Condensed Cyclobutane Aromatic Compounds. XXI. Adducts of Benzocyclobutadienes with 1,3-Diphenylisobenzofuran

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Diphenylisobenzofuran has been found to be an excellent trapping agent for benzocyclobutadiene and for halogenated benzocyclobutadienes. Some chemical transformations of the adducts obtained are reported.

A particularly reactive diene component in the Diels-Alder reaction is 1,3-diphenylisobenzofuran (I), which has given adducts with a number of conventional olefinic and acetylenic dienophiles.[1] Recently this reagent has been employed for the trapping of the nonisolable intermediates benzyne[2] and cyclopentyne[3] as adducts. The success of the latter experiments has led us now to investigate the reaction of 1,3-diphenylisobenzofuran with the transient species benzocyclobutadiene (II), and with several halogenated derivatives of II.

The reaction of *trans*-1,2-dibromobenzocyclobutene (III)[4] with zinc in boiling ethanol in the presence of furan I gave the colorless benzocyclobutadiene adduct IV, m.p. 201–202°. Dehydration of IV took place readily in hot ethanolic solution in the presence of hydrochloric acid to yield a yellow hydrocarbon, m.p. 218–220°, formulated as 5,10-diphenylbenzo[*b*]biphenylene (V). The structure of hydrocarbon V was confirmed by both reductive and oxidative transformations. Reductive cleavage of V by Raney nickel in hot acetic acid occurred slowly to give what appeared to be a mixture of 1,2,4-triphenylnaphthalene (VI) and hydrogenation products of VI. Aromatization of this mixture with chloranil gave pure 1,2,4-triphenylnaphthalene.[5] A close analogy to the reduction of V to VI is found in the similar conversion of the parent benzo[*b*]biphenylene to 2-phenylnaphthalene.[6] Oxidation of V with sodium dichromate in hot acetic acid gave a good yield of a colorless neutral compound, m.p. 230–232°. Reproducible analyses of the usual accuracy could not be obtained for this substance, but it contained clearly three oxygen atoms. It contained also all of the original carbons of hydrocarbon V, since, although it was quite stable to further attack by dichromate or by potassium permanganate in acetone, it was degraded by alkaline hydrogen peroxide in excellent yield to both phthalic acid and *o*-dibenzoylbenzene. The above evidence suggests the indanedione structure XXVII as that of the dichromate oxidation product. This formulation is consistent with the infrared spectrum of the compound, which shows the benzoyl carbonyl at 6.02 μ and the 1,3-indanedione carbonyls as a doublet at 5.75 and 5.88 μ.[7]

Although benzocyclobutadiene itself has been trapped in earlier work both by cyclopentadiene[8,9] and by furan,[9] no adducts of any halogenated benzocyclobutadiene (*e.g.*, VII, VIII, or IX) have been reported, although such products would be of considerable interest for further transformations.[10] The halobenzocyclobutadienes VII, VIII, and IX have been invoked, however, as intermediates in the formation of the benzobiphenylenes X, XI, and XII from various halogenated benzocyclobutenes.[11-13] Adducts of all three species (VII, VIII, and IX) with 1,3-diphenylisobenzofuran have now been prepared and studied chemically.

Dehydrohalogenation of either *trans*-1,2-dibromobenzocyclobutene (III) or the corresponding *cis* isomer (XVI) with potassium *t*-butoxide in the presence of furan I gave good yields of the bromo adduct XIII, m.p. 170–173°. In a similar manner, the iodo adduct XIV, m.p. 208–209°, was formed smoothly from both the *cis* and *trans* isomers of 1,2-diiodobenzocyclobutene (XVII and XVIII).[14] The analogous dibromo adduct XV, m.p. 199–

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[1] J. A. Berson, *J. Am. Chem. Soc.*, **75**, 1240 (1953) and references cited in this paper. See also A. Etienne, A. Spire, and E. Ioromanoff, *Bull. Soc. Chim.*, **19**, 750 (1952).

[2] G. Wittig, W. Stils, and E. Knauss, *Angew. Chem.*, **70**, 166 (1958).

[3] G. Wittig, A. Krebs, and R. Pohlke, *Angew. Chem.*, **72**, 324 (1960).

[4] For recent details of the preparation of this dihalide in pure condition, see M. P. Cava and K. Muth, *J. Org. Chem.*, **27**, 757 (1962).

[5] C. F. H. Allen, A. Bell, and J. W. Gates, Jr., *J. Org. Chem.*, **8**, 373 (1943).

[6] F. R. Jensen and W. E. Coleman, *Tetrahedron Letters*, No. 20, 7 (1959).

[7] Although 1-indanone absorbs in the carbonyl region at 5.88 μ (KBr), both 1,3-indanedione and 2-phenyl-1,3-indanedione show carbonyl doublets at 5.71 and 5.84 μ. Enolization cannot be invoked to explain these observations, since the enol of 1,3-indanedione should contribute an additional band at a wave length *longer* than 5.84 μ. We should like to thank Prof. Peter Yates for the infrared spectra of the model diones.

[8] C. D. Nenitzescu, M. Avram, and D. Dinu, *Chem. Ber.*, **90**, 2541 (1957).

[9] M. P. Cava and M. J. Mitchell, *J. Am. Chem. Soc.*, **81**, 5409 (1959).

[10] Attempts to trap VII and VIII with either furan or cyclopentadiene led only to biphenylenes X and XI (M. J. Mitchell, unpublished experiments).

[11] M. P. Cava and J. F. Stucker, *J. Am. Chem. Soc.*, **79**, 1706 (1957).

[12] M. P. Cava, K. W. Ratts, and J. F. Stucker, *J. Org. Chem.*, **25**, 1481 (1960).

[13] M. P. Cava and K. Muth, *J. Org. Chem.*, **27**, 757 (1962).

[14] F. R. Jensen and W. E. Coleman, *J. Org. Chem.*, **23**, 869 (1958).

201°, was prepared in three different ways. The first method involved the dehydrobromination of 1,1,2-tribromobenzocyclobutene (XIX)[4] in the presence of furan I. In the second method, a mixture of 1,1,2,2-tetrabromobenzocyclobutene (XX)[4] and furan I was heated in solution with sodium iodide. The third method consisted of treating a mixture of furan I and $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene (XXI) with potassium *t*-butoxide. Since it has been shown that the dehydrobromination of tetrabromide XXI does not lead to the generation of 1,2-dibromobenzocyclobutadiene (IX),[13] it is proposed that tetrabromide XXI gives first with base the quinoid tribromide XXII, which undergoes cycloaddition to furan I to give the cyclooctadiene derivative XXIII. Dehydrobromination of XXIII, followed by intramolecular cyclization of the resulting quinomethane XXIV, would give directly adduct XV. The formation of XV from tetrabromide XXI in this reaction adds support to the suggested mechanism of dehydrobromination of XXI in the absence of a trapping agent.[13]

A number of attempts were made to convert adducts XIV and XV to the benzocyclobutadiene derivative XXV, in the hope that the latter structure would be resistant to dimerization or polymerization for steric reasons.

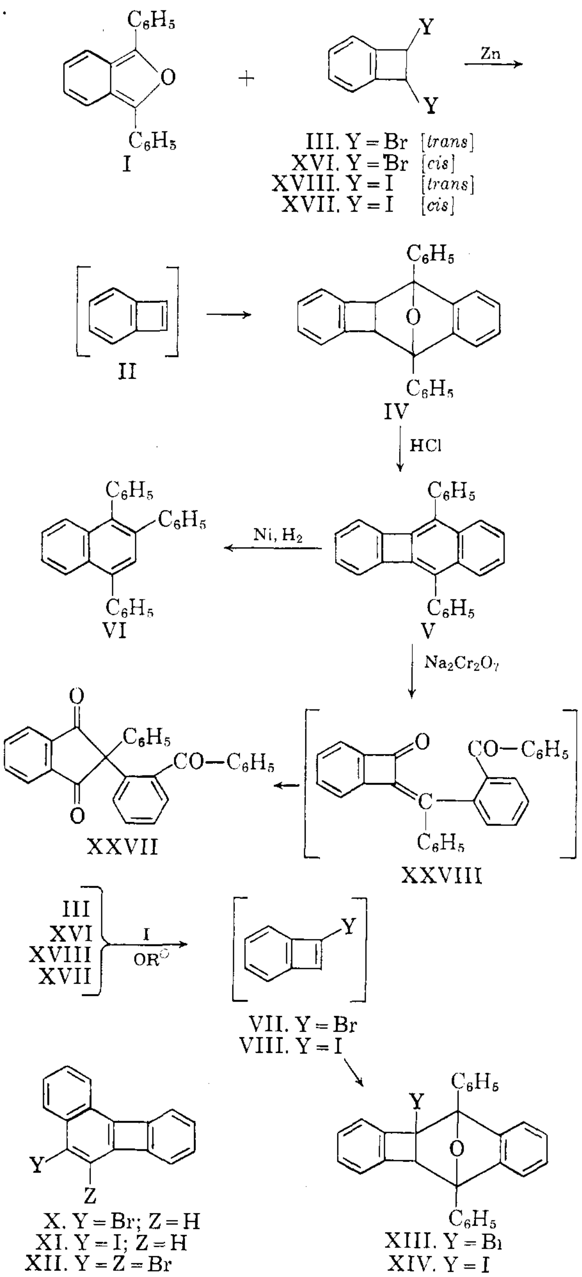
The iodo adduct XIV was surprisingly resistant to dehydrohalogenation, and was recovered quantitatively after refluxing for four days with potassium *t*-butoxide in *t*-butyl alcohol. More vigorous conditions brought about the loss of iodine from the molecule. Either potassium *t*-butoxide in refluxing *p*-xylene or sodium amide in refluxing piperidine gave, however, not the unsaturated adduct XXV but its saturated analog IV. The formation of IV from XIV in these reactions may proceed by attack of the iodine atom by the base, leaving an anion of IV which abstracts a proton from the solvent. It is not impossible, on the other hand, that dehydrohalogenation of XIV to XXV may actually occur, the unstable olefin XXV being reduced to IV by abstraction of hydrogen atoms from the solvent. Evidence exists that the parent cyclobutadiene can abstract hydrogens from other molecules in this manner.[15]

Surprisingly, the reaction of the iodo adduct XIV with potassium *t*-butoxide took a different course in dimethyl sulfoxide solution. The product, obtained in good yield, was the hydrocarbon V. Since the conversion of XIV to V must proceed *via* an anionic intermediate, the result of this experiment would seem to strengthen the hypothesis that the cyclobutadienoid structure XXV is an intermediate in the conversion of XIV to IV by base under the other conditions described above.

More expectedly, adduct XIV was converted readily to V under acidic conditions, free iodine being liberated during the reaction.

The dibromo adduct XV was largely unaffected by zinc dust in dimethylformamide at room temperature for nineteen hours and was completely unchanged after being heated in the same solvent with sodium iodide for one week. Both zinc in boiling ethanol, and lithium amalgam in ether converted XV to hydrocarbon V, the oxide bridge being eliminated as well as the bromine atoms.

It is clear from the evidence presented here that benzocyclobutadiene (II) is generated with much greater ease from comparable precursors than is the cyclobutadienoid compound XXV. It may be that the central double bond of XXV is more highly strained than that of benzocyclobutadiene,



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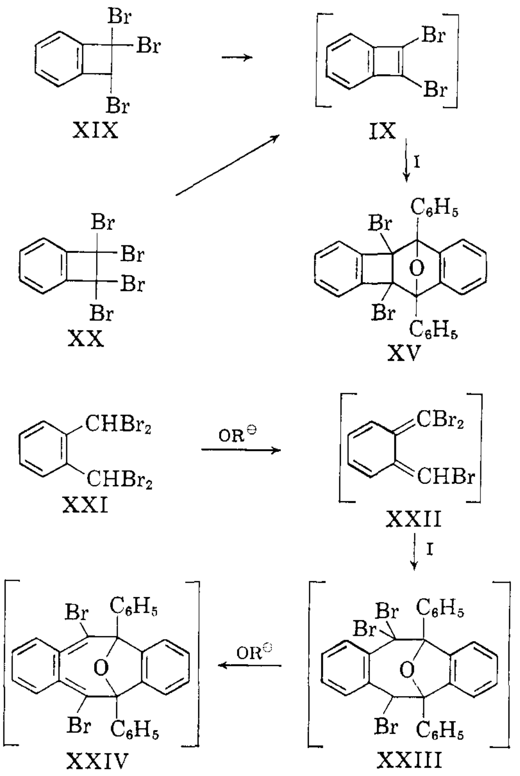
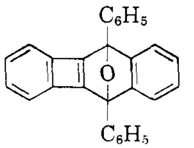
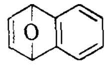
(15) M. Avram, C. D. Nenitzescu, and E. Marica, *Chem. Ber.*, **90**, 1857 (1957).





XXV



XXVI

from which it is formally derived by fusion to the tricyclic nucleus of XXVI. The olefinic bond of XXVI is unusually strained, as evidenced by its reactivity as a dienophile in the Diels-Alder reaction.[16]

Experimental[17]

Adduct of Benzocyclobutadiene with Diphenylisobenzofuran (IV).—A solution of *trans*-1,2-dibromobenzocyclobutene (III, 0.262 g.) and 1,3-diphenylisobenzofuran (I, 0.270 g.) in ethanol (10 ml.) was refluxed with stirring for 6 hr. with zinc dust (0.100 g., activated by treatment with ammonium chloride). The hot solution was filtered and the filtrate was poured into water (200 ml.). Extraction of the precipitate with benzene was followed by chromatography over neutral alumina in benzene, to yield the crude adduct IV (0.206 g., 55%), m.p. 195–200°. Recrystallization from methanol, then petroleum ether, gave the analytical sample, m.p. 200–202°.

Anal. Calcd. for $C_{28}H_{20}O$: C, 90.29; H, 5.41. Found: C, 90.54; H, 5.30.

Adduct of 1-Bromobenzocyclobutadiene with Diphenylisobenzofuran (XIII).—A solution of potassium *t*-butoxide prepared from potassium (0.100 g.) and *t*-butyl alcohol (10 ml.) was added at room temperature to a stirred solution of *cis*-1,2-dibromobenzocyclobutene (XVI, 0.262 g.) and 1,3-diphenylisobenzofuran (I, 0.270 g.) in tetrahydrofuran (10 ml.). After 1 hr. the solution was poured into water and the product isolated by filtration, followed by chromatography in benzene over neutral alumina. Crystallization from petroleum ether gave the crude adduct XIII (0.269 g., 60%), m.p. 150–164°. A second chromatographic purification, followed by crystallization from methanol–chloroform mixture, gave the analytical sample, m.p. 170–173°.

Anal. Calcd. for $C_{28}H_{19}BrO$: C, 74.51; H, 4.24; Br, 17.71. Found: C, 74.51; H, 4.43; Br, 17.79.

A similar reaction using *trans*-1,2-dibromobenzocyclobutene (III) was run at steam bath temperature for 3 hr. The same adduct XIII was obtained in 73% yield.

Adduct of 1-Iodobenzocyclobutadiene with Diphenylisobenzofuran (XIV).—To a solution of *trans*-1,2-diiodobenzocyclobutene (XVIII, 5.57 g.) and 1,3-diphenylisobenzofuran (I, 4.22 g.) in benzene (60 ml.) was added 50 ml. of a 0.5 *M* solution of potassium *t*-butoxide in *t*-butyl alcohol. The mixture was refluxed for 30 min., additional 0.5 *M* potassium *t*-butoxide solution (50 ml.) was added, and refluxing was then continued for a further 5 hr. The resulting solution was poured into water (200 ml.), and the benzene layer was washed with water and dried. Chromatography of the benzene solution on neutral alumina and evaporation of the eluate gave a residue which, on treatment with petroleum ether, afforded crystals of adduct XIV (7.23 g., 92%), m.p. 197–203°. Recrystallization from acetic acid gave the analytical sample, m.p. 208–210°.

Anal. Calcd. for $C_{28}H_{19}IO$: C, 67.48; H, 3.85; I, 25.47. Found: C, 67.90; H, 3.93; I, 25.45.

A similar reaction using *cis*-1,2-diiodobenzocyclobutene (XVII) was run at room temperature for 12 hr. The same adduct XIV was obtained in 73% yield.

Adduct of 1,2-Dibromobenzocyclobutadiene with Diphenylisobenzofuran (XV). A. From Tribromide XIX.—To a solution of 1,1,2-tribromobenzocyclobutene (XIX, 0.341 g.) and 1,3-diphenylisobenzofuran (I, 0.270 g.) in tetrahydrofuran (10 ml.) was added dropwise at room temperature 2 ml. of a 0.54 *M* solution of potassium *t*-butoxide in *t*-butyl alcohol. After 10 hr. an additional 0.5 ml. of the *t*-butoxide solution was added and the mixture was allowed to stand at room temperature overnight. The reaction mixture was worked up in the usual manner to yield, after chromatography from benzene–cyclohexane on neutral alumina, crystals of adduct XV (0.469 g., 88%), m.p. 200°. Recrystallization from ethanol–chloroform gave the analytical sample, m.p. 199–201°.

Anal. Calcd. for $C_{28}H_{18}Br_2O$: C, 63.42; H, 3.42; Br, 30.14. Found: C, 63.70; H, 3.53; Br, 30.66.

B. From Tetrabromide XXI.—A solution of tetrabromo-*o*-xylene (XXI, 0.422 g.) and 1,3-diphenylisobenzofuran (0.270 g.) in tetrahydrofuran (10 ml.) was mixed with 40 ml. of a 0.54 *M* solution of potassium *t*-butoxide in *t*-butyl alcohol. After 4 days at room temperature, the mixture was diluted with water and worked up in the usual manner to yield crude adduct XV (0.266 g., 86%), m.p. 180–200°. Recrystallization gave crystals which were found to be identical by melting point, mixed melting point, and infrared analysis with the authentic material.

C. From Tetrabromide XX.—A mixture of 1,1,2,2-tetrabromobenzocyclobutene (XX, 0.262 g.), 1,3-diphenylisobenzofuran (I, 0.270 g.), sodium iodide (2.0 g.), ethanol (2 ml.), and tetrahydrofuran (45 ml.) was heated on the steam bath for 24 hr. Dilution of the solution with water was followed by the usual isolation procedure to yield, after chromatography, crude adduct XV (0.118 g., 35%), m.p. 190–200°. Recrystallization from methanol gave crystals (m.p. 196–200°) which did not depress the melting point of authentic material.

5,10-Diphenylbenzo[*b*]biphenylene (V).—Concentrated hydrochloric acid (5 ml.) was added to a hot solution of the iodo adduct XVI (0.498 g.) in acetic acid (50 ml.). The mixture was heated for 30 min. on the steam bath, during which time a brown color developed and solid separated.

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[16] G. Wittig, H. Härle, E. Knauss, and K. Niethammer, *Chem. Ber.*, **93**, 951 (1960).

[17] Analyses were carried out by Schwarzkopf Laboratories, Woodside, N. Y. Melting points are uncorrected.

After dilution with water (50 ml.), the mixture was cooled, and the precipitate of fine yellow needles of V (0.344 g., 97%) was washed with ethanol and dried. The hydrocarbon, m.p. 218–220°, was analytically pure without further treatment.

Anal. Calcd. for $C_{28}H_{18}$: C, 94.88; H, 5.12. Found: C, 94.70; H, 5.12.

Adduct IV (0.060 g.), when heated a few minutes in boiling ethanol containing a few drops of concd. hydrochloric acid, gave the same hydrocarbon V (0.052 g.), m.p. 218–220°.

Reductive Cleavage of V to 1,2,4-Triphenylnaphthalene (VI).—A mixture of hydrocarbon V (0.100 g.) and excess Raney nickel (prepared from 7 g. of Raney alloy) was heated for 12 hr. on the steam bath with acetic acid (50 ml.). The filtered solution was diluted with water and extracted with benzene. Concentration of the dried extract, followed by chromatography on neutral alumina, gave colorless crystals (0.086 g., 84%) of crude VI, m.p. 143–147°. The product was, apparently, partially overreduced. A sample (0.070 g.) was rearomatized by refluxing it in benzene (6 ml.) with chloranil (0.170 g.) overnight. After chromatography over alumina the hydrocarbon VI (0.059 g.) melted at 155–157°. The recrystallized material (m.p. 162–163°) did not depress the melting point of authentic 1,2,4-triphenylnaphthalene,[5] and the infrared spectra of both samples were identical.

Oxidation of Hydrocarbon V.—A solution of hydrocarbon V (0.304 g.) and excess sodium dichromate dihydrate in acetic acid (80 ml.) was heated for 2 hr. on the steam bath. The cooled solution was diluted with cold water and the precipitated product was chromatographed in chloroform over neutral alumina. After crystallization from methanol, colorless crystals (0.230 g.), m.p. 230–232° were obtained. Reproducible analyses for this compound could not be obtained.

Anal. Calcd. for $C_{28}H_{18}O_3$: C, 83.57; H, 4.51. Found: C, 84.80; 85.10, 82.72; H, 4.47, 4.96, 4.39.

The above oxidation product (1.25 g.) was dissolved in excess hot methanolic sodium hydroxide solution. The red solution was heated on the steam bath and 30% aqueous hydrogen peroxide was added in portions until the color of the mixture was discharged. The solution was diluted with water and the neutral product, isolated by ether extraction followed by chromatography on neutral alumina, proved to be *o*-dibenzoylbenzene (0.806 g., 95%), m.p. 149–151°, identical in melting point and infrared spectrum with authentic material. The basic aqueous layer from the peroxide oxidation was passed through a column of Amberlite IR-120 resin (hydrogen form) to yield, after evaporation of the water, phthalic acid (0.433 g., 87%), m.p. 204–206°. Sublimation of the latter gave phthalic anhydride (0.350 g., 80%), m.p. 127°, which was identified by lack of mixed melting point depression with an authentic sample.

Reaction of Iodo Adduct XIV with Bases.—A. A mixture of adduct XIV (0.498 g.), potassium *t*-butoxide (0.600 g.), and *p*-xylene (20 ml.) was refluxed for 43 hr. The cooled solution was shaken with water (100 ml.) and the organic layer was worked up in the usual manner to yield, after filtration through alumina, yellowish crystals (0.249 g.), m.p. ~175°. Recrystallization from alcohol containing a few drops of benzene gave colorless crystals (0.120 g., 32%) of adduct IV, m.p. 199–202°. The identity of the material was established by mixed melting point and infrared comparisons.

B. A solution of adduct XIV (0.498 g.) in a small volume of benzene was refluxed for 100 hr. with 5 ml. of a 0.54 *M* potassium *t*-butoxide solution in *t*-butyl alcohol. After the usual work-up there was obtained only starting material (0.492 g., 98%), m.p. 206–210°, identified by mixed melting point and infrared comparisons.

C. A solution of adduct XIV (0.498 g.) in dry dimethyl sulfoxide (18 ml.) was heated on the steam bath for 75 min. with dry potassium *t*-butoxide (0.400 g.). The yellow solution was poured into water and extracted with benzene. After the usual work-up, including chromatography on neutral alumina, there was obtained hydrocarbon V (0.263 g., 74%), m.p. 218–220°, after crystallization from ethanol–benzene. The identity of the sample was confirmed by mixed melting point and infrared comparisons.

D. A solution of adduct XIV (0.498 g.) in dry piperidine (40 ml.) was refluxed with sodium amide (0.400 g.) for 25 hr. Dilution of the cooled mixture with water (150 ml.) afforded fine white needles which were filtered and purified by chromatography and crystallization from methanol–benzene to give adduct IV (0.268 g., 72%), m.p. 197–201°. Recrystallization from ethanol gave a sample, m.p. 200–202°, identified as IV by mixed melting point and infrared comparisons.

Debromination Experiments with Adduct XV.—A. A solution of adduct XV (0.200 g.) in dimethylformamide (20 ml.) was stirred with zinc dust (0.200 g.) at room temperature for 19 hr. After the usual work-up, the only product isolated was starting material XV (0.122 g., 61%), m.p. 202–203°, identified by mixed melting point and infrared comparisons.

B. A solution of adduct XV (0.220 g.) and sodium iodide (1.0 g.) in dimethylformamide (30 ml.) was heated for 7 days in the steam bath. After the usual work-up, starting material XV (0.205 g., 91%), m.p. 195–197°, was isolated. The mixed melting point with authentic XV was 199–202°, and the infrared spectra of the two samples were identical.

C. A solution of adduct XV (0.213 g.) in ethanol (30 ml.) was refluxed for 22 hr. with zinc dust (0.200 g.). After filtration, the hot solution deposited fine yellow needles of hydrocarbon V (0.090 g., 63%), m.p. 215–217°. Mixed melting point behavior and infrared analysis confirmed the identity of the material.

D. A solution of adduct XV (0.200 g.) in dry ether (50 ml. was shaken intermittently with lithium amalgam (from 0.35 g. of lithium and 30 ml. of mercury) at room temperature during a period of 1 day. After the usual work-up, including chromatography on alumina from benzene, the only product isolated was hydrocarbon V (0.040 g., 31%), m.p. 216–218°. The identity of the product was established by mixed melting point behavior and infrared analysis.

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