EXPERIMENTAL

Oximes were prepared by heating the aldehyde with hydroxylamine hydrochloride and sodium acetate in aqueous ethanol, except for phenylacetaldoxime which was made by the method of Weerman.[5] The aldehydes were all commercially available except for pivalaldehyde, prepared according to the method of Roberts and Teague.[6]

The reaction of aldoximes with alkali. The general procedure used was as follows: The aldoxime (10 mmoles) was heated in 100 ml. of the solvent indicated at the temperature indicated in Table I with about 50 mmoles of potassium hydroxide, and the heating was carried out under a nitrogen atmosphere.

At the end of the reaction time, the cooled mixture was diluted with water and extracted four times with half volumes of methylene chloride; these combined extracts being washed with 100 ml. of aqueous sodium chloride solution. Drying the organic extracts over sodium sulfate, filtering, and evaporating the solvent left as a residue the neutral fraction of the reaction mixture. The original aqueous alkaline solution then was acidified with hydrochloric acid to *p*H 7, and again extracted with methylene chloride. A similar treatment of the organic phase yielded the weakly acidic products. Finally, acidification of the aqueous solution to *p*H 2 and similar extraction with methylene chloride yielded the strongly acidic products. The products were then identified by mixed m.p. and infrared comparison with authentic samples.

The thermal dehydration of syn-benzaldoxime. A solution of 1.09 g. of *syn*-benzaldoxime in 80 ml. of 2-methoxyethanol was heated at 120° for 12 hr. under a nitrogen atmosphere with no alkali present. The product was isolated as described above and found to consist entirely of unreacted oxime.

A solution of 1.04 g. benzaldoxime in 50 ml. of diethylene glycol was heated 10 hr. at 200° under a nitrogen atmosphere. The product was entirely neutral and consisted of nitrile and amide. No unchanged oxime or acid was present.

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Condensed Cyclobutane Aromatic Compounds. XVI. Methylenebenzocyclobutene

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This note describes a synthesis of methylenebenzocyclobutene (I), the simplest styrene analog in the benzocyclobutene series.

Benzocyclobutene-1-carboxylic acid (II), prepared by an improved one-step hydrolysis of the corresponding nitrile,[1] was reduced with lithium aluminum hydride to 1-hydroxymethylbenzocyclobutene (III). Reaction of alcohol III with *p*-toluenesulfonyl chloride in pyridine gave the corresponding crystalline tosyl ester (IV). Reduction of tosylate IV with lithium aluminum hydride afforded 1-methylbenzocyclobutene (V), the ultraviolet spectrum of which was virtually superimposable upon that of benzocyclobutene itself.[2] Reaction of IV with potassium *t*-butoxide in *t*-butyl alcohol gave methylenebenzocyclobutene (I), purified at 135° by gas chromatography. The new olefin, which absorbed bromine rapidly, was found to have an ultraviolet spectrum (Fig. 1) somewhat similar to

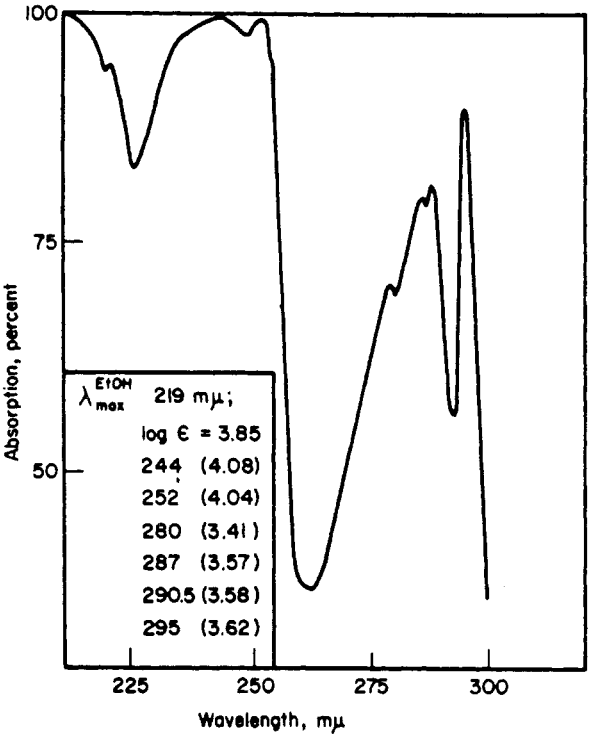
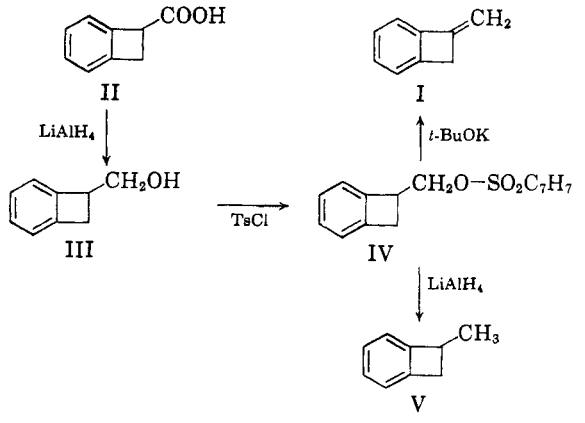


Fig. 1. Ultraviolet spectrum of methylenebenzocyclobutene

that of *o*-methylstyrene.[3] The spectrum of I, however, showed more detail and higher resolution.

As expected, mild catalytic reduction of I occurred readily with saturation of the olefinic double bond to give hydrocarbon V, as evidenced



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by change in the ultraviolet spectrum of the sample.

Some further chemical transformations of I will be reported at a later date.

EXPERIMENTAL[4]

Benzocyclobutene-1-carboxylic acid (II). 1-Cyanobenzocyclobutene[1] (1.0 g.) was dissolved in saturated ethanolic potassium hydroxide (6 ml.). The solution was allowed to stand for twenty-four hours at room temperature, then diluted with water (2 ml.), refluxed for three hours, and poured into water (50 ml.). The resulting suspension was extracted with ether; then the aqueous layer was separated, acidified with 6*N* hydrochloric acid, and re-extracted with ether. The second (acid-containing) ether extract was dried over magnesium sulfate and evaporated to dryness. The residue was taken up in a minimum amount of warm petroleum ether (b.p. 30–60°), and the solution was decanted from an insoluble oily residue, seeded with a crystal of acid, and chilled to 10° to give acid II (0.835 g., 73%), m.p. 72–73°; reported[1] 76.5°.

1-Hydroxymethylbenzocyclobutene (III). A solution of acid II (1.505 g.) in ether (75 ml.) was added dropwise under nitrogen to a stirred solution of lithium aluminum hydride (0.830 g.) in ether. After being stirred overnight, the reaction mixture was treated with a saturated aqueous solution of sodium sulfate (*ca.* 4 ml., added dropwise). The resulting clear ethereal layer was drawn off, and the remaining aqueous sludge was washed with ether (25 ml.). The ether extracts were combined, dried over sodium sulfate, and evaporated to give alcohol III (1.250 g., 86%) as a colorless oil, b.p. 93–95° (4 mm.); n_D^{25} 1.5567, d^{25} 1.071. The analytical sample was obtained by molecular distillation in a semimicro apparatus.

Anal. Calcd. for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.55; H, 7.82.

1-Hydroxymethylbenzocyclobutene tosylate (IV). Finely powdered *p*-toluenesulfonyl chloride (1.24 g.) was added to a solution of alcohol III (0.888 g.) in pyridine (6 ml.). The reaction mixture was allowed to stand at room temperature for twenty-four hours and was then poured into petroleum ether (100 ml.), b.p. 30–60°. The resulting suspension was washed with cold 2*N* sulfuric acid (100 ml.), then with sodium bicarbonate (50 ml., 5%), and finally with water (100 ml.). The organic layer was dried over magnesium sulfate, filtered, and allowed to evaporate slowly at room temperature through a loose cotton plug. After standing for six days, the solution had deposited tosylate IV (1.153 g., 60%) as clusters of pure white needles, m.p. 49–55°. A second crop, obtained by chilling the mother liquor to 5°, raised the total yield of crude product to 1.308 g. (73.6%). The sample, m.p. 73–74°, was recrystallized from *t*-butyl alcohol.

1-Methylbenzocyclobutene (V). A solution of tosylate IV (1.000 g.) in ether (75 ml.) was added dropwise to a solution of lithium aluminum hydride (1.0 g.) in ether (75 ml.). The resulting suspension was stirred for four hours at room temperature and was then treated with a saturated aqueous solution of sodium sulfate to decompose the excess hydride. The dried ether layer was concentrated to a small volume by carefully distilling off the ether through a fractionating column. The residual oil (1.2 g.) was passed through a gas chromatographic column (30% Apiezon M on fire-brick, helium at 105°) to give pure 1-methylbenzocyclobutene (0.157 g., 38%), n_D^{25} 1.5195, d^{25} 0.924.

Anal. Calcd. for C_9H_{10}: C, 91.47; H, 8.53. Found: C, 91.14; H, 8.65.

(4) Melting points are corrected. The analyses were carried out by Galbraith Microanalytical Laboratories, Knoxville, Tenn., and by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

The ultraviolet spectrum (ethanol) showed the following maxima: λ_{max} 260 (log ϵ 3.08), 265.5 (3.24), and 271 (3.19) mμ.

Methylenebenzocyclobutene (I). A solution of tosylate IV (2.000 g.) in warm *t*-butyl alcohol (10 ml.) was added to a solution of potassium *t*-butoxide (prepared from 0.300 g. of potassium and 6 ml. of *t*-butyl alcohol). The reaction mixture was stirred at 75–80° for 15 minutes and was then poured into cold water (15 ml.). The resulting suspension was extracted four times with 5-ml. portions of petroleum ether (b.p. 30–60°). The aqueous layer was filtered to give an amorphous sulfur-free polymer (0.413 g.). The organic extracts were combined, dried over magnesium sulfate, and concentrated to 2 ml. by fractional distillation. Chilling the pot residue to −20° gave unchanged tosylate (0.275 g.), obtained as pure white needles. The mother liquor was vacuum distilled in an all-glass, hermetically sealed apparatus, and the distillate was subjected to gas chromatography (30% Apiezon M on fire-brick, helium at 130°) to give olefin I (0.165 g., 41%) as a colorless liquid, n_D^{25} 1.5679.

Anal. Calcd. for C_9H_8: C, 93.06; H, 6.94. Found: C, 93.87; H, 6.18.

The infrared spectrum of methylenebenzocyclobutene showed absorption bands at 5.96, 6.01, and 11.6 μ, characteristic of the exo methylene group. The ultraviolet spectrum is reproduced in Fig. 1.

Hydrogenation of methylenebenzocyclobutene gave 1-methylbenzocyclobutene. Thus, 0.0162 g. of the olefin was dissolved in ethanol (5 ml.) and was hydrogenated at atmospheric pressure in the presence of palladium (0.001 g., 10%) on charcoal catalyst (reaction time, four minutes). The reaction mixture was filtered quantitatively through Celite, diluted to 10.0 ml. in a volumetric flask, and analyzed spectrophotometrically for 1-methylbenzocyclobutene.

Anal. Calcd. for 1-methylbenzocyclobutene: 0.0165 g. Found: 0.0141 g.

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Some Organofluorosilanes[1]

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Organoalkoxysilanes with the general structure $RSi(OEt)_2R'Si(OEt)_2R$[2,3] are converted readily to the corresponding fluorosilanes when they are treated with boron trifluoride etherate.

The use of covalent halides in the preparation of halosilanes from alkoxysilanes is well known.[4]

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