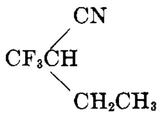
at 1339, 1176, and 1145 cm.$^{-1}$, respectively, are in accord with the literature values,[5] 1321 ± 9, 1179 ± 7, and 1140 ± 9 cm.$^{-1}$ for the CF_3 symmetrical and antisymmetrical deformation modes. Similarly, bands in the 1230–1287- and 3000-cm.$^{-1}$ regions for each sample confirmed[6] the presence of the C–F and C–H stretching modes.

The CF_2 symmetrical and antisymmetrical stretching modes have been well characterized[7] as 1125 ± 10 and 1181 cm.$^{-1}$ in a series of pentafluoroethylhalides. In the $C_7H_6F_7N$ fraction, bands are observed at 1119 and 1198 cm.$^{-1}$, respectively.

Discussion

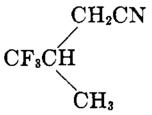
While the microelemental analyses of the 1:1 addition products from propylene with CF_3CN and $CF_3CF_2CF_2CN$, confirm the empirical formulas, $C_5H_6F_3N$ and $C_7H_6F_7N$, respectively, the n.m.r. spectra (and chromatographic analyses for $C_7H_6F_7N$) clearly show that these are two component mixtures in each case. The compounds, $CF_3CH_2CH(CN)CH_3$ and $CF_3CF_2CF_2CH_2CH(CN)CH_3$ are present in large excess (*i.e.*, 89 and 97%), in these mixtures. The predominance of these two compounds is strong support for the viewpoint[1] that $\dot{C}F_3$ is the chain initiator in the propagation cycle of this free-radical reaction. The thermally initiated reactions of perfluoroalkylnitriles with propylene correspond closely, in this respect, with those reported elsewhere[8] for CF_3I and monoolefins.

The results are inadequate for the exact structural characterization of the second component observed in the 1:1 addition fractions. It can nevertheless be inferred (microelemental analysis, infrared spectra, and F^{19} magnetic resonance spectrum) that for the CF_3CN-propylene product two structures are probable.



I

or



II

The presence of this second component in much smaller amounts may thus be attributed to abnormal radical additions of the perfluoroalkylnitriles with propylene. Disappearance of CN radicals in the presence of olefins has been observed[9]; in the present systems this is also a possible route to the formation of an (isomeric) 1:1 addition product.

Acknowledgment.—The authors are indebted to Drs. C. W. Wilson, III, and L. O. Moore of Union Carbide, South Charleston, West Virginia, for the n.m.r. analysis (Table I). J. B. Flannery (Rensselaer Polytechnic Institute) is thanked for helpful discussions. This work was made possible, in large part, by a grant-in-aid from the American Chemical Society Petroleum Research Fund and a Carbide Fellowship in Chemistry.

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Nitrile Oxides. III. Reduction of Nitrile Oxides to Nitriles[1]

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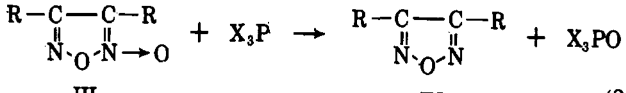
Received February 8, 1965

The reduction of benzonitrile oxide and triphenylacetonitrile oxide to the corresponding nitriles has been achieved by means of zinc dust and acetic acid or tin and hydrochloric acid.[2] In other cases, however, these methods have failed because of side reactions, *e.g.*, addition of the acid to the nitrile oxide with formation of a hydroxamic acid derivative which is no more reduced to the nitrile.[3]

A generally applicable method for the conversion of nitrile oxides (I) into nitriles (II) in excellent yields under very mild conditions was found in the reduction with trivalent phosphorus compounds, especially trialkyl- or triarylphosphines and trialkyl phosphites, as shown in eq. 1. The reduction of the semipolar

$$\underset{\text{I}}{R{-}C{\equiv}N{\rightarrow}O} + X_3P \longrightarrow \underset{\text{II}}{R{-}C{\equiv}N} + X_3PO \qquad (1)$$

$\geqslant$N→O group to $\geqslant$N by trivalent phosphorus compounds is generally known,[4-8] although the ease of reduction depends to a large extent on the nature of the groups attached to nitrogen; *e.g.*, triphenylphosphine does not reduce pyridine and quinoline N-oxides or aromatic nitro groups.[4a] The dimers of nitrile oxides, the furoxans (III, 1,2,5-oxadiazol-2-oxides), are easily deoxygenated to the corresponding furazans (IV, 1,2,5-oxadiazoles),[5,6,8] although claims to the contrary have been made.[7] Reduction of III to IV has been achieved with aliphatic or aromatic tertiary phosphines as well as with trialkyl phosphites (eq. 2).



III IV (2)

For our purpose, we found the lower aliphatic trialkyl phosphites, *e.g.*, trimethyl or triethyl phosphite, especially suitable, since any excess of the reagent is almost instantly hydrolyzed by dilute mineral acids and the trialkyl phosphates formed during the reaction are water soluble, thus rendering the isolation of the nitrile very convenient.[9] The nitriles were identified by analysis and mixture melting point with an authentic sample. In the cases where the nitrile was not known, it was also

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(1) Second communication: C. Grundmann and J. M. Dean, *Angew. Chem.*, **76**, 682 (1964); *Angew. Chem., Intern. Ed. Engl.*, **3**, 585 (1964).

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(9) In case of water-soluble nitriles, one would for the same reasons, preferably employ, for instance, triphenylphosphine.

TABLE I

NITRILES FROM NITRILE OXIDES[a]

$R—C\equiv N\rightarrow O$ (I) $\longrightarrow$ $R—C\equiv N$ (II)

Nitrile oxide I R =	Nitrile II M.p., °C.	Yield, %	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
2,4,6-Trimethylphenyl-[b]	50[c]	98	$C_{10}H_{11}N$	...	...	...	...	9.65	9.56
2,3,5,6-Tetramethylphenyl-[b]	74[d]	91	$C_{11}H_{13}N$	...	...	...	...	8.80	8.81
2,4,6-Trimethoxyphenyl-[b]	143–144[e]	93	$C_{10}H_{11}NO_3$	62.16	61.96	5.74	5.74	7.25	7.28
9-Anthracenyl-[f]	177[g]	98	$C_{15}H_9N$	88.65	88.64	4.46	4.70	6.89	6.81
2,3,5,6-Tetramethylphenylen-1,4[b]	208–209[e,h]	80	$C_{12}H_{12}N_2$	78.22	78.07	6.57	6.52	15.21	15.12

[a] All reductions with trimethyl phosphite, as described in the Experimental section. [b] C. Grundmann and J. M. Dean, *Angew. Chem.*, **76,** 682 (1964); *Angew. Chem., Intern. Ed. Engl.*, **3,** 585 (1964). [c] F. W. Küster and A. Stallberg, *Ann.*, **278,** 212 (1893). [d] O. Jacobsen, *Ber.*, **22,** 1224 (1889). [e] See Experimental section for preparation by another route. [f] Prepared by the procedure described in *b;* yellow needles (from methanol), m.p. 127–128°. *Anal.* Calcd. for $C_{15}H_9NO$: C, 82.19; H, 4.12; N, 6.39; mol. wt., 219. Found: C, 82.39; H, 3.91; N, 6.17; mol. wt., 219. [g] P. Karrer and E. Zeller, *Helv. Chim. Acta*, **2,** 485 (1919). [h] Berl-Block, sealed capillary.

prepared by dehydration of the oxime. The results are summarized in Table I.

This reduction of nitrile oxides to the corresponding nitriles can be of value in establishing the structure, especially in cases where rapid dimerization to the furoxan makes molecular weight determinations difficult. Since, under the applied conditions, the furoxans are reduced no further than to the furazans, the rate of dimerization of a nitrile oxide can be conveniently determined by measuring the consumption of trivalent phosphorus compound by the mixture of nitrile oxide–furoxan,[10] according to eq. 1 and 2.

Experimental[11]

Reduction of Nitrile Oxides to Nitriles.—One millimole of the nitrile oxide was dissolved, if necessary with gentle warming, in 10 ml. of benzene, and 0.4 mmole of trimethyl or triethyl phosphite (practical, Eastman) was added. After heating for 5–10 min. on the steam bath, the reduction was terminated.[12] The cooled reaction mixture was diluted with 10 ml. of benzene, and shaken with 25 ml. of 5% sulfuric acid until the odor of the alkyl phosphite had disappeared. The organic layer was then washed four times with 25 ml. of water each to extract the formed trimethyl or triethyl phosphate and then evaporated *in vacuo* to dryness. The yields of the remaining nitriles are given in Table I, the melting points were generally no more than 1–2° below those given in the table. Except for VI which was purified by vacuum sublimation (110–130° at 0.1 mm) the crude products yielded pure samples by a single recrystallization from methanol or ethanol. **2,4,6-Trimethoxybenzonitrile** (V) and **tetramethylterephthalobisnitrile** (VI) were independently synthesized by refluxing the corresponding oximes with acetic anhydride for 7 hr. From 2,4,6-trimethoxybenzaldoxime,[13] the nitrile V was obtained directly in 92% yield, while tetramethylterephthalodialdoxime (prepared from tetramethylterephthalodialdehyde[14] and hydroxylamine hydrochloride in the usual manner yielding prisms, from ethanol, m.p. 240° dec.) gave a crude product which yielded pure VI only after chromatography from benzene on alumina, followed by vacuum sublimation, 27% (for melting point and analysis of V and VI, see Table I).

Acknowledgement.—The research of which this publication is a part was supported by Public Health Service Research Grants CA 07272-01 and CA 07272-02 of the National Cancer Institute, Bethesda, Maryland.

[10] In this case triphenylphosphine is preferred, because of stability towards autoxidation and ease of preparation of an analytically pure standard.

[11] Melting points were determined with the Fisher-Johns melting point apparatus and are uncorrected. Microanalyses are by Galbraith Laboratories, Knoxville, Tenn.

[12] In batches of 0.01 mole and above the reaction becomes quite exothermic and leads to vigorous boiling of the solvent; dropwise addition of the phosphite and a reflux condenser are recommended.

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[14] L. A. Mikeksa and D. R. Koennecke, U. S. Patent 2,806,883 (to Esso Research & Engineering Co.) (1958); *Chem. Abstr.*, **52,** 5407*g* (1958).

Optical Rotatory Dispersion of Some Deuterium Compounds[1]

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Received February 8, 1965

Many compounds are now known having substantial and useful optical activity due only to hydrogen–deuterium asymmetry. Fickett[3] showed how this optical rotatory power can result from the anharmonicity of the C–H vibrations; *i.e.*, the effective polarizability along a C–D bond differs from that of a C–H bond. According to this theory the optical activity of H–D compounds does not differ in principle from that of normally asymmetric compounds. A corollary is that deuterium compounds should show normal optical rotatory dispersion (O.R.D.).

Little data on this point are available in the literature. The ratio of rotations of 1-butanol-1-*d* and several esters at the mercury green line and the sodium line were reported to be similar to those of other simple alcohols and esters.[4] A recent attempt to measure the O.R.D. curve of cyclopentanone-3-*d* failed when the compound showed insufficient optical activity.[5]

In the course of various studies with optically active deuterium compounds we have had occasion to determine several O.R.D. curves. Earlier measurements were made on a Rudolph photoelectric polarimeter modified with a Beckman monochromator.[6] Rotations on this instrument were taken at selected wave lengths from 650 mμ down to just below 400 mμ. The long path lengths required precluded accurate work at shorter wave lengths. More recently, a number of samples were examined with a Cary 60 recording spectropolarimeter. This instrument has allowed us to measure directly the O.R.D. curves of several deu-

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[3] W. Fickett, *J. Am. Chem. Soc.*, **74,** 4204 (1952).

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[6] Rudolph spectropolarimeter, Model S-80, O. Rudolph and Sons, Caldwell, N. J.