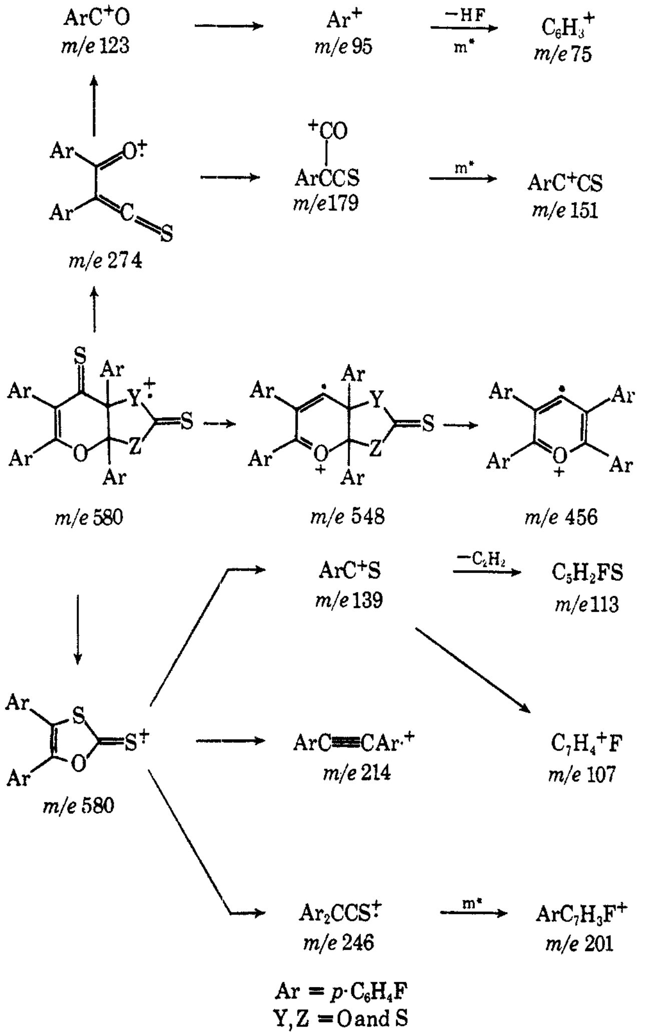
azibenzil and carbon disulfide. Seemingly modest variations in substrate **1**, replacing phenyl with methyl, or phenyl with *p*-fluorophenyl, lead to strikingly different results in reactions with carbon disulfide. The alkylalkoyldiazomethanes give rise to adducts **3**; *p*-fluorophenyl-*p*-fluorobenzoyldiazomethane gives both the expected adduct **2c** and two more complex products $C_{30}H_{16}F_4O_2S_3$. Structural determinations for adducts A and B, and an understanding of how they are formed, will depend upon further experimentation.

SCHEME I

RATIONALIZATION OF MASS SPECTRUM OF $C_{30}H_{16}F_4O_2S_3$ ADDUCTS



Experimental Section

***p,p'*-Difluorobenzil** was prepared in two steps from *p*-fluorobenzaldehyde, according to a procedure described for the conversion of benzaldehyde to benzoin to benzil.[15] *p,p'*-Difluorobenzoin was recrystallized from ethanol and had mp 85–86°.

Anal. Calcd for $C_{14}H_{10}O_2F_2$: C, 67.74; H, 4.06. Found: C, 67.46; H, 4.31.

p,p'-Difluorobenzil was recrystallized from benzene to give yellow needles, mp 119–121° (lit.[16] mp 123–123.5°), in 38% over-all yield.

***p,p'*-Difluorobenzil Monohydrazone.**—*p,p'*-Difluorobenzil (13 g) was converted into the monohydrazone with hydrazine hydrate in ethanol.[17] An 81% yield of fine yellow crystals, mp 183–185°, was obtained. The analytical sample, mp 190–191°, was recrystallized from ethanol.

Anal. Calcd for $C_{14}H_{10}F_2N_2O$: C, 64.63; H, 3.87; N, 10.77. Found: C, 64.33; H, 4.05; N, 10.84.

***p*-Fluorophenyl-*p*-fluorobenzoyldiazomethane** was prepared from 11.1 g of *p,p'*-difluorobenzil monohydrazone through oxidation by mecuric oxide.[18] The crude product (6.8 g) was recrystallized from diethyl ether to give 3.2 g of orange product: mp 102–106° dec; $\bar{\nu}$ ($CHCl_3$) 2080, 1620–1600, 1500, 1340, 1155, 865, and 830 cm^{-1}. Further recrystallizations did not raise the decomposition temperature.

Anal. Calcd for $C_{14}H_8F_2N_2O$: C, 65.13; H, 3.12; N, 10.84. Found: C, 65.23; H, 3.36; N, 10.81.

Reaction of *p*-Fluorophenyl-*p*-fluorobenzoyldiazomethane with Carbon Disulfide.—*p*-Fluorophenyl-*p*-fluorobenzoyldiazomethane (4.4 g, 17 mmol) and 40 ml of carbon disulfide were heated at reflux for 40 hr. The reaction mixture was cooled, filtered, and concentrated. Yellow crystals (4.4 g) were collected, washed with ether, and dried.

The crude product was recrystallized from absolute ethanol to give two crops of yellow crystals, 1.2 and 1.0 g, having mp 90–105°, and a residue insoluble in ethanol (1.2 g of yellow material, mp 267–270°).

The first two crops of crystals were dissolved in hot ethanol and, as the solution was allowed to cool slowly, a flocculent mass of very fine, hairlike yellow needles was obtained. This solid had mp 235–236° after repeated recrystallization from ethanol.

Anal. Calcd for $C_{30}H_{16}F_4O_2S_3$: C, 62.06; H, 2.78. Found: C, 61.43; H, 2.92.

Concentration of the ethanolic mother liquors gave another solid which, after repeated recrystallization from carbon disulfide, had mp 145–146°.

Anal. Calcd for $C_{29}H_{16}O_2S_2$: C, 64.91; H, 3.01; S, 11.95. Found: C, 64.54, 64.58; H, 3.12, 3.15; S, 11.81.

The high-melting residue from the first recrystallization was recrystallized four times from chloroform to obtain lemon yellow plates, mp 274–275° dec.

Anal. Calcd for $C_{30}H_{16}F_4O_2S_3$: C, 62.06; H, 2.78; S, 16.58. Found: C, 61.55; H, 2.98; S, 16.42.

The combined 3.2 g of crops 1, 2, and 3 contained approximately 12% of the adduct of mp 235–236°, 66% of the $C_{29}H_{16}F_4O_2S_2$ adduct, mp 145–146°, and 22% by weight of the high melt-product, mp 274–275°. Spectral data for these three adducts are given in the discussion.

Registry No.—*p,p*-Difluorobenzil monohydrazone, 18598-41-9; **1c**, 18542-79-5; **2c**, 18542-80-8; **4**, 18542-81-9; **5**, 18542-82-0; carbon disulfide, 75-15-0.

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[15] L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass., 1957, p 170.

[16] W. Voegtli and P. Läuger, *Helv. Chim. Acta*, **38**, 46 (1955).

(17) *Cf.* L. I. Smith and H. H. Hoehn, "Organic Syntheses," Coll. Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1955, p 356.

(18) *Cf.* C. D. Nenitzescu and E. Solomonica, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1943, p 496.

Lack of Oxygen-18 Scrambling in the Solvolytic Rearrangement of Bicyclo[2.2.0]hexane-1-methyl *p*-Nitrobenzoate[1a]

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Wagner–Meerwein rearrangements can be considered to fall within two theoretical limits with regard

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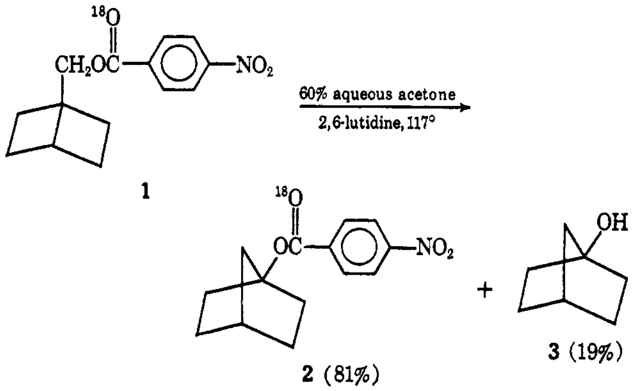
(1) (a) This investigation was supported in part by Grant No. GP 3890, National Science Foundation. (b) National Institutes of Health Predoctoral Fellow, 1966–1968.

to the ionic nature of the starting material and product of migration. At one extreme are those systems which can exist as ion-pair intermediates under the solvolytic conditions employed and in which there is little σ-bond character between the anion and cation during rearrangement. An example of this type of rearrangement is found in the solvolysis of 1,2-dimethyl-*exo*-bicyclo-[2.2.1]heptan-2-yl *p*-nitrobenzoate where k_{eq} is about 50% of k_{rac}.[2,3] At the other extreme are those systems in which neither the starting material nor rearrangement product achieves the ion pair stage under the conditions employed and in which a high degree of σ bonding between migrating ester group and alkyl moiety is maintained throughout the rearrangement. Wiberg has investigated two neopentyl systems, bicyclo[3.2.0]heptane-1-methyl and bicyclo[2.1.1]hexane-1-methyl *p*-toluenesulfonates, which lie at this extreme. The starting neopentyl system does not ionize without participation and the bridgehead product formed, bicyclo[3.2.1]octyl and 1-norbornyl *p*-toluenesulfonates, respectively, would give poor cations; 90% or more of the rearrangement products were internally returned.[4,5] Wiberg has suggested that "the reaction may possibly be best described as an internal rearrangement in which charge separation is minimized."[5] Bicyclo[2.2.0]hexane-1-methyl *p*-nitrobenzoate also lies at this latter extreme[6] and it was felt that a solvolytic study of ^{18}O-labeled bicyclo[2.2.0]hexane-1-methyl *p*-nitrobenzoate might give some additional information about the nature of the leaving group and carbon skeleton bonding during Wagner–Meerwein rearrangement.

Bicyclo[2.2.0]hexane-1-methyl *p*-nitrobenzoate (**1**) containing about 7.5% enrichment of ^{18}O at the carbonyl oxygen was prepared from an ^{18}O-enriched sample of *p*-nitrobenzoyl chloride and a sample of bicyclo-[2.2.0]hexane-1-methanol.[6] A portion of this ester was saved for comparison purposes and the remainder was dissolved in 60% aqueous acetone containing 2,6-lutidine as a buffer (0.02 *M* in ester) and maintained in a sealed ampoule at 117° for 130 hr (ten half-lives of the rearrangement).[6] After standard work-up, the rearranged ester **2** was compared with the starting material **1** by mass spectroscopy. The *p*-nitrobenzoyl fragment at *m/e* 150 was the base peak and the region of *m/e* 151 and 152 was free of signals other than those due to the natural abundance of the minor isotopes of oxygen, carbon, and hydrogen. Therefore, a comparison of the *m/e* 152–150 peaks gave the amount of ^{18}O enrichment at the carbonyl oxygen.[7] On the basis of ten scans each of the starting ester **1** and rearranged ester **2**, there was obtained an average value for the transfer of ^{18}O enrichment from the carbonyl to the ether oxygen of 2% (total ^{18}O enrichment = 100%) with a range of ±3%. Thus within the limits of experimental error there was no transfer of the ^{18}O label.



It was known from earlier work[6] that the 19% 1-norbornanol (**3**) did not come from either bicyclo[2.2.0]-hexane-1-methanol or from 1-norbornyl *p*-nitrobenzoate (**2**) since these two compounds were stable under the solvolytic conditions employed. Therefore, it appeared that the hydroxyl group of the 1-norbornanol came from solvent. To confirm the source of the hydroxyl group, a separate solvolysis was performed on unlabeled bicyclo[2.2.0]hexane-1-methyl *p*-nitrobenzoate in 60% aqueous acetone containing a 20% enrichment of ^{18}O. After the standard work-up, the 1-norbornanol was vpc collected from a 5 ft × 0.25 in. 10% TCEP column and its mass spectrum compared with that of a sample of 1-norbornanol which had no ^{18}O enrichment. The solvolytic sample of 1-norbornanol had a 20% enrichment of ^{18}O; therefore, all of the 1-norbornanol oxygen comes from solvent.

It was shown earlier that the rate of rearrangement of the bicyclo[2.2.0]hexane-1-methyl system is greatly enhanced relative to the parent neopentyl system (7×10^6 faster at 100°) and that migration and ionization are concerted.[6] The large amount of internal return found in this solvent of high nucleophilicity and the large negative entropy of activation indicate that the transition state is highly ordered.[6] Since rearrangement of **1** does not occur in cyclohexane at 117°, the transition state of this rearrangment is reasonably polar. The ^{18}O results show that there is no oxygen equilibration during the rearrangement and that all alcohol produced contains oxygen from the solvent.

The present observations suggest that the essential feature of the rearrangement of the bicyclo[2.2.1]-hexane-1-methyl system is the drive to dissipate internally the positive charge of the developing primary cation by rearranging. The ease of this rearrangement is enhanced by the release of an estimated 34 kcal of hydrocarbon ring strain.[6] As migration begins, the σ bonding of the leaving group to the initial carbon atom is reduced and the formation of the 1-norbornyl cation begins, thereby allowing the alkyl portion to share its electron deficiency between two carbon atoms. However, the 1-norbornyl system prefers to retain s character so that the σ bond is simply shifted from the initial primary center to the developing tertiary center.

Previously, no alkyl *p*-nitrobenzoate has failed to give extensive oxygen equilibration where it could be shown that ionization to an intimate ion pair and re-

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[2] H. L. Goering, private communication.

[3] (a) Also, acetolysis of *threo*-3-phenyl-2-butyl *p*-toluenesulfonate and *endo*-bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonate gives a value for k_{eq} which is about 50% k_{rac}: H. L. Goering and R. W. Thies, *J. Amer. Chem. Soc.*, **90**, 2967, 2968 (1968). (b) Winstein has found that nonrearranging, secondary *p*-toluenesulfonates also undergo internal return with ^{18}O equilibration: A. F. Diaz, I. Lazdins, and S. Winstein, *ibid.*, **90**, 1904 (1968).

[4] K. B. Wiberg, private communication.

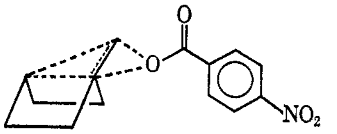
[5] K. B. Wiberg and B. R. Lorry, *J. Amer. Chem. Soc.*, **85**, 3188 (1963).

[6] W. G. Dauben, J. L. Chitwood, and K. V. Scherer, Jr., *ibid.*, **90**, 1014 (1968).

[7] C. G. Swain, G. Tsuchihashi, and L. J. Taylor, *Anal. Chem.*, **35**, 1415 (1963).

turn had occurred.[2,8-11] The complete lack of ^{18}O equilibration during rearrangement of bicyclo[2.2.1]hexane-1-methyl *p*-nitrobenzoate implies that in this system a significant degree of σ bonding is maintained between the leaving group and alkyl portion throughout the entire migration.[12,13] The findings reported here may be in accord with the recent suggestion that two different intermediates might be involved in Wagner–Meerwein rearrangements.[3a] One of these intermediates returns without any oxygen scrambling; the other intermediate allows oxygen equilibration to occur before collapsing. This latter intermediate is captured preferentially by added lithium perchlorate and by solvent.[3a] The exact nature of the correlation between Goering's first intermediate and the migrating species in the solvolysis of bicyclo[2.2.0]hexane-1-methyl *p*-nitrobenzoate remains to be determined.

The formation of 19% 1-norbornanol is interesting in light of the high degree of σ-bond character maintained during this rearrangement. To accommodate both the formation of rearranged but unscrambled *p*-nitrobenzoate and the formation of alcohol resulting from solvent attack, the process can be viewed in the following fashion. As the initial carbon–oxygen bond begins to stretch toward heterolytic cleavage, either the oxygen atom of the leaving group, as in **4**, leading to the ester or the oxygen atom of water, as in **5**, leading to the alcohol could transfer the σ bond to the developing 1-norbornyl bridgehead.[14] A second possibility is that the σ-bond character of **4** is occasionally lost during migration and the ion pair produced gives only alcoholic product.[15] A third, somewhat less attractive explanation is that 1-norbornanol is formed from a frontside displacement on an intermediate such as **6**.[16]



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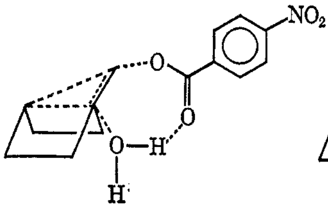

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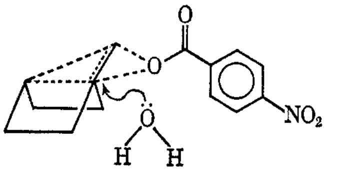

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Thus in 1,2 rearrangements where neither the starting material nor the product ionizes to ion pairs under the conditions necessary to effect the rearrangement, one would anticipate that a high degree of σ bonding is retained at all times.

Experimental Section[17]

***p*-Nitrobenzoyl-^{18}O Chloride.**[9a,13b]—To a solution of 50 mg of water (30% enrichment in ^{18}O) in 800 μl of tetrahydrofuran was added 359 mg of *p*-nitrobenzoyl chloride (Matheson Coleman and Bell) and the solution was stirred at room temperature for 48 hr. The solvent was removed at room temperature and about 2 mm pressure. The residue was refluxed with 480 μl of thionyl chloride in 700 μl of toluene for 24 hr at 95–105°. The solvent was again removed at about 2-mm pressure and the residue was recrystallized from carbon tetrachloride to give pale yellow needles. Mass spectral analysis showed approximately 7% enrichment in ^{18}O.

Bicyclo[2.2.0]hexane-1-methyl *p*-Nitrobenzoate-carbonyl-^{18}O (1).—Bicyclo[2.2.0]hexane-1-methanol[6] (43 mg, collected by vpc from a 10 ft × 0.25 in. 10% Carbowax, 10% KOH column) was dissolved in 8 ml of pyridine (reagent grade, distilled from KOH and dried over BaO) and 500 μl of carbon tetrachloride. The solution was then cooled with stirring in an ice bath and 98 mg of ^{18}O-enriched *p*-nitrobenzoyl chloride was added. The mixture stirred 2.5 hr at 0° and was then isolated in the usual manner.[6] The conversion to ester was incomplete; therefore, the alcohol–ester mixture was resubmitted to the reaction conditions. This time complete conversion to ester **1** was obtained. The mass spectrum indicated a 7.6% enrichment of ^{18}O.

Rearrangement of Bicyclo[2.2.0]hexane-1-methyl *p*-Nitrobenzoate-carbonyl-^{18}O.—The procedure and concentrations were similar to those previously reported.[6] A 40-mg portion of ^{18}O carbonyl labeled bicyclo[2.2.0]hexane-1-methyl *p*-nitrobenzoate was placed in a Pyrex tube containing 30% molar excess of 2,6-lutidine and 6 ml of freshly prepared 60% aqueous acetone [composition based on volumes of pure components (25°) prior to mixing]. The tube was evacuated, with cooling in Dry Ice–acetone, to approximately 2 mm and sealed. The sealed tube was placed in a 117° bath for 130 hr (10 half-lives). The tube was then cooled and opened. The contents were poured into 30 ml of water and the mixture was extracted with six 10-ml portions of pentane. The combined pentane extracts were washed with four 50-ml portions of saturated sodium bicarbonate solution and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the solvent by rotary evaporation, first at aspirator pressure and then at 2 mm for

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[8] (a) H. L. Goering and J. T. Doi, *J. Amer. Chem. Soc.*, **82**, 5851 (1960); (b) H. L. Goering, J. T. Doi, and K. D. McMichael, *ibid.*, **86**, 1951 (1964).

[9] (a) H. L. Goering and M. M. Pombo, *ibid.*, **82**, 2515 (1960); (b) H. L. Goering, M. M. Pombo, and K. D. McMichael, *ibid.*, **85**, 965 (1963).

[10] (a) H. L. Goering and J. F. Levy, *ibid.*, **84**, 3853 (1962); (b) H. L. Goering, R. G. Briody, and J. F. Levy, *ibid.*, **85**, 3059 (1963); (c) H. L. Goering and J. F. Levy, *ibid.*, **86**, 120 (1964); (d) H. L. Goering and J. F. Levy, *Tetrahedron Lett.*, 644 (1961).

[11] Simple tertiary systems were found to undergo no scrambling. However, since no optically active systems were studied, there was no evidence for ionization followed by return; see ref 10b and A. Streitwieser, *Chem. Rev.*, **56**, 663 (1956). It has also been suggested that internal return may be occurring but that the steric requirements of the bulky *t*-butyl grouping may prevent scrambling: G. J. Frisone and E. R. Thornton, *J. Amer. Chem. Soc.*, **90**, 1211 (1968).

[12] An intermediate case has been reported in the acetolysis of ^{18}O-labeled 2-phenylpropyl *p*-toluenesulfonate. Here the starting material cannot ionize easily without participation from the migrating group, but the product of the migration can exist as an ion pair under the rearrangement conditions. During the migration itself, the label underwent 58% scrambling; see D. B. Deeney and B. Goldstein, *ibid.*, **79**, 4948 (1957).

[13] Two other cases of simultaneous double rearrangements with a high degree of σ bonding are found with decalyl perbenzoate and $5\alpha,5\beta$-dibromocholestane: see (a) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 162; (b) D. B. Denney and D. G. Denney, *J. Amer. Chem. Soc.*, **79**, 4806 (1957); D. B. Denney and M. A. Greenbaum, *ibid.*, **79**, 979 (1957); D. B. Denney, *ibid.*, **77**, 1706 (1955); (c) C. A. Grob and S. Winstein, *Helv. Chim. Acta*, **35**, 782 (1952).

[14] One would assume that the *p*-nitrobenzoate is rotating freely under the conditions of the solvolysis. Whether 1-norbornyl *p*-nitrobenzoate is formed or whether 1-norbornanol is formed might depend on the orientation of the carbonyl and its solvation molecules at the time the migration begins. This would mean that the carbonyl and its solvation molecules are close enough to compete favorably with the ether oxygen of the *p*-nitrobenzoate about 20% of the time.

[15] This ion pair might correspond to Goering's second intermediate which allows oxygen equilibration to occur before returning (see ref 3a). Our experimental results would require that this intermediate be trapped by water without undergoing any internal return, whereas allylic *p*-nitrobenzoates in the same solvent system generally undergo complete equilibration during rearrangement (see ref 8 and 9).

[16] An alternate view of these ^{18}O results is that all σ-bond character might be lost during the migration but that the lifetime of the tight ion pair formed is too brief to allow oxygen equilibration in the anion before collapsing either to 1-norbornyl *p*-nitrobenzoate or alcohol.

[17] Mass spectra were determined on a CEC Type 21-103C mass spectrometer. Mass spectral analyses were performed by Miss Sherri Firth, Mass Spectral Laboratory, University of California at Berkeley.

30 min. The mass spectrum of this material showed no diminution of ^{18}O enrichment at the carbonyl position.

Bicyclo[2.2.0]hexane-1-methyl *p*-nitrobenzoate was from previous work; see ref 6.

Rearrangement of Unlabeled Bicyclo[2.2.0]hexane-1-methyl *p*-Nitrobenzoate in ^{18}O-Labeled Aqueous Acetone.—A 100-mg (0.38 mmol) portion of ester (0.076 *M*) was dissolved in 5 ml of ^{18}O-labeled 60% aqueous acetone containing 69 μl of 2,6-lutidine (45% molar excess). The water was 30% enriched in ^{18}O; therefore, the ^{18}O enrichment in the aqueous solvent was 20% after equilibration of acetone and water. This solution was sealed in a Pyrex tube and maintained at 117° for 130 hr (ten half-lives). The tube was then cooled and opened. Its contents were poured into 30 ml of water and extracted with five 10-ml portions of pentane. The combined pentane extracts were washed with two 20-ml portions of saturated sodium bicarbonate solution and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the pentane by distillation at atmospheric pressure through a 5-in. Vigreux column. The residue was dissolved in a small amount of carbon tetrachloride for vpc injection. 1-Norbornanol was collected from a 5 ft × 0.25 in. 10% TCEP [1,2,3-tris(β-cyanoethoxy)propane] column at 110°. The mass spectrum of this white, crystalline solid was measured and compared with that of a sample of 1-norbornanol containing only natural abundance of ^{18}O. This comparison indicated a 20% enrichment of ^{18}O in the 1-norbornanol from this rearrangement study.

Determination of ^{18}O Enrichment.—An average of ten scans per sample was run and the measurements were repeated 48 hr later. In each case unlabeled and labeled material were scanned, one immediately after the other. The precision of these measurements was ±3% out of 100% for an ^{18}O enrichment of 7.5%; for a 20% enrichment of ^{18}O, the precision was even better (see ref 7).

Registry No.—1 (^{18}O), 18542-77-3; 1 (^{16}O), 18542-78-4.

Photochemical Reaction at ~3500 Å of Nitric Oxide with Cyclohexane and Toluene

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Received July 29, 1968

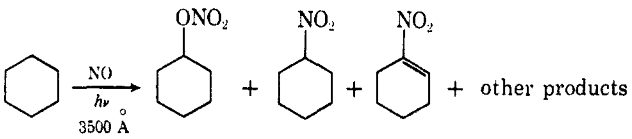
Recently, Piper and Drago[1] have found a new broad, structured absorption band centered at 3700 Å (ϵ 52 ± 1) for nitric oxide when dissolved in various organic solvents such as carbon tetrachloride and acetonitrile. This band is not observed in the gas phase and is attributed to the spin-forbidden transition $^2\pi \rightarrow {}^4\pi$ which becomes less forbidden owing to solvent–molecule interactions in the liquid phase. It occurred to us that irradiation of these solutions with suitable wavelength light might lead to new and useful photoreactions of nitric oxide.

We report here results of a qualitative investigation of the nature of the 3500-Å photoproducts of nitric oxide with cyclohexane and toluene. While nitric oxide has been reported to undergo photosensitized[2] and unphotosensitized short-wavelength photoreactions[3] with alkanes in the gas phase and high-energy radiation-induced reactions[4,5] with alkanes in the liquid phase, the only reaction reported at all similar to ours is that between nitric oxide and benzene under 3130-Å irradiation to give *o*-nitrophenol and 2,4-dinitrophenol.[6]

Results and Discussion

No products were formed upon passing nitric oxide through either solvent without irradiation. In the case of toluene a deep green solution developed over a 1-day period; however, evaporation of the solvent afforded only colorless toluene and no residue.

The product mixture obtained from the photochemical reaction between nitric oxide and liquid cyclohexane after removal of excess solvent was a yellow-green oil having at least eight components by vapor phase chromatography (vpc). The three major peaks were collected and shown to be cyclohexyl nitrate (**1**), nitrocyclohexane (**2**), and 1-nitrocyclohexene (**3**), obtained, respectively, in a ratio of about 6:2:1. Two of the minor peaks showed retention times and peak enhancements corresponding to cyclohexanol and cyclohexanone. A third minor peak showing a retention time corresponding to cyclohexyl nitrite was present in some runs. Adipic acid was found in trace amounts deposited on the wall of the reaction vessel.



1 2 3

It is probable that absorption of 3500-Å light leads to excited nitric oxide which abstracts a hydrogen atom from the solvent to give a cyclohexyl radical. This latter species should combine rapidly with nitric oxide to give nitrosocyclohexane. Subsequent steps leading to the observed products are probably similar to those proposed by Donaruma and Carmody[7] and others[5,8] who have obtained analogous products by reaction of nitric oxide with alkyl radicals or nitrosoalkanes. Since we observed very little cyclohexyl nitrite, it is possible that this material undergoes a further photochemical reaction[9] to give nitric oxide and cyclohexyloxy radical. The latter can combine with nitrogen dioxide present[7] to lead to additional cyclohexyl nitrate. Alternatively, the slow purge of nitric oxide through the system could remove much of the nitrogen dioxide as it is produced, and therefore prevent cyclohexyl nitrite formation. In the *closed system* employed by Donaruma and Carmody[7] cyclohexyl nitrite was presumed to come from buildup of nitrogen dioxide after several hours of reaction.[10]

When toluene was employed as the solvent instead of cyclohexane another complex mixture resulted having at least nine components by vpc. Only one of the major peaks could be conveniently collected. This

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(1) T. S. Piper and R. S. Drago, *J. Chem. Phys.*, **36**, 241 (1962).

(2) O. P. Strausz and H. E. Gunning, *Can. J. Chem.*, **41**, 1207 (1963).

(3) J. Heicklen, *J. Phys. Chem.*, **70**, 2456 (1966).

(4) E. Müller and G. Schmid, *Chem. Ber.*, **94**, 1364 (1961).

(5) E. J. Burrell, Jr., *J. Phys. Chem.*, **66**, 401 (1962).

(6) W. Kemula and A. Grabowska, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **8**, 517 (1960); *Chem. Abstr.*, **60**, 7607*f* (1964).

(7) L. G. Donaruma and D. J. Carmody, *J. Org. Chem.*, **22**, 635 (1957).

(8) J. F. Brown, Jr., *J. Amer. Chem. Soc.*, **79**, 2480 (1957).

(9) M. Akhtar, *Advan. Photochem.*, **2**, 263 (1964).

(10) We thank a referee for suggesting this possibility.