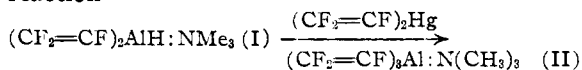


was added. This excess was necessary to bring the alkylation to completion, since the last step of the reaction



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 —C=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.

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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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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 $\text{P}2_1/\text{n}$. 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).