

tion analysis according to the following procedure. Labeled benzyl thiocyanate was prepared (by exchange with Na^{85}SCN) having a specific activity of 0.5 mc./mmole, which in our counting system corresponded to about 150,000 counts/min./per thick-layer sample of BaSO_4 of 0.6 cm.² area. Methyl ethyl ketone solutions (2 ml.) which were 0.1 M in labeled benzyl thiocyanate and 0.1 M in NaClO_4 , were kept at 110° in a thermostat for 225 hr.; afterward, benzyl isothiocyanate carrier (0.2 mmole) was added and the solution extracted with cyclohexane–water. The cyclohexane

layer after washing with water (three times) and drying with Drierite was treated with piperidine. The N-benzyl-N'-piperidinthiourea which precipitated out was oxidized to obtain BaSO_4 , as described previously for a different thiourea.^{2c} The activity found on the thiourea–sulfur corresponded to an isomerization fraction of about 0.2% and was practically undistinguishable from the zero-time fraction, which could be due either to incomplete separation or, more likely, to isothiocyanate initially present in the thiocyanate sample.

Relative Reactivities of Some Benzocyclenes in Aromatic Nitration and Electrophilic Side-Chain Reaction.¹⁻⁵ A Remarkable Effect of the Bicyclo[2.2.1]heptene System

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Relative reactivities and orientations in aromatic nitration of benzonorbornene (I), benzobicyclo[2.2.2]octene (II), indane (III), tetralin (V), 1,3-dimethylindane (VI), and 1,2,3,4-tetrahydro-1,4-dimethylnaphthalene (VII), by means of nitric acid in a mixed solvent of sulfuric acid and nitromethane at 0°, were determined. The relative partial reactivities at their β -positions were 3.63, 1.50, 1.32, 1.01, 1.00, and 0.72, respectively. The relative rates of hydrolyses of the corresponding 1-(α - or β -benzocyclenyl)ethyl chloride in 80% aqueous acetone at 25° were in the β -series, for $I_{\beta\text{-Cl}}$, 6.10; for $II_{\beta\text{-Cl}}$, 2.36; for $III_{\beta\text{-Cl}}$, 1.63; for $IV_{\beta\text{-Cl}}$, 1.36; for $V_{\beta\text{-Cl}}$, 1.22; $VI_{\beta\text{-Cl}}$, 1.00; and for $VII_{\beta\text{-Cl}}$, 0.60. Relative rates in the α -series were for $I_{\alpha\text{-Cl}}$, 1.73; and for $VI_{\alpha\text{-Cl}}$, 1.00, respectively. The remarkable rate enhancement in the bicyclo[2.2.1]heptene system is discussed in terms of internal strain and 1,2- σ bond participation in the transition state. In addition, extraordinarily low nitration at the α -positions of the bridged compounds I and II was observed.

Introduction

The influence of the attached alicyclic ring on the chemistry of benzocyclenes has received considerable attention from three main points of view. The first is

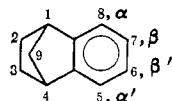
(1) Paper X of a series on Bicyclic Systems. Paper IX: H. Tanida, Y. Hata, Y. Matsui, and I. Tanaka, *J. Org. Chem.*, **30**, 2259 (1965).

(2) Some of the results of this paper appeared in preliminary form: H. Tanida and R. Muneyuki, *Tetrahedron Letters*, No. 38, 2787 (1964).

(3) Presented, in part, at the 15th Organic Reaction Mechanism Symposium of the Chemical Society of Japan in Nagoya, Oct. 1964.

(4) For the designation of the term, electrophilic side-chain reaction, refer to L. M. Stock and H. C. Brown, *J. Am. Chem. Soc.*, **81**, 3323 (1959).

(5) The numbering of bridged benzocyclenes used in this paper is as shown



the almost out-dated hypothesis of bond fixation of Kekulé benzene structures suggested by Mills and Nixon^{6,7} in order to explain the influence of an alicyclic ring condensed with the benzene nucleus on the direction of electrophilic substitution, as in 5-hydroxyindane and 6-hydroxy-1,2,3,4-tetrahydronaphthalene. The second is the influence of strain energy in the ground state, arising from fusion of the alicyclic ring, as evidenced by heats of combustion and hydrogenation.⁸

It is known that the ultraviolet spectra of highly strained benzocyclenes, for example benzocyclobutene, are characteristic. The question of the Baker–Nathan effect (hyperconjugation)¹⁰ of the alicyclic ring, in which the conformation of the ring may be quite significant, is the third main viewpoint. However, to the best of our knowledge, a precise and extensive experimental investigation of the relative reactivities of benzocyclenes using modern analytical tools has not been carried out.

The chemistry of bicyclo[2.2.1]heptane and bicyclo[2.2.2]octane systems is under active investigation. In previous papers,^{11,12} the benzonorbornene system has been demonstrated to be a good model compound for

(6) W. H. Mills and I. G. Nixon, *J. Chem. Soc.*, 2510 (1930).

(7) For reviews of the Mills–Nixon effect, see (a) W. Hüchel, "Theoretische Grundlagen der Organischen Chemie," Vol. II, Akademische Verlagsgesellschaft Geest u. Portig K.-G., Leipzig, 1957, p. 691; (b) M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, p. 197.

(8) Experimental data concerning heats of combustion or hydrogenation of the benzocyclenes themselves seem to be lacking. The only direct data may be those of Kistiakowsky, *et al.*,⁹ who showed the heat of hydrogenation of indane ($-\Delta H$) to be markedly smaller than of *o*-xylene or ethylbenzene. However, many available data on cycloalkenes⁹ suggest the degree of strain of benzocyclenes.

(9) M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, and W. E. Vaughan, *J. Am. Chem. Soc.*, **59**, 831 (1937).

(10) J. W. Baker and W. S. Nathan, *J. Chem. Soc.*, 1844 (1935).

(11) (a) H. Tanida, T. Tsuji, and H. Ishitobi, *J. Am. Chem. Soc.*, **86**, 4904 (1964); (b) H. Tanida, *ibid.*, **85**, 1703 (1963).

(12) (a) P. D. Bartlett and W. P. Gidding, *ibid.*, **82**, 1240 (1960); (b) W. P. Gidding and J. Dirlam, *ibid.*, **85**, 3900 (1963).

study of homobenzylic conjugation; direct conjugate interaction was shown between the C-9 carbonium ion formed in acetolysis of *anti*-9-benzonorbornenyl *p*-bromobenzenesulfonate and the aromatic ring. Our special interests in bridged benzocyclenes led to study of the reactivities of their aromatic rings in comparison with those of nonbridged benzocyclenes.

We have employed two approaches to evaluation of the relative reactivities of aromatic systems. One is kinetic study of an electrophilic substitution reaction, nitration in the present work, and the other is a study of a suitable "nucleophilic" side-chain reaction. For this study, the latter was chosen to be S_N1 solvolysis of 1-arylethyl chlorides, Ar·CHCl·CH₃, in aqueous acetone, partly because the mechanism of the reaction and the nature of the transition state are fairly well understood¹³ and partly because of the similarity of the transition state, as far as electronic effects are concerned, to the transition state in aromatic substitution.¹⁴

The results obtained in the bridged benzocyclenes suggest that an unique factor beyond the three mentioned above might be operating.

Results

The bridged benzocyclenes, benzonorbornene (I)¹⁵ and benzobicyclo[2.2.2]octene (II),¹⁶ were synthesized as reported in the recent literature. The nonbridged model compounds chosen were indane (III), benzocyclobutene (IV), tetralin (V), 1,3-dimethylindane (VI), and 1,2,3,4-tetrahydro-1,4-dimethylnaphthalene (VII). Since the bridged compounds I and II are formally *o*-di-*sec*-alkyl-substituted benzenes, the best nonbridged comparison models are perhaps compound VI and VII. 1,3-Dimethylindane (VI) was prepared by the catalytic reduction of 1,3-dimethylindene¹⁷ and therefore the main portion should have the *cis* configuration.¹⁸ 1,2,3,4-Tetrahydro-1,4-dimethylnaphthalene (VII) was prepared by catalytic reduction of 1,2-dihydro-1,4-dimethylnaphthalene. Properties of this material, including gas chromatographic behavior and infrared spectrum, were indistinguishable from those of an authentic sample of 1,2,3,4-tetrahydro-*cis*-1,4-dimethylnaphthalene independently prepared.¹⁹

Nitration. Treatment of the benzocyclenes (I–VII, except IV) with concentrated nitric acid in a medium composed of 90% aqueous sulfuric acid and nitromethane at low temperature yielded the α - and β -mononitro derivatives without rearrangement or other

(13) Cf. C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter 7; S. Winstein, E. Grundwald, and H. W. Jones, *J. Am. Chem. Soc.*, **73**, 2700 (1951); E. D. Hughes, C. K. Ingold, and A. D. Scott, *J. Chem. Soc.*, 1201 (1937).

(14) Cf. L. M. Stock and H. C. Brown, "Advances in Physical Organic Chemistry," Vol. I, V. Gold, Ed., Academic Press Inc., New York, N. Y., 1963, p. 35.

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

(16) (a) B. A. Kazanskii and P. I. Suirskaya, *Zh. Obshch. Khim.*, **29**, 2588 (1959); (b) K. Kitahonoki and Y. Takano, *Tetrahedron Letters*, No. 24, 1957 (1963).

(17) Regarding the synthesis, see P. A. Platter, A. Fürst, and K. Jirasek, *Helv. Chim. Acta*, **30**, 1320 (1947).

(18) The n.m.r. studies of VI prepared in our laboratories suggest a *cis* configuration of the two methyl groups; these will be reported elsewhere.

(19) Prepared by the route: 1,4-dihydro-1,4-ethanonaphthalene^{16b} (ozone oxidation) \rightarrow *cis*-1,2,3,4-tetrahydronaphthalene-1,4-dialdehyde (LiAlH₄ reduction) \rightarrow *cis*-1,2,3,4-tetrahydro-1,4-dihydroxymethylnaphthalene (conversion into tosylate, then LiAlH₄ reduction) \rightarrow *cis*-1,2,3,4-tetrahydro-1,4-dimethylnaphthalene. Experimental details will be reported elsewhere.

undesired side reactions. The structures and orientations of the new mononitro compounds were established by their n.m.r. spectra. As shown in Table IV, the α -nitrobenzocyclenes show an aromatic proton as a second-order quartet of an ABK system around τ 2.1–2.2 and two aromatic protons as an AB part multiplet of an ABK system around τ 2.7–2.8, and the β -nitrobenzocyclenes show two aromatic protons as an AB part multiplet of an ABK system around τ 2.0–2.1 and an aromatic proton as a second-order quartet of an ABK system around τ 2.7–2.8. In order to confirm these assignments, 6-nitrobenzonorbornene (β -NO₂-I) was converted into 6-aminobenzonorbornene by catalytic reduction and then subjected to the Sandmeyer reaction to yield 6-chlorobenzonorbornene, b.p. 86.5° (5 mm.), *n*^{25D} 1.5655, which was identical with an authentic sample independently prepared from 6-chlorobenzonorbornadiene.²⁰ The isomer ratio of α - and β -nitro compounds was determined by gas chromatography with the isolated pure products being used as internal references. The α -nitro compounds had shorter retention times than the β -nitro compounds. Results are shown in Table I. The isomer ratios ob-

Table I. Nitration of Benzocyclenes and Related Compounds^a

Compd.	Isomer ratio, %		Reactivity (relative to VI)	Relative partial reactivity	
	α	β		α	β
I	6.9	93.1	2.87	0.27	3.63
II	3.3	96.7	1.14	0.05	1.50
III	50.0	50.0	1.94	1.32	1.32
V	51.6	48.4	1.53	1.07	1.01
VI	26.5	73.5	1	0.36	1
VII	23.2	76.8	0.69	0.22	0.72

Compd.	Isomer ratio, %		
	<i>ortho</i>	<i>meta</i>	<i>para</i>
Cumene	23.2	6.3	70.5
<i>t</i> -Butylbenzene	10.3	8.6	81.1

Compd.	Isomer ratio, %		
	α,β - (NO ₂) ₂	α,β' - (NO ₂) ₂	β,β' - (NO ₂) ₂
β -NO ₂ -I ^b	15.9	16.9	67.5
β -NO ₂ -II ^b	10.4	29.3	60.3
β -NO ₂ -II	5.0	19.1	75.9

^a Reagent: HNO₃–H₂SO₄ in CH₃NO₂ at 0°. See General Procedure of Nitrations in the Experimental Section. ^b Reagent: KNO₃–H₂SO₄ at 50–60°.

tained with III and V were approximately the same as reported many years ago.^{21,22} The use of other kinds of reagents in the nitration of I and II did not substantially affect the isomer distribution.²³ For reference purposes, nitration of cumene and *t*-butylbenzene was carried out under the same conditions and the product distribution was determined by gas chromatography.

(20) H. Tanida, R. Muneyuki, and T. Tsuji, *Bull. Chem. Soc. Japan*, **37**, 40 (1964).

(21) The α/β ratio of 2:3 on the nitration of III was reported: J. Linder and J. Bruhin, *Ber.*, **60**, 438 (1927).

(22) The α/β ratio of 1:1 on the nitration of V was reported: G. Schroeter, *Ann.*, **426**, 17 (1922).

(23) Treatment of I with nitric acid–acetic anhydride gave the isomer ratio of α/β = 3.7:96.3. Treatment of I with benzoyl nitrate in carbon tetrachloride gave α/β = 3.3:96.7.

When the β -mononitro bridged compounds, β -NO₂-I and β -NO₂-II, were treated with nitric acid under conditions similar to the above, further nitration easily occurred, and the dinitro products formed were predominantly the β,β' -dinitro derivatives, along with minor amounts of α,β - and α,β' -dinitro derivatives. The n.m.r. spectra of the β,β' -dinitro derivatives show two aromatic protons as a singlet around τ 2.40, thus confirming their symmetrical 1,2,4,5-tetrasubstitution. Their structures were further established by catalytic hydrogenation to give the *o*-diamines, which in turn were characterized as the corresponding imidazole derivatives by reaction with formic acid. The structures of the minor α,β - and α,β' -dinitro compounds were assigned from consideration of n.m.r. spectra, dipole moments, and gas chromatographic behavior, as shown in Table IV.

An extensive study of the electrophilic substitution reactions of benzocyclobutene (IV), including nitration, was recently reported.^{24,25} Because of the formation of complex products due to the cleavage of cyclobutene ring, experimentation with IV has been omitted from this study.

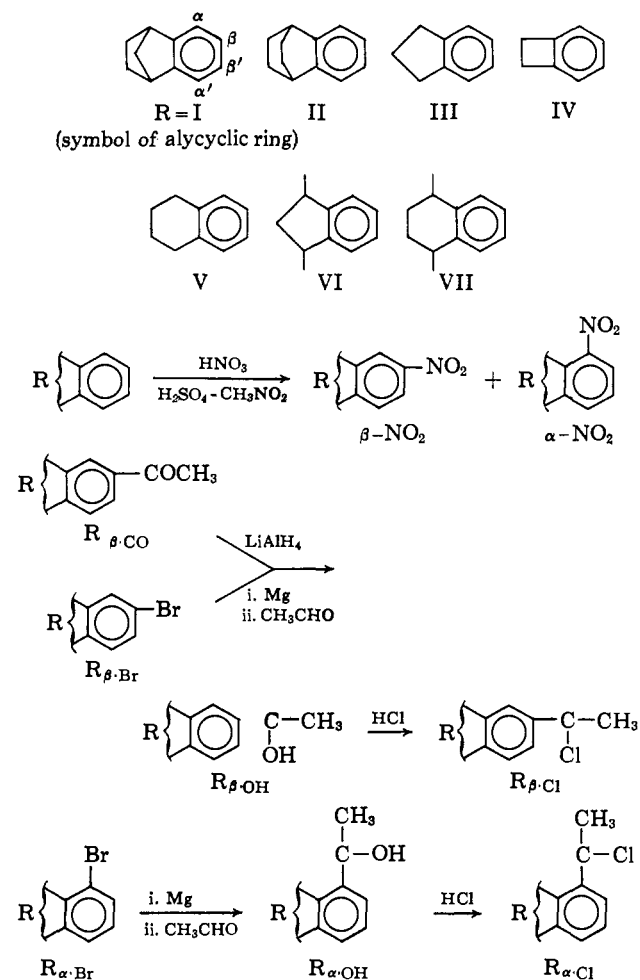
In order to investigate the relative reactivities of the above benzocycloenes, competitive nitration under conditions similar to those used for the isomer ratio study was carried out with hexamethylbenzene as an internal reference for gas chromatographic analyses (see the Experimental Section). Relative reactivities were calculated from the expression of Ingold and Shaw.²⁶ Reactivities relative to VI, chosen as the most suitable nonbridged model compound, are presented in Table I. The relative partial reactivities at the β -positions represent multiplication of the relative reactivities by the relevant isomer ratios. Fusion of a bicyclo[2.2.1]-heptene ring with a benzene ring increases the total reactivity by a factor of 2.87 and the partial reactivity at the β -position by a factor of 3.63. The fused bicyclo[2.2.2]octene ring system causes a 1.5-fold increase in the partial reactivity at β -positions. The influence of fused nonbridged cycloalkenes is significantly smaller.

Preparation of 1-Arylethyl Chlorides. The synthetic route is outlined in Chart I. It is known that Friedel-Crafts acylations of indane and tetralin yield predominantly β -substituted compounds without accompanying isomerization and disproportionation of cycloalkyl groups.²⁷ Therefore, the preparations of 1-(6-benzonorbornenyl)ethanol ($I_{\beta}\cdot OH$), 1-(6-benzobicyclo[2.2.2]octenyl)ethanol ($II_{\beta}\cdot OH$), 1-(5-indanyl)ethanol ($III_{\beta}\cdot OH$), 1-(1,2,3,4-tetrahydro-6-naphthyl)ethanol ($V_{\beta}\cdot OH$), 1-(1,3-dimethyl-5-indanyl)ethanol ($VI_{\beta}\cdot OH$), and 1-(1,2,3,4-tetrahydro-1,4-dimethyl-6-naphthyl)ethanol ($VII_{\beta}\cdot OH$) began with the Friedel-Crafts acylation of the respective benzocycloenes with acetyl chloride in carbon disulfide. The positions of the acyl groups introduced were established by the n.m.r. patterns of aromatic protons, which showed two protons as an AB part multiplet of an ABK system and a

proton as a second-order quartet of an ABK system. The β -ketones thus obtained were reduced with lithium aluminum hydride to the carbinols. Gas chromatographic analyses performed on the carbinols and in some cases additionally performed on the ketones indicated the absence of the α -isomers in amounts more than 1%. Under our conditions, retention times of the β -isomers were considerably longer than those of the α -isomers (see the Experimental Section).

1-(4-Benzocyclobutenyl)ethanol ($IV_{\beta}\cdot OH$), 1-(5-benzonorbornenyl)ethanol ($I_{\alpha}\cdot OH$), and 1-(1,3-dimethyl-4-indanyl)ethanol ($VI_{\alpha}\cdot OH$) were synthesized by reactions

Chart I



of acetaldehyde with the aryl Grignard reagents prepared from the respective bromo compounds. For the synthesis of 4-bromobenzocyclobutene ($IV_{\beta}\cdot Br$), the method used by Cava and Napier²⁸ for the preparation of benzocyclobutene was successfully applied. Treatment of 4'-bromo- $\alpha,\alpha,\alpha',\alpha'$ -tetrabromo-*o*-xylene (prepared by bromination of 4-bromo-*o*-xylene) with sodium iodide afforded 4-bromo-1,2-diodobenzocyclobutene, which was subjected to catalytic hydrogenation in the presence of sodium ethoxide, yielding $IV_{\beta}\cdot Br$. Comparison of the n.m.r. spectra of $IV_{\beta}\cdot Br$ and the derived $IV_{\beta}\cdot OH$ with the reported n.m.r. spectrum of benzocyclobutene²⁹ confirmed the structures of $IV_{\beta}\cdot Br$ and $IV_{\beta}\cdot OH$ (see the Experimental Section).

(28) M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **78**, 500 (1956).

(29) G. Fraenkel, Y. Asahi, M. J. Mitchell, and M. P. Cava, *Tetrahedron*, **20**, 1179 (1964).

(24) (a) J. B. F. Lloyd and P. A. Ongley, *Tetrahedron*, **20**, 2185 (1964); (b) *ibid.*, **21**, 245 (1965).

(25) L. Horner, H. G. Schmelzer, and B. Thompson, *Chem. Ber.*, **93**, 1774 (1960).

(26) C. K. Ingold and F. R. Shaw, *J. Chem. Soc.*, 2918 (1927).

(27) J. v. Brown, G. Krschbaum, and H. Schuhmann, *Ber.*, **53**, 1155 (1920).

Wittig's procedure for the addition of benzynes to cyclopentadiene^{15,20} was used to synthesize 5-bromobenzonorbornadiene. Treatment of 2,6-dibromofluorobenzene (obtained by the Schiemann reaction on 2,6-dibromoaniline) with magnesium in the presence of cyclopentadiene gave 5-bromobenzonorbornadiene, which was reduced over palladium on charcoal to give $I_{\alpha}\text{-Br}$. Its n.m.r. spectrum in carbon tetrachloride shows two C-9 methylene bridge protons as a triplet at τ 7.75, a C-1 bridgehead proton as a multiplet centered at τ 6.10, a C-4 bridgehead proton as a multiplet centered at τ 5.95, two C-2, C-3 vinyl protons as a multiplet centered at τ 3.3, two aromatic protons as an AB part multiplet of an ABK system centered at τ 3.0, and an aromatic proton as a second-order quartet of an ABK system centered at τ 2.6. Comparison of these data with data reported for benzenorbornadiene³⁰ confirmed the structure of 5-bromobenzonorbornadiene.

A synthetic method used for the preparation of VI^{17} was applied for synthesis of 1,3-dimethyl-4-bromindane ($VI_{\alpha}\text{-Br}$). Reformatsky reaction of 2-bromoacetophenone with ethyl α -bromoacetate and subsequent catalytic reduction afforded *o*-bromo- β -methyl-dihydrocinnamic acid ethyl ester, which was converted into the acid chloride and then treated with aluminum chloride to give 4-bromo-3-methylindanone. Treatment of the indanone with methylmagnesium iodide in ether, distillation over potassium bisulfate crystals, and then catalytic reduction yielded $VI_{\alpha}\text{-Br}$ in over-all yield of 22% (see Chart II). Purities of these bromides and the carbinols obtained therefrom were established by gas chromatography.

All of the carbinyl chlorides used for the kinetic studies were prepared by passing dry hydrogen chloride gas into ether solutions of the carbinols; this represented a modification of Brown's procedure for synthesis of phenyldimethylcarbinyl chlorides.³¹ Some of the chlorides were not completely stable and lost a little hydrogen chloride upon attempted distillation, even at pressures as low as 0.5 mm. Experiment revealed that identical rate constants and infinity titers for chloride ion were realized from the chlorides purified by distillation and from those not distilled. Accordingly, we were content to prepare pure samples of the carbinols and to utilize the carbinyl chlorides prepared from these carbinols without distillation. Therefore, we did not prepare samples for analysis in the cases of some of the chlorides.³² The properties of the new compounds prepared in this part of the study are summarized in Table V.

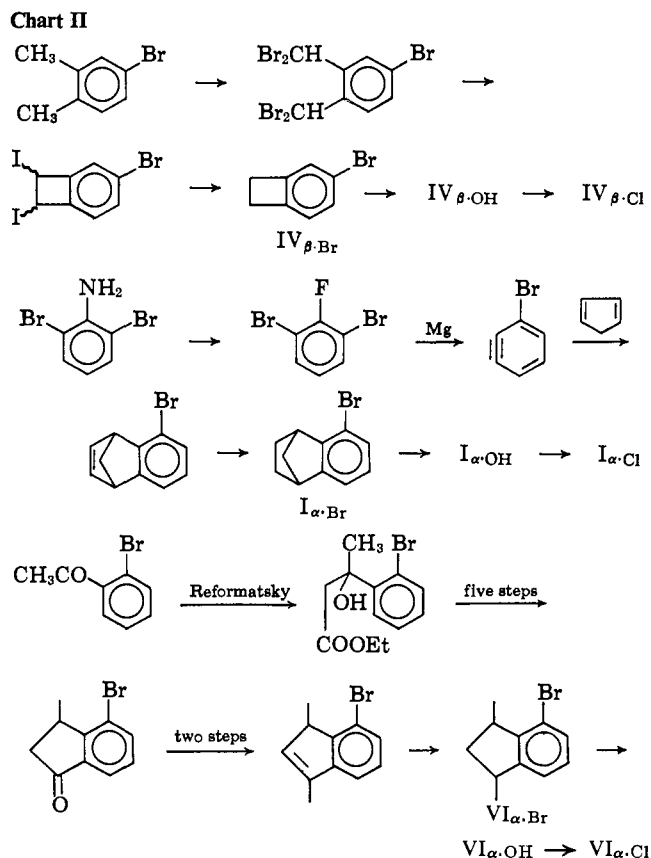
Solvolysis Rates of 1-Arylethyl Chlorides. Rates of solvolysis in 80% aqueous acetone were determined in the usual manner.³³ The solvent was prepared by diluting one volume of water with acetone to five volumes in a volumetric flask at a constant tempera-

(30) K. Tori, Y. Hata, R. Muneyuki, Y. Takano, T. Tsuji, and H. Tanida, *Can. J. Chem.*, **42**, 926 (1964).

(31) H. C. Brown, J. D. Brady, M. Grayson, and W. H. Bonner, *J. Am. Chem. Soc.*, **79**, 1897 (1957).

(32) Brown, *et al.*,³¹ carried out the solvolysis of phenyldimethylcarbinyl chloride with a material of similar history.

(33) *E.g.*, (a) ref. 31; (b) E. Berliner and N. Shieh, *J. Am. Chem. Soc.*, **79**, 3849 (1957); (c) L. Verbit and E. Berliner, *ibid.*, **86**, 3307 (1964). However, it should be pointed out that the preparation of the solvent mixture for kinetics in this study was carried out differently from the method used in these literatures.



ture. The experiments were performed with particular care to avoid minor changes in the water content, and rate constants were easily reproducible to 4–5%. Since structural effects in the present study are comparatively large, this magnitude of experimental error introduces no serious difficulty. The solvolysis rates are summarized in Table II, together with the derived activation parameters. For comparison, rate constants at 25.0° relative to that of VI_{Cl} were calculated, using least-square slopes derived from Arrhenius plots. The plots were good straight lines.

The bicyclo[2.2.1]heptene ring increases the rate at the β -position by a factor of 6.10 and at the α -position by a factor of 1.73. The rate-increasing effect of bicyclo[2.2.2]octene ring also is fairly significant, the factor being 2.36 at the β -position.

Solvolysis Products from 1-Arylethyl Chlorides. The mechanism of hydrolysis of 1-arylethyl chlorides is fairly well understood,¹³ so that a detailed study of the products was not undertaken. However, since aromatic substitutions of IV have been known to be accompanied by cleavage of the cyclobutene ring,^{24,25} we feared the possible occurrence of ring cleavage during the solvolysis of $IV_{\beta}\text{-Cl}$. The n.m.r. spectrum and gas chromatographic retention time of the solvolysis product of $IV_{\beta}\text{-Cl}$ revealed that the product was almost exclusively $IV_{\beta}\text{-OH}$, as in the case in other 1-arylethyl chloride hydrolyses, and accordingly that cyclobutene ring cleavage did not occur.

The Ultraviolet Spectra of Benzocyclenes I–V. In order to obtain information about the lowest excited singlet states of the benzocyclenes prepared, their ultraviolet spectra were determined. The wave lengths of absorption bands appearing in the $\sim 270\text{-m}\mu$ region

Table II. Kinetic Data for the Solvolysis of Arylethyl Chlorides in 80% Aqueous Acetone

Ar in ArCHClCH ₃	Temp., °C. (±0.02°)	<i>k</i> _ψ , sec. ⁻¹	Calcd. at 25.0°								
			Δ <i>H</i> [*] , kcal.	Δ <i>S</i> [*] , cal./deg.	<i>k</i> _ψ , sec. ⁻¹	Rel. rate					
I _β	27.80	5.16 × 10 ⁻⁴	19.7	-7.9	3.78 × 10 ⁻⁴	6.10					
	27.80	5.25 × 10 ⁻⁴									
	19.90	2.08 × 10 ⁻⁴									
	10.02	6.16 × 10 ⁻⁵									
	36.60	5.62 × 10 ⁻⁴									
II _β	27.80	1.96 × 10 ⁻⁴	20.5	-7.2	1.46 × 10 ⁻⁴	2.36					
	27.80	2.05 × 10 ⁻⁴									
	19.90	7.96 × 10 ⁻⁵									
	44.35	9.11 × 10 ⁻⁴									
	36.60	4.22 × 10 ⁻⁴									
III _β	27.80	1.48 × 10 ⁻⁴	20.2	-9.0	1.10 × 10 ⁻⁴	1.63					
	27.80	1.54 × 10 ⁻⁴									
	40.50	5.03 × 10 ⁻⁴									
	29.90	1.49 × 10 ⁻⁴									
	19.41	4.17 × 10 ⁻⁵									
IV _β	44.35	6.54 × 10 ⁻⁴	20.9	-7.1	8.46 × 10 ⁻⁵	1.36					
	36.60	2.96 × 10 ⁻⁴									
	27.80	1.036 × 10 ⁻⁴									
	27.80	1.051 × 10 ⁻⁴									
	44.35	5.89 × 10 ⁻⁴									
V _β	36.60	2.52 × 10 ⁻⁴	20.6	-8.4	7.54 × 10 ⁻⁵	1.22					
	27.80	8.80 × 10 ⁻⁵									
	27.80	8.65 × 10 ⁻⁵									
	27.80	5.35 × 10 ⁻⁵									
	27.80	5.16 × 10 ⁻⁵									
VI _β	35.40	1.79 × 10 ⁻⁵	21.4	-6.1	6.20 × 10 ⁻⁵	1.00					
	I _α	55.20					1.43 × 10 ⁻⁴	19.2	-18.0	5.99 × 10 ⁻⁶	9.66 × 10 ⁻²
		70.00					4.47 × 10 ⁻⁴				
		39.20					1.64 × 10 ⁻⁵				
	VI _α	55.20					8.12 × 10 ⁻⁵				
70.20		3.04 × 10 ⁻⁴									

^a Calculated on the assumption of that the slope of the Arrhenius plots is equal to that of the VI_β.

Table III. Ultraviolet Spectra of Some Benzocyclenes

Compd.	λ _{max} , mμ (ε)	Solvent
I ^a	258.5 (662)	<i>n</i> -Heptane
	264.5 (989)	
	271.3 (1120)	
II ^a	254.7 (361)	<i>n</i> -Heptane
	261.2 (542)	
	268.0 (748)	
III ^b	260 (832)	Isooctane
	266.5 (1260)	
	272.5 (1410)	
IV ^c	260 (1230)	Ethanol
	265.5 (1910)	
	271.5 (1860)	
V ^d	259.5 (347)	Isooctane
	261.5 (372)	
	266.5 (537)	
Benzocycloheptene ^e	273.5 (631) 272 (277)	Isooctane

^a This work. ^b Carnegie Institute of Technology, API Research Project No. 44, II, 1951. Cf. M. J. Kamlet, Ed., "Organic Electronic Spectral Data," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1960, p. 256. ^c Reference 28. ^d Shell Development Co., API Research Project No. 44, II, 1950. Cf. M. J. Kamlet, Ed., "Organic Electronic Spectral Data," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1960, p. 328. ^e Reference 40. The description of the fine structure is omitted.

(¹L_b band by Platt's notation³⁴) are presented in Table III. It is noteworthy that the intensities of absorption maxima of the bridged compound I and II are much weaker than that of the highly strained compound IV and also weaker than that of III. Perhaps this means

(34) J. R. Platt, *J. Chem. Phys.*, 17, 484 (1949).

that perturbation of the aromatic π-electron system is less in the bridged benzocyclenes than in IV and III.

Discussion

Available evidence does not indicate large difference in the effects of alkyl groups upon the rates of electrophilic aromatic substitution.³⁵ For example, Knowles, *et al.*,³⁶ reported that the relative over-all reactivities of alkylbenzenes in nitration by means of fuming nitric acid in acetic anhydride solution at 0° are for toluene, 1; for ethylbenzene, 0.85; for cumene, 0.65; and for *t*-butylbenzene, 0.56. According to their data, the partial rate factors *para* to the alkyl group change less than 1.3-fold and *meta* less than 2.3-fold.³⁷ This is also shown by the fact that the maximum variation of σ⁺ values of alkyl substituents (σ⁺_{*p*-Bu} - σ⁺_{*p*-Me}) is only 0.055, while σ⁺_{*m*-Bu} - σ⁺_{*m*-Me} is only 0.007.³⁸ The maximum rate ratio observed in the solvolyses of *p*-alkyl-substituted phenyldimethylcarbinyl chlorides in 90% aqueous acetone at 25° is 1.81 and in the case of *m*-alkyl-substituted phenyldimethylcarbinyl chloride it is only 1.08.³¹

Benzocyclenes may be considered as *o*-dialkylbenzenes. Although the differences of relative reactivity obtained consistently from the nitration and from the S_N1 solvolyses (Tables I and II, and Figure 1) are not large, they appear to be quite significant. Particularly,

(35) As a review, see ref. 14.

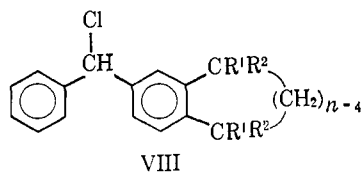
(36) J. R. Knowles, R. O. C. Norman, and G. K. Radda, *J. Chem. Soc.*, 4885 (1960).

(37) Because of the low yield at the *meta* positions, the experimental error must be large.

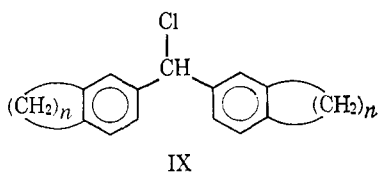
(38) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, 80, 4979 (1958).

the enhanced reactivity of the bridged benzocyclenes is a prominent effect.

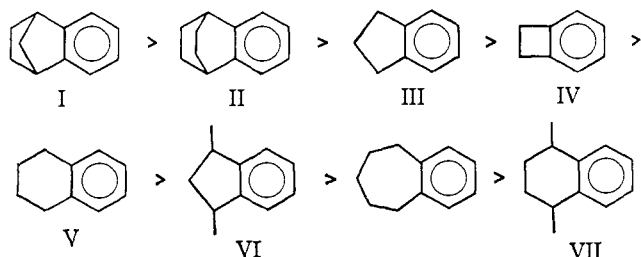
Reactivities at the β -Positions. Previously, Baddeley and Gordon³⁹ found the relative rates of solvolyses of substituted benzhydryl chlorides (VIII) in dry ethanol at 20° to be for VIIIa, 1.28; for VIIIb, 1.07; for VIIIc, 1; for VIIId, 0.81; and for VIIIe, 0.92. Moore,



et al.,⁴⁰ reported that the relative rates of solvolyses of compounds (IX) in aqueous acetone at 25° were for $n = 3$ (indane system), 1.5; for $n = 4$ (tetralin system),



1; and for $n = 5$ (benzocycloheptene system), 0.63. Thus, substantial agreement is found among these results and ours. The following order of relative reactivities at the β -positions is indicated.



Since the variation of inductive effects due to the changes in the alkyl group is quite small, the lesser effect of the more branched alkyl groups on the reactivities of the nonbridged compound VI and VII in comparison with those of III and V, respectively, can be attributed to the decreasing tendency for hyperconjugative contributions in the order, Et > *i*-Pr.⁴¹

One of the most interesting results obtained from the present study is that the solvolysis rate of the benzocyclobutene compound IV β -Cl, is intermediate between those of the indane and tetralin compounds, III β -Cl and V β -Cl. Moore, *et al.*,⁴⁰ observed a relationship between the intensities of ultraviolet absorption (I_{L_b} band) of some benzocyclenes and the solvolysis rates of the corresponding benzhydryl chlorides (IX). This was interpreted in terms of conformational effects on hyperconjugation between the cycloalkeno rings and the condensed benzene nucleus. They predicted a high rate of solvolysis for the benzocyclobutene system, but our results do not bear out their prediction.⁴² The

(39) G. Baddeley and M. Gordon, *J. Chem. Soc.*, 4379 (1958). Also refer to G. Baddeley and M. Gordon, *ibid.*, 2190 (1952), and R. T. Arnold and W. L. Truett, *J. Am. Chem. Soc.*, 73, 5508 (1951).

(40) W. R. Moore, E. Marcus, S. E. Fenton, and R. T. Arnold, *Tetrahedron*, 5, 179 (1959).

(41) For example, refer to V. J. Shiner, Jr., and E. Campaigne, *ibid.*, 5, 105 (1959).

(42) No acceleration of aluminum chloride catalyzed benzoylation of benzocyclobutene in comparison with indane and tetralin was observed by F. R. Jensen and G. Maciel, *J. Org. Chem.*, 25, 640 (1960); also see ref. 25b.

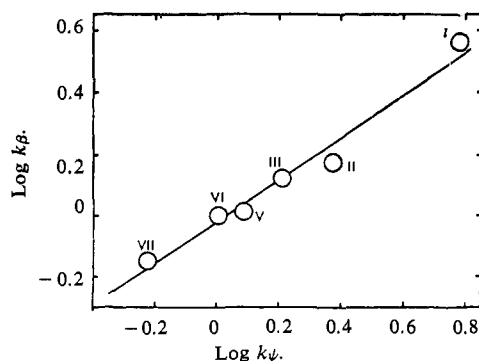
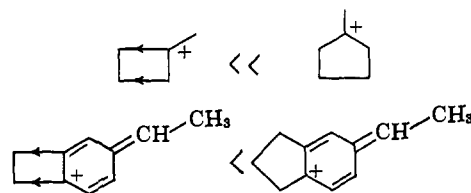


Figure 1. Correlation between the partial relative rates at the β -positions (k_β) on the nitration of benzocyclenes and the relative solvolysis rates (k_ψ) of the corresponding 1-(β -benzocyclenyl)ethyl chlorides.

normal reactivity of benzocyclobutene suggests that, even though there is a certain degree of aromatic destabilization due to the compression of bond angles in benzocyclobutene, as may be reflected in its ultraviolet spectra (Table III),⁴³ this destabilization must be countered by an equal degree of instability in the transition state.

It has been reported by Brown and Borkowski⁴⁴ that the relative solvolysis rates of the 1-chloro-1-methylcycloalkanes (X) in 80% ethanol at 25° are 0.21 for 1-chloro-1-methylcyclobutane ($X_{n=4}$), 125 for 1-chloro-1-methylcyclopentane ($X_{n=5}$), and 1 for 1-chloro-1-methylcyclohexane ($X_{n=6}$). The slowness of the solvolysis of $X_{n=4}$ may be understood with reference to the state of hybridization of the carbon atoms of the four-membered ring. The four-membered ring has bond angles much less than the normal tetrahedral, and the hybrid orbitals comprising this strained ring have considerably more p character than the normal sp^3 orbitals. Consequently, the strained ring system has a greater electron-withdrawing inductive effect than the less strained ring system. In these terms one can understand why IV β -Cl solvolyzes more slowly than III β -Cl.⁴⁵



Relative rates of solvolysis in the decreasing order of III β -Cl > V β -Cl > benzocycloheptene system, although the range of difference is small, have now been found by several workers. They have been discussed in terms of steric inhibition of hyperconjugation of an α -C-H

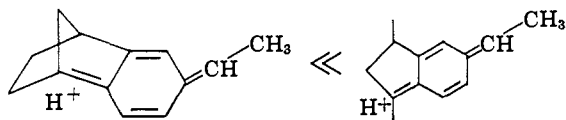
(43) The decreasing forbiddenness of the 270-m μ transition has been interpreted by Dewar in terms of increasing ring strain in this series of hydrocarbons. Refer to M. J. S. Dewar, "Hyperconjugation," The Ronald Press Co., New York, N. Y., 1962, p. 134.

(44) H. C. Brown and M. Borkowski, *J. Am. Chem. Soc.*, 74, 1894 (1952), and references therein.

(45) Recently, J. B. F. Lloyd and P. A. Ongley, *Chem. Ind. (London)*, 1267 (1964), observed that the charge-transfer absorption of the picric acid and tetracyanoethylene complexes of IV, III, and V shifts toward higher wave lengths as the size of the cycloalkene ring is increased, and they interpreted this increasing π -basicity in terms of the inductive effects of the cycloalkene ring.

bond with the benzene ring.^{39,40,46} We shall not attempt to repeat these discussions at the present time.

Let us now consider the most remarkable observation in this study, the enhanced reactivities of I and II. Because the α -carbons of I and II are bridgehead, the hyperconjugative contribution of the α -C-H bonds toward the deficient π -system should be much decreased. Inasmuch as compounds I, II, VI, and VII are all variants of *o*-diisopropylbenzene, it is



reasonable to assume as a first approximation that the inductive effects of all four cycloalkeno rings are nearly the same. Under these circumstances, the interpretation of enhanced reactivities of I and II will be possible in the alternative terms, internal strain or participation.

Since the directly related thermodynamic data of benzocyclenes themselves seem to be lacking, a simplified and admittedly crude calculation for estimation of the internal strain was carried out by a combination of available data. The heat of combustion of cyclopentane relative to cyclohexane is known as 1.3 kcal./mole larger per methylene group ($-\Delta H = -157.4$ kcal.).⁴⁷ Therefore, the strain in the aliphatic chain of indane is given as 3.9 kcal. by multiplication of the number of methylene with the value 1.3 kcal. It is known that the twisted-boat form of cyclohexane has an energy of 5.5 kcal./mole higher than that of the chair form.⁴⁸ Since bicyclo[2.2.2]octane is composed of two-third cycles of the twisted-boat form of cyclohexane,⁴⁸ its strain energy relative to cyclohexane is estimated as 8.3 kcal./mole,⁴⁹ so that the strain in the alicyclic part of II is calculated as $8.3 \times 6/8 = 6.2$ kcal. The strain in norbornane has been estimated to have a value 6.3 kcal./mole larger than bicyclo[2.2.2]octane.⁵⁰ Therefore, the strain energy in the alicyclic part of I becomes $(8.3 + 6.3) \times 5/7 = 10.4$ kcal. The strain in the ring junction was estimated by the available data of heat of hydrogenation of the related cycloalkenes^{9,51} relative to cyclohexene, which show 6.0 for norbornene,⁵¹ 1.2 for bicyclo[2.2.2]octene,⁵¹ and -1.6 kcal./mole for cyclopentene,^{9,52} respectively. Therefore, the relative values of strain energies in I, II, and III would be represented by the sum of those in the alicyclic part and the junction as 16.4, 7.4, and 2.3 kcal./mole, respectively. Therefore, a reasonably good correlation was realized between the observed reactivities and the estimation of internal strain. Only one irregular case is the low reactivity of IV.⁵³

(46) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 98.

(47) Cited from E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 189.

(48) J. B. Hendrickson, *Chem. Eng. News*, **39**, (No. 47) 40 (1961).

(49) P. von R. Schleyer, K. R. Blanchard, and C. D. Woody, *J. Am. Chem. Soc.*, **85**, 1358 (1963), gave the value 8.4 kcal.

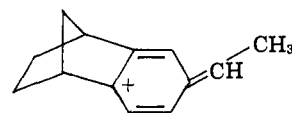
(50) Reference 47, p. 302.

(51) (a) R. B. Turner, W. R. Meador, and R. E. Winkler, *J. Am. Chem. Soc.*, **79**, 4116 (1957); (b) R. B. Turner and W. R. Meador, *ibid.*, **79**, 4133 (1957); in these references ΔH is given at 25° in acetic acid.

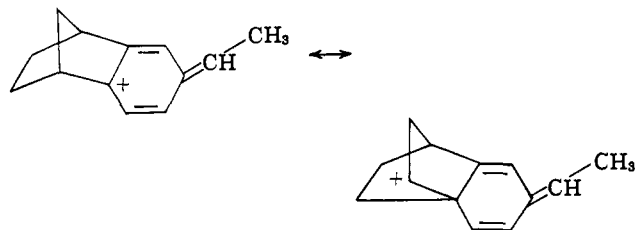
(52) Reference 9 shows ΔH in gas phase at 82°.

(53) The heat of hydrogenation of cyclobutene is not known, but the heat of combustion of cyclobutene per methylene relative to cyclohexane has been reported to be so large as 6.55 kcal./mole.⁴⁷ Accordingly, when the angle strain in the junction calculated by a method (for example, see ref. 47, p. 252) is added, the total strain in IV would be considerably larger than that of I.

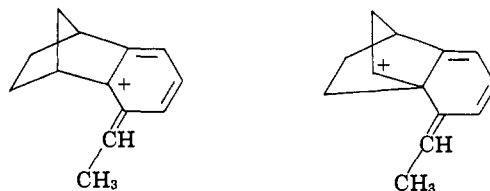
The alternatively possible explanation is based on the comparative study with the solvolytic behavior of bicycloalkanyl systems. As discussed above, the transition state resembles the ion. We may therefore



expect a resemblance between the solvolytic behavior of the 2-norbornyl system and "nucleophilic" reactions of I. The very rapid solvolyses of *exo*-norbornyl derivatives have been attributed to carbon participation in the formation of the transition state (Winstein). The present results may be understood in similar terms. If there is 1,2-bond participation, the contribution of the following resonance structure in the transition state may be held responsible for the observed rate enhancement of the I system.



The significant rate enhancement observed at the α -position of I (the rate of I_{α} relative to VI_{α}) further supports this interpretation. For the evaluation of the net electronic effects at the α -positions, the reference compound is required to have a steric environment



similar to that of I. The suitability of VI as a reference compound is indicated by the fact that solvolyses of both $I_{\alpha-Cl}$ and $VI_{\alpha-Cl}$ yielded almost the same value of entropy of activation (Table II), much more negative than for the other substrates.

To the best of our knowledge, no data are available concerning the solvolysis of 2-methyl-2-bicyclo[2.2.2]octanyl derivatives. However, indications of σ -bond participation in the solvolysis of 2-bicyclo[2.2.2]octanyl system have been reported,⁵⁴ although the rate enhancement was smaller than in the *exo*-2-norbornyl system. Accordingly, it is possible to explain the slightly enhanced rate of solvolysis of $II_{\beta-Cl}$ on the basis of carbon participation.

At the present time, however, because the influence of internal strain toward aromatic substitution is not completely understood and the precise structure and nature of the norbornyl carbonium ion intermediate is highly controversial,⁵⁵ the selection between the above

(54) (a) H. L. Goering and M. F. Sloan, *J. Am. Chem. Soc.*, **83**, 1992 (1961); (b) H. M. Walborsky, M. E. Baum, and A. A. Youssef, *ibid.*, **83**, 988 (1961).

(55) (a) S. Winstein, *et al.*, *ibid.*, **87**, 376, 381 (1965), and references therein; (b) H. C. Brown, Special Publication No. 16, The Chemical Society, London, 1962, p. 155; (c) H. C. Brown, *et al.*, *J. Am. Chem. Soc.*, **86**, 1246, 1248, 5008 (1964).

Table IV. Physical Data of the New Nitro Compounds

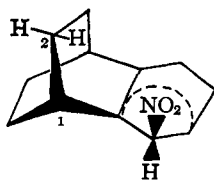
Compd.	M.p. ^a or b.p., °C. (mm.)	Dipole moment, D.	Chemical shift, τ , in CDCl ₃				Coupling constant, J (c.p.s.)	Anal., %					
			H _{α}	H _{β}	H _{β'}	H _{α'}		Calcd.			Found		
							C	H	N	C	H	N	
α -NO ₂ -I	140–141 (6) ^b	4.22	...	~2.22 ^{c,e}	~2.84 ^e	~2.84 ^e	$J_{\beta\beta'}$, 7.9 $J_{\beta\alpha'}$, 1.5	69.82	5.86	7.40	69.86	6.01	7.50
β -NO ₂ -I	140–142 (6) ^f	4.97	~2.0 ^d	...	~2.0 ^d	~2.73 ^c	$J_{\alpha\alpha'}$, ~0 $J_{\beta'\alpha}$, 8.7	69.82	5.86	7.40	69.80	6.04	7.26
β -NO ₂ -II	[69–70]	4.99	~2.0 ^d	...	~2.0 ^d	~2.73 ^c	$J_{\alpha\alpha'}$, ~0 $J_{\beta'\alpha'}$, 7.2	70.91	6.45	6.89	70.80	6.48	6.98
α -NO ₂ -VI	118–120 (7) ^g	~2.14 ^c	~2.7 ^d	~2.7 ^d	$J_{\beta\alpha'}$, 2.0 $J_{\beta\beta'}$, 7.0	69.09	6.85	7.33	69.31	7.02	7.19
β -NO ₂ -VI	[81–82]	...	~2.05 ^c	...	~2.05 ^c	~2.81 ^c	$J_{\alpha\alpha'}$, ~0 $J_{\beta'\alpha'}$, 7.0	69.09	6.85	7.33	69.00	6.85	7.41
β -NO ₂ -VII	[44–45]	...	~2.0 ^d	...	~2.0 ^d	~2.70 ^c	$J_{\alpha\alpha'}$, ~0 $J_{\beta'\alpha'}$, 8.0	70.22	7.37	6.82	69.66	7.40	6.63
α, β -(NO ₂) ₂ -I	[68–69]	2.46 ^h	2.58 ^h	$J_{\beta'\alpha'}$, 8.0	56.41	4.31	11.96	56.20	4.34	12.09
β, β' -(NO ₂) ₂ -I	[146.7–147.2]	7.35	2.40 ⁱ	2.40 ⁱ		56.41	4.31	11.96	56.68	4.39	12.66
α, β' -(NO ₂) ₂ -I	[80.5]	5.13	...	1.29 ^h	...	1.73 ^h	$J_{\beta\alpha'}$, 2.0	56.41	4.31	11.96	56.13	4.25	11.84
β, β' -(NO ₂) ₂ -II	[155.5–156.5]	7.24	2.30 ⁱ	2.30 ⁱ		58.06	4.87	11.29	58.09	4.92	11.08

^a Melting points are shown in brackets. ^b n^{25}_D 1.5789. ^c A second-order quartet of an ABK system. ^d An AB part multiplet of an ABK system. ^e Measured in CCl₄. ^f n^{25}_D 1.5855. ^g n^{25}_D 1.5482. ^h An AB-type quartet. ⁱ A singlet.

alternative mechanisms should be postponed until one has a more suitable evidence and also there may be the possibility of concurrency of the both mechanisms.⁵⁶

Reactivities and Orientation at the α -Positions. The lower yields of α -nitro derivatives of VI and VII than those of III and V are attributed to the steric requirements of their methyl-substituted cycloalkeno rings. However, the orientation observed on nitration of I and II is quite striking. The rates of formation of α -nitro derivatives by I and II are much lower than those of any of the model compounds. Moreover, the yields of α -nitro products from I and II were lower than the yields of *ortho* products in nitration of cumene and *t*-butylbenzene (Table I). The reactivity of α -derivatives of I in solvolysis is augmented, relative to VI derivatives, but the partial reactivity estimated from nitration is diminished. It follows that the mechanism governing the α -position should be one which does not operate at the β -position, most probably a steric effect.

Offhand, the bridged rings of I and II would not appear to be more bulky than the nonbridged rings. Therefore, an important factor appears to be the conformation and flexibility of the bridged rings. The transition state for nitration is believed to resemble a σ -complex, with the nitronium ion approaching the aromatic π -system from out of plane. The rigid bridged ring might provide unusually serious steric hindrance to approach of nitronium ion to an α -position. Indeed, inspection of a molecular model for the σ -complex formed at an α -position suggests large steric interaction between the nitro group at C _{α} and the C-2-methylene. We call this large steric hindrance the "fused *ortho* effect."⁵⁷



(56) This possibility was suggested in the solvolyses of 2,2,2-triphenylethyl tosylate by H. C. Brown, R. Bernheimer, and K. J. Morgan, *J. Am. Chem. Soc.*, **87**, 1280 (1965).

In contrast, the alkyl substituent of a monoalkylbenzene can rotate to minimize the steric hindrance, and a flexible nonbridged ring can avoid the hindrance by ring deformation.^{58,59}

Experimental Section⁶⁰

Properties and analyses of the new compounds prepared in the present study are summarized in Tables IV and V.

Materials. Indane (III) was prepared by catalytic hydrogenation of commercial indene and purified by distillation over sodium wire; b.p. 175–176°. Tetralin (V) was commercial grade and distilled over sodium wire before use, b.p. 85° (14 mm.). 1,3-Dimethylindane (VI) was prepared by the catalytic reduction of 1,3-dimethylindene¹⁷ and had b.p. 80° (12 mm.) and n^{25}_D 1.5170 (lit. b.p. 103° at 15 mm.,¹⁷ b.p. 199–201°).³⁹ 1,2,3,4-Tetrahydro-1,4-dimethylnaphthalene (VII) was prepared by the known methods^{39,61} and had b.p. 102° (19 mm.) (lit.³⁹ b.p. 104–105° at 12 mm.). Benzenorbornene (I) and benzobicyclo[2.2.2]octene (II), m.p. 62–63° (lit.^{16b} m.p. 61–62°), were prepared by the reported method.^{15,16}

4-Bromo- α, α', α' -tetrabromo-*o*-xylene. A substantially similar procedure to that used for the prepara-

(57) Professor H. C. Brown suggested to the authors the name, "fused *ortho*-effect."

(58) The very little " α " nitration of *o*-*t*-butylbenzene recently reported by A. W. Burgstahler, P. L. Chien, and M. O. Abdel-Rohman, *J. Am. Chem. Soc.*, **86**, 5281 (1964), can be explained by the similar argument based on the congested geometry and restricted rotation of the *t*-butyl groups.

(59) Alternatively, a referee favored a view recently suggested by Lloyd and Orgley.^{24b} They have proposed that the high selectivity in favor of β -nitration of I and II must be related to similar phenomena observed in the electrophilic aromatic substitution reactions of benzocyclobutene and biphenylene, and interpreted these observations in terms of stress set up in their aromatic nucleus by the deformed bond angles of the attached ring. The 50% less α -nitration of the less strained II than I (Table I) contrasts to this mechanism, however, we should appreciate this mechanism as a probable factor even at the α -positions.

(60) Melting points were taken by capillary and are corrected. Boiling points are uncorrected. Ultraviolet spectra were recorded on a Beckman DK-2 spectrometer. Unless stated otherwise, infrared spectra were determined with a Nippon Bunko IR-S spectrometer, in carbon tetrachloride and carbon disulfide; n.m.r. spectra were determined at 60 Mc. with a Varian A-60 spectrometer using tetramethylsilane as internal standard.

(61) M. C. Kloetzel, *J. Am. Chem. Soc.*, **62**, 1708 (1940).

Table V. Properties and Analyses of Arylethyl Chlorides and Intermediates

Aryl	Compd.		M.p. ^a or b.p., °C. (mm.)	<i>n</i> _D (°C.)	Formula	Anal., %			
	Subst.	Abbreviation				Carbon		Hydrogen	
	H	I	<i>b</i>			Calcd.	Found	Calcd.	Found
I	β-COCH ₃	I _β -CO	167 (19) [210-211]	1.5703 (23.5)	C ₁₃ H ₁₄ O C ₁₄ H ₁₇ ON ₃ ^d	83.83 69.11	83.33 69.42	7.58 7.04	7.58 7.08
	β-C(OH)CH ₃	I _β -OH	115-116 (2)	1.5580 (24)	C ₁₃ H ₁₆ O	82.93	82.88	8.57	8.60
	β-C(Cl)CH ₃	I _β -Cl	111 (1)	1.5614 (25)	C ₁₃ H ₁₅ Cl ^e	75.54	75.24	7.31	7.33
	α-Br	I _α -Br	111-112 (7)	1.5994 (24)	C ₁₁ H ₉ Br	59.75	59.93	4.10	4.20
	α-C(OH)CH ₃	I _α -OH	85-87 (0.1)	1.5585 (25)	C ₁₃ H ₁₆ O	82.93	82.75	8.57	8.58
II	β-COCH ₃	II _β -CO	141-142 (2)	1.5762 (23.5)	C ₁₄ H ₁₆ O	83.96	83.74	8.05	7.95
	β-C(OH)CH ₃	II _β -OH	[81-81.5]		C ₁₄ H ₁₈ O	83.12	82.91	8.97	9.05
	β-C(Cl)CH ₃	II _β -Cl	[70.5-71.5]		C ₁₄ H ₁₇ Cl	76.17	76.18	7.76	7.77
	β-COCH ₃	III _β -CO	113 (3)	1.5585 (24)	C ₁₁ H ₁₂ O	82.46	82.96	7.55	7.61
	β-C(OH)CH ₃	III _β -OH	118-119 (3) ^h	1.5475 (24)	C ₁₁ H ₁₄ O	81.44	81.14	8.70	8.77
III	β-C(Cl)CH ₃	III _β -Cl	102 (2)	1.5505 (23)	C ₁₁ H ₁₃ Cl ⁱ	73.12	72.99	7.25	7.39
	β-Br	IV _β -Br	101-104 (8)	1.5850 (22)	C ₈ H ₇ Br	52.20	52.21	4.38	4.12
	β-C(OH)CH ₃	IV _β -OH	94-96 (4)	1.5491 (24.5)	C ₁₀ H ₁₂ O	81.04	80.82	8.16	8.25
	β-COCH ₃	V _β -CO	153-154 (10) ^j	1.5596 (24)					
	β-C(OH)CH ₃	V _β -OH	124 (4) ^k	1.5481 (26)	C ₁₂ H ₁₆ O	81.77	81.60	9.15	9.24
IV	β-C(Cl)CH ₃	V _β -Cl	110-112 (2)	1.5530 (24)	C ₁₂ H ₁₅ Cl	74.02	73.86	7.77	7.78
	β-COCH ₃	VI _β -CO	91-92 (0.06) [197.5-198.5]	1.5413 (23)	C ₁₃ H ₁₄ O C ₁₄ H ₁₉ ON ₃ ^m	82.93 68.54	83.34 68.28	8.57 7.81	8.60 7.83
	β-C(OH)CH ₃	VI _β -OH	116-117 (1)	1.5320 (24)	C ₁₃ H ₁₆ O	82.06	81.88	9.54	9.53
	β-C(Cl)CH ₃	VI _β -Cl	76-77 (0.5)	1.5330 (24.5)	C ₁₃ H ₁₇ Cl	74.80	74.63	8.21	8.24
	α-Br	VI _α -Br	111-113 (10)	1.5607 (26)	C ₁₁ H ₁₃ Br	58.68	58.89	5.82	5.91
V	α-C(OH)CH ₃	VI _α -OH	92-94 (0.1)	1.5363 (24.5)	C ₁₃ H ₁₈ O	82.06	82.28	9.54	9.50
	β-COCH ₃	VII _β -CO	164-166 (12)	1.5481 (20)	C ₁₄ H ₁₈ O	83.12	83.25	8.97	9.08
	β-C(OH)CH ₃	VII _β -OH	138-139 (4)	1.5381 (23.5)	C ₁₄ H ₂₀ O	82.30	82.12	9.87	9.90
	β-C(Cl)CH ₃	VII _β -Cl	<i>n</i>	1.5412 (24)	C ₁₄ H ₁₉ Cl	75.48	75.38	8.60	8.65

^a Melting points are presented in brackets. ^b Reference 15. ^c Semicarbazone of the ketone. ^d Calcd.: N, 17.27. Found: N, 17.33. ^e Calcd.: Cl, 17.15. Found: Cl, 17.29. ^f Reference 16. ^g Calcd.: N, 19.34. Found: N, 19.49. ^h B.p. 133° (10 mm.); R. T. Arnold, *J. Am. Chem. Soc.*, **61**, 1450 (1939). ⁱ Calcd.: Cl, 19.62. Found: Cl, 19.78. ^j (a) B.p. 182° (20 mm.); A. R. F. Hesse, *Ber.*, **53**, 1645 (1920); (b) W. Scharwin, *ibid.*, **35**, 2511 (1902). ^k B.p. 119-119.5° (2 mm.), *n*_D²⁰ 1.5484; H. Adkins and H. R. Billica, *J. Am. Chem. Soc.*, **70**, 695 (1948). ^l Reference 39. ^m Calcd.: N, 17.13. Found: N, 16.80. ⁿ Decomposes at the boiling point.

tion of α,α',α'-tetrabromo-*o*-xylene⁶² was employed. The yield of 4-bromo-α,α',α'-tetrabromo-*o*-xylene, m.p. 113.5-114.5°, was 34%.

Anal. Calcd. for C₈H₅Br₅: C, 19.19; H, 1.01. Found: C, 19.29; H, 1.11.

4-Bromo-1,2-diiodobenzocyclobutene was prepared in 77% yield by treatment of the above tetrabromo compound with sodium iodide, according to the method of Cava and Napier²⁸ used for the preparation of benzocyclobutene; colorless crystals, m.p. 72.5-73.5° (from ethanol).

Anal. Calcd. for C₈H₅BrI₂: C, 22.09; H, 1.16. Found: C, 22.25; H, 1.34.

4-Bromobenzocyclobutene (IV_β-Br). Hydrogenolysis of the above diiodo compound at room temperature in ethanol in the presence of palladium-charcoal and sodium ethoxide gave, after careful distillation, pure IV_β-Br in 26% yield. The n.m.r. spectra in deuteriochloroform showed four C-1 and C-2 protons at τ 6.9 (singlet), two aromatic protons *ortho* to bromine at ~2.8 (an AB part multiplet of an ABK system), and one aromatic proton *meta* to bromine at ~3.13 (a second-order quartet of an ABK system), and also *J*_{H₆,H₈} = 7.0 c.p.s.

(62) J. C. Bill and D. S. Tarbell, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p. 807.

This compound was converted into the Grignard reagent by treatment with magnesium turning and then allowed to react with acetaldehyde.

The structure of 1-(4-benzocyclobutenyl)ethanol (IV_β-OH) thus obtained was confirmed by its n.m.r. spectrum in deuteriochloroform, which showed three methyl protons at τ 8.53 (doublet), four cyclobutene ring protons at 6.85 (singlet), one benzylic proton at 5.17 (quartet), and three aromatic protons at ~2.9. Gas chromatography of IV_β-OH showed only one peak.

1,3-Dimethyl-4-bromoindane (VI_α-Br). The synthesis was outlined in the text.

2,6-Dibromofluorobenzene was prepared from 2,6-dibromoaniline⁶³ in 47% yield by the Schiemann reaction⁶⁴ and had m.p. 56-57.5°.

Anal. Calcd. for C₆H₃Br₂F: C, 28.38; H, 1.19. Found: C, 28.52; H, 1.27.

5-Bromobenzonorborene (I_α-Br). Treatment of 2,6-dibromofluorobenzene with magnesium turnings in anhydrous tetrahydrofuran in the presence of cyclopentadiene was carried out according to our modification²⁰ of Wittig's procedure.¹⁵ The work-up procedure and isolation of pure material were carried out

(63) M. K. Seikel, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 262.

(64) A. Roe, *Org. Reactions*, **5**, 193 (1949).

much as in the preparation of 6-bromobenzonorbornadiene.²⁰

The Preparations and Gas Chromatographic Analyses of 1-Arylethyl Alcohols. For the preparation of the carbinols I_β-OH, II_β-OH, III_β-OH, V_β-OH, VI_β-OH, and VII_β-OH, the general procedure of Friedel-Crafts acylation with the respective benzocyclenes and acetyl chloride was applied to obtain benzocycloalkenylmethyl ketones. Although benzocyclenes were not sensitive to isomerization and disproportionation under Friedel-Crafts condition, a modified procedure consisting of the slow addition of aluminum chloride to a mixture of benzocyclene and acetyl chloride in carbon disulfide was used to avoid those complications, according to the suggestion of Brown, *et al.*³¹ The ketones were reduced to the carbinols with lithium aluminum hydride. The positions of the acyl groups introduced were established by n.m.r. spectra as described in the text. The carbinols IV_β-OH, I_α-OH, and VI_α-OH were synthesized by the action of acetaldehyde on the aryl Grignard reagents which were prepared from the respective bromo compounds.⁶⁵ The gas chromatographic analyses were carried out under the following three conditions: (a) on a Hitachi gas chromatograph Model F-6, equipped with a 2 m. × 3 mm. stainless steel column packed with 10 wt. % diethylene glycol succinate polyester on acid-washed, 30–60 mesh Chromosorb W (column A); (b) on a Shimadzu gas chromatograph Model GC-1B, equipped with a 3 m. × 6 mm. stainless steel tubing column packed with 5 wt. % of diethylene glycol succinate polyester on the same support (column B); (c) as a stationary phase, 5 wt. % of polyethylene glycol 6000 was used, and the other conditions were the same to b (column C). Helium was used as a carrier gas. Retention times of the carbinols I_α-OH and I_β-OH were 14.8 and 16.2 min., respectively, at 185° of column A with a pressure of 2.0 kg./cm.² of helium. Those of the ketones I_α-CO and I_β-CO were 4.8 and 7.8 min., respectively, at 160° of column C with a flow rate of 50 ml./min. Those of the ketones III_α-CO and III_β-CO were 10.3 and 15.3 min., respectively, at 170° of column B with a flow rate of 50 ml./min. Those of V_α-CO, V_β-CO, and V_β-OH were 13.5, 21.5, and 25.1 min., respectively, at 185° of column A with a pressure of 1.0 kg./cm.² of helium. Those of the carbinols VI_α-OH and VI_β-OH were 11.8 and 11.1 min., respectively, at 185° of column A with a pressure of 2.0 kg./cm.² of helium. Retention times were for II_β-CO, 18.8 min. (180° of column B and 100 ml. of He); for IV_β-OH, 7.2 min. (164° of column A (1 m. × 3 mm.) and 0.8 kg./cm.² of He); for VII_β-CO, 12.6 min. (180° of column B and 100 ml. of He); for VII_β-OH, 20.2 min. (170° of column B and 100 ml. of He).

Conversion of 1-Arylethyl Alcohols into the Carbinyl Chlorides. Substantially the same procedure to that of Brown, *et al.*,³¹ was used. A solution of about 2.8 mmoles of the carbinol in 10 ml. of anhydrous ether and a few crystals of calcium chloride were placed in a small flask and dry hydrogen chloride was passed over the material for about 30 min. at 0° until it was

saturated. To the ether solution was added about 10 ml. of petroleum ether (b.p. 30–60°), and when possible the separated lower layer of aqueous hydrochloric acid was removed with a fine capillary. The organic layer was dried over calcium chloride and concentrated under reduced pressure below 0°. The concentrated solution was dissolved in petroleum ether and dried over calcium chloride. The solution was evaporated and the residue was pumped for 10–20 min. in a vacuum desiccator. The chlorides thus obtained were mostly analytically pure and were used as such for the purpose of kinetic measurements.^{31,32}

Kinetic Measurements of the Solvolyses. Acetone was purified by the method of Conant and Kirner,⁶⁶ followed by a second distillation from Drierite.⁶⁷ The fraction boiling at 57.0° was collected. A stock solution of 80% aqueous acetone was prepared by diluting 100 ml. of boiled-out distilled water with acetone to the mark of a 500-ml. volumetric flask in a constant temperature room, whose temperature was adjusted at 24°. This constituted the 80% aqueous acetone. Samples of chlorides were weighed into 50-ml. volumetric flasks so that solutions approximately 0.056 M in chloride would be obtained, then filled to 50 ml. with the aqueous acetone solution, in necessary cases with the cold one. Temperatures were controlled to ±0.02°. Kinetic runs below 40° were conducted in 50-ml. volumetric flasks, while for runs above 40°, sealed ampoules were used. Rate constants were determined by the infinity titer method, and zero time was taken as the time that complete solution and thermal equilibrium had been reached. Aliquots, usually ten of 5-ml. volume, were periodically withdrawn and run into 80 ml. of ice-cold acetone, and the liberated HCl was titrated with 0.02 N sodium hydroxide solution using an alcoholic solution of methyl-red and bromocresol green as the indicator. Reaction was usually conducted to between 75–85% completion, but first-order plots remained linear to beyond 90% reaction. "Infinity" ampoules were titrated after 10 half-lives and usually two were taken for each run. The slopes of linear plots of log (A_∞ - A_t) vs. time, where A_∞ and A_t are titers at infinity and at any time, were multiplied by -2.303 in order to obtain the first-order rate constants. Data from a representative run are presented in Table VI.

Table VI. Hydrolysis of I_β-Cl. A Typical Run at 27.80 ± 0.02°^a

Time, min.	NaOH required, ml.	A _∞ - A _t	Log (A _∞ - A _t)
5	1.40	12.37	1.0924
12	3.40	10.37	1.0158
22	6.27	7.50	0.8751
30	7.93	5.84	0.7664
40	9.70	4.07	0.6096
50	10.66	3.11	0.4928
75	12.35	1.42	0.1523
∞	13.80	Mean 13.77	
∞	13.73		

^a The plot of log (A_∞ - A_t) vs. time was linear with slope -1.366 × 10⁻² min.⁻¹ multiplied by -2.303/60; this gave the rate coefficient, 5.25 × 10⁻⁴ sec.⁻¹.

(66) J. B. Conant and W. R. Kirner, *J. Am. Chem. Soc.*, **46**, 232 (1924).

(67) A. Weissberger, E. S. Proskauer, J. A. Riddick, and E. E. Toops, Jr., in "Organic Solvents," Vol. 7, 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1955, p. 383.

(65) For preparation of Grignard reagents from sterically hindered bromo compounds such as I_α-Br, and VI_α-Br, Bowen's procedure is preferable. Refer to D. M. Bowen, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 553.

Calculation of the enthalpy and entropy of activation was performed in the usual method.⁶⁸ Plots of $\log k$ vs. $1/T$ made straight lines for all compounds and their slopes were calculated by the method of least squares.

General Procedure of Nitrations and Products Analyses. A nitrating reagent was prepared by mixing of 10.5 g. of nitric acid (d 1.375 at 22°), 180.0 g. of concentrated sulfuric acid (d 1.835 at 22°), and 16.0 g. of water. Thus the concentration of sulfuric acid in the reagent was 90%. To a solution of 1.8 mmoles of an alkylbenzene in 20 ml. of nitromethane was added dropwise 1 molar equiv. of the above reagent with vigorous stirring. The reaction temperature was kept at 0° through the whole reaction time. After 2 hr. of stirring, the reaction contents was poured onto ice and extracted three times with dichloromethane. The combined organic layers were washed with water, dried over anhydrous sodium sulfate, concentrated, and analyzed by gas chromatography on a Shimadzu gas chromatograph Model GC-1B, equipped with a 2.25 m. \times 4 mm. stainless steel column packed with 8 wt. % of diethylene glycol succinate polyester on acid-washed, 60–80 mesh Chromosorb W. The column temperature was 180° and helium was used as a carrier gas at a flow rate of 50 ml./min. As a general observation, the α -nitro compounds had a considerably shorter retention time than the β -nitro compounds on our analyses.

The relative amounts of α - and β -nitro compounds were determined by comparison of the peak areas. Relative response data were determined by running known amounts of the nitro compounds with an internal reference compound, which was I, V, or VI in approximately those proportions occurring in the reaction mixture.

The work-up procedure on the dinitration of I and II was similar to the above. Isolation of the authentic samples of dinitro compounds was achieved by elution chromatography on alumina. The physical properties of the nitro compounds and the isomer ratios were summarized in Tables I and IV.

(68) Refer to J. F. Bunnett, "Technique of Organic Chemistry," Vol. VIII, Part I, 2nd Ed., S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Interscience Publishers, Inc., N. Y., 1961, p. 200.

Competitive Nitration. Under the identical condition, except for the use of programmed gas chromatography, with those used for the above products analyses, the reactions and the gas chromatographic analyses of the results were carried out. The programmed gas chromatography was performed at the program rate of 5°/min. in a range of 55 to 190°. Samples were injected into column at 60°.

A typical competition run was as follows. The two competing benzocyclenes (3.5 mmoles of each, one of which was usually tetralin) and 3.5 mmoles of hexamethylbenzene as an internal reference on gas chromatographic analyses were dissolved in 50 ml. of nitromethane. To half of the solution was added dropwise 1.8 mmoles of the above nitrating reagent with stirring at 0°. After the addition was completed, the mixture was allowed to react for 1 hr., and then worked up in a way similar to that used for the products analyses. As a preliminary run, the other half of the solution was similarly treated with 90% sulfuric acid not containing nitric acid. The two halves were analyzed by gas chromatography. Hexamethylbenzene used here as an internal reference for gas chromatography proved to be quite stable and caused no trouble during the operation. The ratios of the corresponding peaks, determined from the halves, give the estimation of the amount of residual benzocyclenes.⁶⁹ The relative reactivity was calculated from the expression of Ingold and Shaw²⁶

$$\text{relative rate} = \frac{\log y_0 - \log y}{\log x_0 - \log x}$$

where x_0 , y_0 are the amounts of benzocyclenes in millimoles after the treatment with sulfuric acid only, and x and y are the amounts after nitration. The results are summarized in Table I.

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(69) As an example of the standard procedure, refer to (a) H. C. Brown and A. W. Moerikofer, *J. Am. Chem. Soc.*, 85, 2065 (1963); (b) M. M. Martin and G. T. Gleicher, *J. Org. Chem.*, 28, 3266 (1963).