media, *e.g.*, acetone,[9] by way of undissociated ion pairs,[10] just as do many racemizations, exchanges and a great variety of rearrangements.

By microscopic reversibility, the present type of elimination is related to the reverse reaction of addition of hydrogen halide to certain olefins, carbonium chloride ion pairs being common intermediates. Pertinent cases in acetic acid solvent would appear to be the addition of hydrogen chloride to isobutylene[7] and the mainly *cis* addition of hydrogen chloride and hydrogen bromide to acenaphthylene.[11]

(9) It seems likely that the essentially quantitative first-order elimination which *t*-BuBr undergoes in solvent acetone is of this same type. [See S. Winstein, S. Smith and D. Darwish, *Tetrahedron Letters*, **No. 16**, 24 (1959).]

(10) See, also, S. Winstein, E. Vogelfanger, K. C. Pande and H. F. Ebel, *J. Am. Chem. Soc.*, **84**, 4993 (1962), for elimination from norbornyl ion pairs.

(11) M. J. S. Dewar and R. C. Fahey, Abstracts, American Chemical Society National Meeting, Los Angeles, California, April 1–5, 1963, p. 51M.

(12) National Science Foundation Predoctoral Fellow, 1959–1963.

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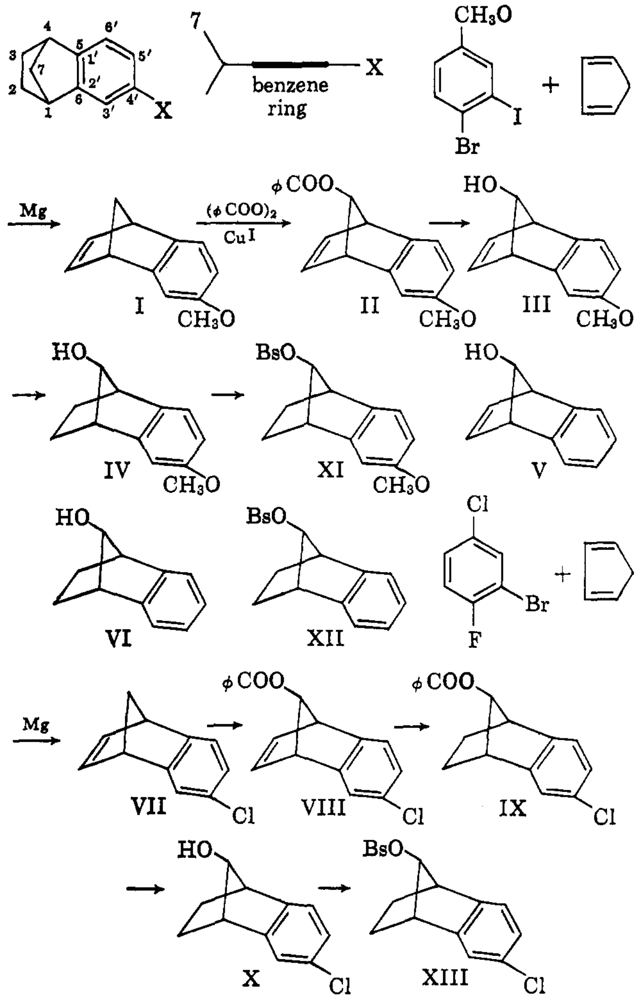
RECEIVED APRIL 18, 1963

SUBSTITUENT EFFECTS ON *anti*-7-BENZONORBORNENYL BROSYLATE SOLVOLYSES

Sir:

Interest in substituent effects on a reaction site not in the same plane as the benzene ring led us to study the acetolysis of substituted *anti*-7-benzonorbornenyl *p*-bromobenzenesulfonates. We wish to report promptly the strikingly large substituent effect observed on a carbonium ion reaction in this rigid homobenzylic[1] system.

Wittig's procedure[2] for the addition of benzynes to cyclopentadiene and our stereospecific benzoyloxylation[3] of the 7-position of benzonorbornadienes were used to synthesize the desired compounds. The cycloaddition was successfully carried out with cyclopentadiene, magnesium and 4-bromo-3-iodoanisole,[4] b.p. 124–126° (2 mm.), $n^{26}\mathrm{D}$ 1.6493, (prepared from 6-bromo-*m*-anisidine by the Sandmeyer reaction) yielding racemic 4'-methoxybenzonorbornadiene (I) in 40% yield, b.p. 99–100° (4 mm.), $n^{23}\mathrm{D}$ 1.5642, $\lambda_{\max}^{\text{cyclohexane}}$ 249 mμ (log ϵ 3.35), 284 mμ (log ϵ 3.26), 290 mμ (log ϵ 3.23). Copper salt-catalyzed reaction of I with benzoyl peroxide yielded *anti*-7-benzoyloxy-4'-methoxybenzonorbornadiene (II), m.p. 90.5–91°. Reaction of II with methylmagnesium iodide gave *anti*-4'-methoxybenzonorbornadien-7-ol (III), m.p. 68.5–70°, which on catalytic reduction over palladium–charcoal afforded quantitatively *anti*-4'-methoxybenzonorbornen-7-ol (IV), m.p. 78–78.5°. *anti*-7-Benzonorbornadienol (V) and *anti*-7-benzonorbornenol (VI) were prepared by a similar sequence, and their structures were confirmed by independent syntheses.[1] Benzyne reaction of 2-bromo-4-chlorofluorobenzene, b.p. 90° (30 mm.), $n^{19}\mathrm{D}$ 1.5549 (obtained by the Schiemann reaction on 2-bromo-4-chloroaniline) with cyclopentadiene gave 4'-chlorobenzonorbornadiene (VII), b.p. 112–112.5° (10 mm.), $n^{21}\mathrm{D}$ 1.5763, $\lambda_{\max}^{\text{cyclohexane}}$ 241 mμ (log ϵ 3.28), 269 mμ (log ϵ 2.83), 276 mμ (log ϵ 2.92), 284 mμ (log ϵ 2.89), in 55.6% yield. Benzoyloxylation afforded *anti*-7-benzoyloxy-4'-chlorobenzonorbornadiene (VIII), m.p. 124–124.5°. Catalytic reduction of VIII gave *anti*-7-benzoyloxy-4'-chlorobenzonorbornene (IX), m.p. 124.5–125°, which was transformed by lithium aluminum hydride into *anti*-4'-chlorobenzonorbornen-7-ol (X), m.p. 114°, in good yield.



The benzoyloxylation reaction gave only *anti*-products, with no evidence of the epimers. Their orientations were established by comparison of the infrared spectra of IV, VI and X with III and V; the latter showed clearly an internal interaction between the hydroxyl group and the π-electrons of the double bond,[5] the ν_{OH} absorptions of IV, VI and X appearing at 2.75 μ,[6] whereas those of III and V were at 2.81 μ.[7] The formation of 2-methoxynaphthalene in high yield by the Oppenauer oxidation of III established unequivocally that the position of the methoxy group was originally 4'. Brosylates of the *anti*-alcohols were prepared in a standard method, *anti*-4'-methoxybenzonorbornen-7-ol *p*-bromobenzenesulfonate (XI), m.p. 94–95°, *anti*-benzonorbornen-7-ol *p*-bromobenzenesulfonate (XII), m.p. 132.5–133.5°, *anti*-4'-chlorobenzonorbornen-7-ol *p*-bromobenzenesulfonate (XIII), m.p. 91–92°.

Solvolysis of the three brosylates in glacial acetic acid containing equivalent sodium acetate[8] yielded the *anti*-7-acetates in quantitative yield. There was no

(1) P. D. Bartlett and W. P. Giddings, *J. Am. Chem. Soc.*, **82**, 1240 (1960).

(2) G. Wittig and E. Knauss, *Ber.*, **91**, 895 (1958).

(3) H. Tanida and T. Tsuji, *Chem. Ind.* (London), 211 (1963).

(4) Satisfactory analyses were obtained for all compounds described.

(5) *Cf.* P. Schleyer, D. S. Trifan and R. Bacskai, *J. Am. Chem. Soc.*, **80**, 6691 (1958); M. Oki and H. Iwamura, *Bull. Chem. Soc. Japan*, **32**, 306 (1959).

(6) The measurements were carried out using Perkin-Elmer Model 12c, LiF prism, 20-mm. cell in carbon tetrachloride solution.

(7) Further support was obtained by behavior of the hydrogen at the 7-position in the n.m.r. spectra, due to diamagnetic anisotropy effects of the double bond: K. Tori, R. Muneyuki, T. Tsuji, Y. Hata and H. Tanida, to be published (presented at the 16th Annual Meeting of the Chemical Society of Japan in Tokyo, April, 1963). Hydrogenation of the double bond causes an upfield shift of the *anti*-7-hydrogen of about 0.15–0.25 p.p.m. Also, *cf.* R.R. Fraser, *Can. J. Chem.*, **40**, 78 (1962).

(8) *E.g.*, S. Winstein, C. Hanson and E. Grunwald, *J. Am. Chem. Soc.*, **70**, 812 (1948); S. Winstein, E. Grunwald and L. L. Ingraham, *ibid.*, **70**, 821 (1948).

TABLE I

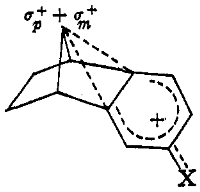
ACETOLYSIS RATES OF THE BROSYLATES

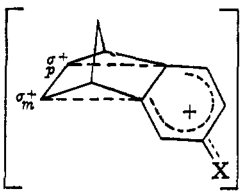
Compound	Temp., °C.	$k\psi$, sec.$^{-1}$	Calculated $k\psi^b$ (77.60°) sec.$^{-1}$	Rel. rate^b (77.60°)
XI	77.65 ± 0.03	8.265×10^{-4}	7.943×10^{-4}	53.3
	77.65 ± 0.03	7.996×10^{-4}		
	64.41 ± 0.03	1.556×10^{-4}		
	59.85 ± 0.03	6.871×10^{-5}		
XII	97.75 ± 0.03	1.235×10^{-4}	1.488×10^{-5}	1
	95.75 ± 0.05	1.058×10^{-4a}		
	77.65 ± 0.03	1.495×10^{-5}		
	74.79 ± 0.05	1.022×10^{-5a}		
XIII	120.55 ± 0.07	1.134×10^{-4}	7.412×10^{-7}	0.050
	103.55 ± 0.04	2.105×10^{-5}		
	77.65 ± 0.03	7.367×10^{-7}		

[a] Cited from ref. 1. [b] Calculated from the least square slopes of the Arrhenius plots.

evidence of *syn*-isomers. The solvolysis rates are summarized in Table I. For comparison, the rate constants at 77.60° were calculated using least square slopes, derived from Arrhenius plots. The relative rates of CH_3O, H and Cl were 53.3:1:0.050.

The large substituent effect and the formation of only *anti*-products strongly suggests a large electron demand from the aromatic ring in the transition state. Although we have insufficient data to establish which kind of σ-value best fits in this homobenzylic system, a plot of log k *vs.* $(\sigma_p{}^+ + \sigma_m{}^+)$ resulted in a good straight line with a ρ of -2.42. A plot of log k *vs.* σ_p also gave a straight line with a ρ of -6.15. However, the latter treatment may be dubious because strongly electron-demanding reactions usually follow σ^+ better than σ; also, the ρ-value is extraordinarily high. All other substituent treatments considered by us did not give a linear relation. It seems reasonable that the aromatic carbons participating in solvolyses at the 7-position will be those which are *para* and *meta* to the 4'-substituent. We tentatively suggest a homoconjugated carbonium ion intermediate, which may be pictured as





If our suggestions are correct, the correlations of homoconjugation on the 3-carbon with $\sigma_p{}^+$ and on the 2-carbon with $\sigma_m{}^+$ would be expected. Further studies in this field are in progress and will be reported later.

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MECHANISMS OF α-ELIMINATION. REACTIONS OF NITROBENZYL 'ONIUM IONS WITH AQUEOUS SODIUM HYDROXIDE

Sir:

It has been found that *p*-nitrobenzyldimethylsulfonium *p*-toluenesulfonate forms *p,p'*-dinitrostilbene (99%) when allowed to react with aqueous sodium hydroxide.[1] An α-elimination mechanism was postulated. An alternative mechanism could be the displacement of dimethyl sulfide by a carbanion (ylide) attack on a second sulfonium ion. The second-order kinetics [(salt)(HO^-)] would eliminate the carbanion displacement mechanism if the removal of the methylene protons were rapidly reversible. The sulfonium salt isolated after partial reaction in D_2O showed infrared absorptions characteristic of C–D bonds.[1] Although the methylene protons would be most likely to be replaced, the infrared evidence does not prove this. By means of n.m.r. it is possible to determine which protons have been replaced. We carried out a deuterium exchange study as described before.[1] The n.m.r. spectrum of the recovered sulfonium salt showed that at least 97% of the methylene protons were exchanged and about 50% of the methyl protons were exchanged. This eliminates the carbanion displacement mechanism.

The nature of the substituent on the phenyl ring is critical. It has been found that unsubstituted, *m*-chloro- and *p*-methylbenzyldimethylsulfonium ions when treated with base do not yield the corresponding stilbenes but give high yields of alcohol.[2]

An aqueous solution 0.1 *M* in *m*-nitrobenzyldimethylsulfonium bromide[3] and an aqueous solution 0.1 *M* in *p*-nitrobenzyltrimethylammonum bromide[3] and 0.2 *M* in sodium hydroxide, after heating on a steam bath for 20 hr., gave a brown amorphous precipitate (I) which was isolated by filtration. The filtrate was extracted with ether and the ether dried with magnesium sulfate. After evaporation of ether and purification on an alumina column, a 5% yield of *m*-nitrobenzyl alcohol was obtained. The brown solid I gave a white crystalline solid which melted at 154–155° and a brown tar after chromatography on alumina. The white solid was homogeneous by thin layer chromatography and was shown to be *m,m'*-dinitrostilbene oxide, in 41% yield. (*Anal.* Calcd. for $C_{14}H_{10}N_2O_5$: C, 58.74; H, 3.52; N, 9.79. Found: C, 58.50; H, 3.62; N, 9.33, mol. wt. (osmom.), 276). An infrared spectrum showed peaks at 1260, 920 and 860 cm.$^{-1}$ (epoxide) and and at 1520 and 1340 cm.$^{-1}$ (nitro group).[4] The n.m.r. spectrum showed absorption in the aromatic region at 7.9 δ[5] and a single sharp peak at 4.0 δ with areas in the ratio 4:1. Ethylene protons of stilbene oxide are known to absorb at 3.9 δ and the phenyl protons at 7.4 δ.[6] A nitro group should shift the absorption of the phenyl protons downfield. The tar is being investigated further. Under nitrogen, with heating for 5 hr., 43% of the stilbene oxide and 5% of *m*-nitrobenzyl alcohol were obtained.

Carbene formation from ammonium salts has been reported.[7] We allowed an aqueous solution 0.1 *M* in *p*-nitrobenzyltrimethylammonium bromide[3] and 0.2 *M* in sodium hydroxide to react on a steam bath for 72 hr. After this period of time a quantitative recovery of ammonium salt was made. Under the same conditions the *p*-nitrobenzyldimethylsulfonium salt gave a quantitative yield of *p,p'*-dinitrostilbene within 1 hr. The relative inertness of the ammonium salt could be due to the fact that trimethylamine is a poorer leaving group than dimethyl sulfide.[8] Also, sulfur has d-orbitals which may help to stabilize the transition state, but

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(1) C. G. Swain and E. R. Thornton, *J. Am. Chem. Soc.*, **83**, 4033 (1961).

(2) C. G. Swain and E. R. Thornton, *J. Org. Chem.*, **26**, 4808 (1961).

(3) This compound gave a satisfactory microanalysis.

(4) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 118, 298.

(5) Obtained with a Varian HR-60 spectrometer in $CDCl_3$; chemical shifts in parts per million downfield from tetramethylsilane.

(6) R. Ketcham and V. P. Shah, *J. Org. Chem.*, **28**, 229 (1963).

(7) V. Franzen, *Chem. Ber.*, **93**, 557 (1960); V. Franzen and G. Wittig, *Angew. Chem.*, **72**, 417 (1960); C. K. Ingold and J. A. Jessop, *J. Chem. Soc.*, 2357 (1929).

(8) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 184; K. Lohmann, Ph.D. Thesis in Organic Chemistry, M.I.T., 1959.