The structural data on 1-methylcyclopropene indicates an sp-type hybrid at C_2. The C_2–C_4 bond distance (longer than methylacetylene[5] and shorter than propylene[6]) can be explained by allowing more p character in the C_2–C_4 bond with a corresponding lengthening over pure sp and more s character in the orbital directed into the ring. The HCH angle at C_3 can also be explained with similar reasoning using sp^2 orbitals with one lobe directed into the center of the ring.

The above interpretation of the bonding in methylcyclopropene is also consistent with the hybridization[14,15] as determined by the $J_{^{13}CH}$ spin–spin coupling constants.

The barrier to internal rotation in methylcyclopropene of 1390 cal/mole has decreased significantly from the value of 2000 cal/mole in propylene.[16] However, the barrier in N-methylmethylenimine[17] is nearly identical with the value in propylene which has caused Dale[18] to question the role of the adjacent vinyl proton in giving rise to the origin of the barrier.[19] Lowe[20] has discussed the equal barriers in N-methylmethylenimine and propylene on the basis of an electrostatic model. The methyl barrier goes down when the vinyl proton is removed, but it also goes up when the angle between the double bond and the methyl rotor axis decreases as in N-methylmethylenimine. According to Lowe, these two compensating factors lead to nearly equal barriers in the two molecules.

In 1-methylcyclopropene we have removed the adjacent proton as in N-methylmethylenimine and we have also increased the double bond–methyl rotor axis angle. Extending Lowe's arguments to this molecule gives the required lowering of the barrier. However, there are other arguments which indicate the electrostatic model may not be the most valuable approach in understanding the origin to the barrier to internal rotation.[19,21]

We are continuing our work on 1-methylcyclopropene in order to determine V_6 and the conformation of the methyl group. These data ought to lead to a better understanding of the bonding and origin to the barrier in small-ring compounds.

Acknowledgment. The support of the National Science Foundation is gratefully acknowledged.

(13) See W. H. Flygare and V. W. Weiss, *J. Chem. Phys.*, **45**, 2785 (1960), for further details in the construction of these hybrid orbitals.
(14) C. Juan and H. S. Gutowsky, *ibid.*, 37, 2198 (1962), and references cited therein.
(15) G. L. Gloss and R. B. Larrabee, *Tetrahedron Letters*, 287 (1965).
(16) E. Hirota, *J. Chem. Phys.*, **45**, 1984 (1966).
(17) K. V. L. N. Sastry and R. F. Curl, *ibid.*, **41**, 77 (1964).
(18) J. Dale, *Tetrahedron*, **22**, 3373 (1966).
(19) For a discussion of recent data in light of theories on the origin of the barrier, see W. H. Flygare, *Ann. Rev. Phys. Chem.*, in press.
(20) J. P. Lowe, *J. Chem. Phys.*, **45**, 3059 (1966).
(21) W. H. Fink and L. C. Allen, *ibid.*, **46**, 2261 (1967).
(22) (a) C. S. Marvel Fellow; (b) Alfred P. Sloan Fellow.

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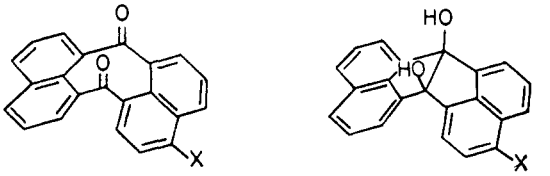
Preparation and Racemization of an Optically Active 1,8-(1′,8′-Naphthalyl)naphthalene[1]

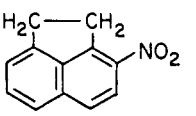
Sir:

We have previously pointed out that in 1,8-(1′,8′-naphthalyl)naphthalene (**1**) simultaneous conrotation or disrotation[2] of the carbonyl groups about the carbon–carbon single bonds is inhibited by the considerable angle strain it introduces, and that a suitably substituted derivative of **1** consequently might be obtained optically active.[3] We now report the preparation of optically active 4-nitro-1,8-(1′,8′-naphthalyl)naphthalene (**2**) and the kinetics of racemization of this new dissymmetric system. The conformational stability of **2** is such that it racemizes on standing in chloroform solution at 25.5° with a half-life of 102 min.

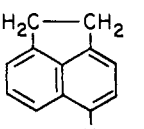


1, X = H
2, X = NO_2

3, X = H
4, X = NO_2



5



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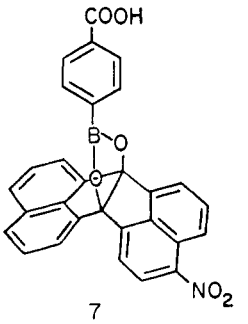

7

Nitration of glycol **3**[4] either with nitric acid in a mixture of acetic acid and nitromethane or with nitryl tetrafluoroborate[5] in nitromethane–acetonitrile solution gave the nitroglycol **4**.[6] The position of nitration follows from the known reactions of acenaphthene[7,8] and was substantiated by comparison of the nuclear magnetic resonance spectra of **4**, the derived diacetate,[6] and the derived acetonide[6] with the spectra of both 3-nitroacenaphthene (**5**)[7] and 5-nitroacenaphthene (**6**).[8] Reaction of the nitroglycol **4** with a slight excess of *p*-boronobenzoic acid[9] in refluxing benzene using a water separator furnished the cyclic boronate ester carboxylic acid **7**.[6] This esterification provided convenient access to a derivative of **4** suitable for optical resolution; the

(1) This investigation was supported by National Science Foundation Grant GB-137 and National Institutes of Health Grant AM-02493.
(2) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).
(3) W. C. Agosta, *Tetrahedron Letters*, 3635 (1966); *J. Am. Chem. Soc.*, **89**, 3505 (1967).
(4) R. L. Letsinger and J. A. Gilpin, *J. Org. Chem.*, **29**, 243 (1964).
(5) G. Oláh, S. Kuhn, and A. Mlinkó, *J. Chem. Soc.*, 4257 (1956); S. J. Kuhn and G. A. Olah, *J. Am. Chem. Soc.*, **83**, 4564 (1961).
(6) This new substance gave acceptable elemental analyses for carbon, hydrogen, and nitrogen.
(7) 3-Nitroacenaphthene (**5**) is available in low yield by nitration of acenaphthene with acetyl or benzoyl nitrate in petroleum ether: G. T. Morgan and H. A. Harrison, *J. Soc. Chem. Ind.* (London), **49**, 413T (1930).
(8) Direct nitration of acenaphthene under a variety of conditions gives 5-nitroacenaphthene (**6**) in good yield: F. Sachs and G. Mosebach, *Ber.*, **44**, 2852 (1911).
(9) A. Michaelis, *Ann.*, **315**, 19 (1901).

boronate ester **7** could be formed reversibly and in high yield under quite mild conditions, and this transformation introduced no change in the symmetry properties of the original array (**4**).

As a carboxylic acid, **7** gave a crystalline salt with quinine which, after four recrystallizations from ethyl acetate, showed $[\alpha]^{25}$ −37.4° (*c* 3.30, methanol).[10] Liberation of **7** by treatment of the salt with aqueous hydrochloric acid gave optically active material, $[\alpha]^{25}$ +39.8° (*c* 4.42, ethyl acetate),[10] which was hydrolyzed in hot aqueous dioxane to **4**, $[\alpha]^{25}$ +57.5° (*c* 2.76, acetone).[10]

Experiments with racemic **4** indicated that it was cleaved to nitro diketone **2** in high yield by lead tetraacetate in benzene.[11] This reaction was now applied to dextrorotatory **4** and the racemization of the isolated product, dextrorotatory **2**, was followed in chloroform solution.[10] First-order rate constants for this process were determined graphically and are recorded in Table I; from these data the following activation

Table I. First-Order Rate Constants

Temp (±0.5°), °C	$k \times 10^5$, sec^{-1}
15.5	2.96
	2.95
25.5	11.4
	11.5
	11.0
30.5	27.2
	27.2

parameters were calculated for 25.5° in conventional fashion: $\Delta F^{\ddagger}$ = 22.9 kcal/mole; E_a = 26.1 kcal/mole; $\Delta H^{\ddagger}$ = 25.5 kcal/mole; $\Delta S^{\ddagger}$ = +9 eu.

(10) All rotations were measured in a 1-dm cell at 5461 A (mercury green line).

(11) Unsubstituted glycol **2** is oxidized to **1** under these conditions; *cf.* ref **4**.

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Neighboring Group Dipolar Effects upon Solvolytic Reactivity

Sir:

Inherent in the hypothesis of neighboring group participation is the difficulty of estimating the rate-retarding effect of the group in the absence of participation.[1] As an approach toward separating the opposing factors of inductive and field destabilization *vs.* the stabilizing effect derived from anchimeric assistance, we have studied the solvolytic behavior of several model compounds which possess a neighboring group locked in a position unfavorable for anchimeric interaction. Rate data for the typical compounds I–IV are given in Table I.

The essential findings of this study are (a) large (factors of 10^4–10^7) rate decelerations relative to the parent compounds, (b) abnormally high infrared carbonyl stretching frequencies for the ketonic carbonyl group derived from the related secondary alcohol, and (c) extensive rearrangement in the product-forming step. We interpret the observed rate retardations in terms of an electrostatic destabilization arising from the interaction of the conformationally fixed dipole of the neighboring group and the developing dipole associated with the departing toxyloxy anion. The related carbonyl compound serves as a model for this transition-state interaction and the high carbonyl stretching frequency is attributable to similar dipolar destabilization in the ground state.[2]

The origin of the very large rate retardations observed for I–IV could be in steric, inductive, or field effects. From a steric standpoint, it is clear that the 2,6-bridging group in compounds I–IV effectively blocks the rear side of the potential cationic center at C_5 and could hinder seriously solvation. However, the corresponding 2,6-ethano-bridged derivative, *exo*-2-brendyl brosylate, solvolyzed at about the same rate as *exo*-2-norbornyl brosylate.[6] As far as the inductive effect of bridged lactone and oxido groups within the norbornyl system is concerned, very little data exist for the rate-retarding influence due to these substituents. Assuming that the lactone function in I might retard the solvolysis to about the same extent as a β-acetoxyl group, one would expect a rate-retardation factor of 10^3 relative to norbornyl tosylate.[7] Neither steric nor simple

(1) For a discussion see E. Grunwald, *J. Am. Chem. Soc.*, **73**, 5458 (1951); S. Winstein, E. Grunwald, and L. L. Ingraham, *ibid.*, **70**, 821 (1948).

(2) These effects are, of course, well recognized; however, attention has not been drawn explicitly to the possible relationship between the carbonyl stretching frequency and the rate of solvolysis in systems possessing neighboring dipolar functions. For example, the carbonyl stretching frequency for an α-bromo ketone possessing an almost coplanar arrangement of the carbonyl group and bromine atom is shifted by 20 cm^{-1} relative to the *trans* orientation. The shift is due to a destabilizing dipolar interaction which is minimized in the *trans* case.[3] Applying the Schleyer-Foote equation[4,5] to this system in which the displacement in the carbonyl stretching frequency is not due to internal angular strain but rather a dipolar effect, one would anticipate a rate retardation of log rel rate = 0.125(20 cm^{-1}) = 2.5. Approximate models exist to test this prediction.[1] At 75°, the relative rates of solvolysis of cyclohexyl brosylate, *trans*-2-bromocyclohexyl brosylate, and *cis*-2-bromocyclohexyl brosylate are 1.00:0.101:1.24 × 10^{-4}. If one assumes that the transition states for solvolysis of the two bromo tosylates have the tosyloxy group in an axial conformation, one can understand the relative rates of solvolysis of the *cis* a,e and *trans* a,a without recourse to anchimeric assistance by bromine in the rate-limiting ionization step.

(3) R. N. Jones, D. A. Ramsay, F. Herling, and K. Dobriner, *J. Am. Chem. Soc.*, **74**, 2828 (1952); E. J. Corey, *ibid.*, **75**, 2301 (1953); N. L. Allinger, J. Allinger, L. A. Freiberg, R. F. Czaja, and N. A. LeBel, *ibid.*, **82**, 5876 (1960).

(4) P. von R. Schleyer, *ibid.*, **86**, 1854, 1856 (1964).

(5) C. S. Foote, *ibid.*, **86**, 1853 (1964); Ph.D. Dissertation, Harvard University, 1961.

(6) Private communication, A. Nickon.

(7) Using the Taft equation with $\alpha^* = 0.85$, $\rho^* = -3.49$, and k_H for norbornyl tosylate at 25° of 2.33 × 10^{-5} sec^{-1}, one may calculate the rate of solvolysis for the β-acetoxyl derivative to be 2.6 × 10^{-8} sec^{-1}. This of course does not take into account the position of the acetoxyl group in space relative to the tosyloxy group.

(8) Thus far, no large solvolytic rate variations have been reported for norbornyl derivatives bearing polar substituents. P. G. Gassman and J. L. Marshall, *J. Am. Chem. Soc.*, **87**, 4648 (1965), essentially discount dipole–dipole interactions as being important in the solvolysis of 7-ketonorbornyl tosylates. H. Kwart and T. Takeshita, *ibid.*, **86**, 1161 (1964), find rate variations of less than a factor of 10 for orientated polar substituents. The work of Roberts and co-workers on the *syn*- and *anti*-7-chloro-2-*exo*-norbornyl tosylates has not disclosed any analogous dipolar interactions. The ratio of rates of the *anti* to *syn* isomers is 1.25. Absence of such an effect is due to the lower dipole moment of the carbon–chlorine bond and also the greater distance between the chlorine atom in the *syn* case and the departing tosyloxy group. This may account for the differences between our work and theirs: W. G. Woods, R. A. Carboni, and J. D. Roberts, *ibid.*, **78**, 5653 (1956).