Reactions of Dinitrogen Tetroxide with Acenaphthylene. Diels–Alder Reactions and Photodimerizations of 1-Nitro- and 1,2-Dinitroacenaphthylenes[1a]

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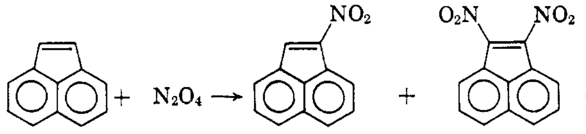
Reaction of dinitrogen tetroxide and acenaphthylene in ethyl ether at 0° yields 1-nitroacenaphthylene (I) and 1,2-dinitroacenaphthylene (II). 1,2-Dinitroacenaphthylene (II) and 1,3-diphenylisobenzofuran react at 25–30° to give an initial Diels–Alder adduct which is converted to a more stable product at elevated temperature. 1-Nitroacenaphthylene (I) also undergoes addition with 1,3-diphenylisobenzofuran. The possible structures of these adducts are discussed. Photolysis of I in ethyl ether yields the *cis*, head-to-head dimer, *cis*-2,3-dinitro-1,2,3,4-di(1,8-naphthylene)cyclobutane (VI), and the symmetrical *trans*, head-to-tail dimer, *trans*-1,3-dinitro-1,2,3,4-di(1,8-naphthylene)cyclobutane (VII), as major and minor products, respectively.

The reactions of dinitrogen tetroxide with olefins to yield vicinal dinitro compounds and nitronitrites have been subjects of extensive chemical and mechanistic investigation.[2] Whereas the free-radical nature of the reaction processes has been established in many systems, the rules and factors concerning the stereochemistry of addition are not yet clear.[2,3] In an effort to delineate the stereochemical preference of the addition of dinitrogen tetroxide to rigid planar olefins, it was decided to investigate the configurations of the vicinal dinitro compounds and nitro alcohols (from hydrolysis of the intermediate nitronitrites) that are expected from dinitrogen tetroxide and acenaphthylene. The stereochemical information originally sought was not obtained because the primary products were too unstable to be isolated. There were derived other results, however, on which we report herein.

Addition of dinitrogen tetroxide in ethyl ether to acenaphthylene in ethyl ether at 0° in the absence of oxygen (eq 1) gave 1-nitroacenaphthylene (I, 12–16%), 1,2-dinitroacenaphthylene (II, 11–14%), amorphous polymer (7–9%), and intractable red products.



I II (1)

Excess acenaphthylene favored formation of the mononitro compound I; thus addition of dinitrogen tetroxide in ethyl ether to a 25% excess of acenaphthylene in ethyl ether in the absence of oxygen gave 26–28% yields of I and 8–11% of II. Indeed, 1-nitroacenaphthylene (I) can be conveniently prepared by this method. Inverse addition, that is addition of acenaphthylene in ethyl ether to dinitrogen tetroxide in ethyl ether, led to much lower yields of I and II and considerable quantities of amorphous polymer.

Polymerization of acenaphthylene by dinitrogen tetroxide is not surprising, particularly if the nitrating agent reacts by a free-radical process; acenaphthylene gives polymeric materials on halogenation under homolytic conditions.[4] At −78°, acenaphthylene and dinitrogen tetroxide gave pale solutions which became dark on stirring for a short time. Adducts such as 1,2-dinitroacenaphthene, 1-nitrito-2-nitroacenaphthene, 1,1,2-trinitroacenaphthene, and 1-nitrito-1,2-dinitroacenaphthene may have been formed; however, they could not be isolated. Careful chromatography of various reaction mixtures on silica gel gave, besides I and II, only dark red or black intractable materials having infrared bands characteristic of hydroxyl, carbonyl, and nitro groups. No well-defined nitro alcohol or nitro ketone was isolated.

Analytical, molecular weight, and spectral data suggest the structural assignments indicated for I and II. 1-Nitroacenaphthylene (I), orange needles, mp 124–125°, exhibits infrared bands at 6.63 and 7.54 μ for a conjugated nitro group; I has ultraviolet absorption maxima at 339 and 242 mμ (ϵ 14,600 and 112,000). 1,2-Dinitroacenaphthylene (II) was obtained as two types of crystals; short brick-red needles and slender crimson needles, both melting with decomposition at 160°. The infrared spectra of the two types of crystals in chloroform are identical and have strong bands at 6.62 and 7.52 μ. The ultraviolet spectrum exhibits maxima at 343 and 246 mμ (ϵ 10,300 and 113,000).

Both I and II react readily with 1,3-diphenylisobenzofuran to give Diels–Alder adducts. On brief treatment of 1,2-dinitroacenaphthylene (II) with 1,3-diphenylisobenzofuran in benzene at room temperature, an unstable adduct (III), mp 160°, could be isolated. This substance reverts to its starting materials on standing in solution or even in the solid state when stored for several days. Heating the unstable adduct (III) or a mixture of II and 1,3-diphenylisobenzofuran in benzene at 80° for a few minutes gives a stable, very insoluble, isomeric adduct, mp 212–213°. The reactivity of II is to be contrasted with that of its parent, acenaphthylene, which forms an adduct with 1,3-diphenylisobenzofuran in refluxing xylene and reacts with ordinary dienes only at temperatures above 175°.[5]

There remains to be answered the question of structures of the adducts of II and 1,3-diphenylisobenzofuran. Consideration of the spectral data (see Experimental Section) and the conditions of formation of the two adducts lead to the conclusion that they are *exo–endo* isomers. In reaction of furan with maleic anhydride, it has been shown that the initial adduct is that in which the anhydride group is *endo,* in accordance

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[1] (a) Abstracted in part from the Ph.D. dissertation of T. S. Cantrell, The Ohio State University, Columbus Ohio, 1964; (b) National Science Foundation Cooperative Fellow, 1961–1962 and 1963–1964; National Science Foundation Graduate Fellow, 1962–1963.

[2] This subject has been recently reviewed by H. Shechter, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **25**, 55 (1964).

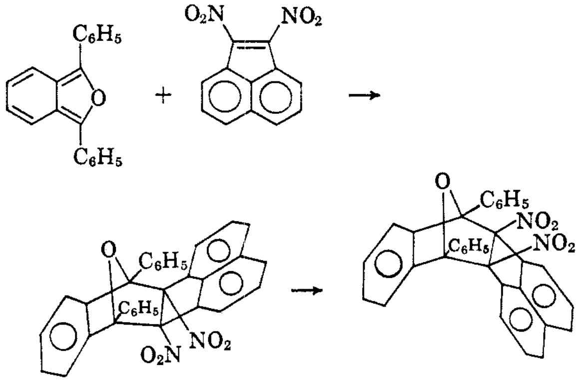
[3] (a) J. C. D. Brand and I. R. Brand *J. Chem. Soc.*, 629 (1958); (b) H. Shechter, J. J. Gardikes, and A. H. Pagano, *J. Am. Chem. Soc.*, **81**, 5420 (1959); (c) T. E. Stevens, *ibid.*, **81**, 3593 (1959).

[4] B. Campbell, *J. Chem. Soc.*, 918 (1915).

[5] (a) E. Bergmann, *J. Am. Chem. Soc.*, **74**, 1075 (1952); (b) M. C. Kloetzel and H. E. Mertel, *ibid.*, **72**, 4786 (1950).

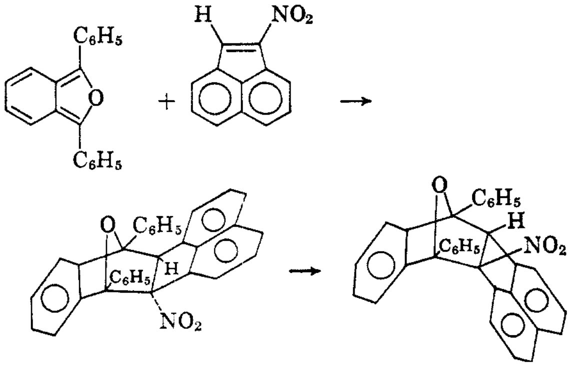
with the rule of maximum overlap of unsaturation, and that this adduct isomerizes readily, even at room temperature, to the more stable *exo* adduct.[6] This latter phenomenon had been rationalized by thermodynamic effects in which the unshared electron pairs on the oxygen atom of the adduct interact with the electron-withdrawing carbonyl groups of the *exo*-anhydride.

The question in the present case is which part of the dienophile is the effective unsaturated group for initial greater overlap, the naphthalene nucleus or the nitro groups. In a fairly analogous case, reaction of cyclopentadiene and *trans*-β-nitrostyrene, the nitro group is more effective than the phenyl group in controlling the stereochemistry of addition in that *endo*-2-nitro-*exo*-3-phenyl-5-norbornene is formed.[7] If indeed the factors of the previous systems[6,7] do apply to that of the present, it may be concluded that the less stable adduct from 1,2-dinitroacenaphthylene (II) and 1,3-diphenylisobenzofuran (eq 2) is the *endo*-dinitro derivative, III, whereas the more stable, higher melting isomer has the *exo*-dinitro structure, IV.



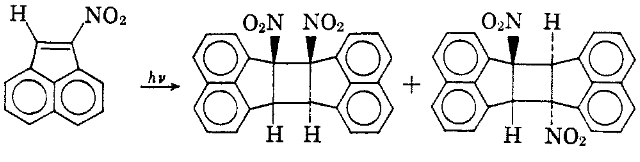
III IV (2)

1,3-Diphenylisobenzofuran also reacts with 1-nitroacenaphthylene (I); in 15 min in boiling tetrahydrofuran an almost quantitative yield of a 1:1 adduct (eq 3), mp 172–173°, was obtained. This adduct was stable and did not isomerize, even when refluxed for 12 hr in xylene. Although one might infer from the adduct's stability that it is of the *exo*-nitro structure (Vb), its infrared spectrum and its solubility behavior resemble much more closely the corresponding properties of the less stable product, III, than of IV in the previous system. It is thus not yet clear whether the present adduct has the structure Va (probable) or Vb.



Va Vb (3)

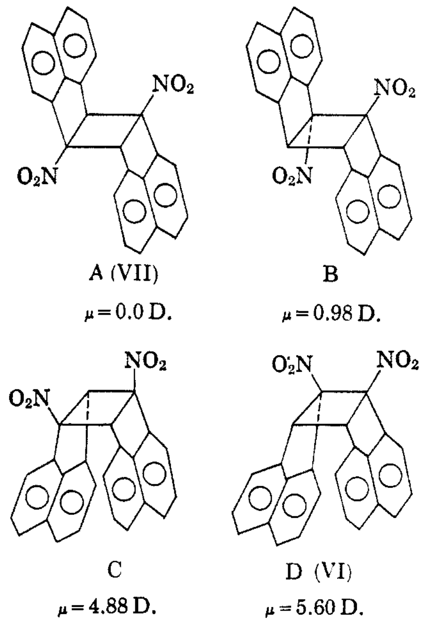
Of particular interest is the facile photodimerization of 1-nitroacenaphthylene (I). Exposure of solutions of I in ethyl ether to sunlight for a few hours gave a mixture of stereoisomeric dimers.[8] Under appropriate conditions a 34% yield of dimer VI, mp 210–211°, and a 3.5% yield of dimer VII, mp 275–277° dec, were obtained (eq 4). The photoproducts (VI and VII) were characterized as dimers of the cyclobutane type on the basis of analyses, molecular weights, and spectra. Both VI and VII exhibited infrared bands for saturated nitro groups at $\sim$6.5 and 7.4 μ; neither VI nor VII displayed ultraviolet absorption above 300 mμ.



I VI VII (4)

There are four possible stereoisomeric structures for the photodimers of I, as shown in Chart I; A and C are isomeric 1,3-dinitro-1,2,3,4-di(1,8-naphthylene)cyclobutanes and B and D are isomeric 2,3-dinitro-1,2,3,4-di(1,8-naphthylene)cyclobutanes. An unambiguous assignment of stereochemistry to the two dimers obtained was made on the basis of their dipole moments. The theoretical values for each of the four possible structures A–D were calculated by vector addition methods; the calculated values obtained are given in Chart I. The dipole moment of the lower melting dimer as determined experimentally was 5.82 ± 0.2 D. (average of two determinations), thus showing it to be the dimer of structure D (VI). The low solubility of the higher melting dimer prevented the preparation of several solutions of the concentration range usually emplyed for the dielectric constant and refractive index measurements. However, the solutions actually employed, although of low concentration, showed the same dielectric constant as the pure solvent, clearly indicating a

CHART I



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[6] R. B. Woodward and H. Baer, *J. Am. Chem. Soc.*, **70**, 1166 (1948).

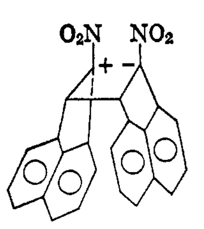
[7] G. I. Poos, H. Kleis, R. R. Wittekind, and J. D. Rosenau, *J. Org. Chem.*, **26**, 4898 (1961).

[8] Irradiation of 1,2-dinitroacenaphthylene (II) gave dark reaction mixtures from which no crystalline dimer was isolated.

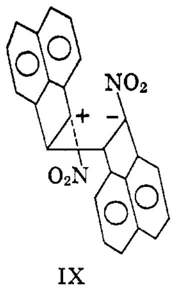
dipole moment of 0 for the high-melting dimer and consequently the structure A (VII). Thus, solar irradiation of 1-nitroacenaphthylene (eq 4) gives the *cis*, head-to-head (VI) and the symmetrical *trans*, head-to-tail (VII) dimers as major and minor products (~10:1 ratio), respectively.

The products and mechanism of codimerization of *trans*-β-nitrostyrene and olefins to cyclobutanes have been studied recently.[9] On the basis of the orientation and the reactivities of electron-rich olefins, *trans*-β-nitrostyrene may react as a n–π* singlet ($C_6H_5\bar{C}H-CHNO_2^{+}$)[9] involving an oriented π complex as has been proposed[10] for photochemical addition of conjugated enones to reactive olefins. For major formation of VI in the present experiments, it is not yet known which excitations are involved since the selective head-to-head orientation is rationalizable on the basis of nonconcerted addition of I in either its n–π* or π–π* excited states to unexcited I.

What is of particular note in the photolysis of I is the selective head-to-head dimerization of the *cis* (D, VI) rather than the *trans* (B) type. The *cis*, head-to-head dimerization of I is similar to major formation of the analogous dimer by direct irradiation of coumarin in alcoholic solution,[11] but it is in contrast to the *trans*, head-to-head dimerization in solution of benzalacetophenone,[12] a less rigid conjugated enone, and to the *trans* stereochemistry of the phenyl groups in 1-nitro-*cis*-2-*trans*-3-diphenylcyclobutane as derived from photochemical cycloaddition of *trans*-β-nitrostyrene and styrene.[9] Evidence has been presented that this coumarin dimer arises from singlet excited coumarin *via* excimers; *trans* dimers are formed from coumarin triplets.[11] It seems reasonable that I, a rigid, planar, conjugated system, may form VI *via* singlet excited states. *cis* dimerization of I, as with coumarin,[11a] may have its origins in the fact that steric interference involving rigid planar aromatic rings and planar nitro or carbonyl groups will be considerably less than that for less rigid or more bulky molecules, *e.g.*, nitrostyrene and benzalacetophenone.[1a] As a result, there will be allowed significantly greater stabilization from intramolecular (transannular) overlap in a transition state such as VIII leading to the *cis* dimer (D, VI) compared with that (IX) for the *trans* (B).[1a,13] The present interpretation also raises the question as to the importance of quantum-mechanical stabilization and orientation resulting from symmetry in transition states of the type N–N* → N*–N in which steric interference is relatively insignificant.[14,14a]



VIII



IX

Experimental Section

Reaction of Acenaphthylene with Dinitrogen Textroxide. Normal Addition, Equimolar Quantities of Reactants.—Dinitrogen tetroxide (1.50 g, 0.0163 mole) in ethyl ether (10 ml) was added dropwise in 45 min to a stirred solution of acenaphthylene (2.50 g, 0.0164 mole) in ethyl ether (100 ml) at 0° under nitrogen. The solution, which had become deep red, was stirred for 1.5 hr and then filtered. The solid was washed twice with cold ether and the combined filtrate and washings were poured into cold water. This tan solid was precipitated from benzene–hexane to give an amorphous material (0.34 g, 0.0015 mole, ~9.5% yield if calculated as a dinitroacenaphthene) having infrared absorption characteristic of saturated nitro groups (6.40 μ) and which exhibited the general behavior of polymeric substances. The analysis indicated approximately 1.6 nitro groups per acenaphthene nucleus.

Anal. Calcd for $C_{12}H_8(NO_2)_{1.6}$: C, 63.8; H, 3.55. Found: C, 64.5; H, 3.86.

The combined ethereal filtrate and washings were washed four times with cold water and dried. Cooling this solution at 0–5° overnight gave 1,2-dinitroacenaphthylene (II, 0.46 g, 0.0019 mole) as short, dark red needles, mp 160° dec. Recrystallization from ethyl acetate gave the analytical sample as dark red needles, mp 160–161° dec.

Anal. Calcd for $C_{12}H_6N_2O_4$: C, 59.56; H, 2.48; N, 11.56. Found: C, 59.64; H, 2.68; N, 11.20.

The ether was evaporated from the filtrate and the residue was chromatographed on a 28- × 340-mm column of silica gel. The column was eluted with 200 ml each of hexane, 20% methylene chloride–hexane, 30% methylene chloride–hexane, 40% methylene chloride-hexane, and 300 ml each of 50% methylene chloride–hexane, 70% methylene chloride–hexane, methylene chloride, 15% ethyl acetate–methylene chloride, and 30% ethyl acetate–methylene chloride. From the various fractions was isolated, first, 1-nitroacenaphthylene (I, 0.53 g, 0.0027 mole, 16% yield), as long orange needles, mp 123–125°. Recrystallization from ethyl acetate gave the analytical sample, mp 124–125°. The product exhibited strong infrared bands at 6.63, 6,83, 7.56, 8.42, 10.53, 11.64, 12.21, 13.07, and 13.64 μ. Its ultraviolet spectrum possessed maxima at 339 mμ (ε 10,200) and 245 mμ (ε 110,000).

Anal. Calcd for $C_{12}H_7NO_2$: C, 73.1; H, 3.55; N, 7.12. Found: C, 73.0; H, 3.65; N, 7.24.

Succeeding fractions contained bright red needles of 1,2-dinitroacenaphthylene (II, 0.13 g), mp 160° dec. The stout dark red needles described above and the slender red needles indicated here have identical infrared spectra in chloroform, with strong maxima at 6.64, 7.10, 7.53, 7.81, 8.42, 12.19, 13.14, and 13.70

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(9) (a) O. L. Chapman, private communication; (b) O. L. Chapman, A. A. Griswold, E. Hoganson, G. Lenz, and J. Reasoner, *Pure Appl. Chem.*, **9** (4), 585 (1964). (c) Photolyses of *trans*-β-nitrostyrene with propylene, methyl vinyl ether, and styrene, respectively, yield the corresponding 1-nitro-2-phenyl-3-substituted cyclobutanes.[9a] (d) The excitations of aromatic nitro compounds and nitroolefins have been discussed by H. H. Jaffé and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p 188 ff; O. L. Chapman, D. C. Heckert, J. W. Reasoner and S. P. Thackaberry, *J. Am. Chem. Soc.*, **88**, 5550 (1966); and R. O. Kan, McGraw-Hill Book Co., Inc., New York, N. Y., 1966, pp 190–191.

(10) E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *J. Am. Chem. Soc.*, **86**, 5570 (1964).

(11) (a) H. Morrison, H. Curtis, and T. McDowell, *ibid.*, **88**, 5515 (1966); (b) G. S. Hammond, C. A. Stout, and A. A. Lamola *ibid.*, **86**, 3103 (1964).

(12) (a) 1-*trans*-2-Dibenzoyl-3-*cis*-4-*trans*-diphenylcyclobutane is the principal photodimer of benzalacetophenone in acetic acid, chloroform, benzene, or ethanol; (b) H. Stobbe and K. Bremer, *J. Prakt. Chem.*, [2] **123**, 1 (1929); (c) W. J. Link, Ph.D. Dissertation, The Ohio State University, 1960.

(13) Effects of this type may also be involved if I undergoes addition as a triplet.

(14) Acenaphthylene is photolyzed to *cis*-bis(1,8-naphthyl)cyclobutane (β-heptacyclene) in ligroin and to *trans*-bis(1,8-naphthyl)cyclobutane (α-heptacyclene) in benzene: K. Dziewonski and G. Rapalski, *Ber.*, **45**, 2491 (1912); K. Dziewonski and G. Rapalski, *ibid.*, **46**, 1986 (1913); E. Bowen and J. Marsh, *J. Chem. Soc.*, 109 (1947). W. J. Link[12c] has suggested that dimerization of acenaphthylene to β-heptacyclene in a noncomplexing solvent such as ligroin may be controlled by symmetrical transannular interaction of acenaphthylene nuclei in an excited transition state such as N–N*, whereas in benzene the energy of the excited transition state leading to α-heptacyclene can be significantly lowered relative to that for β-heptacyclene because of extensive solvation of each acenaphthylene unit.

(14a) NOTE ADDED IN PROOF.—D. O. Cowan and R. L. Drisko [*Tetrahedron Letters*, 1255 (1967), and *J. Am. Chem. Soc.*, **89**, 3068 (1967)] have reported important effects of solvents and heavy atoms on the photodimerization of acenaphthylene.

μ. The total amount of VIII was 0.59 g (0.0024 mole, 14% yield). The methylene chloride and methylene chloride–ethyl acetate fractions from the chromatography contained dark red tars (2.1 g) which showed infrared bands for nitro, hydroxyl, and carbonyl (weak band) groups; no tractable material could be obtained from these fractions. The reaction of equimolar quantities of acenaphthylene and dinitrogen tetroxide in ethyl ether, in the absence of oxygen, thus gave 1-nitroacenaphthylene (I, 15% yield), 1,2-dinitroacenaphthylene (II, 16% yield), and an amorphous polymer (*ca.* 8%). Additional experiments performed in the manner described gave I and II in yields of 12 and 15% and 14 and 16%, respectively.

Reaction of Acenaphthylene with Dinitrogen Textroxide. Normal Addition, Excess Acenaphthylene.—Dinitrogen tetroxide (1.50 g, 0.016 mole) in ethyl ether (10 ml) was added dropwise in 30 min to a stirred solution of acenaphthylene (3.05 g, 0.020 mole) in ethyl ether (150 ml) at 0° under nitrogen. The red solution was stirred for 1.5 hr and then filtered. The tan solid (0.17 g) was similar in properties to the polymeric material obtained at this stage in the previous experiments and was not studied further. The filtrate was poured into ice water and the ether layer was washed four times with cold water; the solution was dried and then evaporated. The red-orange semisolid residue was chromatographed on a 28 × 320 mm column of silica gel. The column was eluted with hexane (200 ml), 20% methylene chloride–hexane (200 ml), 30% methylene chloride–hexane (500 ml), 40% methylene chloride–hexane (300 ml), 50% methylene chloride–hexane (300 ml), 70% methylene chloride-hexane (300 ml), and methylene chloride (400 ml). From the various fractions the following products were isolated: (1) unchanged acenaphthylene (0.04 g), (2) 1-nitroacenaphthylene (I, 0.82 g, 0.0042 mole, 26% yield), (3) 1,2-dinitroacenaphthylene (II, 0.46 g, 0.0019 mole, 12% yield), and (4) a black intractable material (1.7 g).

The reaction of dinitrogen tetroxide with a 20 mole % excess of acenaphthylene in ethyl ether at 0° thus gave 1-nitroacenaphthylene (I, 26% yield) and 1,2-dinitroacenaphthylene (11, 12% yield.) Subsequent experiments performed in this manner gave similar yields of I (26 and 28%) and II (10 and 13%). Experiments were conducted at temperatures as low as −78° in the hope of obtaining primary adducts; however, the solutions still become deeply colored shortly after reaction began and 1,2-dinitroacenaphthene was not isolated.

Reaction of 1,2-Dinitroacenaphthylene (II) with 1,3-Diphenylisobenzofuran.—A solution of 1,3-diphenylisobenzofuran (0.27 g, 1.00 mmole) in benzene (3 ml) was added quickly to a solution of 1,2-dinitroacenaphthylene (II, 0.24 g, 1.00 mmole) in benzene (4 ml) and the solution was stored at room temperature for several hours. Filtration gave a solid which, on visual examination, was a mixture of tiny dull yellow needles and larger, less highly colored prisms. Separation was effected by extracting the mixture with warm benzene, in which the large prisms were much more soluble. Recrystallization of the residue from toluene (charcoal) gave the stable dinitro adduct, IV, as tiny, off-white needles, mp 212–213° (0.13 g, 0.25 mmole, 25% yield).

Anal. Calcd for $C_{32}H_{20}N_2O_5$: C, 75.02; H, 3.92; N, 5.49. Found: C, 75.11; H, 3.77; N, 5.76.

Compund IV displayed strong infrared bands at 6.55, 6.90, 7.47, 9.99, 11.10, 11.91, 12.26, 12.41, 13.08, 13.32, 13.60, and 14.20 μ. Evaporation of the benzene extracts of the reaction product and recrystallization of the residue from benzene–hexane gave the lesser stable dinitro adduct, III, as thick colorless prisms, mp 161–162° dec (0.29 g, 0.57 mmole, 57% yield). The infrared spectrum of compound III possessed strong bands at 6.48, 6.83, 6.93, 7.50, 9.63, 9.80, 10.00, 12.36, 12.70, 13.43, 14.15, and 14.69 μ.

Anal. Calcd for $C_{32}H_{20}N_2O_5$: N, 5.49. Found: N, 5.72.

The adduct dissociated to its components in the solid state. A sample stored for 8 days at room temperature became discolored and was converted to a mixture of 1,2-dinitroacenaphthylene (II) and *o*-dibenzoylbenzene, the oxidation product of 1,3-diphenylisobenzofuran. When a solution of dinitro adduct III (0.20 g, 0.39 mmole) was refluxed in benzene for 6 hr, the more stable dinitro adduct, IV, gradually precipitated during the reflux period. Cooling and filtering gave crude IV (0.17 g, 0.33 mmole, 85% yield). Recrystallization from toluene gave pure adduct, mp 212°. A similar yield was obtained in this manner beginning with II and 1,3-diphenylisobenzofuran.

Reaction of 1-Nitroacenaphthylene (I) with 1,3-Diphenylisobenzofuran.—A solution of 1-nitroacenaphthylene (I, 0.20 g, 1.00 mmole) in benzene (4 ml) was added quickly to 1,3-diphenylisobenzofuran (0.27 g, 1.00 mmole) in benzene (2 ml). A deep purple color formed which faded within a few seconds. The solution was kept at room temperature for 7 hr. During this time an adduct crystallized from the reaction mixture. The mixture was filtered and the solid was washed with a little cold benzene–hexane to give the Diels–Alder adduct V (0.44 g, 0.94 mmole, 94% yield) as off-white prisms, mp 169–171° dec. Two recrystallizations from benzene gave the analytical sample as thick white prisms, mp 171–172° dec.

Table I

N^a	ϵ_{12}^b	n_{12}^c	Dipole moment, D.
	Run I		
0.00733	2.364	1.4994	
0.00516	2.343	1.4990	5.71
0.00271	2.320	1.4986	
0.00000	2.294	1.4981	
	Run II		
0.00657	2.363	1.4991	
0.00453	2.344	1.4987	5.96
0.00210	2.315	1.4982	
0.00000	2.296	1.4979	

[a] N weight fraction of solute. [b] ϵ_{12} dielectric constant of the solution. [c] n_{12} refractive index.

Anal. Calcd for $C_{32}H_{21}NO_3$: C, 82.23; H, 4.71; N, 3.00. Found: C, 82.61; H, 4.93; N, 3.03.

Compound V exhibited strong infrared bands at 6.51, 6.93, 7.45, 7.50, 9.69, 9.85, 10.09, 12.23, 12.65, 12.93, 13.14, 13.64, 14.34, and 14.78 μ. Its nmr spectrum showed, in addition to the multiplets for the aromatic hydrogens, a singlet at τ 4.77.

Photodimerization of 1-Nitroacenaphthylene (I).—A solution of 1-nitroacenaphthylene (I, 0.90 g, 0.0046 mole) in ethyl ether (100 ml) in a Pyrex test tube was flushed with nitrogen and allowed to stand in direct sunlight for 6 hr. The solution was filtered from a small amount of dark amorphous material and the filtrate was evaporated to dryness. The residue was dissolved in warm benzene and chromatographed on a 22 × 260 mm column of silica gel. Elution with 2:1 and 1:2 hexane–benzene (300 ml each) gave a series of fractions which on evaporation yielded *trans*-1,3-dinitro-1,2,3,4-di(1,8-naphthylene)cyclobutane (VII, 0.34 g, 0.000086 mole, 3.8% yield) as an off-white solid, mp 271–274°. Recrystallization from chloroform gave the analytical sample as tiny white prisms, mp 275–277° dec, 0.031 g (3.5%).

Anal. Calcd for $C_{24}H_{14}N_2O_4$: C, 73.10; H, 3.55; N, 7.12. Found: C, 73.38; H, 3.87; N, 7.33.

The longest wavelength ultraviolet absorption band of VII appeared at 294 mμ. The infrared spectrum showed strong bands at 6.47, 7.51, 11.95, 12.11, 12.45, 12.72, 12.92, and 13.50 μ. Evaporation of the latter fractions gave *cis*-2,3-dinitro-1,2,3,4-di(1,8-naphthylene)cyclobutane (VI) as a pale yellow solid, mp 206–209° (0.32 g, 0.0082 mole, 35% yield). Recrystallization from benzene–hexane gave white prisms, mp 210°, containing one molecule of solvated benzene per dimer molecule.

Anal. Calcd for $C_{24}H_{14}N_2O_4 \cdot C_6H_6$: C, 76.27; H, 4.23. Found: C, 75.99; H, 4.27.

Drying this material at 80° for 20 hr, followed by recrystallization from chloroform, gave the pure dimer, VI, as thick white prisms, mp 210–211°.

Anal. Calcd for $C_{24}H_{14}N_2O_4$: C, 73.10; H, 3.55; N, 7.12. Found: C, 73.43; H, 3.74; N, 6.82.

Photodimer VI exhibited its longest wavelength ultraviolet absorption maximum at 289 mμ. It showed strong bands in the infrared at 6.49, 7.39, 11.94, 12.09, 12.21, and 12.81 μ. The aliphatic hydrogen signal in the nmr spectrum was a sharp singlet at τ 3.93.

Succeeding fractions from the chromatographic column gave only red tars. The yields of the two dimers ranged from 3 to 4% for VII and from 27 to 35% for VI. In general, exposure of solutions of I to sunlight for more than 2 days appeared to decrease the yield of dimers and increase the yield of tar. Dimers were formed after only 1 hr in the sun, but 4–6 hr appeared to be the optimum irradiation time. Exposure of solutions of the dinitroacenaphthylene, II, to sunlight for varying periods led only to starting material or tars.

Dipole Moment Measurements.—For determination of the dipole moments of VI and VII, measurements were made of the dielectric constants and refractive indices of several solutions of each compound (0.0–1.1%) in benzene at 30°. The method used for calculating the dipole moments was that of Everard, Hill, and Sutton.[15] For the system, benzene at 30°, eq 5[16] is obtained in

$$\mu = (\text{mol wt})^{1/2}(0.00945\alpha + 0.00024\beta + 0.0287\gamma + 0.0028)^{1/2} \qquad (5)$$

which μ is the dipole moment and α, β, and γ are parameters which represent the changes in dielectric constant, density, and refractive index with composition. For compounds having a dipole moment greater than 1.5 D., β can be neglected without introducing appreciable error.[16]

The apparatus used for measurement of the electrical properties of the solutions was a General Radio Corp. Model 1610-A capacitance bridge. From the capacitance of each solution, the dielectric constant was calculated, using the directions of the manufacturer. Typical data for VI are given in Table I, p 117.

Registry No.—I, 13132-28-0; II, 13132-29-1; III, 13132-30-4; IV, 13132-31-5; Va, 13132-32-6; Vb, 13132-33-7; VI, 13132-34-8; VII, 13132-35-9; acenaphthylene, 208-96-8.

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Neighboring Hydroxyl Group Effect in Solvolysis Reactions of Common Ring *p*-Toluenesulfonates

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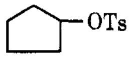
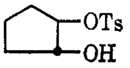
Solvolysis rates of cyclopentyl (1), cyclohexyl (2), cycloheptyl (3), *trans*-2-hydroxycyclopentyl (1-OH), *trans*-2-hydroxycyclohexyl (2-OH), and *trans*-2-hydroxycycloheptyl (3-OH) *p*-toluenesulfonate have been determined in a series of solvents of varying ionizing strength. Analysis of the kinetic data by the mY relationship supports an SN1-type mechanism for the compounds in question. Further analysis of the kinetic data suggests that *I* strain plays a significant role in the competition between the neighboring hydroxyl group assistance and inductive effects while conformational factors have little influence upon the neighboring-group effect. The fact that the enthalpy difference controls the magnitude of the rate ratios k^1/k^2 and $k^{1\text{-OH}}/k^{2\text{-OH}}$ lends additional support to the significant influence of *I* strain upon the neighboring group-effect.

In a recent solvolytic investigation,[1] the slight influence of a neighboring *trans*-hydroxyl group on the reaction rate of cyclooctyl derivatives was rationalized in terms of a balance between opposing neighboring-group assistance and electronic effects upon the free energy of activation. The relative importance of conformational factors in the neighboring-group effect was not specifically described and a more detailed investigation was needed.

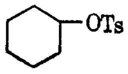
In this paper the kinetic investigation of the solvolytic reactions of cycloalkane derivatives was extended to include the five-, six-, and seven-membered ring compounds. The data indicate that the influence of a neighboring hydroxyl group is sensitive to medium and *I* strain effects but insensitive to conformational effects.



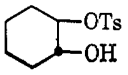
1



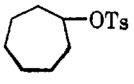
1-OH



2



2-OH



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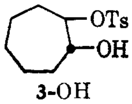

3-OH

The first-order rate constants for solvolysis of **1**–**3** and **1**-OH–**3**-OH in various solvents are summarized in Table I. The solvolysis reaction of **3**-OH in the 1:1 acetic acid–formic acid solvent mixture yielded integrated first-order rate constants that tended to decrease as reaction progressed; consequently, the rate constant was calculated from the initial slope of a plot of log $(a - x)$ *vs.* time. All other reactions were first order in *p*-toluenesulfonate up to at least 80% conversion. The activation parameters were obtained by IBM 1620 computer regression analysis of ln k/T *vs.* $1/T$.

The linear free-energy relationship given by eq 1 is useful for mechanistic classification of solvolysis

$$\log k = \log k^0 + mY \qquad (1)$$

reactions.[2a,3a] The plots of the logarithms of selected rate data from Table I *vs.* Y result in the well-known[4,5] dispersion of points into two nonparallel lines (*cf.* Figures 1–3), one for the aqueous alcohol solvent mixtures and one for the carboxylic acid solvent mixtures. This dispersion of points into two correlation lines can be ascribed to at least two factors. First, the nucleophilic character of the solvent is important to the solvolysis rate of the compounds in question because their solvolysis is not limiting.[4] Second, the presence of multiple solvation mechanisms, neglected[3b] by the mY relationship, will produce plots with different slopes for each different two-component solvent system.

Concerning factor 1, the importance of the solvent nucleophilic character in the solvolysis of **1**–**3**, there is abundant support in the literature[6,7–9] for the

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[1] D. D. Roberts and J. G. Traynham, *J. Org. Chem.*, **32**, 3177 (1967).

[2] A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962: (a) pp 63, 64; (b) p 96.

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[5] S. Winstein, A. H. Fainberg, and E. Grunwald, *ibid.*, **79**, 4146 (1957).

[6] See Table I, footnote *g*.

[7] S. Winstein, E. Grunwald, and L. L. Ingraham, *J. Am. Chem. Soc.*, **70**, 821 (1948).

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[9] A. Streitwieser, Jr., *ibid.*, **78**, 4935 (1956).