and structure study of the polymolybdate species in I is of considerable interest in view of recent discussions about the structure of related heteropoly and isopoly anions.[5–7]

Acknowledgments. We thank the donors of the Petroleum Research Fund administered by the American Chemical Society for the support of part of this work.

(6) M. T. Pope, *Inorg. Chem.*, **11**, 1973 (1972).
(7) H. T. Evans, *Perspect. Struct. Chem.*, **4**, 1 (1971).

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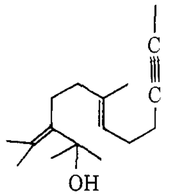
Acetylenic Bond Participation in Biogenetic-Like Olefinic Cyclizations.[1] Wagner–Meerwein Rearrangement of a Linear to a Bent Vinyl Cation

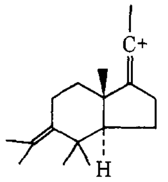
Sir:

Recently we discovered that the diolefinic acetylenic alcohol I undergoes a facile, acid-catalyzed, stereospecific cyclization to produce the bicyclic vinyl cation II which can be captured by various nucleophiles, *i.e.*, formic acid, acetonitrile, and an olefinic bond (supplied intramolecularly in a modification of I where the acetylenic methyl is replaced by an alkenyl side chain).[2,3]

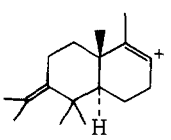
It is noteworthy that a vinyl cation can actually be produced efficiently under extremely mild conditions (see below) from a relatively stable ditertiary allylic cation, the energy being provided by the conversion of π to σ bonds.



I

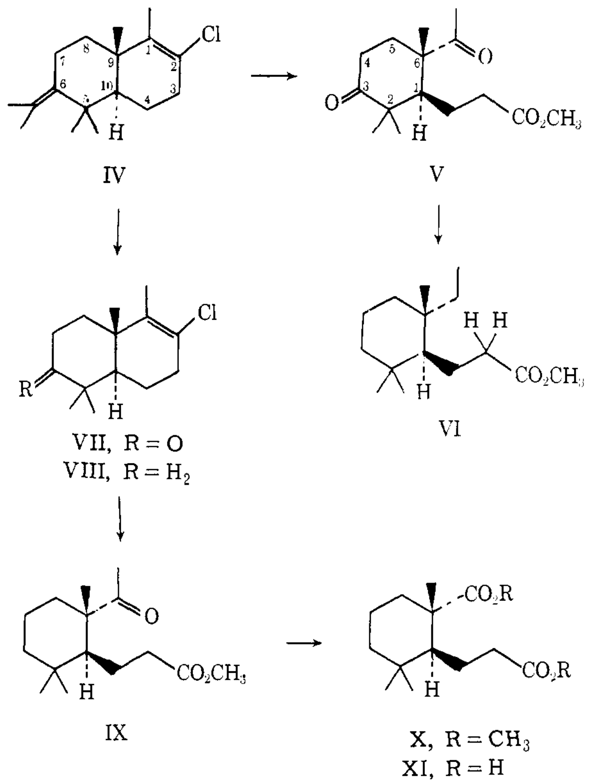


II



III

In the present communication we are concerned with the question of the fate of the vinyl cation II in the absence of a good nucleophile. A solution of 0.67 mmol of dienynol I in 50 ml of methylene chloride (under nitrogen) was cooled to −78°; then 0.5 ml of trifluoroacetic acid was added with vigorous stirring.[4] After 20 min at −78°, the mixture was poured into excess aqueous sodium bicarbonate. The product, isolated in 66% yield by tlc on silica gel (10% ethyl acetate in hexane), proved to be the chlorodiene IV. Bulb-to-bulb distillation gave a low-melting crystalline product (*Anal.* Found: C, 76.8; H, 10.25; Cl, 13.1): mass spectrum m/e 266, M^+; nmr[5] 0.95 (3 H, s), 1.12 (3 H, s), and 1.20 (3 H, s), methyls at C-5 and C-9, 1.66 (3 H, s) and 1.80 (3 H, s), methyls of isopropylidene group, 1.68 (3 H, s), methyl at C-1. The chlorodiene IV, which evidently is derived from the vinyl cation III, appeared to be homogeneous by vpc and tlc, and it contained at most (see below) very small proportions of that isomer derived from the unrearranged cation II and that derived from the cation of alternative rearrangement (*i.e.*, formula III in which the + charge and the adjacent methyl are interchanged).



Proof of the structure and isomeric purity of the chlorodiene IV was obtained as follows. Exhaustive ozonization in 1:3 methanol–ethyl acetate at −78° followed by treatment with dimethyl sulfide gave, after preparative tlc (50% ethyl acetate in hexane), a 40% yield of the diketo ester V. (There was no evidence by tlc or vpc for the presence of *trans*-4,4,8-trimethylhydrindan-1,5-dione,[2] which would have been produced from the chlorodiene arising from cation II.) Bulb-to-bulb distillation at 105° (0.07 mm) afforded an oil (*Anal.* Found: C, 67.1; H, 8.9): nmr[5] 1.13 (6 H, s), methyls at C-2, 1.3 (3 H, s), methyl at C-6, 2.22 (3 H, s), ketone methyl 3.66 (3 H, s), ester methyl. Wolff–Kishner reduction of the diketo ester V by the Huang-Minlon method, followed by esterification with diazomethane and preparative tlc (5% ethyl acetate in hexane), gave the ester VI in 31% yield. Bulb-to-bulb distillation at 65° (0.01 mm) afforded an oil (*Anal.* Found: C, 75.2; H, 11.6): mass spectrum m/e 240, M^+; nmr[5] 0.82 (3 H, s), methyl at C-6, 0.87 (3 H, s) and 0.88 (3 H, s), methyls at C-2, 2.23–2.53 (2 H, m), hydrogens α to carbomethoxy group, 3.68 (3 H, s), ester methyl.

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(1) For the previous paper of this series, see W. S. Johnson, M. B. Gravestock, and B. E. McCarry, *J. Amer. Chem. Soc.*, **93**, 4332 (1971). For the previous paper of the series on Nonenzymic Biogenetic-Like Olefinic Cyclizations, see G. D. Abrams, W. R. Bartlett, V. A. Fung, and W. S. Johnson, *Bioorg. Chem.*, **1**, 243 (1971).

(2) W. S. Johnson, M. B. Gravestock, R. J. Parry, R. F. Myers, T. A. Bryson, and D. H. Miles, *J. Amer. Chem. Soc.*, **93**, 4330 (1971).

(3) We appreciate the possibility that the process may be concerted, in which case the transition state may be regarded as having some degree of vinyl cationic character.

(4) Under these conditions the trifluoroacetic acid is sparingly soluble and is largely out of solution, in the solid phase.

(5) The nmr spectra (60 MHz, TMS internal standard, $CDCl_3$ solvent) are recorded in δ values (ppm). Only absorptions of special significance are recorded here.

Had the skeletal rearrangement during the cyclization occurred in the opposite sense to give the isomer of IV in which the groups at C-1 and C-2 are interchanged, the substance resulting from the aforementioned transformations would be an isomer of the ester VI in which the carbomethoxy group and the ethyl (at C-6) are interchanged. This isomer would have no hydrogens α to the carbomethoxy group. The presence of two such α hydrogens in the substance at hand (see nmr above) was confirmed by a deuterium exchange experiment (treatment for 10 hr at 25° with sodium dissolved in methanol-d_1). Partial exchange was observed by significant diminution of the intensity of the nmr signal at 2.23–2.53.

The configuration of the ring fusion of the chlorodiene IV was proved to be trans as follows. Selective ozonization, using a Rubin ozonizer, with 0.95 mol equiv of ozone in methylene chloride at $-78°$, followed by treatment with dimethyl sulfide and then preparative tlc (10% ethyl acetate in hexane), gave a 72% yield of the ketone VII which crystallized on standing. Bulb-to-bulb distillation at 75° (0.02 mm) afforded colorless, low-melting crystals (*Anal.* Found: C, 70.1; H, 8.8; Cl, 14.7): nmr[5] 1.05 (3 H, s), and 1.11 (6 H, s), methyls at C-9 and C-5, 1.75 (3 H, t, $J = 1$ Hz), methyl at C-1. Wolff–Kishner reduction of the ketone VII by the Huang–Minlon modification[6] gave, after preparative tlc (10% ethyl acetate in hexane), a 57% yield of the chloro olefin VIII. Bulb-to-bulb distillation at 78° (0.04 mm) gave an oil (*Anal.* Found: C, 74.2; H, 10.1; Cl, 15.4): mass spectrum m/e 226, M$^+$; nmr[5] 0.83 (3 H, s), 1.03 (3 H, s), and 1.16 (3 H, s), methyls at C-5 and C-9, 1.70 (3 H, t, $J = 1$ Hz), methyl at C-1. A solution of the chloro olefin VIII in 2:1 ethyl acetate–methanol was treated with excess ozone at $-78°$ and then with dimethyl sulfide. Preparative tlc (20% ethyl acetate in hexane) gave (78% yield) the keto ester IX. Bulb-to-bulb distillation at 105° (0.01 mm) afforded an oil (*Anal.* Found: C, 70.95; H, 10.1): mass spectrum m/e 254, M$^+$; nmr[5] 0.93 (6 H, s), methyls at C-2, 1.20 (3 H, s), methyl at C-6, 2.14 (3 H, s), ketone methyl, 3.64 (3 H, s), ester methyl. The ester IX was saponified with aqueous methanolic sodium hydroxide and the resulting crude keto acid (0.54 mmol) was oxidized with sodium hypobromite (7.7 mmol) in aqueous alkaline solution (6.5 hr, 0°). Treatment of the product with diazomethane, followed by preparative tlc (10% ethyl acetate in hexane), gave the diester X in 43% yield. Bulb-to-bulb distillation at 125° (0.01 mm) afforded an oil (*Anal.* Found: C, 66.4; H, 9.5): mass spectrum m/e 270, M$^+$. Saponification of the diester X with aqueous methanolic sodium hydroxide gave the crystalline diacid XI which on three recrystallizations from ether–hexane melted at 106–109°, undepressed on admixture with authentic material: mp 107–110°[7] (*Anal.* Found: C, 64.3; H, 9.0); mass spectrum m/e 242, M$^+$. The nmr[5] spectrum of the diester X was identical with that of an authentic specimen prepared from the aforementioned authentic diacid. The vpc behavior (coinjection) of these two diester specimens was also identical.

Since the cyclization of the carbinol I evidently proceeds so as to give, as the primary product, the 6/5 fused ring vinyl cation II which is readily trapped by ordinary nucleophiles (see above), the formation of the chlorodiene IV may be rationalized as follows. The vinyl cation II is first formed but, in the absence of a good nucleophile, it undergoes an equilibration, *via* a Wagner–Meerwein shift,[8] with the 6/6 fused ring cation III which, in a relatively slow process, abstracts chloride ion from the solvent (CH_2Cl_2).[9] Evidence from solvolysis experiments supports the view that vinyl cations like II and III, but lacking the fused A ring, "do not differ much in stability."[8] In the present case, the relief of torsional strain in the conversion of a 6/5 to a 6/6 trans-fused ring system could be a factor in determining the course of the reaction.

Acknowledgment. We are indebted to the National Institutes of Health and the National Science Foundation for support of this research.

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(6) The hydrazone formation was conducted at 0° for 12 hr in order to minimize the total heating period and concomitant loss of halogen.

(7) Prepared by Wolff–Kishner reduction of the keto diester **9** of ref 2.

(8) Products of similar rearrangements have been observed with vinyl cations generated by solvolysis of vinyl triflates. See, for example, W. D. Pfeifer, C. A. Bahn, P. v. R. Schleyer, S. Bocher, C. E. Harding, K. Hummel, M. Hanack, and P. J. Stang, *J. Amer. Chem. Soc.*, **93**, 1513 (1971).

(9) *Cf.* E. H. White, H. P. Tiwari, and M. J. Todd, *ibid.*, **90**, 4734 (1968), for the abstraction of chloride ion from methylene chloride by the 1-norbornyl cation.

(10) NIH Postdoctoral Fellow.

(11) Rockefeller Foundation Fellow.

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Raman Depolarization Ratio and Short-Range Order in Liquid Crystals

Sir:

Laser Raman scattering was recently used to investigate the phase transitions in liquid crystals.[1–3] It was found that significant Raman spectral changes occur only in the solid nematic phase transition and not in the nematic liquid transition. The result, consistently with the observation of a very small change of latent heat associated with the nematic liquid phase transition,[4] suggests that Raman spectra of the nematic and isotropic liquid phases are primarily affected by short-range order.

Despite the small change in the intermolecular potential, molecular motions in the nematic and isotropic liquid phases are different. In the nematic phase, only the reorientation around the molecular long axis is possible, whereas in the isotropic phase, reorientation around the short axis is also permitted. As a result, we expect that the depolarization ratio rather than the total scattering intensity should reflect the change of short-range order as the phase transition occurs, but no previous Raman study of the liquid crystals has considered the measurement of the depolarization ratio. Because of this neglect, the reorientational information that Raman scattering can be used to disclose has been overlooked. We report new results on

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(1) N. M. Amer, Y. R. Shen, and H. Rosen, *Phys. Rev. Lett.*, **24**, 718 (1970).

(2) B. J. Bulkin and F. T. Prochaska, *J. Chem. Phys.*, **54**, 635 (1971).

(3) N. M. Amer and Y. R. Shen, *ibid.*, **56**, 2654 (1972).

(4) See, *e.g.*, A. Saupe, *Angew. Chem., Int. Ed. Engl.*, **7**, 97 (1968).