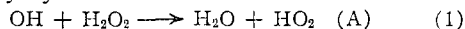


Fig. 3.—Successive stages of e.p.r. spectrum of 10^{-3} M H_2O_2 irradiated with ultraviolet lamp for (1) 30 min., (2) 2 hours, and (3) 12 hours.

ported by Siegel⁸ and his colleagues for the beginning of measurable decay of the spectrum considered by him as possibly representing HO_2 radicals. Finally, the saturation concentration of radicals B produced in H_2O ice by $T\beta$ -particles, applied at a dose rate of 7.6×10^{17} ev./ml. hr. is of the order of 10^{18} spins/ml., whereas the concentration of radicals A, produced in tritiated 6 M H_2O_2 , easily exceeds this value, and for a dose rate of 2.51×10^{17} ev./ml. hr. and a total dose of 2.5×10^{20} ev./ml. approaches 10^{19} spins/ml. Under these conditions the yield of radicals A seems to be higher than that of radicals B by a factor of the order of 10.

Assuming that the primary results of H_2O_2 photolysis are limited to the production of OH radicals, probably represented by spectrum B in Fig. 1, our further experiments were based on the assumption that radical A is produced in H_2O_2 by a secondary process involving OH radicals, most likely by the reaction



Consequently, the influence of H_2O_2 concentration on e.p.r. spectra was investigated.

Photolysis by Ultraviolet Light.—Aqueous H_2O_2 solutions of concentrations ranging from 10^{-3} to 10 M were irradiated in quartz tubes at liquid nitrogen temperature by ultraviolet light (Mineralight Model SL without filter). Varying the concentration of H_2O_2 in the range 10 to 10^{-2} M does not seem to affect the e.p.r. spectrum, which, in all cases, remains identical with spectrum A in Fig. 1. However, on approaching a concentration of the order of 10^{-3} M the spectrum, especially after longer ultraviolet irradiation, changes, as shown in Fig. 3.

Finally, after a long irradiation, the spectrum becomes identical with that in Fig. 1B, believed to represent OH radicals.

Characteristically, even for dilute H_2O_2 solutions, the initial spectrum recorded after short ultraviolet irradiation seems to represent mainly radical A and in course of further irradiation (Fig. 3) is gradually replaced by B. This change of spectrum probably results from the progressive decomposition of H_2O_2 . Thus, as the photolysis proceeds, the number of OH radicals escaping reaction (1) increases.

The doublet spectrum obtained after prolonged irradiation disappears on warming according to curve B in Fig. 2. After reaching the temperature of about -130° , only a weak signal, corresponding to the spectrum of radical A, is left. The concentration of the latter may be estimated as about 10% of the initial concentration of radicals represented by the doublet.

In view of the above facts, we are inclined to believe that the e.p.r. spectra reported hitherto for concentrated (2–98%) solutions of H_2O_2 , irradiated by ultraviolet light at liquid nitrogen temperature, represent mainly HO_2 radicals in reaction (1). OH radicals produced in the primary photolytic process may be observed only in dilute (10^{-3} to 10^{-2} M) H_2O_2 solutions when the occurrence of reaction (1) is limited and a large fraction of OH radicals remains unscavenged by hydrogen peroxide.

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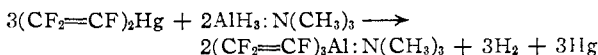
JERZY KROH
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RECEIVED FEBRUARY 25, 1961

A PERFLUOROVINYALUMINUM COMPOUND

Sir:

The preparation of some perfluorovinylboron compounds was reported recently,¹ and a communication also has appeared in print on a perfluoromethylboron derivative.² In our laboratory we have been able to synthesize a perfluorovinylaluminum compound. This has been accomplished by a method which has been found to be of general utility in the preparation of organoaluminum compounds³



To 0.99 g. (0.011 mole) of aluminum hydride trimethylamine⁴ in ethyl ether was added slowly, under stirring, 6.0 g. (0.017 mole) of bis-(perfluorovinyl)-mercury,⁵ likewise dissolved in ethyl ether. A vigorous reaction occurred even at -20° and hydrogen was liberated immediately. After the addition was complete, stirring was continued for 12 hr. at room temperature and then another 0.50 g. (0.0014 mole) of $(CF_2=CF)_2Hg$

(1) S. L. Stafford and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 6238 (1960).

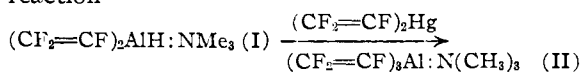
(2) T. D. Parsons, E. D. Baker, A. B. Burg and G. L. Juvinall, *ibid.*, **83**, 250 (1961).

(3) B. Bartocha, A. J. Bilbo, D. E. Bublitz and M. Y. Gray, *Angew. Chem.*, **72**, 36 (1960).

(4) J. K. Ruff and M. F. Hawthorne, *J. Am. Chem. Soc.*, **82**, 2141 (1960).

(5) R. N. Sterlin, Li-Vei-Gan and I. L. Knunyants, *Izvest. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk*, 1506 (1959) [*C.A.*, **54**, 1273c (1960)].

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.

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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 $\text{P}2_1/\text{n}$. 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.*, **225**, 385 (1936).