

nitroform in reactions with potassium nitrite and potassium hydroxide or potassium iodide. The acetate 6 and 2-chloro-2,2-dinitroethyl acetate (12), however, produce the rearranged product 2 with potassium nitrite in the presence of iodide.

Esters of 2-chloro-2,2-dinitroethanol are expected to behave similarly. However, the presence of the labile positive halogen leads to competitive reactions possibly of the dinitroethylation type,⁴ which will be discussed below. In no case was a salt that corresponded to potassium chlorodinitromethane isolated.

However, difficultly hydrolyzed substituents, such as 2,2,2-trinitrochloroethane (1), with nitrogen bases or methoxide lead to the isolation of potassium dinitromethane (3). Most probably the initial attack of base is at the trinitromethyl group. This can be followed by acidic proton abstraction of hydrolysis of chloride resulting in the loss of one carbon as a derivative of formaldehyde. Sodium methoxide or nitrogen bases in reaction with 1, 2,2-dinitro-1,2-dichloroethane (4), and 2,2,2-trinitroethyl fluoride (5) produce this dinitromethane product. The fact that in no case was potassium trinitromethane formed and that in one case the rearranged product 2 was formed gives support to the speculation that the first point of attack occurs at the trinitromethyl group.

Discussion of the rearrangement of 2,2,2-trinitrochloroethane (1) to 2 was presented in ref 2. Since the 2,2,2-trinitroethyl acetate (6) and 2-chloro-2,2-dinitroethyl acetate (12) produce 2 only when reacted with potassium nitrite in the presence of iodide ion, it would seem more probable that a reaction path similar to that proposed in the dinitroethylation type reactions⁴ takes place with dinitroethylene as a common intermediate. Halogenation of intermediate nitronates by sources of positive halogen finds support in work reported by McEwen.⁴

Rearrangement to dipotassium 1,1,3,3-tetranitropropane (8) occurs in the absence of nitrite ion for compounds such as the chlorodinitroethyl acetate (12), the trinitroethyl acetate (6), and the sulfite 10 by reaction with iodide. Formation of the reactive intermediate dinitroethylene followed by Michael addition of 2,2-dinitroethyl acetate leads to the formation of 8.

From the reactions discussed above, it is obvious that many factors are responsible for directing the courses of the many processes involved and that much further study is needed to define the actual processes and steps involved. It is hoped that the speculation presented, along with the interesting chemical evidence, will spur additional fundamental work in the area of aliphatic nitro chemistry.

Experimental Section⁷

Preparation of Nitronate Salt Derivatives (Table I).—A solution of potassium nitrite (plus other reactants, if used) in 25 ml of 60% aqueous methanol was prepared (mole amounts given in Table I). To this solution was added 0.01 mol of nitro aliphatic compound, and the resulting solution was allowed to stand at room temperature for 24 hr. The precipitate was collected and washed with cold aqueous methanol and then air dried. The nitronate salt products were identified by their ir spectrum, melting (decomposition) points, and halogenated derivatives.

(7) Melting points and boiling points are uncorrected. *Caution:* many of the compounds described are explosives and are sensitive to impact, friction, etc.; *handle with care.* Microanalysis by Berkeley Analytical Laboratories; nmr by Varian Associates.

2,2,2-Trinitrochloroethane (1), 1,2-dichloro-2,2-dinitroethane (4), 2,2,2-trinitroethyl sulfite (10), 2,2-dinitrochloropropane (15), 1,3-dichloro-2,2-dinitropropane (13), dipotassium tetranitroethane (2), and potassium dinitromethane (3) were prepared as previously reported.²

2,2,2-Trinitroethyl acetate (6) was prepared as described by Morans and Zelinsky.⁵

2-Chloro-2,2-dinitroethyl acetate (12) was prepared by the method of Ungnade and Kissinger.³

2,2,2-Trinitroethyl Trifluoroacetate (9).—A solution of 36 g (0.2 mol) of 2,2,2-trinitroethanol in 50 g (0.24 mol) of trifluoroacetic anhydride was refluxed for 24 hr. The reaction mixture was fractionated under reduced pressure giving 47 g (85.5%) of product, bp 61–62° (4 mm), n_D^{25} 1.4051.

Anal. Calcd for $C_4H_2N_3O_5F_3$: C, 17.34; H, 0.73; N, 15.17. Found: C, 17.28, 17.37; H, 1.08, 1.01; N, 15.12, 15.14.

2,2,2-Trinitroethyl Tosylate (11).—2,2,2-Trinitroethanol (15 g, 0.082 mol) and *p*-toluenesulfonyl chloride (15 g, 0.078 mol) were heated at 85° for 7 days. After the first 2 hr of heating, 4 drops of pyridine were added. The crude product was recrystallized twice for benzene giving 10.5 g (24.7%) of product, mp 136.5–137°.

Anal. Calcd for $C_9H_9N_3O_6S$: C, 32.22; H, 2.68; N, 12.59; S, 9.56. Found: C, 32.23; H, 2.73; N, 12.62; S, 9.54.

2,2,2-Trinitrofluoroethane (5).—Trinitroethanol was fluorinated with sulfur tetrafluoride by the method of Baum.⁸ A 50% yield of 5 was obtained, bp 52–53° (13 mm). Proton nmr shows a doublet at 310 and 355 ppm from TMS. Principal infrared absorption was consistent with ref 8.

1,2-Difluorotetranitroethane.—Dipotassium tetranitroethane (2) was fluorinated by the aqueous fluorination method of Grakanskas.⁹ A 45% yield of 1,2-difluorotetranitroethane was obtained: bp 60° (35 mm); n_D^{25} 1.4152; F^{19} nmr shows a pentet at 97.3 ppm (relative intensity 1:2:3:2:1 split by 9 cps); principal infrared absorption at 1630 (s), 1340 (m), 1300 (m), 1275 (m), 820 (m), and 770 cm^{-1} (m).

Anal. Calcd for $C_2F_2N_4O_8$: C, 9.75; H, 22.76. Found: C, 9.77; N, 22.71.

1,3-Difluoro-1,1,3,3-tetranitropropane.—This compound was prepared by the aqueous fluorination procedure⁹ and produced a 58% yield of product: bp 75–77° (5 mm); n_D^{25} 1.4425; proton nmr shows a triplet with peaks at 291, 277, and 263 (relative intensity 1:2:1) from TMS; principal infrared absorption at 1620 (s) 1375 (w), 1310 (m), 1110 (w), 850 (w), and 820 cm^{-1} (w).

Anal. Calcd for $C_3H_2F_2N_4O_8$: C, 13.86; H, 0.78; N, 21.54. Found: C, 14.54; H, 0.90; N, 21.18.

Registry No.—1, 4100-02-1; 4, 4100-03-2; 5, 15892-91-8; 6, 4998-90-7; 9, 681-40-3; 10, 10596-61-9; 11, 26332-91-2; 12, 5917-55-5; 13, 4167-16-2; 14, 26329-29-3; 15, 4167-15-1; 1,2-difluorotetranitroethane, 20165-39-3; 1,3-difluoro-1,1,3,3-tetranitropropane, 22692-28-0.

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Radical Reaction of Isocyanide with Disubstituted Phosphine

TAKEO SAEGUSA,* YOSHIHIKO ITO, NAOHIKO YASUDA,
AND TETSUO HOTAKA

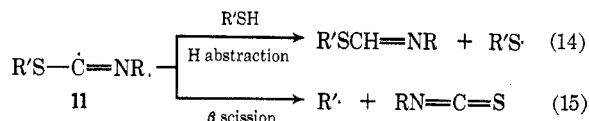
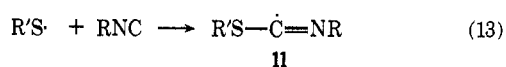
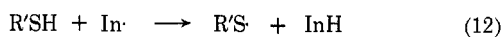
Department of Synthetic Chemistry, Faculty of Engineering,
Kyoto University, Kyoto, Japan

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A series of free-radical reactions of isocyanide have been found by us, which have been schematized by assuming an imido radical as the intermediate. As to the radical reaction of isocyanide with the heteroatom-

* To whom correspondence should be addressed.

and the hydrogen abstraction from thiol determine the whole course of reaction (eq 12-15). Thus three radi-



cal reactions of isocyanide are all summarized by the scheme involving the corresponding imido radicals, 8, 10, and 11, whose reactivities are decisive of determining the reaction courses.

Experimental Section

Materials.—All isocyanides were prepared from the corresponding formamides according to Ugi's procedure⁴ and stored under nitrogen. Diethylphosphine⁵ and diphenylphosphine⁶ were prepared according to the respective literatures and were stored under nitrogen. Benzene as solvent was used after the purification in the usual method. Azobisisobutyronitrile (AIBN) was a commercial reagent and used without further purification.

Representative Procedure for the Reaction of Isocyanide with Phosphine.—A mixture of benzyl isocyanide (30 mmol), diethylphosphine (40 mmol), AIBN (1.5 mmol), and benzene (10 ml) was heated at 70° for 18 hr under nitrogen atmosphere. Then, the reaction mixture was subjected to the fractional distillation under nitrogen. A product, toluene, was analyzed by glpc and nmr. An analytical sample of diethylcyanophosphine (1) was prepared by further purification of the distillation fraction [bp 71-72° (22 mm)] using preparative glpc. The structure of 1 was established by nmr, ir, and mass spectra, and elemental analysis: ir (neat) $\nu_{\text{C}=\text{N}}$ 2210 cm^{-1} (weak); mass spectrum parent mass 115 (mol wt, 115).

Anal. Calcd for $\text{C}_6\text{H}_{10}\text{NP}$: C, 52.16; H, 8.77; N, 12.17; P, 26.90. Found: C, 52.01; H, 9.03; N, 12.06; P, 26.71.

This compound is vulnerable to air.

The other reactions were carried out by the same procedure. The spectra data and elementary analyses of the reaction products are shown below.

***N*-Cyclohexylformimido-diethylphosphine (C_2H_5)₂PCH=N-C₆H₁₁** was analyzed as follows: bp 110-112° (6 mm); ir (neat) $\nu_{\text{C}=\text{N}}$ 1605 cm^{-1} (strong); nmr (CDCl_3) δ 8.35 (doublet, $J_{\text{FH}} = 33$ cps, 1 H, >PCH=N-).

Anal. Calcd for $\text{C}_{11}\text{H}_{22}\text{NP}$: C, 66.30; H, 11.13; N, 7.03; P, 15.54; mol wt, 199. Found: C, 65.94; H, 11.14; N, 7.07; P, 14.69; mol wt (cryoscopy in benzene), 202.

N*-*n*-Hexylformimido-diethylphosphine (3d) (C_2H_5)₂PCH=N-C₆H₁₃-*n was analyzed as follows: bp 105° (8 mm); ir (neat) $\nu_{\text{C}=\text{N}}$ 1614 cm^{-1} (strong); nmr (CDCl_3) δ 8.35 ppm (doublet, $J_{\text{FH}} = 36$ cps, 1 H, >PCH=N-), 3.50 (triplet, 2 H, -CH=NCH₂CH₂-).

Anal. Calcd for $\text{C}_{11}\text{H}_{24}\text{NP}$: C, 65.62; H, 12.04; N, 6.96. Found: C, 65.11; H, 12.46; N, 6.98.

Diphenylcyanophosphine (C_6H_5)₂PCN was analyzed as follows: 113.5° (0.13 mm); ir (neat) $\nu_{\text{C}=\text{N}}$ 2180 cm^{-1} (weak).

Anal. Calcd for $\text{C}_{13}\text{H}_{10}\text{NP}$: C, 73.92; H, 4.78; N, 6.63; P, 14.67. Found: C, 73.83; H, 5.43; N, 6.38; P, 14.56.

Registry No.—1, 26306-14-9; 3c, 19911-05-8; 3d, 26306-16-1; diphenylcyanophosphine, 4791-48-4; *tert*-butyl isocyanide, 7188-38-7; benzyl isocyanide, 10340-91-7; cyclohexyl isocyanide, 931-53-3; *n*-hexyl isocyanide, 15586-23-9; diethylphosphine, 627-49-6; diphenylphosphine, 829-85-6.

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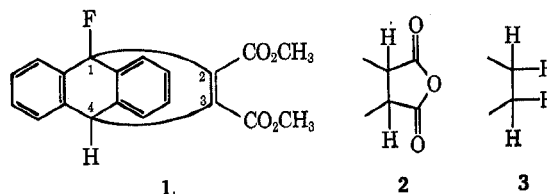
On the Stereochemistry of $^5J_{\text{HF}}$

LEON M. STOCK AND MICHAEL R. WASIELEWSKI^{1a}

Department of Chemistry, The University of Chicago, Chicago, Illinois 60637

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Long-range proton fluorine spin-spin coupling over five bonds is a well-known phenomenon.¹ The magnitude of the coupling constant depends importantly on the distance between the nuclei^{1c} and on the spatial arrangement^{1g} of the nuclei in the molecule under examination. Although the available data are not wholly consistent, the evidence suggests a direct,² or a very specific indirect,^{1g} coupling mechanism is important.¹ We have examined this question by an investigation of the nmr spectra of three rigid bicyclic molecules (1-3) in which the hydrogen and fluorine nuclei have the geometry (a trans coplanar relationship between F and C₂ and between H and C₃) that is thought to be ideal for a completely indirect² coupling mechanism but in which the hydrogen and fluorine nuclei are separated by approximately 5 Å.



The signal for the bridgehead hydrogen atom of 1 was a broadened doublet. Double resonance experiments with irradiation in the aryl hydrogen atom region narrowed the signal from $\Delta\nu_{1/2} = 2.6$ Hz to 2.1 Hz and enabled the confident definition of $^5J_{\text{HF}}$ as 0.88 ± 0.05 Hz (Figure 1).

Similar experiments with compounds 2 and 3 do not yield definitive values for $^5J_{\text{HF}}$ but do establish the value of this coupling constant as certainly less than 0.5 Hz. For 2, the resonance of the bridgehead hydrogen atom was a somewhat broadened doublet $^3J_{\text{HH}} = 1.7 \pm 0.1$ Hz. Double resonance experiments with irradiation in the region of H₂ and H₃ confirmed the assignment of the doublet and decreased $\Delta\nu_{1/2}$ to 1.8 Hz. For 3, the resonance of the bridgehead hydrogen atom was a broadened triplet, $^3J_{\text{HH}} = 1.9 \pm 0.1$ Hz. Double resonance work with H₂ and H₃ confirmed the origin of the triplet and decreased $\Delta\nu_{1/2}$ to 2.2 Hz. Irradiation in the aryl hydrogen atom region narrowed the signal for H₄ by about 0.5 Hz for 2 and 3. These results and the closely related behavior of 1 in similar experiments suggest that $^5J_{\text{HF}}$ is less than 0.5 Hz for 2 and 3, but probably greater than 0.3 Hz.

The nmr spectrum of 1-fluorobicyclo[2.2.2]octane has

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(2) The terminology of M. Barfield and M. Karplus, *ibid.*, **91**, 1 (1969), has been adopted.