

reported for the ruthenium crystals are 0.550:1.000:0.986, $\beta = 100^{\circ}46'$, point group $2/m$; from our data for the osmium compound $a:b:c = 0.547:1.000:0.974$, $\beta = 100^{\circ}27'$, point group $2/m$. Even though the compound is not isomorphous with $[\text{Fe}(\text{CO})_4]_3$,³ the volumes per molecule are equivalent within experimental error.

Three-dimensional Weissenberg and precession intensity data involving over 2000 reflections were obtained with $\text{MoK}\alpha$ radiation. The positions of the osmium atoms were located from Patterson projections of $h0l$, $hk0$, and $0kl$ data. Least squares refinement of the 400 observed reflections for the three zones places the osmium atoms at the corners of an equilateral triangle; the average distance between the osmium atoms in the triangle is 2.87 Å. For isotropic refinement the discrepancy factor $R_1 = 16\%$. A complete three-dimensional analysis now under way will be required to locate the positions of the carbonyl groups.

The absence of symmetrical bridging carbonyls is to be expected since the long Os-Os distances are of the magnitudes found in $\text{Mn}_2(\text{CO})_{10}$ (2.93 Å),^{4,5} $\text{Re}_2(\text{CO})_{10}$ (3.02 Å),⁴ and $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ (3.22 Å)⁶ all of which dimerize only by direct metal-metal bonds. The infrared spectrum of this trinuclear osmium carbonyl apparently does not show frequencies characteristic of bridging carbonyls.⁷ The presence of symmetrical bridging carbonyls in 1st row transition metal compounds⁸⁻¹² has been shown from X-ray work; in all these cases the metal-metal distances found are 2.54 Å. or less. The larger metal atoms in the 2nd and 3rd row transition metal carbonyls may well be expected to lead to metal-metal repulsion of a magnitude to render ketonic carbonyls unstable. This may be why $\text{Ru}_2(\text{CO})_9$ and $\text{Os}_2(\text{CO})_9$ as yet have not been isolated as the decomposition products of the pentacarbonyls.

A closer examination of previous work supports a tetracarbonyl species. The chemical analyses² reported for the presumed ruthenium enneacarbonyl may be interpreted as fitting either the formula $\text{Ru}_2(\text{CO})_9$ or $[\text{Ru}(\text{CO})_4]_3$. The molecular weight determinations are definitely inconclusive; furthermore it is easy to envision a change in molecular formula when the carbonyl compound is dissolved. Manchot and Manchot² observed no pressure change during the decomposition of $\text{Ru}(\text{CO})_5$ to give the yellow carbonyl. This may be readily explained by the reaction $3 \text{Ru}(\text{CO})_5(\text{g}) \rightarrow [\text{Ru}(\text{CO})_4]_3(\text{s}) + 3 \text{CO}$, which they did not consider. Furthermore, $[\text{Ru}(\text{CO})_4]_3$ and $[\text{Os}(\text{CO})_4]_3$ are the only trinuclear molecular species which obey the "inert gas rule." The nature of the green ruthenium carbonyl² is being investigated.

(3) L. P. Dahl and R. E. Rundle, *J. Chem. Phys.*, **26**, 1751 (1957).

(4) L. P. Dahl, E. Ishihara and R. E. Rundle, *J. Chem. Phys.*, **26**, 1750 (1957).

(5) L. P. Dahl and R. E. Rundle, to be published.

(6) F. C. Wilson and D. P. Shoemaker, *J. Chem. Phys.*, **27**, 809 (1957).

(7) E. O. Fischer, private communication.

(8) H. M. Powell and R. V. G. Ewens, *J. Chem. Soc.*, 283 (1939).

(9) G. G. Sumner, H. P. Kling and L. E. Alexander, abstracts of papers, National Meeting of the American Crystallographic Association, Washington, D. C., January, 1960.

(10) P. Corradini, *J. Chem. Phys.*, **31**, 1076 (1959).

(11) O. S. Mills and G. Robinson, *Proc. Chem. Soc.*, 156 (1959).

(12) O. S. Mills, *Acta Cryst.*, **11**, 620 (1958).

Our results further suggest that the structures of $\text{Rh}_2(\text{CO})_8$ ¹³ and $\text{Ir}_2(\text{CO})_8$ ¹⁴ may differ from that of $\text{Co}_2(\text{CO})_8$ ⁹. A structure with trigonal bipyramidal symmetry around each Rh or Ir with a direct metal-metal bond would make bridging carbonyls unnecessary. Toward this end structural work on the rhodium and iridium carbonyls is now in progress.

NOTE ADDED IN PROOF.—Single crystals of the presumed ruthenium enneacarbonyl recently have been prepared and examined by X-ray diffraction techniques (L. F. Dahl, E. R. Corey and E. E. deGill, to be published). The X-ray data agree well with the previously cited optical results for this compound,² and further confirm the isomorphism of the ruthenium and osmium compounds. Infrared spectra of the ruthenium carbonyl in both Nujol mull and KBr pellet reveal absorption bands only in the 2000 cm^{-1} region. Three-dimensional X-ray intensity data also are being taken for this compound to provide more accurate positional parameters for the carbonyl groups than will be obtained from the three-dimensional osmium carbonyl data.

We wish to thank the Petroleum Research Advisory Board (Fund No. 471A) for financial support and the Numerical Analysis Laboratory at the University of Wisconsin for the use of their computing facilities.

(13) W. Hieber and H. Lagally, *Z. anorg. Chem.*, **251**, 96 (1943).

(14) W. Hieber and H. Lagally, *ibid.*, **245**, 321 (1940).

(15) Petroleum Research Fellow.

DEPARTMENT OF CHEMISTRY

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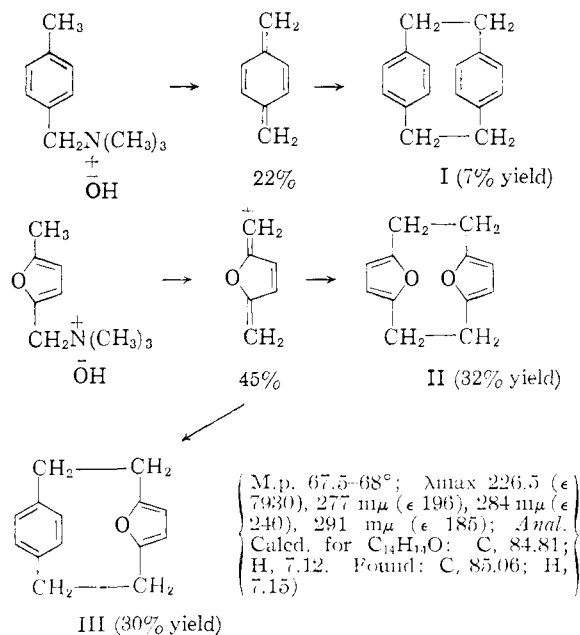
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RECEIVED MARCH 2, 1961

A CROSS-BREEDING REACTION, A BENT BENZENE RING, AND A MULTIPLE DIELS-ALDER REACTION¹

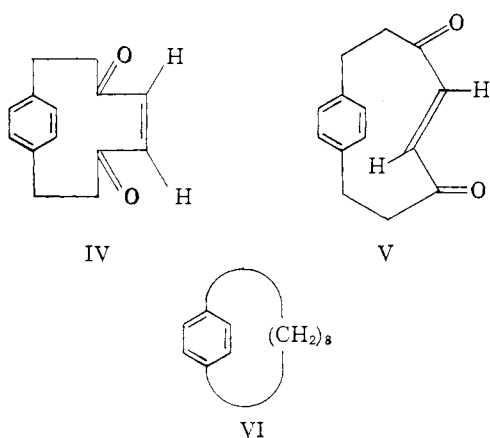
Sir: Publication² of practical means of preparing I and II suggested a route which proved successful for synthesis of III by the cross-breeding reaction formulated. Treatment of III with bromine in



methanol at -30° ,^{2,3} then with water, gave a mixture

(1) This work was supported by the Office of Ordnance Research, U. S. Army.

(2) H. E. Winberg, F. S. Fawcett, W. E. Moehl and C. W. Theobald, *J. Am. Chem. Soc.*, **82**, 1128 (1960).



ture of *cis* and *trans* isomers, IV and V. The high melting yellow isomer (m.p. 162.5°; λ max 219 $m\mu$, ϵ 11,560; shoulder at 250 $m\mu$, ϵ 3,000; shoulder 310 $m\mu$, ϵ 480. *Anal.* Calcd. for $C_{14}H_{14}O_2$: C, 78.50; H, 6.58. Found: C, 78.31; H, 6.57) is tentatively assigned the *cis*-configuration on the basis of its ready thermal conversion to the lower melting, colorless isomer (m.p. 132.5-133°; λ max 223 $m\mu$, ϵ 7,300, λ max 249 $m\mu$, ϵ 3,350, shoulder 310 $m\mu$, ϵ 480. *Anal.* Found: C, 78.66; H, 6.82). Support for this assignment is found in the presence of a band at 968 cm^{-1} in the infrared spectrum (potassium bromide pellet) of the *trans* isomer (out-of-plane C-H deformation) which was absent in the *cis*-isomer. Attempts to isomerize the lower to the higher melting isomer (*trans* to *cis*) failed.

Molecular models indicate that the *trans* isomer is less strained than the *cis*. Clemmensen reduction of V gave [8]paracyclophane (VI), a camphoraaceous smelling liquid. *Anal.* Calcd. for $C_{14}H_{20}$: C, 89.28; H, 10.70. Found: C, 89.36; H, 10.35.

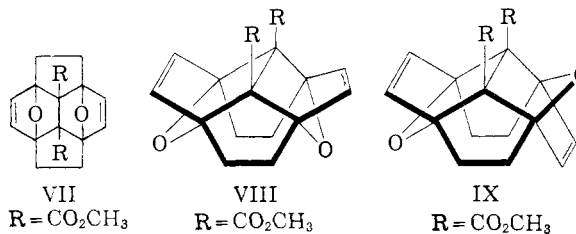
The ultraviolet absorption spectrum of VI (λ max 224 $m\mu$, ϵ 6,840, λ max 265.5 $m\mu$, ϵ 403, λ max 274 $m\mu$, ϵ 407, shoulder 315 $m\mu$, ϵ 28) indicates that the benzene ring is seriously bent from its normal planar configuration. Comparison of the spectrum of VI and of [2.2]paracyclophane suggests that some but not all of the spectral abnormalities of the latter compound are associated with the deformations of the benzene rings.^{4,5}

Molecular models of V and of derived compounds that retain the *trans* double bond suggest that the substance is a racemate because of steric stabilization of conformation. The stereochemistry of the system is currently being investigated.

Although compounds I, II or III do not react with ordinary dienophiles, reaction of II (not I or III) with dicarbomethoxyacetylene occurred readily at 100° to give VII,⁶ m.p. 162.5-163° (decomposition). *Anal.* Calcd. for $C_{18}H_{18}O_6$: C, 65.45; H, 5.50. Found: C, 65.39; H, 5.38. On pyroly-

sis VII gave back starting materials, a fact that indicates absence of a deep-seated rearrangement in formation of VII. Reduction of VII with hydrogen and platinum gave the thermally stable tetrahydro derivative, m.p. 229-230°. *Anal.* Calcd. for $C_{18}H_{22}O_6$: C, 64.66; H, 6.64. Found: C, 64.84; H, 6.62.

The interesting question of whether VII possesses detailed structure VIII or IX is under investigation.



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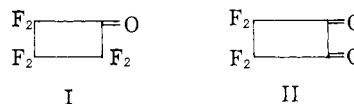
DONALD J. CRAM
GRAHAM R. KNOX⁷

RECEIVED MARCH 27, 1961

PERFLUOROCYCLOBUTANONES

Sir:

We wish to report the synthesis of two extraordinary perfluoroketones starting with tetrafluoroethylene (TFE). Perfluorocyclobutanone (I) is light yellow in the liquid state, absorbs at 5.4 μ in the infrared (the lowest recorded for any ketone) and is quantitatively converted to perfluorocyclopropane and carbon monoxide by light. Perfluorocyclobutane-1,2-dione (II) is deep blue in the gaseous, liquid and solid states.



Both compounds are exceptionally reactive and undergo a variety of addition reactions involving the carbonyl groups.

To synthesize I, methyl trifluorovinyl ether, available from sodium methoxide and TFE,¹ was treated with TFE at 175° to give a 65% yield of methoxyheptafluorocyclobutane, b.p. 56° (*Anal.* Calcd. for $C_5H_3F_7O$: F, 62.7. Found: F, 62.6). Hydrolysis of this ether in 95% sulfuric acid at 175° in a sealed vessel gave a solution of perfluorocyclobutanone hydrate. On heating this solution at atmospheric pressure, I distilled at 1° in 75% yield (*Anal.* Calcd. for C_4F_6O : F, 64.0; mol. wt., 178. Found: F, 63.4; mol. wt. by vapor density, 176) then its hydrate, b.p. 128°, m.p. 52°, 14% yield (*Anal.* Calcd. for $C_4H_2O_2F_6$: C, 24.5; H, 1.0; neut. eq., 196. Found: C, 24.0; H, 1.3; neut. eq., 195). When phosphorus pentoxide was added to the above sulfuric acid solution of the hydrate, the distillation gave only I in over 90% yield.

Perfluorocyclobutanone (I) is very stable thermally, being recovered unchanged after heating

(1) S. Dixon, U. S. Patent 2,917,548 (1959).

(3) N. Clauson-Kaas, *Kgl. Danske Videnskab. Selskab. Mat.-fys. Medd.*, **24** [6] 18 p. (1947).

(4) C. J. Brown and A. C. Farthing, *Nature*, **164**, 915 (1949).

(5) D. J. Cram, R. H. Bauer, N. L. Allinger, R. A. Reeves, W. J. Wechter and E. Heilbronner, *J. Am. Chem. Soc.*, **81**, 5977 (1959).

(6) O. Diels and S. Olson [*J. prakt. Chem.*, **156**, 285 (1940)] observed that one mole of dicarbomethoxyacetylene reacted readily with two moles of furan to give a compound similar to VII, but lacking the two extra methylene bridges.