indication for the existence of a second conformer was obtained from the matrix spectra.

Recently, Hawkins and Andrews[2] reported the observation of vibrational transitions of vinyl alcohol produced in reactions of oxygen atoms with ethylene in an argon matrix after UV irradiation. The analysis of their spectra was less complete since more products were formed simultaneously and the transitions of vinyl alcohol were weaker than in our investigation. Our results confirm their observations and assignments of strong transitions. They observed additional absorption lines in regions of strong transitions which were not present in our spectra. They might be due to increased site splittings in the matrix after the photolytic reactions or indicate interactions between vinyl alcohol and other products.

The normal coordinate analysis produced the first rather complete GVFF of a simple enol compound. Comparison with force constants of molecules with analogous partial structures revealed some characteristic features of the GVFF of *syn*-vinyl alcohol. The partial double bond character of the C—O bond arising from the interaction of the lone pairs at the oxygen with the C=C double bond is reflected in the large C—O stretching force constant of 6.14 mdyn/Å. Formic acid which is isoelectronic with vinyl alcohol shows a similar increase of the C—O stretching force constant of 6.1–6.23 mdyn/Å[17] compared to methanol with 5.27–5.28 mdyn/Å.[13b,18] The increase of the C—O stretching force is also reflected in the decrease of the C—O bond length going from methanol to vinyl alcohol.[3] The partial double bond character of the C—O bond is further demonstrated by the increase of the frequency of OH torsion in vinyl alcohol with respect to methanol (413 vs. 271 cm^{-1}). The corresponding force constant of 0.073 mdyn Å in vinyl alcohol is almost tripled compared to 0.027 mdyn Å in methanol.[13b,18]

Acknowledgment. Financial support by the Swiss National Science Foundation (project No. 2.407-0.82) is gratefully acknowledged. We thank Dr. R. Gunde for his advice. We are indepted to Mr. G. Grassi for his help with some of the isotopic syntheses. The computer center at ETH Zurich granted free computer time.

Registry No. $H_2C{=}CHOH$, 557-75-5; $H_2C{=}CH^{18}OH$, 90134-15-9; $H_2C{=}CHOD$, 64066-40-6; $H_2C{=}CDOH$, 90134-16-0; $D_2C{=}CHOH$, 90134-17-1; (*E*)-HDC=CHOH, 90134-18-2; (*Z*)-HDC=CHOH, 90134-19-3; $D_2C{=}CDOH$, 90134-20-6; (*E*)-HDC=CDOH, 90134-21-7; (*Z*)-HDC=CDOH, 90134-22-8.

---

[17] (a) Davis, R. W.; Robiette, A. G.; Gerry, M. C. L.; Bjarnov, E.; Winnewisser, G. *J. Mol. Spectrosc.* **1980**, *81*, 93. (b) Ha, T. K.; Meyer, R.; Günthard, Hs. H. *Chem. Phys. Lett.* **1978**, *59*, 17.

[18] (a) Serrallach, A.; Meyer, R.; Günthard, Hs. H. *J. Mol. Spectrosc.* **1974**, *52*, 94. (b) Mallinson, P. D. *Ibid.* **1975**, *58*, 194.

Communications to the Editor

Reaction of Cyclic Ketene Acetal and Carbon Disulfide through Macrozwitterion

Takeshi Endo*

Research Laboratory of Resources Utilization
Tokyo Institute of Technology
Nagatsuta, Midori-ku, Yokohama 227, Japan

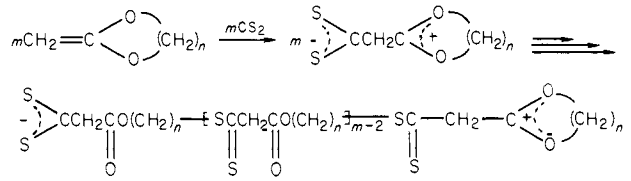
Hiroyuki Fukuda* and Masahiro Hirota

Nagoya Municipal Industrial Research Institute
4-41, Rokuban 3-chome
Atsuta-ku, Nagoya 456, Japan

Received October 26, 1983

It has been reported that ketene *N*,*N*- and *N*,*S*-acetals, which belong to a class of the most electron-rich olefins, react easily with heterocumulenes to give betaines.[1] It is also known that the unsaturated carbon–carbon double bond of ketene acetals is highly polarized and the β-carbon atom has a strong anionoid character because of the electron-donating property or the mesomeric effect of oxygen atom. Therefore, most of ketene acetals are susceptible to attack by the protic substrates and undergo cationic polymerization.[2-3] From a different viewpoint, radical ring-opening polymerizations have been also reported.[4]

It is anticipated that cyclic ketene acetals may react with carbon disulfide to form betaines, which react successively with each other to afford macrozwitterions.



We now report a new reaction of 4-methyl-2-methylene-1,3-dioxolane (I) with carbon disulfide and a structure of the resulting product.

The reaction of I with CS_2 was carried out at 80 °C for 48 h in a glass ampule treated with 3-(triethoxysilyl)propylamine to prevent cationic homopolymerization of I on the glass surface.[5] If the reaction of I with CS_2 proceeds via the zwitterion mechanism, the resulting copolymer should be the alternating structure. However, the elemental analyses indicated that the obtained copolymer consists of I and CS_2 with the ratio of 2:1, contrary to our expectation. Here, we must call attention to the copolymer (composition of I and CS_2; 2:1) containing dithioester structure of malonic acid. It has been reported that the dithioester of cyanomalonic acid exists exclusively as an enthiol form at equilibrium.[6] Therefore, it can be assumed that dithiomalonate formed by the reaction of I with CS_2 tautomerizes to enthiol form, which may react easily with I to give monothio ortho acetate. The IR spectrum of the copolymer showed characteristic absorption bands at 1745 and 1700 cm^{-1} attributable to ester C=O and 1530 cm^{-1} assignable to unsaturated C=C. ^1H NMR spectrum indicated the peaks at 5.90 (s, 1 H), 5.21 (m, 2 H), 3.02–3.40 (br,

---

[1] Gompper, R.; Elser, W. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 366. Gompper, R. *Ibid.* **1969**, *8*, 312.

[2] McElvain, S. M.; Corry, M. J. *J. Am. Chem. Soc.* **1948**, *76*, 3781.

[3] Cho, I.; Song, M. S. *J. Polym. Sci., Polym. Lett. Ed.* **1982**, *20*, 361. Fukuda, H.; Hirota, M.; Nakashima, Y. *Ibid.* **1983**, *21*, 171.

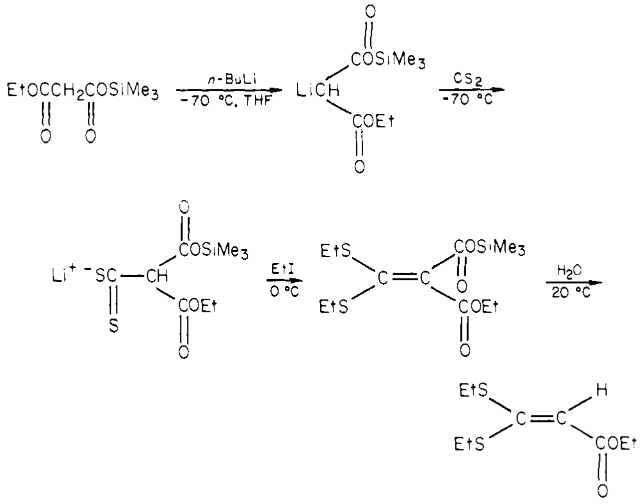
[4] Bailey, W. J.; Ni, Z.; Wu, S. R. *Makromol. Chem.* **1982**, *183*, 1913; *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 3021. Endo, T.; Okawara, M.; Bailey, W. J.; Azuma, K.; Nate, K.; Yokono, H. *J. Polymn. Sci., Polym. Lett. Ed.* **1983**, *21*, 373.

[5] In a 100-mL sealed polymerization tube, 2 g (0.02 mol) of I and 5 g (0.06 mol) of CS_2 were heated at 80 °C for 48 h. After the tube was cooled and opened, the reaction mixture was poured into a large excess of *n*-hexane to precipitate the copolymer. Purification of the copolymer was carried out by the reprecipitation from chloroform to methanol. The precipitated gum-like material was dried under reduced pressure at room temperature for 2 days to give 2.45 g of an orange red copolymer: M_w 11 000 (by GPC); softing point 65–75 °C. Anal. Calcd for $(C_5H_8O_2)_2(CS_2)_1$: C, 47.79; H, 5.85; S, 23.20. Found: C, 47.47; H, 5.91; S, 22.87.

[6] Hartke, K.; Meissner, F. *Tetrahedron* **1972**, *28*, 875.

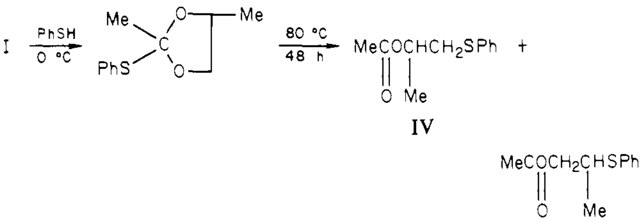
4 H), 2.08 (s, 3 H), and 1.20–1.50 ppm (m, 6 H). The absorption at 5.90 ppm is assignable to olefinic methine proton without any coupling, and the peaks at 5.21 and 3.02–3.40 ppm are due to methine and methylene protones adjacent to oxygen and sulfur atoms, respectively. Further, the peaks at 2.0, and 1.28–1.50 ppm are attributable to the methyl protones of acetate unit and propylene unit, respectively. From these data, P-I should be proposed as the structure of the copolymer.

In order to clarify this assumption, it was carried out to prepare the model compound [ethyl 2,-bis(ethylthio)acrylate (II)[7]] similar to the repeated unit by the following schemes.



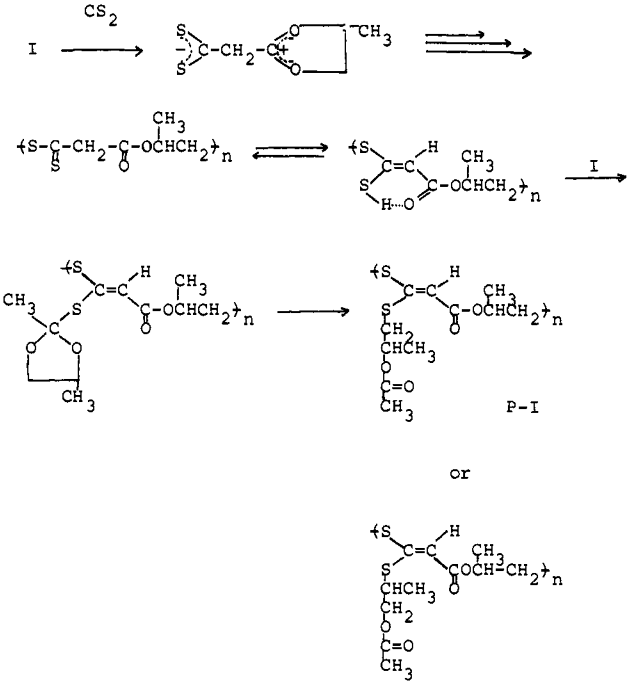
II

The reaction of I with thiophenol was also carried out to find that 2,4-dimethyl-2-(phenylthio)-1,3-dioxolane (III) was produced quantitatively by the equimolar reaction at 0 °C. Furthermore it was ascertained that III underwent the isomerization at 80 °C quantitatively to the mixture of 1-methyl-2-(phenylthio)ethyl acetate (IV) and 2-(phenylthio)propyl acetate (V).[8] The ratio of IV and V was estimated to be 90:10 by the ^{1}H NMR spectrum.



IV

The IR spectra of the mixture of II and IV–V were in good agreement with that of the resulting copolymer (P-I). From these data the plausible mechanism of the reaction of I with CS_2 might be as follows.



We can expect to prepare new compounds or new types of polymers by developing the reactions of cyclic ketene acetals with heterocumulenes such as carbon dioxide, isocyanates, isothiocyanates, carbodiimides, etc. on the basis of this reaction.

Registry No. I, 85079-89-6; II, 18224-54-9; III, 90369-21-4; IV, 32300-28-0; V, 32300-63-3; (I)·(CS_2) (copolymer), 90369-22-5; CS_2, 75-15-0; EtI, 75-03-6; PhSH, 108-98-5; $EtO_2CCHLiCO_2SiMe_3$, 49775-36-2.

---

[7] To a solution of 20 mL of tetrahydrofuran containing 4.1 g (0.02 mol) of ethyl trimethylsilyl malonate, prepared by the reaction of monoethyl malonate and trimethylsilyl chloride, 15 mL of *n*-butyllithium in hexane (1.6 mmol/mL) was added dropwise at −70 °C, and the mixture was left at −70 °C for 10 min. After 2.3 g (0.03 mol) of CS_2 was added dropwise to the solution at −70 °C, 6.2 g (0.04 mol) of ethyliodide was added to the mixture. After reaction mixture was allowed to warm to 0 °C overnight, 50 mL of water was added, and the solvent was removed by a rotary evaporator. The residue was poured into 100 mL of water and the organic layer was extracted with ether 3 times. After the etheral solution was dried over magnesium sulfate, the solvent was removed and the residue was distilled under reduced pressure to give 2.52 g (57%) of II; bp 124–125 °C (4 mmHg); ^{1}H NMR (100 MHz, $CDCl_3$) δ 1.20–1.48 (3 t, 9 H, CH_3), 2.85–3.20 (2 q, 4 H, SCH_2), 4.25 (q, 2 H, OCH_2), 5.78 (s, 1 H, C=CH). Anal. Calcd for $C_9H_{16}O_2S_2$: C, 49.05; H, 7.33; S, 29.10. Found: C, 48.90; H, 7.62; S, 29.20.

[8] To a mixture of 1.1 g (0.01 mol) of thiophenol and 5 mL of carbon tetrachloride 1.0 g (0.01 mol) of I was added dropwise at 0 °C. A portion of the reaction mixture was poured into a NMR tube, and then NMR measurement was carried out to find that 2,4-dimethyl-2-(phenylthio)-1,3-dioxolane (III) was obtained quantitatively. After the solvent was removed by using a rotary evaporator, the oily residue was heated at 80 °C for 48 h and then distilled under reduced pressure to give 1.92 g (87%) of 1-methyl-2-(phenylthio)ethyl acetate (IV) containing 10% of 2-(phenylthio)propyl acetate (V): bp 109–111 °C (3 mmHg); ^{1}H NMR (100 MHz, $CDCl_3$) δ 1.50 (d, 3 H, CH_3), 1.96 (s, 3 H, CH_3CO), 2.90–3.20 (m, 2 H, SCH_2), 5.10 (m, 1 H, OCH), 7.40–7.70 (m, 5 H, Ar H's). Anal. Calcd for $C_{11}H_{14}O_2S$: C, 62.81; H, 6.72; S, 15.25. Found: C, 62.80; H, 6.78, S, 15.21.

Multisite Kinetics by Quantitative Two-Dimensional NMR

Charles L. Perrin* and Robert K. Gipe

Department of Chemistry, D-006
University of California, San Diego
La Jolla, California 92093

Received October 17, 1983

Two-dimensional NMR[1] is a promising technique for kinetics,[2] especially in multisite systems. Previous applications[3,4] have been qualitative, designed to display exchange pathways. Quantitative application has been limited, owing to the use of absolute-value transforms to produce suitable peak shapes. We now report that rate constants can be evaluated from two-dimensional NMR spectra obtained with a program of phase cycling[5] that produces

---

[1] McFarlane, W.; Rycroft, D. S. *Nucl. Magn. Reson.* **1982**, *11*, 157; **1983**, *12*, 158.

[2] Jeener, J.; Meier, B. H.; Bachman, P.; Ernst, R. R. *J. Chem. Phys.* **1979**, *71*, 4546.

[3] Meier, B. H.; Ernst, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 6441. Huang, Y.; Macura, S.; Ernst, R. R. *Ibid.* **1981**, *103*, 5327.

[4] Cutnell, J. D. *J. Am. Chem. Soc.* **1982**, *104*, 362. Schwartz, A. L.; Cutnell, J. D. *J. Magn. Reson.* **1983**, *53*, 398. Szeverenyi, N. M.; Bax, A.; Maciel, G. E. *J. Am. Chem. Soc.* **1983**, *105*, 2579.

[5] States, D. J.; Haberkorn, R. A; Ruben, D. J. *J. Magn. Reson.* **1982**, *48*, 286.

0002-7863/84/1506-4036$01.50/0