enthalpy and entropy, respectively. The negative activation entropy indicates that the rate-determining step involves formation of either **3** or **7**.

Uncertainties in the interpretation of solvent effects make it impossible to rule out **7** as an intermediate in the alkyl isocyanate reactions. At least two cases exist in which the formation of a polar intermediate from less polar reactants will not be reflected in solvent effects. A reaction which proceeds through an electronically early transition state which does not reflect the character of the intermediate will be solvent insensitive.[9] A more likely consideration for the alkyl isocyanate reactions is the possibility of offsetting solvent effects in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$,[10] a point which is difficult to probe because of the stringent requirements on the precision of the rate constants.[11] The probability that the measured rate constants contain contributions from partitioning of **7** between starting materials and **3** has been discussed by Huisgen.[12]

Experimental Section

Spectra were obtained from the following instruments: IR, Beckman IR20; NMR, Hitachi Perkin-Elmer R-20; MS, DuPont Instruments 21-491. Melting points and boiling points are uncorrected.

***N,N*-Diethyl-2-methyl-3-(alkylimino)-2-propenamides 4a–c.** A solution of 0.03 mol of isocyanate and 0.03 mol of diethylamino-1-propyne in 50 mL of dry carbon tetrachloride or benzene was allowed to stand 3–5 days under nitrogen at room temperature. After concentration under reduced pressure, the residue was distilled.

From methyl isocyanate **4a** was obtained in 78% yield: bp 73–6 °C (0.3 mm) [lit.[3b] bp 70 °C (0.2 mm)]; IR (CCl_4) 2010, 1615 cm^{-1}; NMR (CCl_4) δ 1.10 (t, 6 H), 1.73 (s, 3 H), 3.21 and 3.31 (overlapping s and q, 7 H).

From ethyl isocyanate **4b** was obtained in 67% yield: bp 67–9 °C (0.3 mm); IR (CCl_4) 2010, 1615 cm^{-1}; NMR (CCl_4) δ 1.09 and 1.27 (overlapping triplets, 9 H), 1.73 (s, 3 H), 3.30 and 3.47 (overlapping quartets, 6 H); mass spectrum, *m/e* 81 (B), 109, 167, 182. Anal. Calcd for $C_{10}H_{18}N_2O$: C, 65.90; H, 9.95; N, 15.37. Found: C, 65.67; H, 9.90; N, 15.39.

From *n*-butyl isocyanate **4c** was obtained in 51% yield: bp 89–91 °C (0.3 mm); IR (CCl_4) 2010, 1615 cm^{-1}; NMR (CCl_4) δ 1.10 (t, 3 H), 0.9–1.7 (m, 10 H), 1.72 (s, 3 H), 3.29 and 3.42 (overlapping q and t, 6 H). Anal. Calcd for $C_{12}H_{22}N_2O$: N, 13.32. Found: N, 13.25.

***N,N*-Diethyl-2-methyl-3-(2,6-dimethylphenylimino)-2-propenamide (4d).** To a solution of 2.94 g (0.02 mol) of 2,6-dimethylphenyl isocyanate in 10 mL of acetonitrile under nitrogen and in a room-temperature water bath was added a solution of 2.72 g (0.02 mol) of diethylamino-1-propyne in 10 mL of acetonitrile dropwise with stirring over 20 min. The resulting solution was concentrated under reduced pressure at 50 °C. The residue showed only product NMR absorptions. Distillation gave a small forerun of unchanged isocyanate and 1.8 g (35%) of the ketenimine: bp 144–9 °C (0.4 mm); IR (CCl_4) 2015, 1610 cm^{-1}; NMR (CCl_4) δ 1.08 (t, 6 H), 1.90 (s, 3 H), 2.34 (s, 6 H, 3.36 (q, 4 H), 6.93 (s, 3 H). A large pot residue appeared to be polymeric material. Anal. Calcd for $C_{16}H_{22}N_2O$: C, 74.38; H, 8.58; N, 10.84. Found: C, 74.17; H, 8.65; N, 11.02.

***N*-Alkyl-*N′,N′*-diethyl-2-methylpropanediamides 5b and 5c.** The addition of 1.0 g of the ketenimine to 15 mL of cold, 6 M hydrochloric acid resulted in a clear solution which was extracted several times with chloroform. The extracts were dried over anhydrous sodium sulfate and concentrated, and the residue was distilled.

The amide **5b** was obtained in 50% yield: bp 85–90 °C (0.3 mm); IR (CCl_4) 3340, 1675, 1635, 1530 cm^{-1}; NMR (CCl_4) δ 1.07 (t), 1.16 (t), 1.31 (d) all overlapping (12 H), 3.0–3.5 (m, 6 H), 6.9 (broad s, 1 H).

The amide **5c** was obtained in 75% yield as a waxy solid: bp 90–95 °C (0.3 mm); mp 43–5 °C; IR (CCl_4) 3340, 1675, 1632, 1530 cm^{-1}; NMR (CCl_4) δ 0.8–1.6 (m, 16 H), 2.9–3.6 (m, 7 H), 7.2 (broad s, 1 H). Anal. Calcd for $C_{12}H_{24}N_2O_2$: C, 63.12; H, 10.59; N, 12.27. Found: C, 63.32; H, 10.80; N, 12.48.

***N*-(1-Butyl)-*N*-acetyl-*N′,N′*-diethyl-2-methylpropanediamide (6c).** To a solution of 1.6 g (9.5 mmole) of ketenimine **4c** in 10 mL of CCl_4 under nitrogen was added a solution of 0.57 g (9.5 mmol) of anhydrous acetic acid in 5 mL of CCl_4. An exothermic reaction occurred which was complete within an hour. The solution was concentrated and the residue was distilled giving 1.0 g of **4c**: bp 58–60 °C (0.3 mm); IR (CCl_4) 1660 cm^{-1}, unresolved band; NMR (CCl_4) δ 1.03 (t, 6 H), 1.50 (d, 3 H), 1.87 (s, 3H), 2.85 and 2.92 (overlapping s and q, 7 H), 4.13 (q, 1 H). Anal. Calcd for $C_{11}H_{26}N_2O_3$: C, 57.87; H, 8.83; N, 12.27. Found: C, 57.75; H, 8.80; N, 12.38.

Kinetics. Diethylamino-1-propyne was obtained from Columbia Organic Chemicals and redistilled under nitrogen. Methyl isocyanate was redistilled immediately before use. Solvents were reagent grade, redried, and distilled. For 34 °C runs (ambient probe temperature for the thermostated permanent magnet) 0.5 to 1 M solutions of the two reactants were mixed at 34 °C and an aliquot in a NMR sample tube was kept in the probe throughout the entire run. For high- or low-temperature runs, the reaction was carried out in a constant temperature bath (± 0.2 °C) and aliquots were withdrawn periodically. The probe was maintained at the same temperature (± 1 °C) as determined by ethylene glycol or methanol calibration spectra. Integrals were recorded as the average of four sweeps at 60 or 120 Hz sweep widths and 1 Hz/s sweep times. The rf level was kept well below saturation, generally 500 μV. The integrals were reproducible within ±4% and the instrument stability was such as to necessitate no rebalancing of the integration circuit throughout the course of a run. The peaks monitored were those of the C-methyl singlets of the ynamine, ketenimine, and isocyanate. Trial runs indicated that the ketenimine did not react with either the ynamine or the isocyanate under the reaction conditions.

The rate constants reported in Table I are averages of three independent runs. Second-order plots for the reactions in benzene were linear through 75% completion. In other solvents, curvature was noticeable after 50% completion.

Registry No.—**1a**, 624-83-9; **1b**, 109-90-0; **1c**, 111-36-4; **1d**, 28556-81-2; **2**, 4231-35-0; **4a**, 36277-29-9; **4b**, 63815-28-1; **4c**, 63797-98-8; **4d**, 63797-99-9; **5b**, 63798-00-5; **5c**, 63798-01-6; **6c**, 63798-02-7.

References and Notes

(1) Supported by grants from the Research Corporation and the Simmons College Fund for Research.

(2) Deceased.

(3) (a) J. U. Piper, M. B. Allard, and V. Lee, Abstracts, 162nd National Meeting of the American Chemical Society, Washington, D.C., September 1971, ORGN 103; (b) J. Ficini and J. Pouliquen, *Tetrahedron Lett.*, 1139 (1972).

(4) C. L. Stevens and M. E. Munk, *J. Am. Chem. Soc.*, **80**, 4065 (1958).

(5) (a) M. E. Kuehne and P. J. Sheeran, *J. Org. Chem.*, **33**, 4407 (1968); M. E. Kuehne and H. Linde, *ibid.*, **37**, 1846 (1972); (b) H. J. Gais and K. Hafner, *Tetrahedron Lett.*, 5101 (1970); (c) G. J. Mikol, Abstracts, 166th National Meeting of the American Chemical Society, Chicago, Ill., August 1973, ORGN 102.

(6) M. E. Kuehne and H. Linde, *J. Org. Chem.*, **37**, 1846 (1972).

(7) R. Huisgen, *Acc. Chem. Res.*, **10**, 117 (1977).

(8) J. Ficini, *Tetrahedron*, **32**, 1449 (1976).

(9) D. C. Wigfield and B. Lem, *Tetrahedron*, **31**, 9 (1975).

(10) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", Wiley, New York, N.Y., 1963, p 324.

(11) R. C. Petersen, J. H. Markgraf, and S. D. Ross, *J. Am. Chem. Soc.*, **83**, 3819 (1961).

(12) R. Huisgen and G. Steiner, *Tetrahedron Lett.*, 3769 (1973).

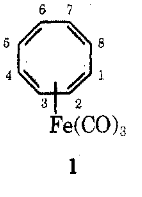
Organometallic Chemistry. 16.[1a] Carbon-13 Nuclear Magnetic Resonance Spectroscopic Structural Investigation of Protonated Cyclooctatetraeneiron Tricarbonyl in Superacid Solution

George A. Olah,*[1b] Gao Liang, and Simon Yu

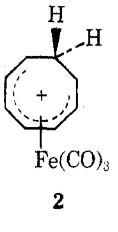
Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

Received February 8, 1977

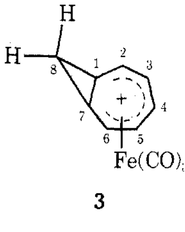
Cyclooctatetraeneiron tricarbonyl **1**[2] has been extensively studied as one of the earliest examples of the fluxional behavior of organometallic compounds.[3] Both proton[4] and carbon-13[5] NMR spectroscopic studies have unequivocally



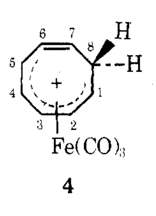
1



2



3



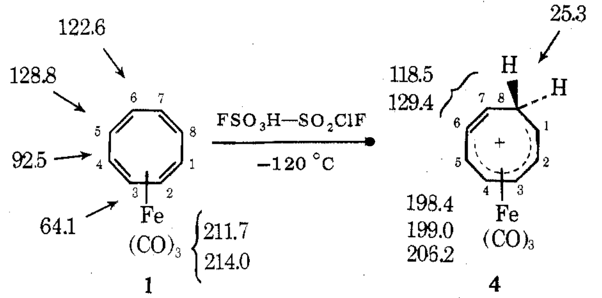
4

shown that simple 1,2″ shifts are responsible for the fluxional behavior of 1 and its analogues.[5] Complex 1 was first converted, via protonation in etheral solution of fluoroboric acid, into a tetrafluoroborate salt by Schrauzer and thought to be cyclooctatrienyliron tricarbonyl cation 2.[6] A year later, Davison, McFarlane, Pratt, and Wilkinson refuted structure 2 and unequivocally presented structure 3 to be the actual cation formed.[7] At even lower temperature (−120 °C), Brookhart and co-workers were able to obtained the monocyclic cyclooctatrienyliron tricarbonyl cation 4 initially formed from 1 by protonation in FSO_3H-SO_2F_2 solution.[8] Structure 4 was confirmed by their proton NMR spectroscopic study. Furthermore, upon warming the solution of 4 to −60 °C, cation 3 was quantitatively formed via a first-order electrocyclic ring-closure reaction.

Our recent report of the ^{13}C NMR study of σ–π complex formation in strong acid solution[9] prompts us to describe the ^{13}C NMR study of protonated cyclooctatetraeneiron tricarbonyl 1 under stable ion conditions.

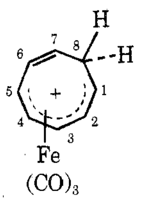
Results and Discussion

^{13}C NMR Spectroscopy Study of Protonated Cyclooctatetraeneiron Tricarbonyl at −120 °C. Cotton[5a] and Giacometti[5c] separately reported the ^{13}C NMR spectra of cyclooctatetraeneiron tricarbonyl 1 at various temperatures. 1 shows only a doublet at δ 102.1 (J_{CH} = 160 Hz) and a carbonyl singlet at δ 213.5 at 0 °C. The doublet splits into four doublets at δ 128.8, 122.6, 92.5, and 63.7 at −120 °C, while the carbonyl splits into two singlets at δ 214.0 and 211.7 in a ratio of 2:1. Addition of the solution of 1 in SO_2ClF to FSO_3H-SO_2ClF at −120 °C results in a light-yellow solution which gives an ^1H NMR spectrum identical with that reported by Brookhart.[8]



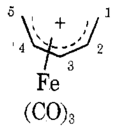
1 4

The proton-decoupled ^{13}C NMR spectrum of 4 in FSO_3H-SO_2ClF solution at −90 °C consists of eight carbon resonances in the organic region and three in the carbonyl region. According to the off-resonance ^{13}C NMR spectrum, the signal at δ 25.3 is a triplet which naturally can be assigned to the methylene carbon C_8. The two lowest field shifts δ 118.5 and 129.4 (both are doublets) in the olefinic region can be attributed to C_6 and C_7 since they resemble the olefinic carbon (uncomplexed) atoms (C_5–C_8) of 1. C_6 should experience inductive deshielding from the neighboring positive charge more than C_7 does. The lower field shift at δ 129.4 is thus assigned to C_6. The other five carbon shifts at higher field are divided into three groups: δ 94.1 and 98.1 (both show J_{CH} ~ 174 Hz), 70.9 and 73.4 (J_{CH} ~ 160 Hz), and 105.7 (J_{CH} = 184.0 Hz). These shifts are assigned to the five pentadienyl carbon atoms (C_1–C_5) since they are apparently complexing with $Fe(CO)_3$ which induces substantial shielding toward these carbon atoms. This is clearly seen in the case of the open-chain analogue 5 previously reported by us.[9] The terminal positions (C_1 and C_5) in ion 5 show the smallest magnitude of J_{CH} (in Hz), and the central position (C_3) shows the largest value of J_{CH}. According to this order, chemical shifts are assigned to ion 4 as shown. The ^{13}C NMR thus confirms 4 as the initially formed ion from 1 and the former contains a methylene group and an olefinic bond remaining intact by the iron tricarbonyl group. Other structures such as 6 or 7 can be excluded.



4

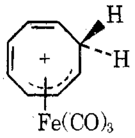
positions	$\delta^{13}C$
1,5	70.9 (d, 159.7 Hz) 73.4 (d, 158.2 Hz)
2,4	94.1 (d, 174.5 Hz) 98.1 (d, 173.0 Hz)
3	105.7 (d, 184.0 Hz)
6	129.4 (d, 161.0 Hz)
7	118.5 (d, 170.7 Hz)
8	25.3 (t)



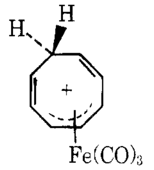
5

$\delta^{13}C$

65.4 (d d, 165, 4, 164.4)
104.6 (d m, 170.8)
98.6 (d t, 180.3)

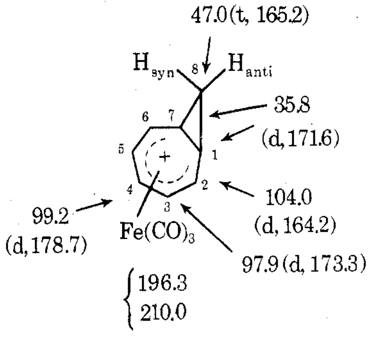


6

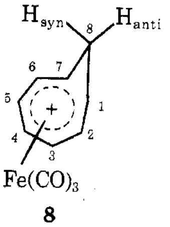


7

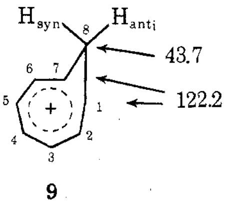
Thermal Rearrangement of the Protonated Cyclooctatetraeneiron Tricarbonyl. When the solution of protonated cyclooctatetraeneiron tricarbonyl 4 was allowed to stand at −60 °C, a clean transformation of the ion took place giving the bicyclo[5.1.0]octadienyliron tricarbonyl cation 3.[8] The eight carbon resonances in the organic and three in the carbonyl region originally present in the ^{13}C NMR spectrum of 4 are now replaced by five and three carbon resonances, respectively. In the proton-coupled ^{13}C NMR spectrum the two



3



8



9

Table I. ^{13}C Chemical Shifts of Carbonyl Groups of Olefiniron Tricarbonyls and Their Related Ions

δ ^{13}C CO, ppm	3	4	5	10	11	12	13	14	15	16	17	18
Apical or axial	210.0	206.2	206.0	209.0[a]	218.3[a]	207.5	208.1	207.9	203.1	205.9[b]	202.7	205.6
Basal or equatorial	196.3	198.4 199.0	197.3	209.0[a]	218.3[a]	198.1 198.5	198.4	198.2	196.0 199.2	204.6[b] 205.5[b]	200.0	191.3

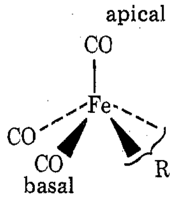
[a] Averaged shift at −90 °C in SO_2 solution. [b] Interchangeable values.

high-field signals at $\delta_{^{13}C}$ 35.8 and 47.0 are a doublet and a triplet, respectively. These are assigned to the cyclopropane ring carbons formed via a first-order electrocyclic ring closure reaction.[8] They are substantially deshielded from other neutral cyclopropane-ring carbons, obviously due to charge delocalization into the three-membered ring. They do, however, show chemical shifts in the aliphatic region which confirm the assigned structure **3** for the observed ion. Otherwise in a complexed homotropylium ion **8** both C_1 and C_7 should have chemical shifts of about $\delta_{^{13}C}$ 100 (olefinic region). The NMR data thus exclude the homotropyliumiron tricarbonyl ion **8** structure. Using **5** as the model ion, the chemical shifts for ion **3** are summarized as shown.

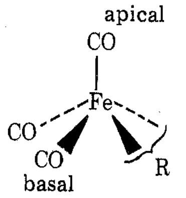
Study of the Carbonyl Absorptions. In recent carbon-13 NMR studies of the fluxional behavior of 1,3-dieneiron tricarbonyl complexes, only two resonances were observed in the carbonyl region, even at temperatures below −90 °C, usually in a ratio of 2:1, corresponding to the basal and apical carbonyl groups, respectively.[11] 1,3-Butadiene **10** and norbornadiene **11**–iron tricarbonyls both undergo fast fluxional exchange and even at −90 °C they only show a single averaged carbonyl shift at $\delta_{^{13}C}$ 209.0 and 218.3, respectively.[9a] Upon protonation, i.e., **15** from **10** in excess acid, **16** (the neutral HCl adduct) from HCl solution, and **18** from **11**, the octahedral organoiron tricarbonyl cations show either two or three carbonyl absorptions depending whether they are symmetrical or unsymmetrical. For example, **15** and **16** are unsymmetrical and thus they show one axial and two equatorial carbonyl resonances. The former is found more deshielded than the latter. On the other hand, the symmetrical ion **18** which undergoes fast equilibration shows only one axial and one equatorial carbonyl absorption in a ratio of 1:2.[9a] The symmetrical σ–π complex ion **17** derived from cyclobutadieneiron tricarbonyl via protonation also shows two carbonyl resonances[9b] (Table I).

For organoiron tricarbonyl complex ions **3**–**5** and **12**–**14** which adopt tetragonal-pyramidal configuration, the possibility arises of observing apical and both of the basal carbonyl absorptions, which indeed was the case. This depends, however, on whether the complexed ions are symmetrical or unsymmetrical. The carbonyl shifts of these ions are summarized in Table I.

Chemical shifts of the carbonyl carbons in transition-metal carbonyls are sensitive to the electron density on the metal atom.[12] The less the positive charge on the metal atom, the more carbonyl groups become shielded. The shieldings found for the basal (tetragonal-pyramidal configuration) and equatorial (octahedral configuration) carbonyl groups thus indicate significant positive charge density on iron. Contribution to the total shielding due to other factors (i.e., anisotropic shielding from organic moiety) should also be considered. However, the neutral species **10**, **11**, and **16** which do not bear formal positive charge on iron only display unchanged carbonyl absorptions (relative to their parent neutral iron carbonyl complexes). This indicates that the development of positive charge density on iron arising from strong complexation between the olefinic and iron tricarbonyl groups may be the key factor toward the total shielding of the carbonyl absorptions for organoiron tricarbonyl complexed ions.

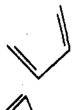


tetragonal pyramid

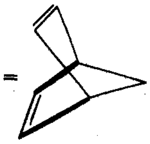


tetragonal pyramid

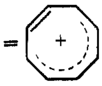
10, R =



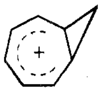
11, R =



4, R =



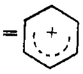
3, R =



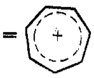
5, R =

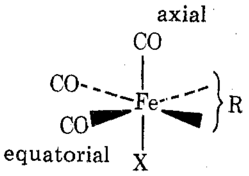
12, R =

13, R =



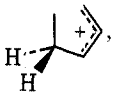
14, R =





octahedral

15, R =

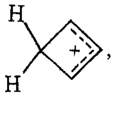


, X = H

16, R =

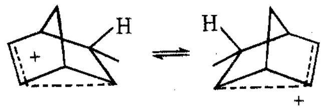
, X = Cl

17, R =



, X = H

18, R =



, X = H

Experimental Section

Cyclooctatetraeneiron Tricarbonyl 1 was prepared according to the literature procedure.[5a]

Protonation of Cyclooctatetraeneiron Tricarbonyl (1) in FSO_3H-SO_2ClF Solution at −120 °C. Ion **4** was prepared by addition of **1** in SO_2ClF solution to excess FSO_3H-SO_2ClF solution with vigrous stirring at ethanol–liquid nitrogen bath temperature (ca. −120 °C) under dry-nitrogen atmosphere to give an approximately 5% solution of 4. The yellow solution formed this way was then transferred under dry nitrogen into a precooled NMR tube.

The Thermal Rearrangement of 4 to Bicyclo[5.1.0]octadienyliron Tricarbonyl Cation 3. When a solution of 4 was allowed to warm up to −60 °C, ^1H NMR signals due to ion 4 completely disappeared and were replaced by those of 3 formed quantitatively.

^{13}C NMR Spectroscopic Study. The ^{13}C NMR spectra were obtained using a Varian XL-100-15 NMR spectrometer equipped with FT accessory, spin decoupler, and a variable temperature probe. A Varian 620L computer was used to accumulate data. An external lock (fluorobenzene) was used and all chemical shifts are referred to the ^{13}C signal of the enriched (5) Me_4Si capillary.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

Registry No.—**1**, 12093-05-9; **3**, 41853-19-4; **4**, 41370-96-1; **5**, 45977-75-1; **10**, 12078-32-9; **11**, 12307-07-2; **12**, 46134-85-4; **13**, 49654-90-2; **14**, 46236-85-1; **15**, 63765-50-4; **16**, 61216-90-8; **17**, 63765-51-5; **18**, 63765-52-6.

References and Notes

(1) (a) Organometallic Chemistry, 15: G. A. Olah, G. K. Prakash, G. Liang, K. L. Henold, and G. B. Haigh, *Proc. Natl. Acad. Sci. U.S.A.*, in press. Address correspondence to this author at the Institute of Hydrocarbon Chemistry, Department of Chemistry, University of Southern California, Los Angeles, Calif.

(2) (a) T. A. Manuel and F. G. A. Stone, *Proc. Chem. Soc., London*, 90 (1959); *J. Am. Chem. Soc.*, **82**, 366 (1960); (b) M. D. Rausch and B. N. Schrauzer, *Chem. Ind. (London)*, 957 (1959); (c) K. Nakamura and N. Hagihara, *Bull. Chem. Soc. Jpn.* **2**, 880 (1959); (d) B. Dicken and W. N. Lipscomb, *J. Am. Chem. Soc.*, **83**, 4862 (1961); *J. Chem. Phys.*, **37**, 2084 (1962); (e) C. E. Keller, G. F. Emerson, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 1388 (1965).

(3) (a) F. A. Cotton, *Acc. Chem. Res.*, **1**, 257 (1968); *J. Chem. Soc.*, 400 (1960); (b) F. A. Cotton, "Dynamic NMR Spectroscopy", L. M. Jackman and F. A. Cotton, Ed., Academic Press, New York, N.Y., 1975; (c) D. A. Brown, *J. Inorg. Nucl. Chem.*, **10**, 39 49 (1959).

(4) (a) C. G. Kreiter, A. Maasbol, F. A. L. Anet, H. D. Kaesz, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 3444 (1966); (b) F. A. Cotton, A. Davison, and J. W. Faller, *ibid.*, **88**, 4507 (1966); (c) C. E. Keller, B. A. Shoulders, and R. Pettit, *ibid.*, **88**, 4760 (1966); (d) F. A. Cotton, J. N. Faller, and A. Musco, *ibid.*, **90**, 1438 (1968); (e) S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *ibid.*, **87**, 5267 (1965); (f) F. A. L. Anet, *ibid.*, **89**, 2491 (1967); (g) A. Carbonaro, A. Greco, and G. Dall'Aota, *Tetrahedron Lett.*, 2037 (1967); (h) W. K. Bratton, F. A. Cotton, A. Davison, J. W. Faller, and A. Musco, *Proc. Natl. Acad. Sci. U.S.A.*, **58**, 1324 (1967); (i) M. I. Bruce, M. Cooke, M. Green, and F. G. A. Stone, *Chem. Commun.*, 523 (1967); (j) R. Grubbs, R. Breslow, R. Herber, and S. J. Lippard, *J. Am. Chem. Soc.*, **89**, 6864 (1967).

(5) (a) F. A. Cotton and D. L. Hunter, *J. Am. Chem. Soc.*, **98**, 1413 (1976); (b) F. A. Cotton, D. L. Hunter, and P. LaLuerta, *ibid.*, **96**, 7926 (1974); (c) G. Rigatti, G. Boccalon, A. Accon, and G. Giacometti, *Chem. Commun.*, 1165 (1972).

(6) G. N. Schrauzer, *J. Am. Chem. Soc.*, **83**, 2966 (1961).

(7) A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *Chem. Ind. (London)*, 555 (1961); *J. Chem. Soc.*, 482 (1962).

(8) (a) M. Brookhart and E. R. Davis, *J. Am. Chem. Soc.*, **92**, 7622 (1970); (b) M. Brookhart, E. R. Davis, and D. L. Harris, *ibid.*, **94**, 7853 (1972).

(9) (a) G. A. Olah, S. H. Yu, and G. Liang, *J. Org. Chem.*, **41**, 2227, 2383 (1976); (b) G. A. Olah and G. Liang, *ibid.*, **41**, 2659 (1976).

(10) G. A. Olah, G. Liang, L. A. Paquette, M. J. Broadhurst, and P. Warner, *J. Am. Chem. Soc.*, **95**, 3386 (1973).

(11) (a) L. Kruczynski and J. Takats, *J. Am. Chem. Soc.*, **96**, 932 (1974); (b) F. A. Cotton, V. W. Days, B. A. Frenz, K. I. Hardcastle, and J. M Troup, *ibid.*, **95**, 4522 (1973).

(12) (a) G. M. Bodner and L. J. Todd, *Inorg. Chem.*, **13**, 360, 1335 (1974); (b) L. Vancea, R. K. Pomeroy, and W. A. G. Graham, *J. Am. Chem. Soc.*, **98**, 1407 (1976); (c) L. F. Farnell, E. W. Randall, and E. Rosenberg, *Chem. Commun.*, 1078 (1971); (d) H. L. Retcofsky, E. N. Frankel, and H. S. Gutowsky, *J. Am. Chem. Soc.*, **88**, 2710 (1966); (e) C. G. Kreiter, M. Lang, and H. Strack, *Chem. Ber.*, **108**, 1502 (1975); (f) J. Evans and J. R. Norton, *Inorg. Chem.*, **13**, 3042 (1974).

A Synthesis of
6-Hydroxy-1-benzoxepin-3,5(2*H*,4*H*)-dione

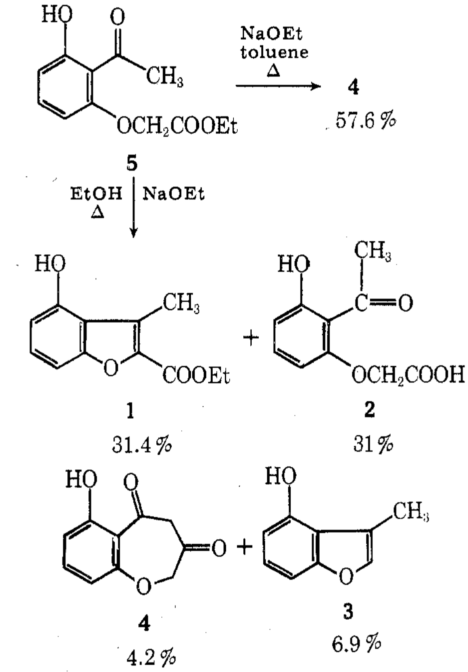
B. K. Wasson,* P. Hamel, and C. S. Rooney

Medicinal Chemistry Department, Merck Frosst Laboratories, Pointe Claire/Dorval, Quebec H9R 4P8, Canada.

Received June 2, 1977

Recently, a relatively large quantity of the known ethyl 4-hydroxy-3-methyl-2-benzofurancarboxylate (1) was required. Repetition of Whalley's[1] procedure in a modified form afforded not only 1 in 31.4% yield, but three additional products (see Scheme I). Two of these, (2-acetyl-3-hydroxyphenoxy)acetic acid (2) and 4-hydroxy-3-methylbenzofuran (3) isolated in 31 and 6.9% yields, respectively, had been reported by Whalley.[1] Compound 3 could also be formed from 2 when the latter was heated with acetic anhydride.[1] The fourth product, identified as the hitherto unknown 6-hydroxy-1-benzoxepin-3,5(2*H*,4*H*)-dione (4), was isolated along with 2 and 3 after silica gel column chromatography in 4.2% yield. The assignment of structure to 4 was based on microanalysis, NMR, IR, UV, and mass spectrometry. Spectral evidence supports the diketo form rather than the enolic in both the solid state and in solution. Thus, the NMR spectrum exhibits two $-CH_2-$ peaks at δ 4.32 and 4.50 and one exchangeable proton at δ 12.31. Similar conclusions have been reported for the structure of 1-benzoxepin-3,5(2*H*,4*H*)-diones.[2-5] The pK_a of 4 is 4.83—presumably representing dissociation of the diketone function.

Scheme I



When ester 5 was allowed to react with sodium ethoxide in dry toluene, 4 was obtained in 57.6% yield. However, similar treatment of ethyl 2-(2-acetylphenoxy)acetate (6) gave only the benzofurans 8 and 9, and no 1-benzoxepin-3,5(2*H*,4*H*)-dione (7) was observed. It thus appears that the phenolic hydroxyl plays an essential role in the formation of the benzoxepin 4. Compound 4 remained unchanged after heating at 65 °C in sodium ethoxide–ethanol. Thus, 4 is not an intermediate

Scheme II