B. 10b.—The reaction was conducted as above and gave **2a** (32.6% yield), **3a** (50.3% yield), and **3b** (2.8% yield).

C. 15 and 16.—The reactions of **15**[2] and **16** were carried out essentially as described above. The product was a brown-black solid; no α- or β-tetralone was detected by gc analysis (comparison with authentic samples, 5% DC-710 on Chromosorb W, 80–100 mesh, 5 ft × 1/4 in., 150°). It was subsequently shown that β-tetralone, but not α-tetralone, reacts readily (to give a black gum) when stirred at 0° with a mixture of 9% aqueous hydrochloric acid to which sodium nitrite is added.

Registry No.—**10b**, 34402-93-2; **11**, 34410-05-4; **12**, 34402-94-3; **13**, 34402-95-4; **14**, 34402-96-5; **16**, 34402-97-6; **19**, 34402-98-7; 3-ethoxyindene, 34402-99-8.

Benzocyclobutene and 2-Phenylethyl Chloride as Alkylating Agents in the Friedel–Crafts Reaction[1]

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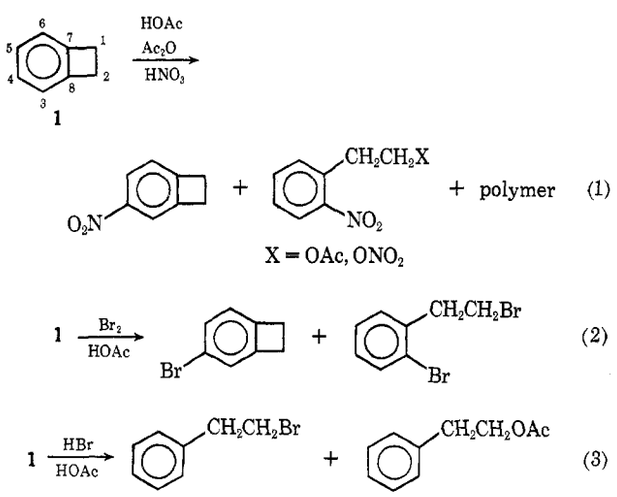
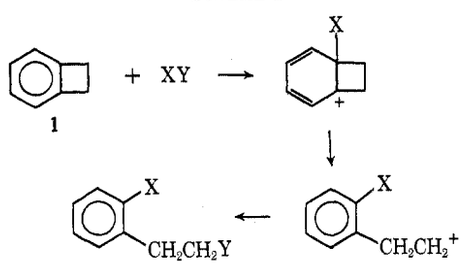
Friedel–Crafts reactions of benzocyclobutene and 2-phenylethyl chloride with benzene and toluene are studied at various temperatures. On the basis of identical product ratios with toluene, lack of positional rearrangement at the aryl rings of 1-chloro-2-*p*-tolylethane and 1-chloro-2-*m*-tolylethane on reaction with benzene, and various stereochemical arguments, it is concluded that in the presence of $AlCl_3$, benzocyclobutene is directly converted to 2-phenylethyl chloride before reaction with the aromatic hydrocarbon. Incomplete reaction of 1,1-dideuterio-2-*p*-tolylethyl chloride with benzene at 40° in the presence of $AlCl_3$ reveals that the starting material undergoes partial isomerization of the CH_2 and CD_2 groups. This differs with previous results with 2-phenylethyl-*1*-^{14}C chloride at −5° and suggests that in our case the intermediate phenonium ion, or its equivalent, reverts in part to starting material.

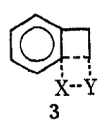
This paper reports the results of a study of benzocyclobutene (**1**) and 2-phenylethyl chloride (**2**) as alkylating agents under Friedel–Crafts conditions. The reactions of benzocyclobutene (**1**) and its derivatives with electrophilic reagents generally follow two competing pathways.[3] Aromatic substitution may occur, mainly at the 4 position with possibly minor amounts of substitution at the 3 position, or electrophilic attack may occur at a bridgehead carbon to open the four-membered ring and give ortho-substituted 2-phenylethyl derivatives. Some examples are nitration (eq 1),[3a,d] bromination (eq 2),[3f] and reaction with HBr in acetic acid (eq 3).[3d] Lloyd and Ongley have presented



SCHEME I



arguments concerning the mechanism of the ring-opening reaction.[3f] They have argued that the pathway involving a benzenonium ion (Scheme I) is not involved, since the formation of the benzenonium ion would be precluded by strain effects. It was further argued that this pathway requires generation of an ortho-substituted 2-phenylethyl cation, which is energetically improbable. It was concluded that the mechanism for ring opening involves a multicentered transition state (**3**).



3

The Friedel–Crafts reaction of 2-phenylethyl chloride (**2**) with aromatic hydrocarbons has been studied by isotopic labeling. Lee, Forman, and Rosanthal have found that 2-phenylethyl-*1*-^{14}C chloride with excess $AlCl_3$ in the presence of anisole yields *p*-methoxybibenzyl with the ^{14}C equally distributed between the methylene groups.[4] Two general mechanisms were discussed which could not be distinguished: (1) the same intermediate is involved in rearrangement and alkylation; (2) rearrangement and alkylation occur by separate processes. McMahon and Bunce studied the

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(3) (a) L. Horner, H.-G. Schmelzer, and B. Thompson, *Chem. Ber.*, **93**, 1774 (1960); (b) L. Horner, P. V. Subramaniam, and E. Eiben, *Tetrahedron Lett.*, 247 (1965); (c) *Justus Liebigs Ann. Chem.*, **714**, 91 (1968); (d) J. B. F. Lloyd and P. A. Ongley, *Tetrahedron*, **20**, 2185 (1964); (e) *ibid.*, **21**, 2281 (1965); (f) *ibid.*, **21**, 245 (1965).

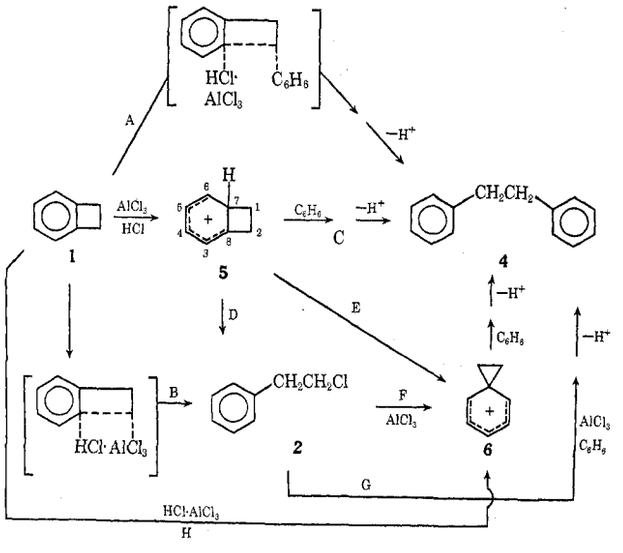
(4) C. C. Lee, A. G. Forman, and A. Rosenthal, *Can. J. Chem.*, **35**, 220 (1957).

reaction of 2-phenylethyl-1-^{14}C chloride with toluene.[5] Recovered starting material was found to be isotopically unrearranged, while the product, 1-phenyl-2-*p*-tolylethane, showed slightly greater than 50% rearrangement of the ^{14}C label. These results were interpreted in terms of a single process for both rearrangement and alkylation. The reaction was pictured as proceeding through a symmetrical phenonium ion which attacked toluene in the rate-determining step.

Results and Discussion

The reaction of benzocyclobutene (**1**) with a large excess of benzene in the presence of approximately 20 mol % $AlCl_3$ at 40° for 0.5 hr gave a quantitative yield of bibenzyl (**4**). A variety of pathways, both multicentered and stepwise, can be envisioned for this reaction. These are shown in Scheme II. Path A

SCHEME II

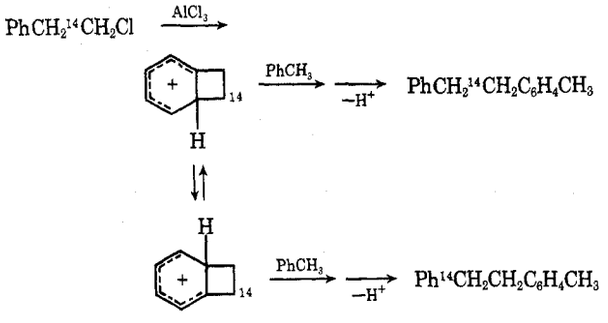


involves a multicentered transition state with direct formation of the product, **4**. Path B involves a multicentered transition state to form 2-phenylethyl chloride (**2**), which yields the product (**4**) either through route F[6] or route G (a direct displacement path). Path C involves direct displacement by benzene at C-1 of benzenonium ion **5**. In addition, ion **5** could lead to the product by directly forming phenonium ion **6** (path E) or by forming 2-phenylethyl chloride (**2**) (path D) which can lead to product as indicated above.

Under the reaction conditions, 2-phenylethyl chloride (**2**) also gave a quantitative yield of bibenzyl (**4**). In an attempt to distinguish between pathways which involve 2-phenylethyl chloride (**2**) (B, D) and those which do not, we studied the reactions of **1** and **2** with toluene. Under identical conditions at 40°, **1** yielded a mixture of 1-phenyl-2-tolylethanes of composition 47.8 ± 0.8% ortho (**7**), 18.2 ± 1.0% meta (**8**), and 34.0 ± 0.2% para (**9**), while **2** yielded a mixture of composition 46.1 ± 0.3% ortho (**7**), 18.8 ± 0.8% meta (**8**), and 35.1 ± 1.1% para (**9**). Suitable control experiments were carried out which established that the products were stable to both the reaction conditions and the subsequent work-up procedure. These isomer distributions therefore represent the kinetically controlled products.[7] The identity of the two product mixtures strongly suggests that the reactions of benzocyclobutene (**1**) and 2-phenylethyl chloride (**2**) proceed through a common intermediate. If this is the case, path A is eliminated.

One possible common intermediate is the benzenonium ion **5**. Formation of **5** from **2** would have to involve reversal of either step D or step E (Scheme II). By invoking reversible and rapid 1,2-hydride shifts (or rapid deprotonation–protonation), such an intermediate could accommodate the earlier labeling results of McMahon and Bunce,[5] which were interpreted in terms of a symmetrical phenonium ion. This is shown in Scheme III.

SCHEME III



In an attempt to obtain further information on the possible intermediacy of a benzenonium ion from the 2-arylethyl chloride system, we studied the reaction of 1-chloro-2-*p*-tolylethane (**10**) and 1-chloro-2-*m*-tolylethane (**11**) with benzene. Let us consider a step similar to the reversal of step D. If rapid 1,2-hydride shifts occur in the intermediate benzenonium ion (Scheme III), both **10** and **11** could yield mixtures of 1-phenyl-2-tolylethanes. This is shown in Scheme IV. Careful glc analyses of the reaction products revealed that **10** yielded only 1-phenyl-2-*p*-tolylethane (**9**) and none of the corresponding ortho (**7**) or meta (**8**) isomers, and **11** yielded only 1-phenyl-2-*m*-tolylethane (**8**) and none of the ortho (**7**) or para (**9**) isomers. We interpret these results together with those of previous investigators[8] and the ^{14}C labeling results of McMahon and Bunce[5] as ruling out the reversal of step D followed by step C as the pathway leading from **2** to bibenzyl (**4**). If this were the route leading to the ^{14}C scrambling results of McMahon and Bunce,[5] we would expect to obtain a mixture of products from **10** and **11**.

However, the pathways, reversal of D followed by E, and F followed by the reversal of E, cannot be ruled out unless it is established that under the reaction conditions 1,2-hydride shifts, as pictured in Schemes III and IV, are relatively rapid. These routes could account for the observed ^{14}C scrambling,[5] without the need to invoke shifts of the type pictured in Schemes III and IV. Mixtures of products from **10** and **11**

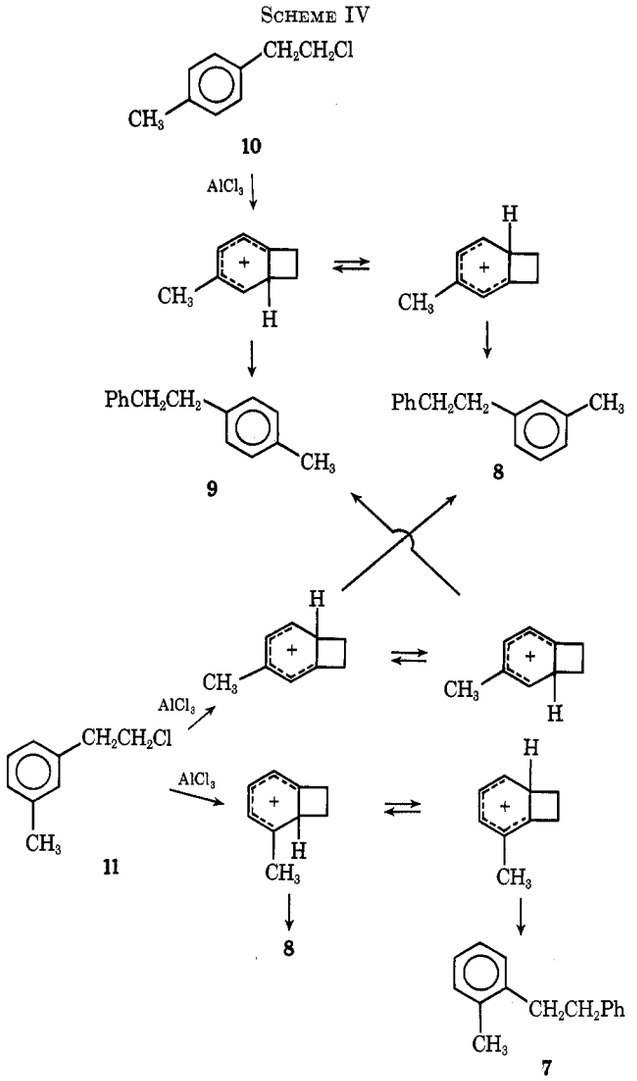
(5) M. A. McMahon and S. C. Bunce, *J. Org. Chem.*, **29**, 1515 (1964).

(6) For simplicity of representation, a phenonium ion (**6**) rather than rapidly equilibrating classical 2-phenylethyl cations is used. This work does not allow these species to be differentiated.

(7) Under somewhat different conditions, McMahon and Bunce[5] found virtually complete para alkylation of toluene by 2-phenylethyl chloride (**2**) at 0°.

(8) The 2-arylethyl system has been the subject of numerous studies in past years. To our knowledge there is no reported case of a substituent on the aromatic ring changing position.

SCHEME IV



would not be required if 1,2-hydride shifts were relatively slow. If such shifts were relatively rapid, **10** would be predicted to yield at least some **8**. This prediction is based on the work of Horner, Schmelzer, and Thompson.[3a] These workers showed that the reaction of 4-acetamidobenzocyclobutene with concentrated HCl yielded, after acetylation, 2-(3-acetamidophenyl)ethyl chloride. The electron-donating acetamido group directs the ring opening toward the meta product. A similar result would be expected from **10**.

Molecular models of ion **5** indicate a small dihedral angle, of the order of 10–15°, between the C_7–H bond and the empty p orbital, and a dihedral angle of approximately 55° between the C_1–C_7 bond and the empty p orbital (Figure 1). Recent work by Brouwer and Hogeveen,[9] Majerski, Schleyer, and Wolf,[10] and Schleyer and coworkers[11] has pointed out the angular requirement for 1,2 shifts between carbonium ions. The difference of five or more orders of magnitude between the rates of 1,2-hydride shifts in the adamantyl ion, on the one hand, and acyclic and monocyclic ions, on

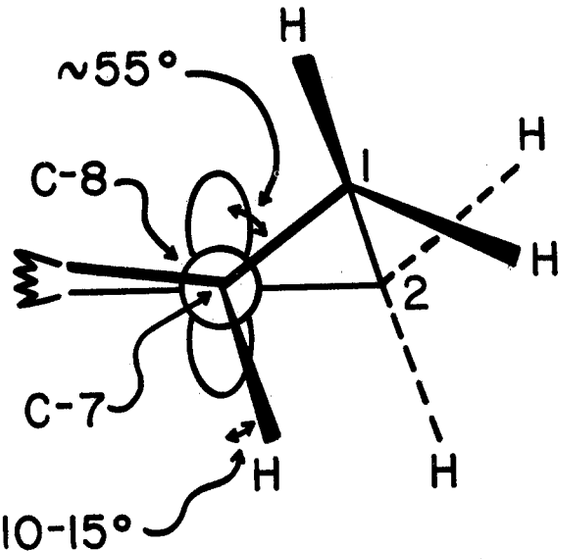


Figure 1.—Molecular model picture of ion **5**.

the other hand, was attributed to unfavorable orbital orientation in the adamantyl ion.[9,11] In order to achieve a most facile rearrangement, the dihedral angle between the sp^3 orbital of the migrating group and the adjacent empty p orbital should be 0°. In the adamantyl case, a 1,2-hydride shift would involve the interconversion of carbonium ions with dihedral angles of 90 and 60°. The mechanism for the interconversion of bridgehead and bridge adamantyl ions was shown to be intermolecular.[11] Similar interconversion of methyladamantyl ions was shown to proceed by skeletal isomerization steps rather than by 1,2-methyl shifts between bridgehead and bridge ions.[10]

Three arguments can be offered against the pathways, reversal of D followed by E, and F followed by the reversal of E. (1) Since orbital orientation in favorable (Figure 1), a 1,2-hydride shift of the type depicted in Schemes III and IV should be relatively facile, especially when such a shift would lead to a more stable ion as in the case of **10**. (2) Both paths under discussion involve the interconversion of ions **5** and **6**. Such a process should be unfavorable, since ion **5** involves a dihedral angle of approximately 55° and ion **6** a dihehdral angle of 60°. The transition state for the interconversion of these ions will be unfavorably twisted.[10,11] (3) Concerning the reversal of step D, to our knowledge, of the many reported studies of the 2-arylethyl system, not a single case of ring closure to a four-membered ring has been found. In an effort to detect such ring closure during the reaction of **2**, we looked for the deprotonation product of **5**, benzocyclobutene (**1**). Careful glc analysis did reveal traces of ethylbenzene and styrene, but no **1** could be found. Based upon the above results and arguments, we conclude that ion **5** is not the common intermediate in the reactions of **1** and **2**.

The remaining possible common intermediates are 2-phenylethyl chloride (**2**) formed from benzocyclobutene (**1**) either through path B or D and phenonium ion **6** formed from **1** either through path E or H. In a number of our early reactions of **1** with toluene, at 40°, glc analysis of the product mixture revealed the presence of very small quantities of 2-phenylethyl chloride

(9) D. M. Brouwer and H. Hogeveen, *Recl. Trav. Chim. Pays-Bas*, **89**, 211 (1970).
(10) Z. Majerski, P. v. R. Schleyer, and A. P. Wolf, *J. Amer. Chem. Soc.*, **92**, 5731 (1970).
(11) P. v. R. Schleyer, L. K. M. Lam, D. J. Raber, J. L. Fry, M. A. McKervey, J. R. Alford, B. D. Cuddy, V. G. Keizer, H. W. Geluk, and J. L. M. A. Schlatmann, *ibid.*, **92**, 5246 (1970).

(2) (<1%). Similar experiments at 0° with equimolar mixtures of **1** and **2** indicated that **2** builds up to approximately 20% of the initial concentration of **1** during the reaction. Since McMahon and Bunce had not found any ^{14}C rearrangement in recovered 2-phenylethyl-*1*-^{14}C chloride (at −5°),[5] which indicated that the reversal of step F does not occur, the formation of **2** from **1** suggested that path B and/or D was being followed *at least* in part. However, since our product distribution (at 40°) was different from that found by McMahon and Bunce (at 0°),[7] we decided to reinvestigate the possibility of rearrangement, under our reaction conditions, of **2** prior to reaction to form product. There are two points that we wished to establish simultaneously: (1) the possibility of rearrangement preceding reaction in the 2-arylethyl system; (2) the possibility of simultaneous isomerization of a substituent on the aromatic ring.[8] The reaction of 1,1-dideuterio-2-*p*-tolylethyl chloride (**10**-*1*-d_2) with benzene was studied at 40° (eq 4). The

$$p\text{-}CH_3C_6H_4CH_2CD_2Cl \xrightarrow[AlCl_3]{C_6H_6} \begin{matrix} p\text{-}CH_3C_6H_4CH_2CD_2C_6H_5 \\ \textbf{9}\text{-}\textit{1}\text{-}d_2 \end{matrix} + \begin{matrix} p\text{-}CH_3C_6H_4CD_2CH_2C_6H_5 \\ \textbf{9}\text{-}\textit{2}\text{-}d_2 \end{matrix} \qquad (4)$$

$$\textbf{10}\text{-}\textit{1}\text{-}d_2$$

reaction was quenched after only partial conversion. Analysis of the starting material by glc–mass spectrometry indicated essentially complete equilibration between CH_2 and CD_2 groups (48% H at C-1 and 52% H at C-2). The product showed 47% H at C-2 (**9**-*1*-d_2) and 53% H at C-1 (**9**-*2*-d_2) (53% rearrangement). Glc analysis further established that no positional rearrangement of the methyl group on the aromatic ring had occurred.

We cannot reach a conclusion concerning the difference between our results and those of McMahon and Bunce.[5] This is due to the fact that we used the reaction of a 2-*p*-tolylethyl chloride derivative with benzene rather than a 2-phenylethyl chloride derivative with toluene to investigate the possibility of rearrangement preceding reaction in the 2-arylethyl system. The difference in results could be caused by the different experimental conditions employed, or by the different reactions chosen for study. Furthermore, the fact that we do observe rearrangement in the starting chloride negates our statement in the preceding paragraph that path B and/or D is followed at least in part. Ion **6** might be the only common intermediate in the reactions of **1** and **2** leading to product, and which by reversal of step F could also lead to the formation of **2** from **1**.

The essentially complete equilibration of the methylene groups in the recovered starting material also raised the possibility that the Friedel–Crafts reaction of **10**-*1*-d_2 could be proceeding by a prior equilibration followed by a direct displacement on the starting material (path G, Scheme II). To test this pathway, the rearrangement of the deuterium label was followed in the starting material (**10**-*1*-d_2) and the product (**9**-*1*-d_2 and **9**-*2*-d_2) during the reaction (at 7°) by removing aliquots, separating the starting material from the product by preparative glc, and analyzing by mass spectrometry. The results are shown in Table I. The per cent rearrangement of the starting material increases during the reaction, while the per cent rearrangement of the product is constant throughout. In order to establish that the deuterium distribution of the product was not the result of a subsequent equilibration, **9**-*1*-d_2 was subjected to the reaction conditions (at 40°). Our results indicated little (3–4%), if any, deuterium scrambling. Path G is eliminated, since this route would predict equal scrambling of product and reactant throughout the reaction.

TABLE I

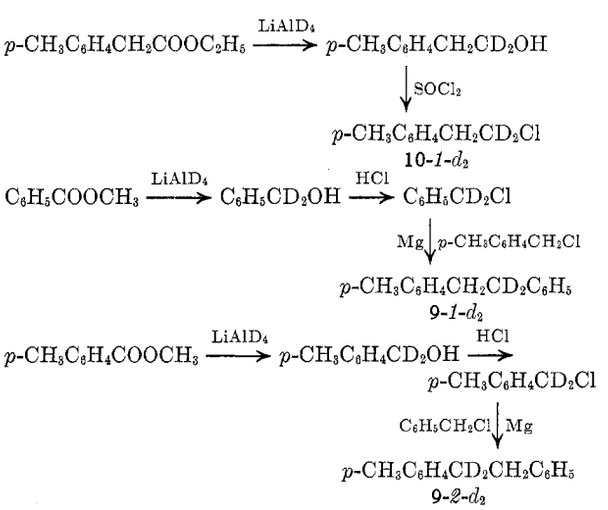
PER CENT REARRANGEMENT OF STARTING MATERIAL AND PRODUCTS DURING THE REACTION OF *p*-$CH_3C_6H_4CH_2CD_2Cl$ (**10**-*1*-d_2) WITH BENZENE (7°)

	Extent of reaction, %	Per cent rearrangement
	5	2
Starting Material	20	6
	70	39
Product	*a*	52

[a] The per cent rearrangement of the product remained invariant throughout the reaction.

The synthesis of **10**-*1*-d_2 and products **9**-*1*-d_2 and **9**-*2*-d_2, which were necessary as standards for mass spectrometry analysis, are outlined in Scheme V and described in the Experimental Section.

SCHEME V



We have already presented an argument against the interconversion of ions **5** and **6** (path E) based on unfavorable twisting in the transition state. A similar argument would apply to path H, where the transition state would have a geometry approaching that of ion **5**. Path D can also be argued against in terms of transition-state strain. A dihedral angle of 0° between the C_1–C_7 bond (Figure 1) and the empty p orbital at C-8 would be most favorable for the conversion of ion **5** to **2**. However, this angle appears to be approximately 55°. Although we cannot offer a quantitative estimation, such a large deviation from the optimum dihedral angle suggests that step D will be an unfavorable process. These arguments lead us to the conclusion that **2** is the common intermediate, and that it arises by way of step B. This is in agreement with the previous conclusion of Lloyd and Ongley[3f] concerning the multicentered nature of the ring opening of benzocyclobutene (**1**).

Experimental Section[12]

Phenyl 2-, 3-, and 4-Methylbenzyl Ketones.—A mixture of 25 g (0.167 mol) of the appropriate tolylacetic acid and 11.5 g (0.084 mol) of PCl_3 were heated under reflux for 1 hr. Anhydrous benzene (119 g, 1.52 mol) was added, and the organic layer was decanted in small portions, with cooling, into a flask containing 25.9 g (0.195 mol) of $AlCl_3$. The mixture was heated under reflux for 1 hr, cooled, and poured into a mixture of 165 g of ice and 65 ml of concentrated HCl. The organic layer was washed with water and dried, and the solvent was removed under vacuum. Distillation afforded the product. Phenyl 2-methylbenzyl ketone (77%) had bp 143–151° (1.3–2.2 mm); mp (from methanol) 67–68°; nmr ($CDCl_3$) δ 2.22 (3 H, s, CH_3), 4.23 (2 H, s, CH_2), 7.12 (4 H, broad s, ArH), 7.2–8.1 (5 H, m, ArH); ir (KBr) 1685 cm^{-1}. Phenyl 3-methylbenzyl ketone (76%) had bp 140–147° (1.5–1.7 mm); nmr ($CDCl_3$) δ 2.20 (3 H, s, CH_3), 4.09 (2 H, s, CH_2), 7.02 (4 H, broad s, ArH), 7.2–8.1 (5 H, m, ArH); ir (liquid) 1678 cm^{-1}. Phenyl 4-methylbenzyl ketone (64%) had bp 150–160° (2.1–2.2 mm); mp (from methanol) 95–96°; nmr ($CDCl_3$) δ 2.27 (3 H, s, CH_3), 4.18 (2 H, s, CH_2), 7.10 (4 H, s, ArH), 7.2–8.1 (5 H, m, ArH); ir (KBr) 1692 cm^{-1}.

1-Phenyl-2-*o*-, -*m*-, and -*p*-tolylethanes (7, 8, 9).—A solution of the appropriate phenyl methylbenzyl ketone (27 g, 0.13 mol), 25.4 g (0.39 mol) of KOH, and 22.5 g (0.45 mol) of hydrazine hydrate in 155 ml of diethylene glycol was heated at reflux for 1.25 hr, distilled until the head temperature reached 198°, and finally heated at reflux for an additional 3.25 hr. After cooling, 150 ml of H_2O was added, and the mixture was extracted with pentane. The pentane solution was washed with water and dried, and the solvent was removed under vacuum. Distillation afforded the product, 1-phenyl-2-*o*-tolylethane (86%): bp 119–120° (2.0–2.2 mm); nmr (CCl_4) δ 2.14 (3 H, s, CH_3), 2.75 (4 H, s, CH_2), 6.95 (4 H, s, ArH), 7.04 (5 H, s, ArH).

Anal. Calcd for $C_{15}H_{16}$: C, 91.78; H, 8.22. Found: C, 91.71; H, 8.48.

1-Phenyl-2-*m*-tolylethane (85%) had bp 118° (2 mm); nmr (CCl_4) δ 2.20 (3 H, s, CH_3), 2.70 (4 H, s, CH_2), 6.65–6.95 (4 H, m, ArH), 7.02 (5 H, s, ArH).

Anal. Calcd for $C_{15}H_{16}$: C, 91.78; H, 8.22. Found: C, 91.73; H, 8.27.

1-Phenyl-2-*p*-tolylethane (92%) had bp 115–119° (1.8–1.95 mm); nmr (CCl_4) δ 2.18 (3 H, s, CH_3), 2.75 (4 H, s, CH_2), 6.87 (4 H, s, ArH), 7.01 (5 H, s, ArH).

Anal. Calcd for $C_{15}H_{16}$: C, 91.78; H, 8.22. Found: C, 92.03; H, 8.11.

Friedel–Crafts Reaction of Benzocyclobutene (1) and 2-Phenylethyl Chloride (2) with Toluene. Product Studies.—The appropriate starting material (1 or 2) (0.0047 mol) was stirred with 500 ml (4.71 mol) of toluene and 0.001 mol of $AlCl_3$ at 40° for 0.5 hr. After quenching with 3 *N* HCl, the organic layer was dried and carefully distilled at atmospheric pressure to remove excess toluene. The residue was subjected to glc analyses. An Apiezon L column (16 ft, 14%, 218°) separated 1-phenyl-2-*m*-tolylethane (8) from the ortho (7) and para (9) isomers, which were not separated. A QF1-0065 column (12 ft, 20%, 189°) separated the ortho isomer from the meta and para isomers. The product distribution from 1 was 47.8 ± 0.8% 7, 18.2 ± 1.0% 8, and 34.0 ± 0.2% 9. In addition, trace amounts of ethylbenzene, styrene, benzocyclobutene (1), and 2-phenylethyl chloride (2) were found. The product distribution from 2 was 46.1 ± 0.3% 7, 18.8 ± 0.8% 8, and 35.1 ± 1.1% 9. Traces of ethylbenzene, styrene, and 2-phenylethyl chloride (2) were also found.

Friedel–Crafts Reactions of 1-Chloro-2-*p*-tolylethane (10) and 1-Chloro-2-*m*-tolylethane (11) with Benzene. A Search for Positional Rearrangement on the Aromatic Ring.—Individually, chlorides 10 and 11 (0.014 mol) were stirred with 0.003 mol of $AlCl_3$ and 300 ml of benzene at 40° for 0.5 hr. After the usual work-up, the products were analyzed by glc. Comparison with known samples indicated that 10 yielded only 9 and 11 yielded only 8.

Stability of the 1-Phenyl-2-tolylethanes (7, 8, 9) under Friedel–Crafts Reaction Conditions.—Two types of experiments were carried out. (1) Various standard mixtures of 7, 8, and 9 were subjected to the reaction conditions described above. Recovery of starting material was essentially quantitative. Analyses by glc showed no alterations in the isomer distributions. (2) Three aliquots were removed at 10-min intervals from a reaction of 2-phenylethyl chloride (2) with toluene (described above). At the 30-min mark, a sample of 9 was added to the reacting mixture. Three additional aliquots were removed at 10-min intervals. Glc analyses indicated the first three aliquots to have identical compositions. The last three aliquots all had the composition expected on the basis of the amount of added 9 and no rearrangement.

1,1-Dideuterio-2-*p*-tolylethyl Alcohol.—Ethyl *p*-tolylacetate (6.89 g, 0.031 mol) was reduced with 1.22 g (0.029 mol) of $LiAlD_4$ in ethyl ether for 5 hr. The nmr spectrum indicated the crude product, which was obtained in 72% yield, to be pure. It was not further purified: nmr ($CDCl_3$) δ 2.25 (3 H, s, CH_3), 2.70 (2 H, broad s, CH_2), 3.62 (1 H, s, OH), 7.05 (4 H, s, ArH).

1,1-Dideuterio-2-*p*-tolylethyl Chloride (10-*1*-d_2).—Thionyl chloride (15 ml) was slowly added to a solution of 5.57 g (0.04 mol) of 1,1-dideuterio-2-*p*-tolylethyl alcohol in 30 ml of pyridine. After heating at 100° for 5 min, the reaction mixture was quenched with 100 ml of cold H_2O and extracted with ether. The ether solution was extracted with H_2O, dilute $NaHCO_3$ solution, and saturated NaCl solution, dried, and evaporated under vacuum. Distillation afforded the product (57%): bp 113° (22 mm); nmr ($CDCl_3$) δ 2.30 (3 H, s, CH_3), 2.97 (2 H, broad s, $ArCH_2$), 7.09 (4 H, s, ArH).

α,α-Dideuteriobenzyl Alcohol.—Methyl benzoate (13.6 g, 0.10 mol) was reduced with 2.53 g (0.055 mol) of $LiAlD_4$ in ethyl ether for 4 hr. The crude alcohol was used without further purification: nmr ($CDCl_3$) δ 2.99 (1 H, s, OH), 7.43 (5 H, s, ArH), 4.66 ($^1/_8$ H, s, starting material).

α,α-Dideuteriobenzyl Chloride.—α,α-Dideuteriobenzyl alcohol (10.9 g, 0.10 mol) was shaken intermittently with 200 ml of concentrated HCl for 2 hr and the mixture was extracted with $CHCl_3$. The $CHCl_3$ solution was washed with H_2O and saturated NaCl solution, dried, and evaporated under vacuum. Distillation afforded the product (20%): bp 173–175°; nmr ($CDCl_3$) δ 7.31 (s, ArH).

1,1-Dideuterio-1-phenyl-2-*p*-tolylethane (9-*1*-d_2).—A solution of 0.87 g (0.01 mol) of α,α-dideuteriobenzyl chloride and 0.97 g (0.01 mol) of 4-methylbenzyl chloride in 40 ml of ether was added over a 0.5-hr period to 0.24 g (0.01 mol) of Mg turnings under a nitrogen atmosphere. The mixture was heated at reflux for 42.5 hr, cooled, and quenched with ice followed by 10% HCl. The ether layer was washed with water, dried, and evaporated under vacuum. The product, 9-*1*-d_2, was separated from the other two possible coupling products by preparative glc (OV-1 column): nmr ($CDCl_3$) δ 2.31 (3 H, s, CH_3), 2.87 (2 H, broad s, CH_2), 7.08 (4 H, s, ArH), 7.22 (5 H, s, ArH).

α,α-Dideuterio-*p*-methylbenzyl Alcohol.—Methyl *p*-toluate (13.2 g, 0.088 mol) was reduced with 2.32 g (0.055 mol) of $LiAlD_4$ in ethyl ether for 5 hr. The crude alcohol, which was obtained in 84% yield, was used without further purification: nmr ($CDCl_3$) δ 2.27 (3 H, s, CH_3), 3.62 (1 H, s, OH), 7.10 (4 H, AA′BB′, ArH).

α,α-Dideuterio-*p*-methylbenzyl Chloride.—α,α-Dideuterio-*p*-methylbenzyl alcohol was treated with concentrated HCl as described above for the preparation of α,α-dideuteriobenzyl chloride: bp 99° (52 mm) (64%); nmr ($CDCl_3$) δ 2.29 (3 H, s, CH_3), 7.19 (4 H, AA′BB′, ArH).

2,2-Dideuterio-1-phenyl-2-*p*-tolylethane (9-*2*-d_2).—9-*2*-d_2 was prepared from α,α-dideuterio-*p*-methylbenzyl chloride and benzyl chloride as described above for the preparation of 9-*1*-d_2: nmr ($CDCl_3$) δ 2.31 (3 H, s, CH_3), 2.87 (2 H, broad s, CH_2), 7.08 (4 H, s, ArH), 7.22 (5 H, s, ArH).

Friedel–Crafts Reaction of 1,1-Dideuterio-2-*p*-tolylethyl Chloride (10-*1*-d_2) with Benzene at 40°. Incomplete Reaction.—A solution of 1.19 g (0.01 mol) of 10-*1*-d_2 and 0.21 g (0.0016 mol) of $AlCl_3$ in 300 ml benzene were heated at 40° for 0.5 hr. After the usual work-up, the crude product was subjected to glc–mass spectrometry analysis (50 ft × 0.02 in. support-coated open tubular column, Apiezon L, connected through a Watson–Biemann separator to a Hitachi RMU-6E mass spectrometer). Two major peaks whose retention times corresponded to starting material and 1-phenyl-2-*p*-tolylethane were observed.

Analysis of the recovered starting material was based on the corrected relative intensities of the *m/e* 105 ($CH_3C_7H_6$) and 107 ($CH_3C_7H_4D_2$) peaks. For reference, 10 and 10-*1*-d_2 were sub-

(12) Nmr spectra were determined at 60 MHz using a Varian A-60 spectrometer with tetramethylsilane as internal standard. Infrared spectra were determined using a Perkin-Elmer 137 spectrophotometer. Boiling points are uncorrected. Melting points are corrected. All Friedel–Crafts reactions were performed under a dry inert atmosphere with anhydrous solvents (Dri-Na).

jected to identical glc–mass spectrometry analyses. The recovered chloride was found to consist of 52% 10-*1*-d_2 and 48% rearranged material, 10-*2*-d_2.

Analysis of the 1-phenyl-2-*p*-tolylethane fraction was based on the corrected relative intensities of the *m/e* 105 ($CH_3C_7H_6$) and 107 ($CH_3C_7H_4D_2$) peaks. For reference, 9-*1*-d_2 and 9-*2*-d_2 were subjected to identical glc–mass spectrometry analyses. The product was found to consist of 47% 9-*1*-d_2 and 53% 9-*2*-d_2.

Friedel–Crafts Reaction of 1,1-Dideuterio-2-*p*-tolylethyl Chloride (10-*1*-d_2) with Benzene at 7°. Analysis of the Starting Material and Product during the Reaction.—A mixture of 2.09 g (0.011 mol) of 10-*1*-d_2, 0.457 g (0.0034 mol) of $AlCl_3$, 1.385 g of *p*-dichlorobenzene (internal standard for glc analyses, inert), and 300 ml of benzene were stirred at 7° for approximately 1.5 hr. Periodically, 50-ml samples were removed, subjected to the usual work-up conditions, and separated into starting material and product by preparative glc. Mass spectral analyses were performed on these samples as well as on appropriate reference materials by Morgan–Schaffer Corp., Montreal, Canada, using a Hitachi RMU-6 mass spectrometer. The results are reported in Table I.

Registry No.—**1**, 694-87-1; **2**, 622-24-2; 10-*1*-d_2, 34403-01-5; phenyl 2-methylbenzyl ketone, 5033-67-0; phenyl 3-methylbenzyl ketone, 34403-03-7; phenyl 4-methylbenzyl ketone, 2430-99-1; 1-phenyl-2-*o*-tolylethane, 34403-05-9; 1-phenyl-2-*m*-tolylethane, 34403-06-0; 1-phenyl-2-*p*-tolylethane, 14310-20-4; α,α-dideuteriobenzyl chloride, 33712-34-4; α,α-dideuterio-*p*-methylbenzyl chloride, 33712-36-6.

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Dealkylation of Di-*tert*-butylhalo-1,4-benzoquinones

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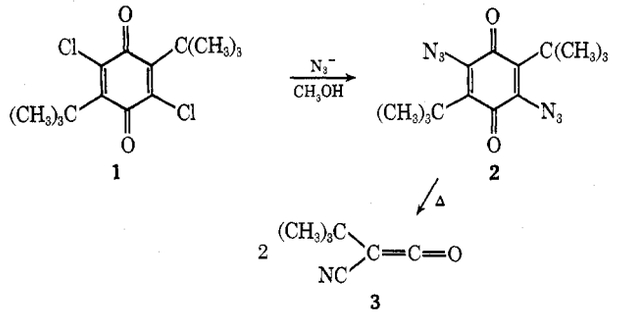
3-Chloro- and 3-bromo-2,5-di-*tert*-butyl-1,4-benzoquinone as well as 3-chloro-2,6-di-*tert*-butyl-1,4-benzoquinone react with anhydrous hydrohalic acids, resulting in dealkylation. This is a synthetically useful reaction for the preparation of 2,3-dihalo-5-*tert*-butyl-1,4-benzoquinones, specifically the 2,3-dichloro-2,3-dibromo-, 3-bromo-2-chloro, and 2-bromo-3-chloro isomers. The mechanism of this dealkylation involves an initial oxidation–reduction yielding the corresponding hydroquinones and molecular halogen. Electrophilic substitution by the halogen then results in elimination of the *tert*-butyl cation.

Recently the synthesis of 2,5-dichloro-3,6-di-*tert*-butyl-1,4-benzoquinone (**1**) was described.[1] This compound upon treatment with sodium azide gives the corresponding 2,5-diazido-3,6-di-*tert*-butyl-1,4-benzoquinone (**2**) which can be pyrolytically cleaved to *tert*-butylcyanoketene (**3**).[2] During our early attempts to synthesize the dichloroquinone **1**, some very interesting de-*tert*-butylation reactions were discovered. These dealkylation reactions are of synthetic utility and can be used to conveniently prepare 2,3-dichloro- (**13**), 2,3-dibromo- (**16**), 3-bromo-2-chloro- (**14**), and 2-bromo-3-chloro-5-*tert*-butyl-1,4-benzoquinone (**15**), from the readily available 2,5- and 2,6-di-*tert*-butyl-1,4-benzoquinones.



The mechanism of these dealkylation reactions is of interest and suggests that the "1,4 addition" of HCl and HBr to certain quinones is not a simple addition, but instead may involve an initial oxidation–reduction to the hydroquinone and molecular halogen followed by electrophilic substitution (halogenation) of the hydroquinone.

(1) H. W. Moore and W. Weyler, Jr., *J. Amer. Chem. Soc.*, **93**, 2812 (1971).

(2) H. W. Moore and W. Weyler, Jr., *ibid.*, **92**, 4132 (1970).

Synthetic Scope.—2,5-Di-*tert*-butyl-1,4-benzoquinone (**4**) was converted to its chloro and bromo derivatives **7** and **8** in high yield. These transformations were accomplished by an initial halogen addition to the carbon–carbon double bond to give the dihalo adducts **5** and **6**. These derivatives were then dehydrohalogenated upon reaction with diethylamine to the 3-halo-2,5-di-*tert*-butyl-1,4-benzoquinones **7** and **8**. Reaction of these haloquinones, 3-chloro-2,5-di-*tert*-butyl- (**7**) and 3-bromo-2,5-di-*tert*-butyl-1,4-benzoquinone (**8**) with anhydrous HCl in glacial acetic acid gave, respectively, 2,3-dichloro- (**9**) and 3-bromo-2-chloro-5-*tert*-butyl-1,4-benzoquinol (**10**). In completely analogous reactions, the monohalo-2,5-di-*tert*-butylquinones, **7** and **8**, were respectively converted to 2-bromo-3-chloro- (**11**) and 2,3-dibromo-5-*tert*-butyl-1,4-benzoquinol (**12**) upon reaction with anhydrous HBr. Oxidation of the above quinols with nitrogen oxides[3] gave the corresponding 2,3-dihalo-5-*tert*-butyl-1,4-benzoquinones, **13**–**16**.

2,3-Dichloro-5-*tert*-butyl-1,4-benzoquinone (**13**) and 3-bromo-2-chloro-5-*tert*-butyl-1,4-benzoquinone (**14**) were also obtained when 2,6-di-*tert*-butyl-1,4-benzoquinone (**17**) was converted to its monochloro derivative and then treated, respectively, with anhydrous HCl and HBr in glacial acetic acid. Oxidation of the resulting quinols gave the quinones in excellent yields.

Structural Assignments.—The structures of the 2,3-dihalo-5-*tert*-butyl-1,4-benzoquinones **13**–**16** are based upon both spectral (Table I) and chemical data. They all react with excess sodium azide to give the same diazide, 2,3-diazido-5-*tert*-butyl-1,4-benzoquinone (**20**),[4]

(3) L. Fieser and M. Fieser, "Reagents for Organic Synthesis," Vol. 1, Wiley, New York, N. Y., 1967, p 738.

(4) In general, azidoquinones are readily prepared by treating a dilute alcoholic solution of the corresponding halo-substituted quinone with aqueous sodium azide: H. W. Moore, H. R. Shelden, D. W. Deters, and R. J. Wikholm, *J. Amer. Chem. Soc.*, **92**, 1675 (1970).