on Varian Associates A-60, A-60D, and T-60 spectrometers with tetra-
methylsilane as internal standard. Data are reported in parts per million
(δ) from Me₄Si. Infrared spectra were obtained from Perkin-Elmer 137
or 247 spectrophotometers. Mass spectra were measured on an LKB 9
combined GLC–mass spectrometer by direct insertion. Analyses were
conducted by Galbraith Laboratories, Inc., Knoxville, Tenn.

(12) This heating was not necessary for the formation of 2, but was done in
an effort to achieve cyclodehydration.
(13) M. Stiles, J. Am. Chem. Soc., 81, 2598 (1959).
(14) This was done in an effort to isolate a methyl ester of carboxylated ma-
terial.
(15) This was done in an effort to isolate intermediate acid.

Isolation of a Cyclopropene from Dehydrochlorination of a gem-Dichlorocyclopropane

W. E. Billups,[*1] John H. Cross, and Andrew J. Blakeney

Department of Chemistry, Rice University, Houston, Texas 77001
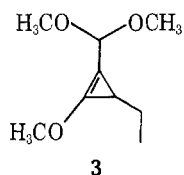
Received June 3, 1974

Although the direct observation of cyclopropenes from dehydrochlorination of chlorocyclopropanes has been reported,[2] usually isomerization products[3] or adducts with nucleophiles[4] are obtained. We report here an unusual example of cyclopropene formation from dehydrochlorination which we observed while attempting to prepare 1, a potentially interesting receptor of singlet oxygen.[5]

Thus addition of KO-t-Bu (2.36 equiv) in dimethyl sulfoxide (DMSO) to a solution of 2 (eq 1) in DMSO did not
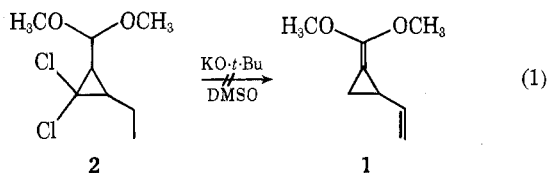
give the expected 1; however, the reaction was reproducible and gave a single major product (decomposition occurred on GLC columns) whose NMR, ir, and mass spectrum allowed assignment of structure 3. The mass spectrum re-

vealed the absence of chlorine and showed a parent ion at m/e 172. The NMR spectrum showed methoxyl signals at δ 3.27, 3.37, and 3.92. The dimethyl acetal proton appeared as a singlet at δ 5.1, in good agreement with the one at δ 5.0 in cis-2-pentenal dimethyl acetal. A triplet at δ 0.9 (3 H) and a multiplet at δ 1.4 (2 H) showed that the ethyl group was undisturbed. A strong, broad ir band at 1880 cm⁻¹ was so unusual that it was relatively simple to assign it to the C=C stretch of a disubstituted cyclopropene.[6] These data and the absence of olefinic protons in the NMR spectrum showed that the ethyl, dimethyl acetal, and methoxyl were bound to different cyclopropene carbons. The collapse of the triplet at δ 2.25 upon irradiation of the methylene group identified the methine carbon of the cyclopropene.

A plausible mechanism for the formation of 3 is shown in Scheme I. The failure of product 3 (or 4) to undergo double-bond isomerization[3] to the exocyclic position is unprecedented; we conclude, on the basis of a study by Davis and Brown,[7] that the cause was steric hindrance of the approach of t-BuO⁻ to the acetal methine proton.

Scheme I
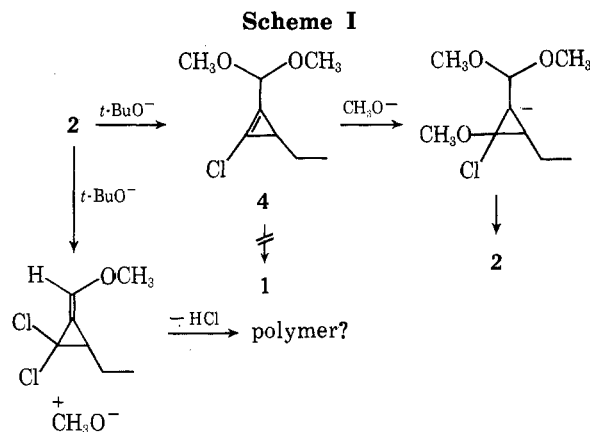
Experimental Section

Infrared spectra were run on a Beckman IR-8 instrument and NMR spectra were recorded on a Varian A-56/60 spectrometer. The mass specta were recorded on a CEC 21-110B instrument. All reactions were conducted in a nitrogen atmosphere.

cis-2-Pentenal Dimethyl Acetal (5). Ethylmagnesium bromide (2 mol) in THF was prepared by the method of Skattebøl, Jones, and Whiting.[8] The flask was then equipped with a Dry Ice–acetone condenser and 1-butyne (Farchan Research Laboratories, 100 g, 1.85 mol) was added dropwise over a 7-hr period at 25° with evolution of ethane. The solution was allowed to stand for 15 hr and trimethyl orthoformate (244 g, 2.3 mol) was added. The resulting brown transparent solution was heated with stirring to about 50° for 5 days and then 1 l. of THF was removed by distillation. CuCl (1%) was then added and the reaction mixture was refluxed for 11 hr. The remaining THF was distilled until the stillhead temperature reached 95°. The black reaction mixture was cooled and diluted with 500 ml of ether and the magnesium salts were filtered and washed with an additional 50 ml of ether. A 38% solution of NH₄Cl was used to destroy any remaining Grignard. The ethereal solution was decanted, dried through a cone of MgSO₄, and stored over Na₂SO₄. Distillation provided 122.4 g (50%) of alkyne, bp 77–78° (47 mm).

Reduction to the olefin was carried out as follows. The alkyne (40 g, 0.312 mols), quinoline (800 mg, 2% by wt), 5% Pd/CaCO₃ (800 mg, 2% by wt), and 200 ml of pentane were shaken in a Parr apparatus under H₂ (5 lb) until 1 equiv was absorbed. The product was then filtered through Celite and the pentane removed in vacuo. The light-yellow product, containing the quinoline, weighed 40.8 g (99% yield). GLC on a 10 ft × 0.25 in. 10% Apiezon J on 80–100 mesh Chromosorb W (acid washed) column at 100° showed only a single peak. Spectra: NMR δ 9.0 (t, J = 7 Hz, 3 H), 2.15 (quintet, J = 7 Hz, 2 H), 3.2 (s, 6 H), 5.0 (d, J = 5 Hz, 1 H), 5.15–5.9 (m, 2 H); ir 3040, 2830, 1665, 1190, 1112, and 1050 cm⁻¹. Spectral properties match reported values.[9]

cis-2,2-Dichloro-3-ethylcyclopropanecarboxaldehyde Dimethyl Acetal (2). The olefin 5 (40.8 g, 0.314 mol, 1 equiv) and ethanol-free CHCl₃ (94 g, 0.785 mol, 0.015 equiv) were stirred rapidly in a 1-l. Morton flask, after which 50% aqueous NaOH was added. The reaction mixture quickly warmed to 60° and turned black. More NaOH was added when the reaction mixture had cooled to 50° until a total of 110 g (1.37 mol, 4.38 equiv) was added. When the reaction mixture had cooled to 45°, about 2 hr, it was poured into a separatory funnel and extracted with ether, and the ethereal solution was washed three times with water. The ethereal solution was then washed with saturated sodium chloride solution and dried over sodium sulfate. After removal of pentane in vacuo, distillation afforded first a reaction weighing 10.5 g, bp 50° (40 mm), followed by 2, bp 60° (4 mm) (12.9 g, 19.3%). The product gave a single GC peak on the Apiezon J column described above. Spectra: NMR δ 1.09 (t, J = 5 Hz, 3 H), 1.3–1.9 (m, 4 H), 3.27 (s, 3 H), 3.37 (s, 3 H), 4.18 (d, J = 7 Hz, 1 H); ir 2980, 1450, 1195, 1142, 1110, 1065, and 810 cm⁻¹. The mass spectrum had no parent ion but showed peaks at m/e 211 (M − 1) and 181 (M − OCH₃); exact m/e calcd for C₇H₁₁OCl₂ (M − OCH₃), 181.0186; found, 181.0188.

2-Methoxy-3-ethylcycloprop-1-enecarboxaldehyde Dimethyl Acetal (3). The cyclopropane 2 (1 g, 4.96 mmol, 1 equiv) and DMSO (7 ml) were placed in a 50-ml flask equipped with a magnetic stirring bar and pressure-equalizing addition funnel.

KO-*t*-Bu (1.2 g, 10.7 mmol, 2.16 equiv) dissolved in 10 ml of DMSO was then added dropwise over 2.3 hr at 25°. The resulting dark solution was stirred for an additional 1 hr, poured into water, and extracted with pentane. The aqueous layer was saturated with NaCl to break the emulsion. The pentane extracts were washed twice with water and twice with saturated sodium chloride solution. Removal of pentane in vacuo gave nearly pure **3** (330 mg, 38%): mass spectrum parent ion *m/e* 172; exact *m/e* calcd for $C_9H_{16}O_3$, 172.1099; found, 172.1094.

References and Notes

(1) Alfred P. Sloan Foundation Fellow, 1973–1975.
(2) S. W. Tobey and R. West, *Tetrahedron Lett.*, 1179 (1963); T. C. Shields, B. A. Loving, and P. D. Gardner, *Chem. Commun.*, 556 (1967); P. Binger, *Synthesis*, 190 (1974).
(3) W. E. Billups, T. C. Shields, W. Y. Chow, and N. C. Deno, *J. Org. Chem.*, **37**, 3676 (1972), and references cited therein.
(4) T. C. Shields and P. D. Gardner, *J. Am. Chem. Soc.*, **89**, 5425 (1967), and references cited therein.
(5) P. D. Bartlett and A. P. Schaap, *J. Am. Chem. Soc.*, **92**, 3223 (1970); S. Mazur and C. S. Foote, *ibid.*, **92**, 3225 (1970).
(6) D. F. Eggers, J. W. Schultz, K. B. Wiberg, E. L. Wagner, L. M. Jackman, and R. L. Erskine, *J. Chem. Phys.*, **47**, 946 (1967); G. L. Closs, L. E. Closs, and W. A. Böll, *J. Am. Chem. Soc.*, **85**, 3796 (1963).
(7) H. A. Davis and R. K. Brown, *Can. J. Chem.*, **49**, 2321 (1971).
(8) L. Skattebøl, E. R. H. Jones, and M. C. Whiting, "Organic Syntheses", Collect. Vol. IV, Wiley, New York, N.Y., 1963, p 792.
(9) H. Esterbauer and W. Weger, *Monatsh. Chem.*, **98**, 1884 (1967).

Organometallic Chemistry. VI. Carbon-13 Nuclear Magnetic Resonance Spectroscopic Study of α-Ferrocenylcarbenium Ions[1]

George A. Olah* and Gao Liang

*Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106*

Kinetic studies of the solvolysis of α-ferrocenylcarbinyl derivatives and actual isolation of stable salts demonstrate the remarkable stability of α-ferrocenylcarbenium ions.[2] Although extensive work has been done in the past, the nature of ferrocenyl-stabilized carbocations is still under dispute.[3] Carbon-13 nuclear magnetic resonance spectroscopy

provides an understanding of distribution of positive charge in carbocations, in a more quantitative way than does the proton NMR. This is also indicated by several earlier investigations on ferrocenylcarbenium ions.[3,4] Interested in the nature of these ions, we wish to report our further ^{13}C NMR spectroscopic investigation of a series of α-ferrocenylcarbenium ions.

Results and Discussion

Cations 1–4 were prepared in sulfuric acid solution at 0° from their corresponding alcohols.[5] The proton NMR spec-
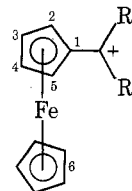
1, $R_1 = R_2 = H$
2, $R_1 = H$; $R_2 = CH_3$
3, $R_1 = R_2 = CH_3$
4, $R_1 = CH_3$; $R_2 = CH_2CH_3$

tra of α-ferrocenylcarbenium ions were in accordance with those previously reported.[6] The carbon-13 NMR spectra of the cations were obtained by the Fourier-transform method. Carbon shifts (δ ^{13}C, in parts per million from external Me_4Si), multiplicities, and coupling constants (J_{CH}, in hertz) are summarized in Table I. The assignments of the carbon resonances were made with the aid of either off-resonance or proton-coupled spectra.

The present results reveal several interesting features of the carbon-13 NMR spectra of α-ferrocenylcarbenium ions. First of all, the carbocationic centers in these ions are unusually shielded, instead of being deshielded as observed in conventional carbenium ions. Secondly, the replacement of a hydrogen atom in primary ion 1 by a methyl group causes about 30 ppm deshielding of the carbenium center. Further replacement of the second hydrogen by a methyl group causes additional deshielding of about 37 ppm. Ethyl substitution causes about 43 ppm deshielding from **3** to **4**. Thirdly, consecutive methylation at carbenium centers from primary to tertiary ions causes slight shielding at C_1, C_2, and C_3, while C_4 (and C_5) and C_6 (cyclopentadienyl carbons) are almost unaffected. A deshielding of 5 ppm at carbons (C_1) adjacent to the carbenium center is observed for substitution of each methyl going from primary to tertiary ions.

It is also interesting to see that C_3 (and C_4) are more deshielded than the carbenium center (C^+) in the primary

Table I
Carbon-13 NMR Parameters of α-Ferrocenylcarbenium Ions in Sulfuric Acid Solution[a]

Ion	C^+	C_1	C_2	C_3	C_4	C_5	C_6	Δ_1[b]	Δ_2[b]
1	87.8	110.6	84.8	94.5	94.5	84.8	82.4	+22.8	9.7
	(t, 168.9)	(s)	(d, 188.0)	(d, 183.7)	(d, 183.7)	(d, 188.0)	(dt, 184.1, 6.0)		
2[c]	117.9	105.6	81.0[d]	93.9[d]	94.2[d]	81.8[d]	82.3	−12.3	11.9
	(d, 164.9)	(s)	(d, 187.6)	(d, 183.0)	(d, 183.0)	(d, 190.0)	(dt, 182.9, 6.0)		
3[e]	155.1	100.1	78.3	93.6	93.6	78.3	82.2	−55.0	15.3
	(s)	(s)	(dd, 187.5, 5.0)	(d, 185.0)	(d, 185.0)	(as C_2)	(dt, 180.0, 6.0)		
4[f]	160.6	100.3	78.9[d]	93.8[d]	94.0[d]	78.4[d]	82.2	−60.3	15.1
	(s)	(s)	(d, 178.2)	(d, 183.3)	(d, 183.3)	(d, 180.9)	(dt, 182.5, 6.0)		

[a] Carbon shifts (δ ^{13}C) are in parts per million from external Me_4Si (capillary). Multiplicities and coupling constants (J_{CH}, in hertz) are given in parentheses: d, doublet; dt, doublet of triplets; t, triplet; dd, doublet of doublets; s, singlet; and q, quartet. [b] $\Delta_1 = \delta$ $^{13}C_1 - \delta$ $^{13}C^+$, $\Delta_2 = \delta$ $^{13}C_3 - \delta$ $^{13}C_2$. [c] $\delta_{CH_3} = 19.8$ (q, 129.8). [d] Interchangeable values. [e] $\delta_{CH_3} = 26.6$ (q, 127.5). [f] $\delta_{CH_3} = 25.7$ (q, 129.5), $\delta_{CH_3} = 16.6$ (q, 129.1), and $\delta_{CH_2} = 35.9$ (t, 131.0).