(73) with the Agricultural Research Service, U. S. Department of Agriculture, administered by the Athens, Ga. Area, Richard B. Russell Agricultural Research Center, Athens, Ga. 30604.

Registry No.—Phenylacetonitrile, 140-29-4; diphenylmethane, 101-81-5; *o*-methylbiphenyl, 643-58-3; *o*-hydroxybiphenyl, 90-43-7; phenyl ether, 101-84-8.

Steric Factors in the Solvolysis of Haloallenes

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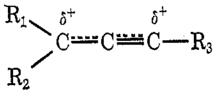
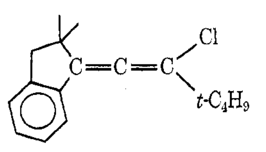
Earlier work[1-3] has established the mechanism of solvolysis of trisubstituted haloallenes in aqueous acetone and aqueous ethanol solutions as a unimolecular C–X bond heterolysis yielding the resonance-stabilized cation, 1. The solvolysis reaction of the haloallenes studied parallels the S$_N$1 reaction of saturated systems in every respect. First-order rate laws are obeyed, a large excess of added nucleophile has no effect on the rate of solvolysis, a common ion rate depression is observed, the substituent effects and temperature and solvent dependence of the reaction rate are consistent with a carbonium ion mechanism, and products derived from reaction at each end of 1 are observed.



1

It was noted, however, that an aromatic ring at C-1 had a much larger effect on the rate of solvolysis than one placed at C-3. For example, 1-chloro-1-phenyl-3-*tert*-butyl-4,4-dimethyl-1,2-pentadiene ($R_3 = C_6H_5$; $R_1 = R_2 =$ *tert*-butyl) solvolyzes eight times as rapidly as 3-chloro-2,2,6,6-tetramethyl-5-phenyl-3,4-heptadiene ($R_1 = R_3 =$ *tert*-butyl; $R_2 = C_6H_5$) in 50:50 (v/v) acetone–water at 35°. This is apparently due to the inability of an aromatic ring in the 3 position to achieve the coplanarity necessary for overlap with the developing electron-deficient π MO of the cation. A similar situation obtains in the solvolysis of aralkyl chlorides where 1-chloro-2,2-dimethylindane is reported to solvolyze 10^4 times as fast as 1-chloro-1-phenyl-2,2-dimethylpropane in 80% ethanol at 45°.[4,5]



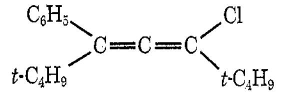
2

To test this hypothesis in our system the allenyl halide 2 was prepared. Treatment of the propargyl alcohol obtained upon nucleophilic addition of *tert*-butylethynyllithium to 2,2-dimethylindan-1-one with $SOCl_2$ afforded the desired chloroallene. The data in Table I support the conclusion that 2 reacts by a mechanism identical with that of other trisubstituted haloallenes. A plot of these data *vs. Y* yields $m = 0.73$. The temperature dependence of the rate constant yields $\Delta H^{\ddagger} = 20.0$ kcal/mol and $\Delta S^{\ddagger} = -11.0$ eu at 25°. These data also point up the remarkable rate enhancement over the structurally similar compound 3 ($R_1 = R_3 =$ *tert*-butyl; $R_2 = C_6H_5$). The indanyl derivative, 2, reacts 6800 times as fast as the open-chain analog, 3, in 90:10 acetone–water at 35°.

Table I

Rates of Solvolysis of 2 in Aqueous Acetone Solvent

Acetone–water (v/v)	*T*, °C	10^4k, sec^{-1}
70:30	24.62 ± 0.01	13.0 ± 0.3
80:20	24.62 ± 0.01	2.89 ± 0.03
90:10	24.62 ± 0.01	0.463 ± 0.004
90:10	34.68 ± 0.02	1.68 ± 0.03
90:10	45.30 ± 0.02	4.47 ± 0.03



3

It is likely that some of this rate acceleration is due to the presence of an ortho alkyl substituent in the fused-ring compound which is not present in the open-chain compound. However, for this rate acceleration to be accounted for solely by the substituent effect, ρ must equal -12, a value at least twice as large as that observed for any other solvolysis reaction. Furthermore, since no hybridization changes occur at C-3, any strain introduced by the five-membered ring remains the same in the ground state and transition state. Thus, no change in rate due to the introduction of strain in the ground state is to be expected. It seems likely therefore that a major portion of the rate enhancement is associated with the constrained coplanarity of the aromatic ring and vacant π MO and the attendant stabilization of 1. We have attempted unsuccessfully thus far to prepare analogs of 2 and 3 having substituents in the aromatic ring in an attempt to assess the magnitude of substituent effects on this system.

Experimental Section

All melting points and boiling points are uncorrected. Ir spectra were obtained using a Perkin-Elmer Model 457 spectrophotometer or a Bausch and Lomb Model 250 spectrophotometer. Nmr spectra were obtained using a Perkin-Elmer Model R-20B spectrometer. Microanalyses were performed by Atlantic Microlabs, Atlanta, Ga.

2,2-Dimethyl-1-indanone was prepared by dialkylation of 1-indanone with methyl iodide and potassium *tert*-butoxide in *tert*-butyl alcohol according to Woodward, *et al.*[6] Distillation at reduced pressure (80-81° at 0.7 mm) afforded the ketone in

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[1] M. D. Schiavelli, S. C. Hixon, and H. W. Moran, *J. Amer. Chem. Soc.*, **92**, 1082 (1970).

[2] M. D. Schiavelli, S. C. Hixon, H. W. Moran, and C. J. Boswell, *J. Amer. Chem. Soc.*, **93**, 6989 (1971).

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[5] G. Baddeley, J. W. Rasburn, and R. Rose, *J. Chem. Soc.*, 3168 (1958).

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55% yield: mp 42–43° (lit.[6] mp 42–43°); ir (CCl_4) 1710 cm^{-1} (C=O); nmr (CCl_4) δ 1.15 (s, 6), 2.9 (s, 2), 7.3 (m, 4).

1-*tert*-Butylethynyl-2,2-dimethylindan-1-ol was prepared as described earlier[3] for the general synthesis of tertiary propargyl alcohols by addition of *tert*-butylethynyllithium to 2,2-dimethyl-1-indanone. Distillation afforded the alcohol in 82% yield (99–100° at 0.5 mm): ir (neat) 3460 cm^{-1} (O—H), 2250 cm^{-1} (C≡C); nmr (CCl_4) δ 1.0 (s, 3), 1.15 (s, 3), 1.23 (s, 9), 2.02 (s, 1), 2.55 (s, 1), 2.78 (s, 1), 7.05 (m, 4).

1-(*tert*-Butylchlorovinylidene)-2,2-dimethylindan (2) was prepared according to the general procedure for the preparation of chloroallenes by Jacobs and Fenton.[7] After three successive distillations from a small amount of sodium borohydride to remove unreacted alcohol, the desired chloroallene was obtained in 23% yield: bp 96–100° at 0.3 mm; ir (neat) 1945 cm^{-1} (C=C=C); nmr (CCl_4) δ 1.22 (s, 9), 1.29 (s, 6), 2.86 (s, 2), 7.08 (m, 4).

Anal. Calcd for $C_{17}H_{21}Cl$: C, 78.31; H, 8.06; Cl, 13.63. Found: C, 78.40; H, 8.12; Cl, 13.46.

Kinetic Procedure.—The rate of appearance of HCl was measured conductometrically as described earlier.[2,3] All rates are the average of triplicate determinations. Acetone was purified according to Denoon.[8] Kinetic solvent solutions exhibited initial measured conductances of less than 2 μmho.

Acknowledgments.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. The senior author acknowledges the support of the College of William and Mary Faculty Research Fellowship Program.

Registry No.—**2**, 40548-49-0; 2,2-dimethyl-1-indanone, 10489-28-8; 1-*tert*-butylethynyl-2,2-dimethylindanol, 40548-50-3; *tert*-butylethynyllithium, 37892-71-0.

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(7) T. L. Jacobs and D. M. Fenton, *J. Org. Chem.*, **30**, 1808 (1965).

(8) C. E. Denoon, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 16.

A New Synthesis of Benzocyclobutene[1]

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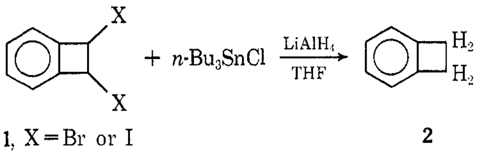
In connection with current studies of transition metal complexes of strained cyclic olefins, we required a supply of benzocyclobutene. The preparations of benzocyclobutene (2) previously reported in the literature are inconvenient for large-scale synthesis. Hydrogenation of 1,2-diiodobenzocyclobutene with palladium on carbon[3] requires a specially aged sodium ethoxide catalyst and involves lengthy purifications. High temperature pyrolyses *in vacuo* (without or with uv irradiation) of 1,3-dihydroisothianaphthene 2,2-dioxide[4,5] require special apparatus. A recent synthetic route to 2 involves the dissolving metal reduction of benzocyclobutenyl acetate[6] which is prepared by the cycloaddition of vinyl acetate to benzenediazonium-2-carboxylate, an explosive benzyne[7] precursor requiring special handling.

We devised a convenient reduction of the mixture of 1,2-dibromo- and 1,2-diiodobenzocyclobutene[3b] (**1**) which is readily prepared in 90% yields from the commercially available α,α,α′,α′-tetrabromo-*o*-xylene (Columbia Organic Chemicals, Co., Inc.). Reduction of **1** with lithium aluminum hydride in refluxing tetrahydrofuran gave **2** in 20% yields. This method was inconvenient since large quantities of lithium aluminum hydride were required and much polymeric material was formed, thus making purification tedious. A more expedious method involved the reduction of **1** with tri(*n*-butyl)tin hydride generated *in situ* from tri(*n*-butyl)tin chloride with lithium aluminum hydride. Since the reduction of **1** with the hydride gives **2** and tri(*n*-butyl)tin halide (which can be reduced to the hydride), only a limited amount of tri(*n*-butyl)tin chloride is needed. Thus this route is convenient for a large-scale synthesis since the reaction is carried out in one reaction vessel with no special apparatus required, the course of the reaction is readily monitored by nmr spectroscopy, and the purification procedures are straightforward. Assuming the reactants to be pure 1,2-dibromobenzocyclobutene, yields of >50% of **2** have been realized.



1, X = Br or I

2

Experimental Section

Benzocyclobutene (2).—To a 1000-ml round-bottom flask fitted with a magnetic stirrer, heating mantle, and reflux condenser was added tetrahydrofuran (200 ml), tri(*n*-butyl)tin chloride (70 g, 0.22 mol), and 100 g of a mixture of 1,2-dibromo- and 1,2-diiodobenzocyclobutene.[3b] Lithium aluminum hydride (10 g, 0.26 mol) was added in 0.5-g portions over a period of 6 hr. while a gentle reflux was maintained. The mixture was allowed to cool to room temperature, transferred to a 1000-ml erlenmeyer flask, treated sequentially with 10 ml of H_2O, 10 ml of 15% NaOH, and 30 ml of H_2O, and shaken after each addition. The resulting mixture was filtered through a large sintered-glass filter, and the residue was washed with two 50-ml portions of THF. The filtrate was rapidly distilled under reduced pressure (12 mm) into a trap cooled in liquid nitrogen until 202 ml of volatile material had been collected and the pot temperature reached 60°. While at 60°, the residue was placed under high vacuum (10^{-2} mm) and an additional 6 ml of volatile material collected. The nmr spectrum of the residue showed no remaining benzocyclobutene. The volatile fractions were combined (208 ml) and poured into 1250 ml of water in a large separatory funnel. The lighter organic layer was separated from the aqueous layer and then extracted three times with 50-ml portions of water, dried over $MgSO_4$, and filtered through a sintered-glass funnel. The remaining solvent was removed by distillation through a 25-cm Vigreux column until the head temperature reached 80°. The product (**2**) was collected *via* short-path distillation of the residue: 20 g, ∼50% yield; bp 143°; uv max (95% EtOH) 260, 265.5, 271.5 nm; nmr (CCl_4) τ 6.88 (s, 4), 3.03 (m, 4).

Registry No.—**1** (X = Br), 22250-72-2; **1** (X = I), 6639-21-0; **2**, 694-87-1; tri(*n*-butyl)tin chloride, 1461-22-9.

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(1) We gratefully acknowledge support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Graduate School of Boston University.

(2) An EPDA, Part E Fellowship from the Office of Education is gratefully acknowledged.

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