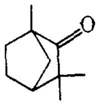
The power of the new method of analysis is illustrated best by the following chemical shift data (ppm) of nonprotonated sites of eight structurally diverse terpenic compounds;[10] quaternary carbons: fenchone (**1**), 138.7, 145.3; cedrol (**2**), 138.1, 148.5; totarol acetate (**3**), 154.5, 159.1; manool (**4a**), 152.5, 158.7; sclareol (**4b**), 153.4, 159.2; retinyl (vitamin A) palmitate (**5**), 158.4; cholesterol (**6**), 150.0, 155.9; friedelin (**7**) (in chloroform), 153.6, 155.9, 157.2, 158.1, 165.3, 167.4; tertiary carbinols: **2**, 118.0; **4a**, 119.3; **4b**, 118.3 (C-8), 119.4 (C-13); disubstituted methylidene moieties: **4a**, 45.2 (C-8); **5**, 54.8, 54.8, 57.1, 64.1.



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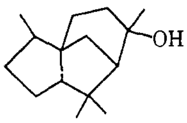

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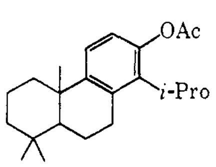

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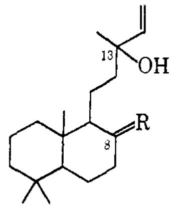
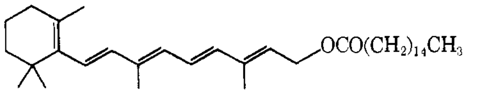


4a, R = CH_2
b, R = CH_3, OH



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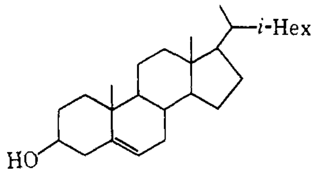

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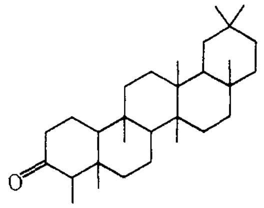

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(9) Natural-abundance ^{13}C nmr spectra were determined by the procedure described by A. O. Clouse, D. Doddrell, S. B. Kahl, and L. J. Todd, *Chem. Commun.*, 729 (1969), at 15.074 MHz. Noise decoupling followed the method of Ernst.[1]

(10) The noise resonance and off-resonance decoupling spectra of carbon tetrachloride solutions showed identical band widths of *ca.* 3 Hz at half-height. Less than 250 scans on a Varian C-1024 time-averaging computer were required. Chemical shifts in ppm, accurate to ±0.4 ppm, are cited relative to carbon disulfide ($\delta_{CS_2} = \delta_{CCl_4} + 96.5 = \delta_{CHCl_3} + 115.2$).

(11) Public Health Service Predoctoral Fellow, 1967–present.

Ernest Wenkert, A. O. Clouse
David W. Cochran,[11] David Doddrell
Department of Chemistry, Indiana University
Bloomington, Indiana 47401

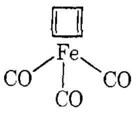
Received August 8, 1969

Flash Vacuum Pyrolysis. VI. Cyclobutadieneiron Tricarbonyl[1]

Sir:

The discovery of stable cyclobutadiene transition metal complexes[2] has naturally led to attempts to generate and characterize the free organic ligand. For example, Pettit and coworkers[3a,b] have concluded that free cyclobutadiene (**1**) is generated by the oxidation of cyclobutadieneiron tricarbonyl (**2**) on the basis of its dimerization and reactions with dienophiles. They also reported results suggesting that **1** had a finite lifetime in the gas phase and in the condensed phase at −196°. Flash photolysis of **2** generates transients having *m/e* 52 and 104 and lifetimes of 1–2 and 20 msec, respectively, at 0.010–0.250 Torr.[3c] More recently, the pyrolysis of **2** has been reported[4] to give **1** "as a stable compound" which could be distilled from a cold surface at −105° into a mass spectrometer.

1



2

Here we report on our investigation of the flash vacuum pyrolysis (FVP) of **2**. On the basis of these results and those recently reported on the FVP of photo-α-pyrone,[1] we conclude that the only detectable C_4H_4 thermal product from **2** is vinylacetylene. Moreover, we believe that the data of Li and McGee[4a,b] are more consistent with a similar assignment.

2 was first pyrolyzed at low pressures (~1 μ) and short contact times (~1 msec) in a tubular oven coupled to the ionization chamber of a mass spectrometer.[5] Significant decomposition occurred at about 450° giving major thermal fragments at *m/e* 52, 28, and 26, moderately intense signals at *m/e* 54 (C_4H_6) and 78 (C_6H_6), and minor signals at *m/e* 104 (C_8H_8) and 80 (C_6H_8). The thermal fragments maximized at temperatures between 560 and 700° except for that having *m/e* 26 which maximized at about 1000°: AP[6] (*m/e*, oven temperature); 9.8 eV (52, 700°), 11.5 eV (26, 900°), 9.4 eV (54, 700°), 9.7 eV (78, 560°), 8.6 eV (104, 560°). These appearance potentials can be compared with the independently determined ionization potentials for vinylacetylene (9.9 eV), acetylene (11.4 eV),[7] butadiene (9.2 eV),[7] benzene (9.7 eV), and cyclooctatetraene (8.4 eV). Radical titration experiments with methyl radicals generated by copyrolysis of ethyl nitrite led only to minor signals at *m/e* 67 and 68 and no new signals at *m/e* 66 and 82.

The thermal products were ultimately identified by the FVP of **2** at 560° and *ca.* 50 μ in the apparatus previously described,[8] where the pyrolysate was rapidly quenched on the surface of a large liquid nitrogen dewar closely coupled to the tubular oven. The products were isolated by distillation into a small vacuum manifold

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(1) Part V: E. Hedaya, R. D. Miller, D. W. McNeil, P. F. D'Angelo, and P. Schissel, *J. Amer. Chem. Soc.*, **91**, 1875 (1969).

(2) For a review see: M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press, New York, N. Y., 1967.

(3) (a) L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Amer. Chem. Soc.*, **87**, 3253 (1965); (b) R. Pettit, *Pure Appl. Chem.*, **17**, 253 (1969); (c) W. J. R. Tyerman, M. Kato, P. Kebarle, S. Masamune, O. P. Strausz, and H. E. Gunning, *Chem. Commun.*, 497 (1967).

(4) (a) H. A. McGee, Jr., Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, PHYS-061; (b) P. H. Li and H. A. McGee, Jr., *Chem. Commun.*, 592 (1969); (c) *Chem. Eng. News*, **47**, 51 (April 21, 1969).

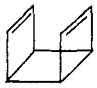
(5) P. Schissel, D. J. McAdoo, E. Hedaya, and D. W. McNeil, *J. Chem. Phys.*, **49**, 5061 (1968).

(6) AP, appearance potential; IP, ionization potential.

(7) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y., 1957.

(8) E. Hedaya and D. W. McNeil, *J. Amer. Chem. Soc.*, **89**, 4213 (1967).

and characterized by glpc, ir, and nmr. Glpc analysis (mol/100 mol **2**) exhibited the following: acetylene (1.2), vinylacetylene (2.6), butadiene (3.8), benzene (5.3), cyclooctatetraene (0.2), and styrene (0.9). These determinations were confirmed by a less precise nmr analysis. No *anti* or *syn* dimer of cyclobutadiene (**3**) could be detected either by glpc or nmr. Finally, a copious iron-containing deposit formed in the oven during the pyrolysis.



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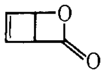

4

The results of our previous work on the FVP of photo-α-pyrone (**4**)[1] can be summarized for comparison. A *m/e* 52 fragment was thermally generated having a low ionization potential (8.2 eV) and diradical character on the basis of its dimerization and reactivity with radicals and oxygen. Chemical experiments showed that rapid quenching of the pyrolysate gave the *syn* dimer of cyclobutadiene (**3**) exclusively while benzene and acetylene were formed either in the gas phase or on warm walls prior to quenching. No vinylacetylene, butadiene, or other C_4 fragment was detected. On the basis of these experiments, we concluded that the transient *m/e* 52 thermal product was cyclobutadiene, and that this has a significant but short lifetime at FVP conditions.

In contrast, we believe that the appearance potential measurements, radical titration experiments, and chemical experiments all indicate that the only C_4H_4 product which survives the pyrolysis of **2** is vinylacetylene. The absence of the *syn*-dimer **3** in the rapidly quenched pyrolysate is particularly significant.

The different behavior of **2** and photo-α-pyrone (**4**) under FVP conditions most likely involves both surface thermal activation and decomposition for the former and only surface thermal activation for the latter. This would allow for the highly exothermic formation of metallic iron from **2** and is consistent with the copious deposition of iron on the oven surface as well as the low yield of organic products.[9] The precise nature of the reactions leading to vinylacetylene, benzene, acetylene, cyclooctatetraene, and styrene is extremely interesting, but obscure. Any surface reaction must occur very rapidly owing to the short residence times of activated molecules on the hot oven walls.

We must conclude that Li and McGee[4a,b] also did not detect cyclobutadiene from the low-pressure pyrolysis of **2** in contrast to their claim. Their ionization potential measurement for the *m/e* 52 fragment (9.6 eV) from **2** is much closer to vinylacetylene (9.9 eV) than cyclobutadiene (8.2 eV).[1] Furthermore their fragmentation pattern for *m/e* 52, which was obtained after subtraction of the fragments due to 1,3-butadiene, was essentially the same as that for vinylacetylene except for the low masses: for *m/e* 52 from **2**, *m/e* (relative intensity) 52 (100), 51 (59), 50 (51), 49 (17), 48 (1), 39 (5), and 26 (26); for vinylacetylene, 52 (100), 51 (56), 50 (49), 49 (19), 48 (8), 39 (1), and 26 (12). Finally, their reported ionization potential for C_8H_8 (9.1 eV) is very different from that of **3** (8.4 eV) as well as cyclooctatetraene and styrene (8.86 eV).[7]

Acknowledgment. We wish to thank Professor Leo Paquette for supplying us with our initial sample of cyclobutadieneiron tricarbonyl.

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[9] Nickelocene was also found to undergo surface decomposition at FVP conditions.[5,10]

[10] E. Hedaya, D. W. McNeil, P. Schissel, and D. J. McAdoo, *J. Amer. Chem. Soc.*, **90**, 5284 (1968).

[11] Union Carbide Corporation Postdoctoral Fellow, 1968–1969.

[12] Union Carbide Corporation Postdoctoral Fellow, 1967–1968.

E. Hedaya, I. S. Krull,[11] R. D. Miller[12]
M. E. Kent, P. F. D'Angelo, Paul Schissel
Union Carbide Research Institute
Tarrytown, New York 10591

Received August 9, 1969

Molecular Structure of the Decamolybdodicobaltate(III) Ion

Sir:

When solutions of cobalt(II) ion and heptamolybdate ion ($Mo_7O_{24}{}^{6-}$) are mixed in the presence of an oxidizing agent (such as bromine), Kurnakov,[1] Hall,[2] and others found that an emerald green complex is formed as the main product, namely, the heteropoly complex ion hexamolybdocobaltate(III), which forms salts such as $(NH_4)_3[H_6CoMo_6O_{24}]\cdot 12H_2O$. Friedheim and Keller[3] showed that at the same time a small amount of another complex is also formed, having a Co:Mo ratio of 1:5. Tsigdinos, *et al.*,[4] found that if a hot solution of the hexamolybdocobaltate complex ion is treated with activated charcoal or Raney nickel the 1:6 complex is converted almost entirely to the 1:5 complex. These workers[4] proved the latter to be a dimer, and formulated the ammonium salt (earlier prepared by Friedheim and Keller[3]) as $(NH_4)_6[Co_2Mo_{10}O_{36}]\cdot 10H_2O$. We have now completed a crystal structure analysis of this interesting compound, which shows the proper formula to be $(NH_4)_6[H_4Co_2Mo_{10}O_{38}]\cdot 7H_2O$.

Solutions of the complex ion deposit large black crystals of two different ammonium salts, as follows: form A, monoclinic, space group C2/c or Cc, $a = 44.18 \pm 0.03$ Å, $b = 12.60 \pm 0.01$ Å, $c = 15.36 \pm 0.01$ Å, $\beta = 106.89 \pm 0.02°$, $Z = 8$, $V = 4 \times 2044$ Å^3; form B, monoclinic, space group Pc, $a = 12.59 \pm 0.01$ Å, $b = 12.72 \pm 0.01$ Å, $c = 15.48 \pm 0.01$ Å, $\beta = 121.70 \pm 0.01°$, $Z = 2$, $V = 2110$ Å^3.

The two forms may appear simultaneously, though form A seems to be the more stable, especially in warm solutions. Our study was carried out on form B (prepared from a sample kindly supplied by Drs. Tsigdinos and Baker), to which the formula given applies. Using Mo Kα radiation, 4105 X-ray intensity data were collected for this crystal with a Picker automatic diffractometer. The data were normalized and subjected to the symbolic addition procedure of phase determination, assuming the space group to be P2/c. A structure was readily found in this way, but complete convergence of the refinement to $R = 0.071$ could only be accomplished in space group Pc. In the refinement, individual, isotropic thermal parameters were assumed, and no corrections were made for absorption, extinction, or dis-

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[1] N. S. Kurnakov, *Chem. Ztg.*, **14**, 113 (1890).

[2] R. D. Hall, *J. Am. Chem. Soc.*, **29**, 692 (1907).

[3] C. Friedheim and F. Keller, *Ber.*, **39**, 4301 (1906).

[4] G. A. Tsigdinos, *Dissertation Abstr.*, **22**, 732 (1961); G. A. Tsigdinos, M. T. Pope, and L. C. W. Baker, Abstracts 135th National Meeting of the American Chemical Society, Boston, Mass., April 1959.