Reduction of *m*-Nitroanisole with Sodium Borohydride in Dimethyl Sulfoxide.—To a stirred solution of sodium borohydride (3.405 g, 0.09 mol) in 25 ml of DMSO maintained at 85° was added dropwise a solution of *m*-nitroanisole (2.297 g, 0.015 mol) in 12 ml of DMSO over a 10-min period. After 1.5 hr, the solution was poured into 150 ml of water and extracted with three 25-ml portions of $CHCl_3$. The $CHCl_3$ solution was diluted to 100 ml and analyzed for yields of *m*-anisidine and *m*-azoanisole by glpc using standard solutions of the products (13.2 and 75.9% *m*-anisidine and *m*-azoanisole, respectively). The solution was washed with dilute HCl, then with water, and dried ($MgSO_4$). Removal of solvent on a rotary evaporator gave a red oil which solidified (1.96 g). A 208-mg sample was chromatographed on Florisil. Elution with 1:1 pentane-benzene afforded an orange-red solid, mp 75–76° (111.1 mg, representing a 61% yield). The ir and nmr spectra were consistent with *m*-azoanisole. One sublimation at reduced pressure gave the analytical sample.

Anal. Calcd for $C_{14}H_{14}N_2O_2$: C, 69.40; H, 5.82; N, 11.56. Found: C, 69.65; H, 5.73; N, 11.56.

***p,p'*-Azobenzamide.**—In a similar manner as above, *p,p'*-azobenzamide was obtained from *p*-nitrobenzamide in 49% yield. Three recrystallizations from DMF afforded the analytical sample, mp 360–363° (dec).

Anal. Calcd for $C_{14}H_{12}N_4O_2$: C, 62.68; H, 4.51; N, 20.88. Found: C, 62.68; H, 4.42; N, 20.86.

Registry No.—Sodium borohydride, 16940-66-2; *m*-azoanisole, 6319-23-9; *p,p'*-azobenzamide, 27332-13-4.

Acknowledgment.—We wish to thank the Petroleum Research Foundation, administered by the American Chemical Society, for partial support of this study.

Reactions of 2,2-Dinitroalkyl Tosylates with Nucleophiles

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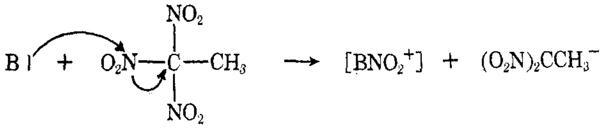
Some reactions of 2-fluoro-2,2-dinitroethyl tosylate (1) and 2,2-dinitropropyl tosylate (2) with nucleophiles were investigated. Weak bases lead to tosylate displacement, in some instances in preparatively useful yields. With strong bases side reactions such as nitrous acid elimination prevail. The reactivity of these tosylates is discussed, and some properties of 2,2-dinitroalkyl azides prepared from them are given.

The effects of β substituents on the S_N2 reactivity of alkyl halides and sulfonates have been the subject of extensive studies. No completely unequivocal rationalization of these effects in terms of steric and electronic properties of the substituents has been achieved. It seems clear, however, that β substitution generally decreases reaction rates rather strongly due to steric crowding in the transition state; if the β substituent is electron withdrawing (*e.g.*, halogen), a further smaller decrease is frequently observed.[1] A combination of these factors has been invoked, for example, to account for the observation that 1,1-di-*H*-perfluoroalkyl halides and tosylates are much less reactive toward KI in acetone or NaI in alcohols than the corresponding unsubstituted alkyl substrates.[2]

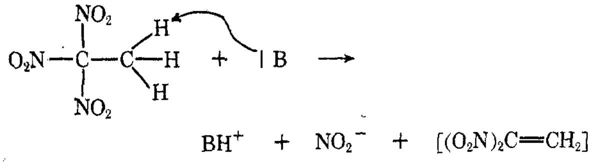
If this trend were to continue with bulkier and still more electron-withdrawing substituents such as nitro, it could result in 2-nitroalkyl sulfonates being essentially unreactive in S_N2 displacement reactions. The extent of our knowledge on this subject appeared confined to a single statement to the effect that "2,2-dinitropropyl benzenesulfonate is unreactive toward LiCl and KOAc in boiling ethanol."[3] We therefore investigated the reactions of several nucleophiles with some 2,2-dinitroalkyl tosylates which became available to us in the course of other studies with 2,2-dinitroalkanols.[4]

This paper deals primarily with the course of such reactions of 2-fluoro-2,2-dinitroethyl tosylate (1) and, to a lesser extent, of 2,2-dinitropropyl tosylate (2); quantitative rate data regarding their relative reactivities will be presented elsewhere. That these tosylates are, in fact, surprisingly reactive is demonstrated by the following experiment. Refluxing 1 with LiBr in acetone for 5 hr results in precipitation of *ca.* 90% of the theoretical amount of lithium tosylate, most of which deriving from a direct displacement reaction (see below), while trifluoroethyl tosylate is recovered unchanged after a reaction time of 150 hr.

Displacement reactions on 2,2-dinitroalkyl tosylates are likely to be complicated by the fact that polynitroalkanes themselves are subject to attack by nucleophiles. Thus, 1,1,1-trinitroethane undergoes two general reactions with nucleophiles under relatively mild conditions:[5] (1) attack by the nucleophile on one of the nitro groups with displacement of the 1,1-dinitroethane anion, and (2) abstraction by the nucleophile of a β-hydrogen atom resulting in elimination of nitrous acid and formation of 1,1-dinitroethene as an intermediate. 1-Halo-1,1-dinitroalkanes react similarly. When hal = Cl or Br, dinitrocarbanion formation occurs (reaction 1);[5] with hal = F, fluoronitroethene intermediates are formed (reaction 2).[6] Simple *gem*-dinitroalkanes with nonterminal dinitromethylene groups are more resistant to attack by nucleophiles. In particular, proton ab-



$$B| + O_2N-\overset{NO_2}{\underset{NO_2}{C}}-CH_3 \longrightarrow [BNO_2^+] + (O_2N)_2CCH_3^- \quad (1)$$



$$O_2N-\overset{NO_2}{\underset{NO_2}{C}}-\overset{H}{\underset{H}{C}}-H + |B \longrightarrow BH^+ + NO_2^- + [(O_2N)_2C{=}CH_2] \quad (2)$$

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[1] A. Streitweiser, Jr., *Chem. Rev.*, **56**, 691 (1956); J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1962, p 163 ff.

[2] G. V. D. Tiers, H. A. Brown, and T. S. Reid, *J. Amer. Chem. Soc.*, **75**, 5978 (1953); E. T. McBee, R. D. Battershell, and H. P. Braendlin, *ibid.*, **84**, 3157 (1962).

[3] L. W. Kissinger, T. M. Benziger, H. E. Ungnade, and R. K. Rohwer, *J. Org. Chem.*, **28**, 2491 (1963).

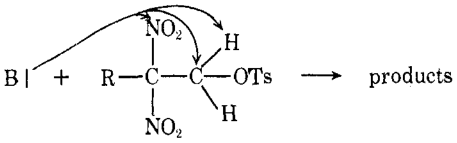
[4] H. G. Adolph and M. J. Kamlet, *ibid.*, **34**, 45 (1969).

[5] L. Zeldin and H. Shechter, *J. Amer. Chem. Soc.*, **79**, 4708 (1957).

[6] L. A. Kaplan, this laboratory, private communication.

straction from the adjacent carbon does not occur readily. For example, no deuterium uptake (or any other change) was detected by nmr over a period of 5 days when 2,2-dinitropropane was allowed to react with CD_3O^- in CD_3OD at room temperature.

One must therefore expect, at least in the reactions of **1** with nucleophiles, that denitrosation (2) and other side reactions resulting from proton abstraction at C_1 by the nucleophile or from its initial attack on the dinitromethylene group may come into play.



1, R = F
2, R = CH_3

The results of the reactions of **1** and **2** with several nucleophiles are listed in Table I. It is seen that the reaction conditions vary considerably, and interpretation of the results is further complicated by the possibility that the tosylate displacement products may be unstable to varying extents under the reaction conditions. Further reaction of the primary products with the nucleophile by paths 1 or 2 could lead to a decrease in yield or, possibly, to a complete disappearance from the product mixture. Except for the reaction with potassium fluoride, a distinct effect of the basicity of the nucleophile on the course of the reaction is nevertheless evident. The weakest base, bromide ion, gives the best yield of tosylate displacement product. The considerably stronger base, azide ion, yields much less of it. Finally, the strongly basic cyanide and methoxide ions give no substitution products at all. There is also strong indication that C_1-proton abstraction by the nucleophile either in the substrate or in the product does occur. Thus, in the fluorodinitroethyl system which should be more vulnerable to such attack, the yield of dinitroalkyl azide is much lower than in the dinitropropyl series. In addition, the reaction of **1** with $KOCH_3$ and, under certain conditions with NaN_3, gave products which probably in the latter and definitely in the former case arise from a denitrosation reaction (see below).

TABLE I
REACTION OF 2,2-DINITROALKYL TOSYLATES WITH NUCLEOPHILES

Substrate	Nucleophile	Reaction conditions	Products, yield
1	Br^-	LiBr/acetone, 5 hr at 55°	2-Fluoro-2,2-dinitroethyl bromide (**3**), 75%
1	F^-	KF/DMSO, 15 hr at 75–80°	**1** recovered, 20%; no other products isolated
1	N_3^-	NaN_3/80% aq DMSO, 15 hr at 25–30°	**1** recovered, 30%; 2-fluoro-2,2-dinitroethyl azide (**4**), 20–25% of reacted **1**
2	N_3^-	NaN_3/80% aq DMSO, 48 hr at 60°	**2** recovered, 35%; 2,2-dinitropropyl azide (**5**), 73% reacted **2**
1	CN^-	NaCN/80% aq DMSO, 24 hr at 25–30°	**1** recovered, 50%; no other products
2	CN^-	NaCN/80% aq DMSO, 48 hr at 50–60°	**2** recovered, 57%; no other products
1	CH_3O^-	2 KOH/MeOH, 15 min at 0°	No **1** recovered; major product, 1-fluoro-1-nitro-2,2-dimethoxyethane (**8**), 30%

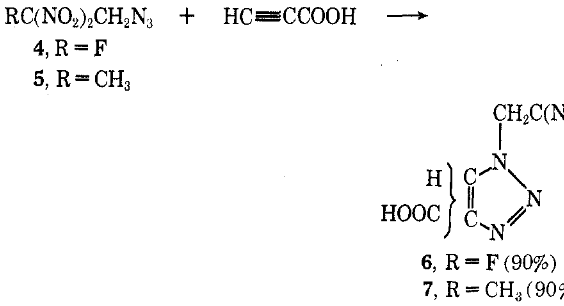
No other evidence was obtained during this work as to the fate of that portion of the substrate that was consumed but not converted to a tosylate displacement product. It is clear that for synthetic purposes the results of the attempted displacement reactions are not encouraging in the case of **1** but do suggest some usefulness of the reaction for 2,2-dinitroalkyl sulfonates such as **2**. A more detailed discussion of some of the reactions and products listed in Table I follows.

2-Fluoro-2,2-dinitroethyl bromide (**3**), the product of the reaction of **1** with lithium bromide in acetone, was also prepared from 2-fluoro-2,2-dinitroethanol by reaction with triphenylphosphine dibromide in acetonitrile.[7]

$$CF(NO_2)_2CH_2OH + (C_6H_5)_3P + Br_2 \xrightarrow[40\%]{\text{reflux in MeCN}} \underset{\mathbf{3}}{CF(NO_2)_2CH_2Br}$$

The structure of 2-fluoro-2,2-dinitroethyl azide followed from its ir spectrum (azide band at 2150 cm^{-1}, asymmetric and symmetric nitro stretching frequencies at 1595 and 1315 cm^{-1}, respectively) and from analytical and spectral data for its adduct to propiolic acid, 1-(2-fluoro-2,2-dinitroethyl)-4- (or 5-) carboxy-1,2,3-triazole (**6**). **4** was also obtained in *ca.* 10% yield from 2-fluoro-2,2-dinitroethyl mesylate in 80% aqueous DMSO. When the reaction between **1** and sodium azide was conducted in anhydrous DMSO, no **4** was obtained at all. Instead, a small amount of a material was isolated which, from comparison of its ir and nmr spectra with those of **8**, is believed to be a fluoromononitro species of the partial structure $HCF(NO_2)CHN_3$. The formation of this structure would seem to lend further support to the view that increased basicity of the nucleophile, here due to decreased solvation of the azide ion, favors the denitrosation reaction.

2,2-Dinitropropyl azide (**5**) also added to propiolic acid in essentially one direction to give **7** in excellent yield.



4, R = F
5, R = CH_3

6, R = F (90%)
7, R = CH_3 (90%)

2-Nitroalkyl azides such as **4** and **5** have apparently not been described in the literature. It is noteworthy that these compounds are surprisingly stable in view of the facile conversion to furoxanes of the structurally

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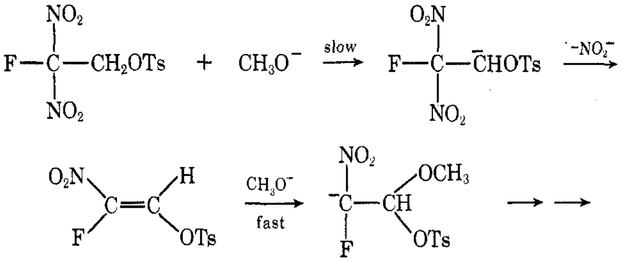
[7] G. A. Wiley, R. L. Hershkowitz, B. M. Rein, and B. C. Chung, *J. Amer. Chem. Soc.*, **86**, 964 (1964).

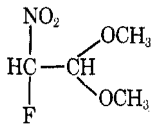
similar *o*-nitrophenyl azides.[8] Thus, *o*-nitrophenyl azide readily loses nitrogen on heating to 100° in toluene solution. In contrast, when **4** was refluxed in toluene for 5 hr or heated neat or in acetic acid to 110–115° for 5 hr, no change was detected by glpc. Heating for 1 hr at 150° also had little effect; on prolonged heating at this temperature **4** did decompose, but no furoxane was formed. Apparently this conversion does not take place in the aliphatic series.

The reaction of **1** with methanolic potassium hydroxide was comparatively rapid. When equimolar amounts were allowed to react, half of the tosylate was recovered unchanged. Two equivalents of base consumed all of the starting material. The products were the same in both cases and consisted of a mixture of at least five compounds with a main component amounting to about 80% of the isolated material. This was shown to be 1-fluoro-1-nitro-2,2-dimethoxyethane (**8**) on the basis of elemental analyses and uv, ir, and nmr spectral data. None of the minor products were identified, but it was shown that the product of a direct displacement of the tosyloxy group, fluorodinitroethyl methyl ether, was not among them by comparison of the glpc retention times with that of an authentic sample of the latter.[9]

The formation of **8** very likely involves initial denitrosation of **1**. The fact that with 1 mol of base only half of the tosylate was converted suggests that a slow, base-consuming step is followed by a rapid one which consumes a second equivalent of base. **9** might lose a tosylate ion and add methanol to give the final product.



9



8

Attempts to obtain a dinitrophenylhydrazone from **8** failed, neither were we able to obtain the parent aldehyde by acid hydrolysis. **8** was stable in aqueous acids but decomposed completely in concentrated sulfuric acid.

Experimental Section

General.—*Caution:* Some of the materials described here are explosives of moderate to considerable sensitivity to initiation by impact, shock, friction, and other means and should be handled with *care*. 2-Fluoro-2,2-dinitroethanol is also a strong skin irritant.

Microanalyses and molecular weight determinations were by Professor M. H. Aldridge, American University, Washington, D. C., and by Mr. D. J. Glover of this laboratory. Melting and boiling points are uncorrected. Nmr spectra were obtained on a Varian HA-100 spectrometer; chemical shifts are in parts per million relative to TMS (δ 0.00) as internal standard.

2,2-Dinitropropyl Tosylate (2).—To a solution of 15 g of 2,2-dinitropropanol and 38 g of *p*-toluenesulfonyl chloride in 100 ml of chloroform was added 19 g of pyridine *N*-oxide, and the mixture was heated to a gentle reflux for 5 hr. After cooling, the solids were filtered off and washed with methylene chloride. The filtrate was washed with dilute sulfuric acid, water, and dilute $NaHCO_3$ solution, and concentrated to *ca.* 100 ml. Hexane was added to the cloud point and the solution was chilled to give 26.0 g (85%) of crude **2** in two crops. The analytical sample was obtained from CCl_4, mp 84–85°.

Anal. Calcd for $C_{10}H_{12}SN_2O_7$: C, 39.48; H, 3.98; N, 9.21; mol wt, 304.28. Found: C, 39.57; H, 3.70; N, 9.15; mol wt ($CHCl_3$), 297.

2-Fluoro-2,2-dinitroethyl Bromide (3) from 1 and LiBr.—A solution of 10 g of anhydrous lithium bromide and 19.5 g of **1**[4] in 100 ml of dry acetone was refluxed for 5 hr. A precipitate of lithium tosylate appeared soon. The mixture was poured into ice–water, the product extracted into methylene chloride, and the extract washed once with water, dried, and distilled to give 10.3 g (75%) of **3**, bp 46–48° (2 mm).

Anal. Calcd for $C_2H_2BrFN_2O_4$ (216.96): N, 12.91; F, 8.76; Br, 36.83. Found: N, 12.90; F, 8.81; Br, 36.94.

2-Fluoro-2,2-dinitroethyl Bromide (3) from 2-Fluoro-2,2-dinitroethanol and Triphenylphosphine Dibromide.—To a suspension of 17 g of triphenylphosphine in 80 ml of acetonitrile was added with ice cooling a solution of 10.4 g of bromine in 20 ml of acetonitrile. To this mixture was added within a few minutes and without further cooling 10 g of 2-fluoro-2,2-dinitroethanol[4] dissolved in 20 ml of acetonitrile. After 2 hr of stirring at room temperature, the mixture was refluxed for 5 hr and then stirred into 150 ml of water. The lower organic phase was separated and washed once with water. At 0.2 mm and a bath temperature rising gradually to 100°, the volatile material was distilled into a trap immersed in ice–water. The product thus collected weighed 5.6 g (40%) and was found to be **3** of excellent purity. It was identical with material prepared from **1** as evidenced by superimposable ir spectra and identical glpc retention times.

2-Fluoro-2,2-dinitroethyl Azide (4).—A solution of 12.5 g of sodium azide in 100 ml of 50% aqueous DMSO was added at room temperature to a solution of 40 g of **1** in 150 ml of DMSO, and the mixture was stirred for 15 hr. After pouring the mixture into ice–water, the organic material was extracted into methylene chloride, the extract was washed once with water, concentrated to about 50 ml, washed again with water to remove residual DMSO, and dried ($MgSO_4$), and the solvent was distilled off. The azide **4** was distilled from the residue at 0.2 mm and a bath temperature up to 90–100°, and the distillate collected in a receiver cooled with ice–water. Obtained was 3.5 g of **4** of good purity; refractionation gave a material of bp 35° (0.25 mm) showing no impurities in the glp chromatogram. It was analyzed as its propiolic acid adduct. Upon recrystallization of the distillation residue from methanol, 12.5 g of unreacted **1** was recovered; the yield of **4** was thus 22%.

Reaction of 1 with Sodium Azide in Anhydrous DMSO.—Sodium azide, 6 g, was dissolved in 70 ml of warm DMSO, and the solution was cooled to room temperature (partial reprecipitation of NaN_3). **1** (8 g) was added and the mixture was stirred at 25–30° for 20 hr. Drowning the reaction mixture in 250 ml of ice–water gave a clear solution, indicating the absence of unreacted **1**. The drowning liquors were extracted with methylene chloride, and the extracts were concentrated, washed with water to remove DMSO, dried ($MgSO_4$), and freed from the remaining solvent *in vacuo*. The residual oil was partially distilled at 0.01 mm to a bath temperature of 60°. About 1 g of an oil was collected which had the following spectral characteristics: ir 2140 (azide), 1585 cm^{-1} (asymmetric mononitro stretch); nmr ($CHCl_3$) δ 5.28 (double d, $J_{HF} = 51$, $J_{HH} = 5$ cps, FCHCH). Attempts to isolate a pure material from this oil were not successful.

2,2-Dinitropropyl Azide (5).—A solution of 4.05 g of sodium azide in 26 ml of 50% aqueous DMSO was added to 13 g of **2** in 49 ml of DMSO, the mixture was stirred for 48 hr at 60° and drowned in ice–water, and the products were extracted into methylene chloride. The extracts were washed with water and concentrated to 50 ml, and hexane was added to the cloud point. Upon cooling 3.2 g of **2** was recovered. The filtrate was washed with water and dried ($MgSO_4$), and the solvents were removed *in vacuo*. The residue was distilled at 0.1 mm, bath temperature up to 90°, to give 3.6 g of **5** of excellent purity (glpc). Crystallizing the distillation residue from methylene chloride–hexane

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[8] P. A. S. Smith and J. H. Boyer, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 75.

[9] M. J. Kamlet and H. G. Adolph, *J. Org. Chem.*, **33**, 3073 (1968).

gave an additional 1.3 g of unreacted **2**. The yield of crude **5** is thus 73.5% of the reacted **2**, bp 60° (0.5 mm). It showed the expected azide and nitro absorption in the ir and was analyzed as the adduct to propiolic acid.

1-(2-Fluoro-2,2-dinitroethyl)-4- (or 5-) carboxy-1,2,3-triazole (6).—To 2.15 g of **4** in 10 ml of chloroform was added 0.9 g of propiolic acid, and the mixture was allowed to stand at room temperature for 3 days. The solid was filtered off and washed with a small amount of chloroform, and a second crop was obtained by chilling the filtrate. After recrystallization from acetonitrile–carbon tetrachloride (1:1), there was obtained 2.65 g (88.5%) of **6**: mp 160° with gassing (decarboxylation); nmr (acetone-d_6) δ 8.73 (s), 6.37 (d, J_{HF} = 16 cps), 4.64 (s, COOH); relative areas, 1:2:1.

Anal. Calcd for $C_5H_4FN_5O_6$: N, 28.11; F, 7.63; mol wt and neut equiv, 249.12. Found: N, 27.91; F, 7.80; mol wt (acetonitrile), 242; neut equiv, 242.[10]

1-(2,2-Dinitropropyl)-4- (or 5-) carboxy-1,2,3-triazole (7).—Azide **5**, 0.75 g, was reacted with propiolic acid in chloroform as described for **4**. **7** (0.95 g, 90.5%) was obtained: mp (after recrystallization from acetonitrile) 157–158° dec; nmr (acetone-d_6) δ 8.67 (s), 5.89 (s), 4.21 (s, COOH); relative areas, 1:2:1.

Anal. Calcd for $C_6H_7N_5O_6$ (245.15): C, 29.40; H, 2.88; N, 28.57. Found: C, 29.71; H, 2.84; N, 28.39.

Reaction of 1 with Potassium Hydroxide in Methanol.—Tosylate **1**, 50 g, was dissolved in 500 ml of warm methanol, the solution was cooled in an ice bath, and a precooled solution of 25 g of potassium hydroxide in 150 ml of methanol was added rapidly with stirring. Potassium tosylate precipitated immediately. The mixture was stirred for 15 min with continued cooling, the precipitate filtered off, and the filtrate freed from most of the methanol at 50° (25 mm). The residue and the previously obtained filter cake were triturated with 500 ml of water, the resulting two-phase mixture was extracted with methylene chloride, the extract was dried ($MgSO_4$), and the solvent was distilled off. A glp chromatogram of the remaining oil showed the presence of at least five compounds. The material was distilled at 0.1 mm and 8.3 g went over at 38–43°. The distillate was a 9:1 mixture of two components which were separated readily by chromatography on silica (G. F. Smith, Columbus, Ohio) with methylene chloride as the eluent. The impurity was eluted first. Thus obtained was 7.4 g (30%) of **8** of good purity: ir 1585, 1355 cm^{-1} (asym and sym NO_2 stretch); nmr (CCl_4) δ 5.64 (double d, J_{HF} = 49, J_{HH} = 4.5 cps), 4.73 (double d, J_{HF} = 10.6, J_{HH} = 4.5 cps), 3.50 (s), 3.47 (s); relative areas, 1:1:3:3; uv λ_{max} (0.01 N NaOH) 232.5 nm (ϵ 10,200) [compare 1-chloro-1-nitroethane, λ_{max} (0.1 N NaOH) 237 nm (ϵ 10,000)].[11]

Anal. Calcd for $C_4H_8FNO_4$: N, 9.15; F, 12.41. Found: N, 8.90; F, 12.71.

Registry No.—**1**, 18138-91-5; **2**, 27396-49-2; **3**, 27396-50-5; **4**, 27396-51-6; **5**, 27396-52-7; **6**, 27378-67-2; **7**, 27378-68-3; **8**, 27396-53-8.

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[10] Base was consumed rapidly past the point of neutralization which was therefore difficult to determine.

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

Nuclear Magnetic Resonance Anisotropic Effects of the Epoxy Group and Averaging of Coupling Constants in *trans*- and *cis*-4,5-Epoxy-*trans*-2-(*p*-chlorophenyl)nitrocyclohexane and Derivatives

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The long-range anisotropic effects of the epoxy group in *trans*- (1) and *cis*-4,5-epoxy-*trans*-2-(*p*-chlorophenyl)-nitrocyclohexane (2) cause deshielding of both axial hydrogens cis to the epoxy group and have little effect on the chemical shift of the axial hydrogen trans to, and two carbons removed from, the epoxy group. The deshielding of the cis axial hydrogen, two carbons removed, is of the same magnitude as the deshielding of the same hydrogen caused by the anisotropic effect of the double bond in the parent alkene. The nmr spectra establish the presence of very high populations of the half-chair conformations with the substituents in equatorial orientations for both epoxides and for the parent alkene. The configurational assignment of the isomeric epoxides has been verified from the nmr spectra of the derived diols, monoacetates, and diacetates from the difference between the spatial 1,3-diaxial deshielding effects of hydroxyl and acetoxy groups. Anisotropic deshielding effects of the epoxy, hydroxyl, and acetoxy groups are responsible for significant averaging of coupling constants, involving geminal hydrogens, observed in the spectra of the epoxides and their derivatives.

Epoxidation of *trans*-4-(*p*-chlorophenyl)-5-nitrocyclohexene (**3**)[2] with *m*-chloroperbenzoic acid in ethyl ether yielded the isomeric epoxides *trans*- (**1**) and *cis*-4,5-epoxy-*trans*-2-(*p*-chlorophenyl)nitrocyclohexane (**2**) with a much larger proportion of the trans isomer **1**. The nmr spectra of **1** and **2**, Figure 1, are significantly different. Analysis of the spectra shows that the observed differences are not due to conformational differences, as might be suspected, but result from long-range shielding effects of the epoxy group and from averaging of coupling constants caused by these effects. Complications resulting from averaging of coupling constants due to strong coupling effects in ABX (or higher spin) systems, in which A and B are geminal hydrogens with small chemical shift differences, have been fully described.[3-6] The important thing to keep in mind is that in such systems strong coupling effects tend to average the individual values of J_{XA} and J_{XB}, thus causing changes in the pattern of the signal involved, but the sum of the coupling constants and, therefore, the width of the signal are not affected.[3]

Conformation of Epoxides, Anisotropic Effects, and Averaging of Coupling Constants.—Figure 1 gives portions of the 60-MHz spectra of the two epoxides measured in chloroform-*d*. The width of the signal of H-1 (27.2 Hz at δ 4.89, spectrum A) of the major epoxide **1** and the widths of the signals of H-1 (29 Hz) and H-2 (27.9 Hz) of the minor epoxide at δ 4.68 and 3.34, re-

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[1] NSF Undergraduate Participant, 1968.

[2] A. C. Huitric and W. D. Kumler, *J. Amer. Chem. Soc.*, **78**, 614 (1956).

[3] W. F. Trager, B. J. Nist, and A. C. Huitric, *J. Pharm. Sci.*, **56**, 698 (1967).

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