A part of AB system, J = 11.5, 4.5, 1.5 Hz, H_{8i}); (90 MHz, $CDCl_3$, TMS) 149.69, 140.87, 134.37, 127.81, 127.60, 125.08, 121.82, 120.15, 56.71, 53.05, 50.17, 39.45; IR (KBr, cm^{-1}) 2940, 1580, 1465, 1295, 1230, 1160, 940, 860; MS *m/e* 390/392/394/396 (M^+). Anal. Calcd for $C_{12}H_9Br_3$: C, 36.68, H, 2.31; Br, 67.46. Found: C, 35.72; H, 2.20; Br, 60.49.

(1*SR*,2*RS*,5*RS*)-2,3-Dibromo-6,7-benzobicyclo[3.2.1]octa-2,6-diene (1). To a suspension of 0.58 g (15.26 mmol) of $LiAlH_4$ in 100 mL of dry and freshly distilled ether was added dropwise a solution of 3 g (7.63 mmol) of tribromide **4** in 30 mL of dry ether during 30 min. The resulting reaction mixture was stirred magnetically at room temperature for 20 h. Wet ether was added to the resulting reaction mixture (while cooling with an ice bath) as long as no reaction was observed. The formed precipitate was dissolved by adding dilute HCl solution. The organic layer was washed 3–4 times with water, dried over anhydrous $MgSO_4$, filtered, and concentrated to give an oil. The residue was filtered over 20 g of silica gel, eluting with petroleum ether to give endo dibromide as a colorless liquid: 1.74 g, yield 73%; ^1H NMR (60 MHz, CCl_4, TMS) 7.38–7.60 (m, 1 H, aromatic), 7.15–7.35 (m, 3 H, aromatic), 6.71 (d, 1 H, J = 6.8 Hz, H_4), 5.2 (d, 1 H, J = 4.6 Hz, H_2), 3.70 (t, 1 H, J = 4.6 Hz, H_1) 3.35 (dd, 1 H, J = 6.8 and 3.8 Hz, H_5), 2.45 (dt, B part of AB system, J = 10.4 and 3.8 Hz, H_{8i}), 2.20 (d, A part of AB system, J = 10.4 Hz, H_{8e}); IR (neat, cm^{-1}) 3060, 2950, 2860, 1610, 1465, 1310, 1160, 940, 860. Anal. Calcd for $C_{12}H_{10}Br_2$: C, 45.92; H, 3.21; Br, 50.89 Found: C, 45.73; H, 3.06; Br, 50.45.

Direct Irradiation of 1 in CCl_4. A solution of 50 mg (0.15 mmol) of **1** in 0.5 mL of CCl_4 was placed into a NMR tube. Deoxygenation was followed by irradiation by a 150-W projector lamp for 5 h. The ^1H NMR analysis indicated the formation of the equilibrium mixture consisting of **1** and **2** in a ratio of 13:87. Prolonged irradiation did not change this ratio. The same equilibrium mixture was also obtained starting from pure **2**. When irradiation was carried out in the presence of radical inhibitors, no isomerization was observed.

Thermal Reaction of 1 and 2. An 80-mg (0.25-mmol) sample of **1** (or **2**) was placed in a NMR tube and heated at 150 °C for 2 h. After the mixture was to room temperature, 0.5 mL of CCl_4 was added. The ^1H NMR analysis of the mixture indicated the formation of equilibrium mixture consisting of **1** and **2** in a ratio of 14:86.

(1*SR*,4*SR*,5*RS*)-2,5-Dibromo-7,8-benzobicyclo[2.2.2]octa-2,7-diene (5). Equilibration of 5, 2, and 1. Neat endo dibromide **1** (0.25 g, 0.79 mmol) was mixed with a trace of ferric bromide and heated at 100 °C for 2 h. The product was dissolved in ethyl ether, washed with water, and dried ($CaCl_2$). Evaporation of the solvent left an oil whose ^1H NMR spectrum indicated a mixture of **5**,[9] **2**, and **1** in a ratio of 46:38:16, respectively. The same reaction was also done with pure **2** and **5**. In both cases, the same equilibrium mixture was obtained.

(1*SR*,2*RS*,5*RS*)-2,3-Dibromo-2-deuterio-6,7-benzobicyclo[3.2.1]octa-3,6-diene (11). To a suspension of 0.2 g (4.76 mmol) of $LiAlD_4$ in 30 mL of dry and freshly distilled ether was added dropwise to a solution of 1 g (2.54 mmol) of tribromide **4** in 10 mL of dry ether during 30 min. The resulting reaction mixture was stirred magnetically at room temperature for 20 h. Same workup was done as described by the synthesis of **1**: ^1H NMR (60 MHz, CCl_4, TMS) 7.40–7.60 (m, 1 H, aromatic), 7.15–7.35 (m, 3 H, aromatic), 6.71 (d, 1 H), 3.70 (t, 1 H), 2.45 (dt, 1 H), 2.20 (d, 1 H).

Bromine-Catalyzed Configuration Isomerization of 1. To a solution of 500 mg (1.59 mmol) of endo dibromide **1** in 5 mL of chloroform was added a solution of 255 mg (1.59 mmol) of bromine in 2 mL of CCl_4 in 2 min. The reaction mixture was stirred magnetically at room temperature for 10 min. The solvent was evaporated, and the ^1H NMR analysis of the residue has revealed the existence of the equilibrium mixture consisting of 1 and 2 in a ratio of 14:86. The same equilibrium mixture was also obtained starting from 2 under the same reaction conditions.

Reaction of the Endo Dibromide 1 with Bromine in the Presence of Radical Inhibitors. To a solution of 40 mg (0.12 mmol) of endo dibromide 1 in 0.5 mL of $CDCl_3$ in a NMR tube was added 16 mg of 2,4,6-tri-*tert*-butylphenol (0.06 mmol) (or 2,4,6-tri-*tert*-butylnitrosobenzene) and followed by addition of 20 mg (0.12 mmol) of bromine. After 10 h no configuration isomerization was observed.

Acknowledgment. We are indebted to Atatürk University (Grant 1987/40) and Department of Chemistry for financial support of this work and to wish the express their appreciation to Prof. Dr. M. Schlosser (University of Lausanne) for ^{13}C NMR spectra and to both the referees for their very helpful suggestions concerning the radical mechanism.

Registry No. 1, 132748-50-6; 2, 117404-71-4; 3, 117269-29-1; 4, 117269-30-4; 5, 117404-74-7; 11, 132699-64-0; Br_2, 7726-95-6.

Reactivity of [(Alkylthio)methylene]ketenes in the Gas Phase and Photoelectron Spectra of Thiophen-3(2*H*)-ones[1]

F. Chuburu, S. Lacombe, and G. Pfister-Guillouzo*

Laboratoire de Physico-Chimie Moléculaire, URA CNRS 474, Avenue de l'Université, 64000 Pau, France

A. Ben Cheik, J. Chuche, and J. C. Pommelet

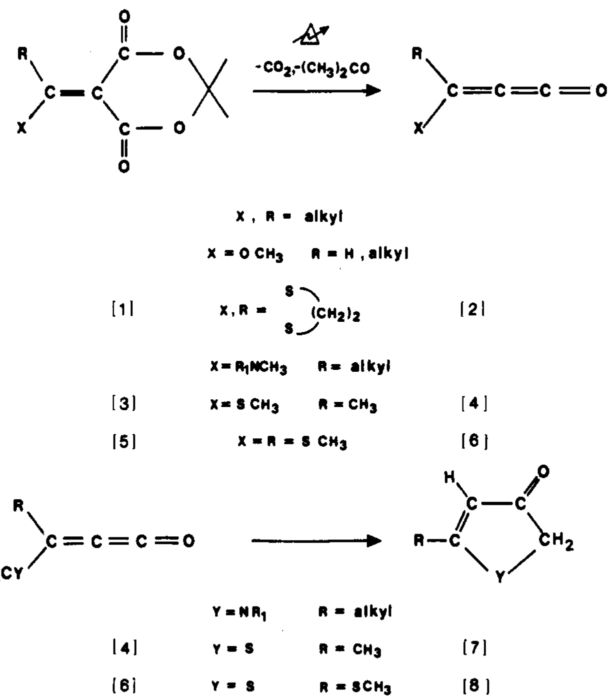
Laboratoire de Chimie Organique Physique, URA CNRS 459, Université de Reims, Faculté des Sciences, Moulin de la Housse, BP 347, 51062 Reims, France

Received October 11, 1990

Flash vacuum pyrolysis of substituted Meldrum's acid derivatives is known to give methyleneketenes (alkyl[2] and alkoxy[3,4] compounds) (Scheme I). However, alkylthio[3,5] and alkylamino[6] derivatives further react to the corresponding five-membered heterocycles, and thiophen-3-(2*H*)-ones or pyrrol-3(2*H*)-ones are generally characterized in solution as the reaction products. The only exception concerns the sterically strained bis(alkylthio) Meldrum's acid derivative 1 [isopropylidene (1,3-dithiolan-2-ylidene)malonate], for which the gas-phase characterization of [bis(alkylthio)methylene]ketene 2 could be performed.[4]

As photoelectron spectroscopy (PES) has proved to be a highly efficient tool for the gas-phase characterization of elusive compounds,[7] the PES detection of other [(alkylthio)methylene]ketenes has been attempted and their gas-phase reactivity is described.

Scheme I



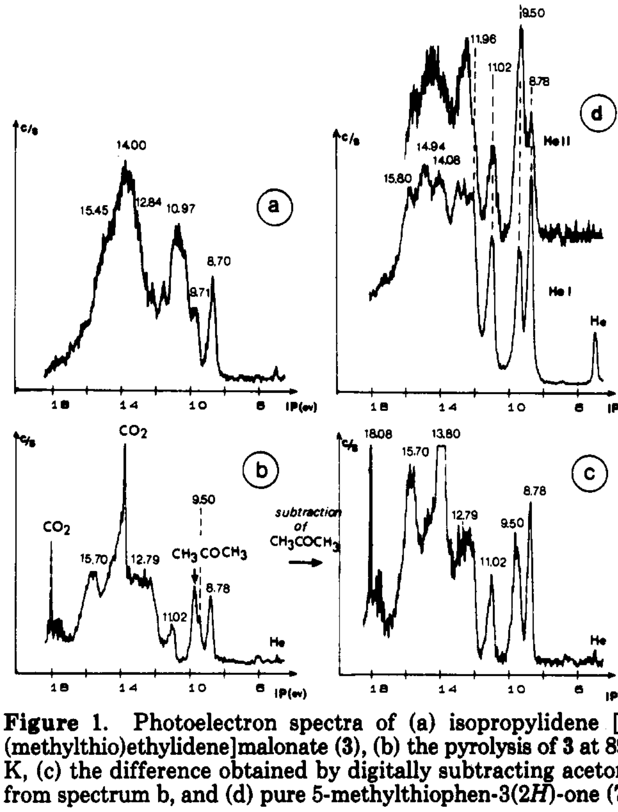


Figure 1. Photoelectron spectra of (a) isopropylidene [1-(methylthio)ethylidene]malonate (3), (b) the pyrolysis of 3 at 893 K, (c) the difference obtained by digitally subtracting acetone from spectrum b, and (d) pure 5-methylthiophen-3(2*H*)-one (7).

The flash vacuum pyrolysis of the alkylthio Meldrum's acid derivatives is monitored "in situ" by photoelectron spectroscopy: the compounds are pyrolyzed in the ionization chamber of the spectrometer (short path pyrolysis: SPP). See ref 8 for a detailed description of the apparatus.

When submitted to SPP, alkylthio compounds 3 and 5 begin to split off acetone and CO_2 at 673 K and the re-

---

[1] Application of Photoelectron Spectroscopy to Molecular Properties. 45. Part 44: Lacombe, S.; Pfister-Guillouzo, G.; Guillemin, J. C.; Denis, J. M. *J. Chem. Soc., Chem. Commun.*, in press.

[2] Mohmand, S.; Hirabayaschi, T.; Bock, H. *Chem. Ber.* **1981**, *114*, 2609.

[3] Ben Cheikh, A.; Dhimane, H.; Pommelet, J. C.; Chuche, J. *Tetrahedron Lett.* **1988**, *29*, 5919.

[4] Chuburu, F.; Lacombe, S.; Pfister-Guillouzo, G.; Ben Cheikh, A.; Chuche, J.; Pommelet, J. C. *J. Am. Chem. Soc.*, submitted for publication.

[5] Hunter, G. A.; McNab, H. *J. Chem. Soc., Chem. Commun.* **1990**, 375.

[6] McNab, H.; Monahan, L. C. *J. Chem. Soc., Perkin Trans. 1* **1988**, 863, 869.

[7] (a) Bock, H.; Solouki, B. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 427. (b) Bock, H. *Phosphorus, Sulfur Silicon Relat. Elem.* **1990**, *49–50*, 3. (c) Westwood, N. P. C. *Chem. Soc. Rev.* **1989**, *18*, 317–343. (d) Schulz, R.; Schweig, A. In *Structure and Reactivity*; Libman, J. F., Ed.; VCH: New York, 1988; Chapter 8.

[8] Vallee, Y.; Ripoll, J. L.; Lacombe, S.; Pfister-Guillouzo, G. *J. Chem. Res. Synop.* **1990**, 40; *J. Chem. Res., Miniprint* 401.

0022-3263/91/1956-3445$02.50/0 © 1991 American Chemical Society