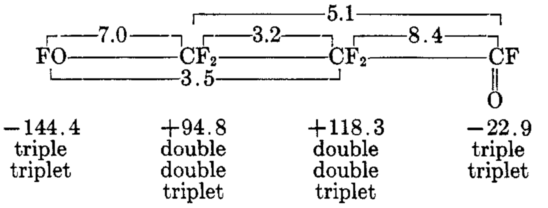

Figure 1.—Schematic representation of the nmr spectrum of 3-fluoroxyperfluoropropionyl fluoride.

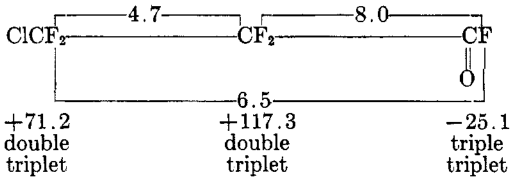

Figure 2.—Schematic representation of the nmr spectrum of 3-chloroperfluoropropionyl fluoride.

rate from the mass spectrometer, was 184 (calcd 182). Elemental analyses were in good agreement with theory.

Anal. Calcd for $C_3F_6O_2$: C, 19.8; F, 62.6. Found: C, 19.9; F, 62.5.

The compound which eluted with perfluoro-1,2-dioxolane is believed to be 3-fluoroxyperfluoropropionyl fluoride (III). This structural assignment was made on the basis of its F^{19} nmr spectrum. Figure 1 shows the absorptions (ϕ^*) and coupling constants (cycles per second) attributed to this compound. The peak areas were found to be in the ratio of 1:2:2:1. 3-Fluoroxyperfluoropropionyl fluoride is found to be oxidizing toward ferrocene and aqueous potassium iodide. Prolonged stability studies were not carried out on this compound. However, in a 22-day period no decomposition was observed in a sample containing only this compound and its coeluent, perfluoro-1,2-dioxolane.

Perfluoroethylene Oxide.—Preliminary isolation of perfluoroethylene oxide (I) was accomplished by trap-to-trap fractionation, followed by gas chromatography at −30° on a column of acid-washed Celite coated with perfluorotributylamine. The fraction having a retention time of 35 relative to dichlorodifluoromethane was subjected again to gas chromatography at −27° on a column of acid-washed Celite coated with Dow Corning SE-30 (a silicone polymer). In the second chromatographic procedure, perfluoroethylene oxide was separated from CF_3CFO, SO_2F_2, and SF_6 (the latter two are present in small amounts in fluorine). Perfluoroethylene oxide was identified by spectral means. Its F^{19} nmr spectrum shows a single sharp peak at ϕ^* 111.0. This value is consistent with the average found for the CF_2 group in higher members of this series. It differs substantially (after appropriate corrections) from that reported by Caglioti and co-workers.[7] However, a comparison of their infrared spectrum with ours leaves no doubt that both materials are the same. The mass spectrum fragmentation pattern of perfluoroethylene oxide exhibits the peaks shown in Table II. The molecular weight, determined by effusion rate from the mass spectrometer, was 118 (calcd 116).

TABLE II

MASS SPECTRUM OF PERFLUOROETHYLENE OXIDE

m/e	Ion	Relative intensity
19	F^+	2.6
31	CF^+	43.1
47	CFO^+	73.3
50	CF_2^+	100.0
51	$C^{13}F_2^+$	1.4
66	CF_2O^+	2.8
69	CF_3^+	57.1
97	$C_2F_3O^+$	2.0
100	$C_2F_4^+$	4.7

Nmr Spectra.—Some further F^{19} nmr data are given below. Perfluoromalonyl fluoride exhibits an absorption (a triplet) at ϕ^* −20.2 for the fluorines attached to carbonyls and one (also a triplet) at ϕ^* 111.6 for the CF_2 group. The coupling constant is 10.9 cps. Figure 2 shows the absorptions (ϕ^*) and coupling constants (cycles per second) for $ClCF_2CF_2CFO$.

Acknowledgment.—The author wishes to express her gratitude to Dr. John J. McBrady, who interpreted the nmr spectra with skill, and to Dr. Richard L. Talbott, who examined the decomposition reaction of the bifunctional fluoroxy compound.

Alkali Sensitivity of a Dinitro Compound in the Cyclopropane Series[1]

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Received August 16, 1965

The synthesis of *trans*-1,2-dinitro-3,3-dimethylcyclopropane was accomplished by monobromination of 1,3-dinitro-2,2-dimethylpropane and subsequent elimination with potassium acetate. It displays the expected high level of cyclopropyl hydrogen lability as revealed by hydrogen exchange under acetate catalysis at room temperature. With sodium hydroxide it is converted irreversibly to the salt of 1,2-dinitro-3-methyl-2-butene, which is liberated upon acidification in the presence of urea; otherwise, a reaction with nitrite ion leads to the formation of 3,4-dinitro-5,5-dimethyl-2-isoxazoline.

Despite the very great immunity of nitrocyclopropane[2] to basic reagents, there are good reasons to suppose that a vicinal dinitrocyclopropane might be exceedingly sensitive and possibly not accessible synthetically by ring closures with alkaline reagents. The known propensity of nitrocyclopropyl ketones to undergo ring-opening reactions with bases under mild conditions is conditional, as Smith and Engelhardt[3] established, upon having a cyclopropyl hydrogen α to a nitro group and a carbonyl function on the adjoining carbon. A second nitro group would be expected to serve even more effectively than carbonyl to provide the necessary activation for ionization and to facilitate rearrangement of the anion to a more stable open-chain species. Secondly, there is an instability associated with *vic*-dinitroalkanes, illustrated, for example, by the elimination of the elements of nitrous acid from 1,2-dinitrocyclohexane on treatment with sodium hydroxide.[4] Nevertheless, it seemed that an entry might be made into the series by cyclization under the mildest possible conditions starting from the readily available 1,3-dinitroneopentane where,

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(1) Work performed under Air Force Office of Scientific Research, Grant No. AFOSR-80-63.

(2) H. B. Hass and H. Schechter, *J. Am. Chem. Soc.*, **75**, 1382 (1953).

(3) L. I. Smith and V. A. Engelhardt, *ibid.*, **71**, 2676 (1949).

(4) A. T. Nielsen, *J. Org. Chem.*, **27**, 2001 (1962).

it was hoped, the *gem*-dimethyl effect would assert itself favorably.

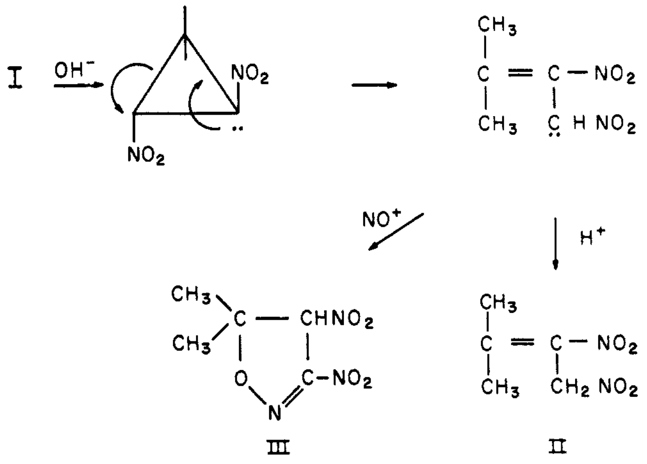
Attempted 1,3 coupling by oxidative procedures was unsuccessful. These efforts included oxygenation of an alkaline solution of dinitroneopentane under conditions that Russell[5] had found favorable in forming 2,3-dimethyl-2,3-dinitrobutane from 2-nitropropane, and also, following a procedure of Angeli and Allesandi[6] for 2,3-dinitrobutane, treatment of an alkaline solution with silver nitrate. However, the cyclization was accomplished readily, though not in high yield, by the classical two-step procedure of monobromination followed by a 1,3 elimination in alcoholic potassium acetate. The product is almost certainly the *trans* isomer of 1,2-dinitro-3,3-dimethylcyclopropane; all efforts to isolate a *cis* isomer, or to convert *trans* to *cis*, were fruitless.

The structure of the product follows unambiguously from the analytical data, infrared and ultraviolet spectra, absence of unsaturation, and the simple nmr spectrum with peaks at τ 8.48 and 4.72, in $CDCl_3$. Deuterium exchange, revealed by diminishing intensity of the low-field nmr peak as well as by the appearance of a C–D infrared stretching frequency, occurred at room temperature in dioxane–deuterium oxide containing potassium acetate. The exchange was evidence for the availability of a mechanism for *cis–trans* equilibration, and the recovery of the same substance from this treatment, or from even more drastic treatment with refluxing alcoholic potassium acetate, shows that the isomer at hand is the more stable one and supports the *trans* assignment.

The occurrence of hydrogen exchange under such mild conditions serves also as a demonstration that the cyclopropyl hydrogens are indeed labile and that a cyclic carbanion can be formed reversibly. An attempt to intercept the anion through a condensation with formaldehyde in the presence of acetate was unsuccessful, though the conditions were such that 2-nitropropane reacted readily. A further indication that the acidity falls below the normal for secondary nitroalkanes is the observation that the material is not immediately soluble in sodium hydroxide solution; its eventual solution is the consequence of an irreversible transformation to an open-chain species.

The behavior of 1,2-dinitro-3,3-dimethylcyclopropane (I) in aqueous sodium hydroxide, in which it dissolves on shaking at room temperature for 1–1.5 hr, is somewhat complicated because the rearrangement to an open-chain anion is accompanied by the appearance of nitrite ion. Upon acidification, unless measures are taken to destroy nitrite, the product then consists in part of 3,4-dinitro-5,5-dimethyl-2-isoxazoline (III), but if urea has been added the product is 1,2-dinitro-3-methyl-2-butene (II). The evidence for these relationships, as depicted in Scheme I, and in support of the product identifications, is detailed in the Experimental Section. The course of the anionic rearrangement can be followed spectrophotometrically by scanning the ultraviolet absorption of an aqueous solution of the dinitrocyclopropane that has been made alkaline by the addition of sodium hydroxide. In the first few minutes the absorption at 270 mμ, which may be due to the anion of I, is present but is soon masked by the 320-mμ absorption, characteristic of the anion of II. It is probable that the nitrite ion has its origin in the prolonged action of alkali on the dinitro olefin rather than by a direct nitrite elimination from the dinitrocyclopropane.

SCHEME I



There is a paradox in the apparently different behavior of the stable cyclopropyl carbanion generated by acetate ion and the short-lived carbanion generated by hydroxyl ion attack. Of the several possible explanations, one that could be checked in future work is that the rearrangement of the anion may not be a simple unimolecular process as represented but may entail reaction of an *aci* form with hydroxide ion somewhat after the pattern of the ter Meer reaction as elucidated by Hawthorne.[7]

Experimental Section

1,3-Dinitro-1-bromo-2,2-dimethylpropane.—A 250-ml aqueous solution of 1,3-dinitro-2,2-dimethylpropane[8] (4.68 g, 0.0288 mole) with a 1 molar equiv of sodium hydroxide (1.148 g, 0.0287 mole) was added dropwise during 45 min at 0° to a vigorously stirred suspension of bromine (4.98 g, 0.031 mole) in water. The precipitated solid was collected, dried, and sublimed at 60° under 1-mm pressure, to furnish 3.1 g of a white amorphous solid in 45% yield, mp 73–77°. In chloroform solution, nitro group absorption was found at 1565, 1372, and 1350 cm^{-1}.

Anal. Calcd for $C_5H_9BrN_2O_4$: Br, 33.15. Found: Br, 31.8.

***trans*-1,2-Dinitro-3,3-dimethylcyclopropane** (I). A.—In a procedure that did not entail isolation of the intermediate bromo compound, a solution of 1,3-dinitro-2,2-dimethylpropane (25.0 g, 0.154 mole) in 200 ml of dry methanol with sodium methoxide (from 3.54 g, 0.154 g-atom, of sodium) was added to a solution of bromine (24.7 g, 0.15 mole), in 250 ml of methanol at 0°. Potassium acetate (45 g, 0.45 mole) in 250 ml of methanol was added and the mixture was refluxed for 1 hr, then concentrated under reduced pressure. After the addition of water and chloroform to the mushy residue, the product was obtained from the chloroform extracts as a yellow oil. A solid product was obtained by chilling an aqueous methanol solution in a Dry Ice bath. This was sublimed at 70° and 1 mm and then recrystallized from aqueous methanol to provide 4.14 g, of the material (16% yield) as white crystals, mp 98.4–98.5°.

Anal. Calcd for $C_5H_8N_2O_4$: C, 37.50; H, 5.04; N, 17.49. Found: C, 37.41; H, 4.90; N, 17.57.

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[5] G. A. Russell, *J. Am. Chem. Soc.*, **76**, 1595 (1954).

[6] A. Angeli and Z. Allesandi, *Atti Accad. Nazl. Lincei Rend. Classe Sci. Fis.*, [5] **19**, *I*, 784 (1910); *Chem. Abstr.*, **4**, 2634 (1910).

[7] M. F. Hawthorne, *J. Am. Chem. Soc.*, **78**, 4980 (1956).

[8] The material was prepared as described by A. Lambert and A. Lowe, *J. Chem. Soc.*, 1517 (1947). The nitro group frequencies occur at 1560, 1555, and 1370 cm^{-1} in CCl_4. The nmr peaks, in CCl_4, occur at τ 8.79 and 5.56.

The substance in acetone solution did not decolorize aqueous permanganate; its solution in chloroform did not decolorize bromine in carbon tetrachloride. The compound was further characterized by its nmr spectrum at 40 Mc, peaks at τ 8.48 and 4.72 in $CDCl_3$[9]; ultraviolet spectrum in methanol, λ_{max} 270 mμ (ϵ_{max} 136); and infrared spectrum in $CHCl_3$, 3080 (m) 3020 (w), 2960 (w), 1560 (sh), 1550 (s), 1462 (m), 1360 (s), 1297 (m), 1258 (w), 1054 (m), 972 (m), 945 (m), 928 (m), and 845 (w) cm^{-1}.

B.—The cycloelimination reaction was performed on 1,3-dinitro-1-bromo-2,2-dimethylpropane (20.0 g, 0.083 mole) by refluxing it 3 hr in a solution of 700 ml of absolute ethanol containing freshly fused potassium acetate (24.4 g, 0.244 mole). The crude product, obtained as a yellow oil from the chloroform extract, was placed on a 70-g Celite–silicic acid (1:3, 3 × 25 cm) column and, by means of a continuous extractor operated for 10 hr on petroleum ether (bp 30–60°), a crystalline material was eluted (3.0 g, 22%) that was identical with that described above. It was obtained in 34% yield when the reflux period was 30 min. There was no reaction in 40 hr at room temperature.

Deuterium Exchange.—Deuterium exchange was followed by nmr observations on the ratio of methyl to ring hydrogen peak areas in the recovered material as well as by the appearance of a C–D stretching frequency at 2280 cm^{-1}. The experiments were performed by mixing 3.00 ml of 0.07 M potassium acetate in deuterium oxide with 5 ml of a 0.19 M solution of the dinitro compound I in dioxane. The solutions were kept at 25.5° while protected from air and light. The extent of exchange after 44 hr, as estimated from peak areas, varied from 61 to 93% of completion for exchange of two hydrogens.

Reaction with Formaldehyde.—A mixture of I (0.320 g, 2.00 mmoles), paraformaldehyde (0.120 g, 4 mmoles), and potassium acetate (0.038 g, 0.39 mmole) in 30 ml of methanol became homogeneous after standing overnight and was allowed to stand for 18 days. The dinitrocyclopropane was recovered (0.308 g, 96%) unchanged. Under similar conditions, 2-nitropropane reacted to provide the known formaldehyde condensation product[10] in 60% yield.

Action of Sodium Hydroxide.—The dissolution of I (101 mg, 0.631 mmole) in 10% aqueous sodium hydroxide (2.37 g, 5.92 mmoles) occurred slowly on stirring for 1–1.5 hr, at room temperature, and I was not regenerated upon acidification with sulfuric acid at 0°. The organic product, extracted by chloroform (three 10-ml portions) and fractionated by liquid chromatography on 5 g of silicic acid–Supercel (3:1, 1 × 10 cm) with elution by benzene–petroleum ether (3:2), was a mixture consisting mainly of II (48 mg) with approximately 2 mg of III. These were characterized as indicated in the following sections. Nitrite ion was detected in the aqueous solution. When urea was added prior to acidification, and acidification was performed at 0° by addition of acetic acid–urea reagent,[11] only II was isolated. When nitrite ion, in fourfold excess, was added prior to acidification with glacial acetic acid at 0°, with subsequent warming to 25°, the product was almost exclusively III.

The action of sodium hydroxide in very dilute solutions was observed spectrophotometrically on aqueous solutions, 0.46 × 10^{-4} M in I and in sodium hydroxide. In the first 2 min maxima were observed at 320 and 270 mμ, but the latter was quickly obscured as the 320-mμ absorption increased to maximum intensity at about 25 min and thereafter gradually decreased. After 1.8 hr a maximum at 270 mμ could again be seen; at 22 hr the 320-mμ band was barely perceptible. Compound II with sodium hydroxide, each at 0.46 × 10^{-4} M, exhibited absorption, gradually decaying, at 320 mμ.

1,2-Dinitro-3-methyl-2-butene (II).—The product from the acidification (12 ml of 20% aqueous acetic acid–urea) of alkaline solutions (25 ml of 0.124 M NaOH) of I (511 mg, 3.19 mmoles) in the presence of urea (4.0 g, 67 mmoles) was obtained, after several short-path vacuum distillations, as a pale yellow liquid (375 mg, 75%) with a lachrymatory odor: bp 70° (1 mm); $n^{20}\mathrm{D}$ 1.4972; λ_{max}^{EtOH} 251 mμ (ϵ_{max} 5560); nmr, τ 7.71 (3), 7.51 (3), and 4.06 (2); infrared, 1648 (m), 1566 (s), 1525 (s), 1417 (m), 1368 (s), 1340 (s), and 889 (m) cm^{-1}.

Anal. Calcd. for $C_5H_8N_2O_4$: C, 37.50; H, 5.04; N, 17.49. Found: C, 37.63; H, 5.27; N, 17.40.

The compound darkens on standing and is largely decomposed in a period of one to several weeks depending upon the initial purity. It decolorizes aqueous permanganate instantly.

Ozonolysis of the compound (185 mg, 1.16 mmoles) in 50 ml of methylene chloride at −78°, with work-up by treatment with zinc dust followed by 2,4-dinitrophenylhydrazine reagent (229 mg, 1.16 mmoles), furnished acetone 2,4-dinitrophenylhydrazone (120 mg, 44%), mp 124.2°.

3,4-Dinitro-5,5-dimethyl-2-isoxazoline (III).—The product of acidification in the presence of nitrite ion was a colorless solid (194 mg from 337 mg of I) which could be purified by recrystallization from petroleum ether and sublimation: mp 97.0–97.2°; λ_{max}^{alc} 268 mμ (ϵ_{max} 5910); nmr (40 Mc), τ 8.40 (double) and 4.36; infrared ($CHCl_3$), 1595, 1575, 1546, 1367, and 1015 cm^{-1}.

Anal. Calcd for $C_5H_7N_3O_5$: C, 31.75; H, 3.73; N, 22.22. Found: C, 31.84; H, 3.77; N, 22.13.

The absorption peaks at 1595 and 1575 cm^{-1} agree well with literature reports[12] on a series of phenyl-substituted 2-isoxazolines.

There appeared to be no available data on the nitro-group frequency for the $-C(NO_2){=}N-$ grouping. Accordingly, two known compounds were prepared and were found to exhibit nitro-group frequencies as follows: ethylnitrolic acid, $CH_3C(NO_2){=}NOH$, mp 75–90°, lit[13] mp 81° dec, 1545 (s) and 1376 (m) cm^{-1} in chloroform; and benzoylethylnitrolic acid, $CH_3C(NO_2){=}N{-}OBz$, mp 132–135°, lit[14] mp 135°, 1555 (s) and 1375 (m) cm^{-1} in chloroform. All data are thus consistent with the formulation of III as 3,4-dinitro-5,5-dimethyl-2-isoxazoline.

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[9] The nmr peaks for 2,3-dinitrobutane in $CDCl_3$ were found at τ 8.22 and 4.78.

[10] B. M. Vanderbilt and H. B. Hass, *Ind. Eng. Chem.*, **32**, 34 (1940).

[11] N. Kornblum and G. E. Graham, *J. Am. Chem. Soc.*, **73**, 4041 (1951).

[12] G. W. Perold, A. P. Steyn, and F. V. K. von Rieche, *ibid.*, **79**, 462 (1957).

[13] V. Meyer, *Ann.*, **175**, 84 (1875).

[14] V. Meyer, *Ber.*, **27**, 1600 (1894).

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cis- and *trans-*1,3-Diphenylpropene

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Received July 13, 1965

The preparation and physical properties of *cis-* and *trans-*1,3-diphenylpropene are described, as is the ultraviolet photoisomerization of the *cis* into the *trans* isomer. Configurational assignments are made on the basis of infrared and nmr spectroscopy and by the relative rates of methoxylation–acetoxymercuration shown by the two isomers.

A compound, mp 57°, purported to be 1,3-diphenylpropene, was obtained in 1899 by Francis[2] as a byproduct to the α-ethylation of 1,3-diphenyl-2-propanone with ethyl iodide and sodium ethoxide, followed by atmospheric-pressure distillation of the crude product. The compound produced a dibromide, mp 231°, on bromination in benzene solution. A second compound designated as 1,3-diphenylpropene was prepared by Dieckmann and Kämmerer[3] in

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[1] NSF Science Teaching Faculty Fellow, 1962–1963.

[2] F. E. Francis, *J. Chem. Soc.*, **75**, 865 (1899).

[3] W. Dieckmann and M. Kämmerer, *Ber.*, **39**, 3046 (1906).