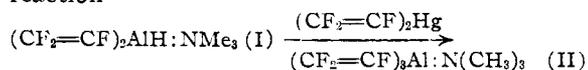


was added. This excess was necessary to bring the alkylation to completion, since the last step of the reaction



is a very slow one. Progress can be followed by means of the infrared spectrum. Compound I gives a very sharp Al-H peak at 5.35μ , a $\text{C}=\text{C}$ peak at 5.85μ , and a broad C-F absorption at 9.1μ . The band at 5.35μ is absent in the spectrum of II.

The solution was stirred overnight, allowed to settle, and then decanted. The ether was removed and the resulting residue was distilled in vacuum, b.p. 42.5° ($> 10^{-3}$ mm.).

Anal. Calcd. for $\text{C}_9\text{H}_9\text{F}_9\text{NAl}$: C, 32.84; H, 2.75; F, 51.95; N, 4.25; Al, 8.19. Found: C, 32.76; H, 2.84; F, 51.23; N, 4.41; Al, 8.38.

Tris-(perfluorovinyl)-aluminum trimethylamine (II) is a clear, colorless, air-sensitive liquid, which may be stored at -20° for weeks. On standing at room temperature, it becomes somewhat dark and viscous. With water at elevated temperature a weighed amount releases 80% of its perfluorovinyl groups as trifluoroethylene. A cryoscopic molecular weight determination in cyclohexane showed the compound to be highly associated.

Anal. Calcd. for $(\text{C}_9\text{H}_9\text{F}_9\text{NAl})_3$: form. wt., 987.4. Found: form. wt., 995.0.

Acknowledgments.—This research was supported by the Advanced Research Projects Agency, through the Bureau of Weapons, Navy Department. The authors wish to thank Dr. Charles P. Haber for his helpful suggestions during the course of the work.

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RECEIVED FEBRUARY 27, 1961

A NEW GENERAL SYNTHESIS OF AROMATIC NITRILES FROM ALDEHYDES

Sir:

We wish to report a unique one-step synthesis of aromatic nitriles *via* the interaction of aldehydes with ammonium dibasic phosphate, nitropropane and acetic acid. The preparation of *p*-N,N-dimethylaminobenzonitrile (77%), 3,4,5-trimethoxybenzonitrile (74%), *p*-chlorobenzonitrile (50%), indole-3-carbonitrile (38%), 5-bromoindole-3-carbonitrile (41%, m.p. 188.5° – 190.5° . Found: C, 48.60; H, 2.40; N, 12.58) and 7-azaindole-3-carbonitrile (31%) from their corresponding aldehydes proceeds readily. A typical procedure is illustrated by the preparation of *p*-N,N-dimethylaminobenzonitrile.

***p*-N,N-Dimethylaminobenzonitrile.**—A mixture of 1.1 g. (0.0073 mole) of *p*-N,N-dimethylaminobenzaldehyde, 7.0 g. of ammonium dibasic phosphate, 30 ml. of nitropropane and 10 ml. of glacial acetic acid was refluxed for 16 hours. During the period of reflux the colorless solution became dark brown and then changed to light brown to yellow. After removal of the volatile reactants *in vacuo*, the residual oil was added to 100 ml. of water with stirring and allowed to stand at room temperature

for one hour. Filtration yielded 0.95 g., m.p. 70 – 78° , of *p*-N,N-dimethylaminobenzonitrile which on crystallization from water-methanol gave 0.82 g. (77%) of pure product, m.p. 75 – 77° .¹

The infrared spectra of the crude and pure products are virtually superimposable and show a characteristic strong —CN band at 2238 cm.^{-1} .

In all cases we have studied to date, the crude product appears to consist mostly of desired nitrile. Thus, although the yields of pure nitriles from the indoles are only fair, the yield of crude product is significantly higher.

Possible mechanisms envisioned include an oxidation-reduction reaction of a transient aldimine with nitropropane to give nitrile directly or, alternatively, an oxime which then undergoes dehydration.

The simplicity of this method makes it apparent that it could potentially be the method of choice for the preparation of aromatic nitriles.²

Further investigations of the mode and limitations of this method are currently under way.

We wish to acknowledge a stimulating discussion with Professor Ernest Wenkert during the preliminary stages of this project and to thank Dr. E. Schlittler for his interest and encouragement.

(1) The literature reports a melting point of 75 – 76° ; R. T. Arnold, V. J. Webers and R. M. Dodson, *J. Am. Chem. Soc.*, **74**, 368 (1952).

(2) See D. J. Mowry, *Chem. Rev.*, **42**, 189 (1948), and E. Müller, Houben-Weyl's "Methoden der Organischen Chemie," 1952, Band VIII, G. Thieme Verlag, Stuttgart, pp. 265–345, for pertinent reviews on the preparation of nitriles.

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RECEIVED MARCH 30, 1961

TRINUCLEAR OSMIUM AND RUTHENIUM CARBONYLS AND THEIR IDENTITIES WITH PREVIOUSLY REPORTED $\text{Os}_2(\text{CO})_9$ AND $\text{Ru}_2(\text{CO})_9$

Sir:

We wish to report direct structural evidence that the widely accepted metal carbonyls $\text{Os}_2(\text{CO})_9$ and $\text{Ru}_2(\text{CO})_9$ are in fact trinuclear molecular species with probable formulas $[\text{Os}(\text{CO})_4]_3$ and $[\text{Ru}(\text{CO})_4]_3$. This and other evidence suggests that the carbonyls of the 2nd and 3rd row transition metals possess distinct structural differences from those of the 1st row transition metals.

Yellow crystals of the presumed enneacarbonyl, $\text{Os}_2(\text{CO})_9$, were prepared by the high pressure reaction of OsO_4 with carbon monoxide.¹ X-Ray diffraction data reveal the compound to be monoclinic with $a = 8.09 \text{ \AA.}$, $b = 14.79 \text{ \AA.}$, $c = 14.40 \text{ \AA.}$ and $\beta = 100^\circ 27'$. The probable space group, as determined by systematic absences, is $\text{P}2_1/n$. There are twelve osmium atoms per unit cell related to one another by the four-fold positions of the space group. These data agree excellently with optical data obtained by Steinmetz and reported by Manchot and Manchot² for the yellow crystals of the presumed ruthenium enneacarbonyl and leave no doubt as to the isomorphism of the two compounds. The $a:b:c$ ratios and symmetry

(1) W. Hieber and H. Stallman, *Z. Elektrochem.*, **49**, 288 (1943).

(2) W. Manchot and W. J. Manchot, *Z. anorg. allgem. Chem.*, **223**, 385 (1936).

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

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

(5) L. F. 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.*, 288 (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**, 1676 (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.

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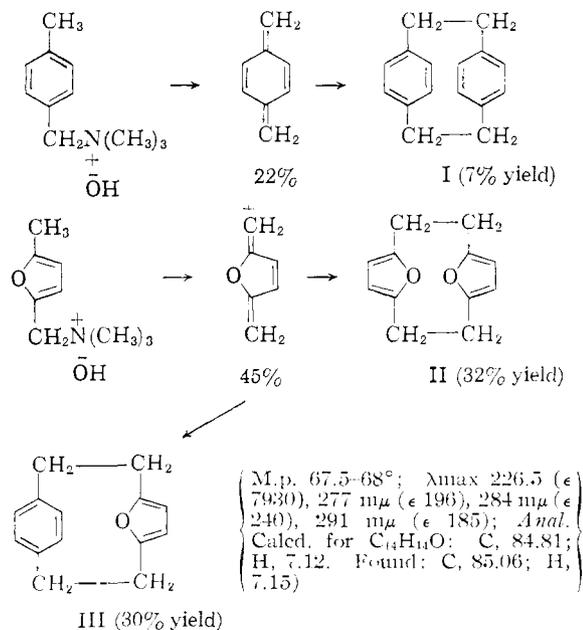
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RECEIVED MARCH 2, 1961

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

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° ,³ then with water, gave a mix-

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

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