570. *Benzocyclobutenes. Part II.* A New Synthesis of Benzocyclobutene and of* 1,2-*Diphenylbenzocyclobutene.*

By WILSON BAKER, J. F. W. McOMIE, and D. R. PRESTON.

Benzocyclobutene (II), accompanied by some 1,2:5,6-dibenzocyclooctadiene, is obtained when the N-toluene-*p*-sulphonamido-derivative of 1,3-dihydroisoindole (I) is treated with aqueous sodium hydroxide. Similarly 1,2-diphenylbenzocyclobutene (VIII) is formed by the spontaneous decomposition of 1,3-dihydro-1,3-diphenyl-*N*-toluene-*p*-sulphonamidoisoindole (VII) in pyridine solution.

BENZOCYCLOBUTENES have been prepared by five different methods, three of which are of general application; they are mentioned in a preliminary communication [1] reporting a new general synthesis now recorded in detail.

The oxidation of 1,1-dibenzylhydrazines, $(Ph\cdot CH_2)_2N\cdot NH_2$, with mercuric oxide to bibenzyl and nitrogen was first recorded by Busch and Weiss;[2] other oxidising agents have since been employed.[3] The closely related reaction due to Bamford and Stevens by which benzaldehyde benzenesulphonylhydrazone, $Ph\cdot CH{:}N\cdot NH\cdot SO_2Ph$, is converted into benzenesulphinic acid and phenyldiazomethane by treatment with alkali,[4] led Carpino to develop a process for the preparation of bibenzyls in which *NN*-dibenzylbenzene(or toluene-*p*-)sulphonylhydrazides are decomposed by alkali to give the bibenzyl, sodium benzene(or toluene-*p*-)sulphinate and nitrogen:[5]

$$(Ph\cdot CH_2)_2N\cdot NH\cdot SO_2\cdot Ph \xrightarrow{OH^-} Ph\cdot CH_2\cdot CH_2Ph + N_2 + {}^-SO_2\cdot Ph + H_2O$$

This suggested that it should be possible to prepare benzocyclobutene (II), which is in a

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* Part I, preceding paper.

[1] Baker, McOmie, and Preston, *Chem. and Ind.*, 1960, 1305.

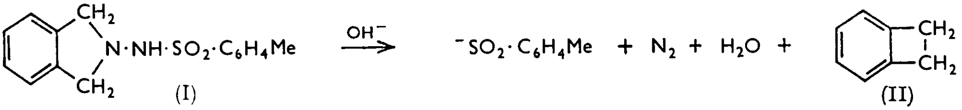
[2] Busch and Weiss, *Ber.*, 1900, **33**, 270.

[3] Overberger and Marks, *J. Amer. Chem. Soc.*, 1955, **77**, 4104.

[4] Bamford and Stevens, *J.*, 1952, 4335.

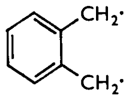
[5] Carpino, *Chem. and Ind.*, 1957, 172; *J. Amer. Chem. Soc.*, 1957, **79**, 4427.

sense a bibenzyl, by a similar reaction from the toluene-*p*-sulphonyl derivative of *N*-amino-1,3-dihydroisoindole (I):

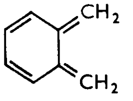


(I) (II)

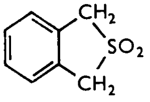
This expectation has been realised. The toluene-*p*-sulphonyl derivative (I) reacts with 20% aqueous sodium hydroxide at 70—80°, giving in a small-scale reaction a 16% yield of a hydrocarbon mixture, containing benzocyclobutene (II) and *o*-xylene in a ratio of about 10 : 1. The hydrocarbons were identified by their infrared spectra. Their relative proportions were established by observation of the infrared spectra and gas–liquid chromatographic behaviour of mixtures of the two pure substances, the benzocyclobutene required for purposes of comparison being prepared by the method of Cava and Napier.[6] A relatively non-volatile product isolated from the reaction mixture in 12% yield was proved to be 1,2:5,6-dibenzocyclo-octadiene.



(III)



(IV)

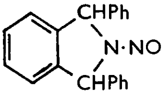


(V)

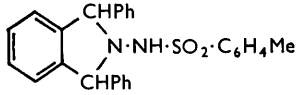
The reaction doubtless proceeds *via* the diradical (III), a canonical form of the dimethylene-*o*-quinone (IV), which then cyclises to benzocyclobutene (II), dimerises to 1,2:5,6-dibenzocyclo-octadiene, or combines with hydrogen to give *o*-xylene. The free-radical nature of the reaction is strongly indicated by the fact that the thermal decomposition of 2-thiaindane dioxide (V) likewise gives benzocyclobutene, *o*-xylene, and 1,2:5,6-dibenzocyclo-octadiene in almost the same proportions as now found.[7]

The reaction has been extended to the preparation of 1,2-diphenylbenzocyclobutene (VIII). 1,3-Dihydro-*N*-nitroso-1,3-diphenylisoindole (VI) was reduced with aluminium amalgam to the *N*-amino-compound which was isolated as the hydrochloride. When this hydrochloride was treated in pyridine with toluene-*p*-sulphonyl chloride 1,3-dihydro-1,3-diphenyl-*N*-toluene-*p*-sulphonamidoisoindole underwent spontaneous decomposition at room temperature to give a mixture, separated chromatographically, of 1,2-diphenylbenzocyclobutene (VIII), m. p. 93—94°, in about 40% yield, and 9,10-dihydro-9-phenylanthracene in about 13% yield. The 1,2-diphenylbenzocyclobutene (VIII) had almost exactly the same m. p. and ultraviolet and infrared spectra as those recorded for the material prepared by treating αα′-dibromo-*o*-dibenzylbenzene with sodium iodide and described in a preliminary note by Jensen and Coleman.[8]

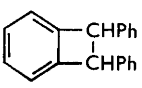
(VI)



(VII)



(VIII)



EXPERIMENTAL

1,3-*Dihydro*-N-*nitrosoisoindole*.—Toluene-*p*-sulphonamide and *o*-xylylene dibromide gave 1,3-dihydro-N-toluene-*p*-sulphonyl-isoindole,[9] which was hydrolysed by aqueous hydrobromic acid in propionic acid in presence of phenol to give 1,3-dihydroisoindole, characterised as its picrate,[9,10] m. p. 195—196·5° (Found: C, 48·9; H, 3·8; N, 16·1. Calc. for $C_8H_9N,C_6H_3N_3O_7$:

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[6] Cava and Napier, *J. Amer. Chem. Soc.*, 1958, **80**, 2255.
[7] Cava and Deana, *J. Amer. Chem. Soc.*, 1959, **81**, 4266.
[8] Jensen and Coleman, *J. Amer. Chem. Soc.*, 1958, **80**, 6149.
[9] Bornstein, Lashua, and Boisselle, *J. Org. Chem.*, 1957, **22**, 1255.
[10] Fenton and Ingold, *J.*, 1928, 3295.

C, 48·3; H, 3·5; N, 16·1%). The derived 1,3-dihydro-*N*-nitrosoisoindole [11] formed needles, m. p. 95—97°, from ethanol (lit.,[11] m. p. 96—97°).

2-*Amino*-1,3-*dihydroisoindole*.—1,3-Dihydro-*N*-nitrosoisoindole (1·37 g.) in dry ether (50 ml.) was stirred during the addition (1 hr.) at room temperature of lithium aluminium hydride (370 mg.; 1·05 equiv.) in ether (30 ml.). The mixture was shaken with damp ether (40 ml.) and then with 20% aqueous sodium hydroxide (40 ml.), the ethereal layer dried (K_2CO_3) and evaporated under reduced pressure and then distilled, giving 2-amino-1,3-dihydroisoindole as an almost colourless liquid (880 mg., 69%), b. p. 115—120°/24 mm., which rapidly darkened in air. The hydrochloride, precipitated from hot ethanolic solution by addition of ether, formed light grey needles, m. p. 189—195° (decomp.) (Found: N, 16·1. Calc. for $C_8H_{11}ClN_2$: N, 16·4%) (lit.,[12, 5] m. p. 190—194° and 185—195°).

1,3-*Dihydro*-2-*toluene*-p-*sulphonamidoisoindole* (I).—The preceding hydrochloride (0·75 g.) in dry pyridine (4 ml.) was stirred at 0° during the addition (5 min.) of toluene-*p*-sulphonyl chloride (0·53 g.). After a further ¼ hr. at 0° water (20 ml.) was added and the solid collected, dissolved in hot acetone, and precipitated by the addition of water, giving light-brown needles (0·70 g., 56%), m. p. 130—135° (decomp.) (Carpino [5] prepared the compound in dimethylformamide and gives m. p. 136—138° for the pure compound).

Action of Alkali on 1,3-*Dihydro*-2-*toluene*-p-*sulphonamidoisoindole. Isolation of Benzocyclobutene* (II) *and* 1,2:5,6-*Dibenzocyclo-octadiene*.—The sulphonamido-derivative (I) (0·70 g.) was added in portions to 20% aqueous sodium hydroxide (5 ml.) at 70—80° (½ hr.). When gas evolution had ceased the cooled solution was extracted with ether, and the extracts were washed with dilute hydrochloric acid, dried ($MgSO_4$), and distilled, giving a colourless oil (40 mg.), b. p. 95—102°/100 mm. The infrared spectrum of this oil showed peaks at 715 and 780 cm.$^{-1}$ (split band corresponding to four adjacent aromatic hydrogen atoms in benzocyclobutene [6]) and at 740 cm.$^{-1}$ (four adjacent aromatic hydrogen atoms in *o*-xylene). Comparison of the spectrum of the product with those of mixtures of the two compounds in known proportions indicated that the ratio of benzocyclobutene to *o*-xylene was approximately 10 : 1, and this was confirmed by gas–liquid chromatography of the product and of mixtures of the two compounds. If high temperatures and low flow rates were used on the column, benzocyclobutene tended to isomerise to a compound identified as styrene by comparison of its retention time with genuine material (cf. Cava and Deana [7]). Gas-chromatography was effected in an 8 ft. column, packed with 20% Apiezon L on Silocel C-22, at 250° with a flow rate of 40 ml. of nitrogen per min.

The residue from the distillations was sublimed several times at 100—120°/0·2 mm., giving 1,2:5,6-dibenzocyclo-octadiene (30 mg., 12%), m. p. 106—108°, mixed m. p. with an authentic specimen,[13] 107—108·5°.

1,3-*Dihydro*-2-*nitroso*-1,3-*diphenylisoindole* (VI).—To 1,3-dihydro-1,3-diphenylisoindole [14] (4·7 g.) in water (200 ml.) and concentrated sulphuric acid (1·3 ml.) was added during 20 min. with ice-cooling, sodium nitrite (1·45 g.) in water (10 ml.), and the mixture was stirred for a further 3 hr. The solid was washed, dried, and crystallised from ethanol, giving 1,3-dihydro-2-nitroso-1,3-diphenylisoindole (VI) (3·6 g., 70%) as colourless needles, m. p. 175·5—176·5° (lit.,[14] m. p. 175—175·5°) (Found: C, 80·3; H, 5·7; N, 9·6. Calc. for $C_{20}H_{16}N_2O$: C, 80·0; H, 5·4; N, 9·4%).

2-*Amino*-1,3-*dihydro*-1,3-*diphenylisoindole*.—Finely powdered 1,3-dihydro-2-nitroso-1,3-diphenylisoindole (VI) (300 mg.) was added during ½ hr. to a stirred suspension of aluminium amalgam (from 1·0 g. of aluminium [15]) in ether (25 ml.), water (6·0 ml.) was then added dropwise during ½ hr., and stirring was continued for a further 1 hr. The ethereal suspension was then shaken with 10% aqueous sodium hydroxide (50 ml.), dried (K_2CO_3), and filtered, and anhydrous hydrogen chloride was passed through the solution. The precipitated 2-*amino*-1,3-*dihydro*-1,3-*diphenylisoindole hydrochloride* (270 mg., 83%), crystallised from water, had m. p. 225—228° (decomp.) (Found: N, 8·9. $C_{20}H_{17}ClN_2$ requires N, 8·7%).

1,2-*Diphenylbenzocyclobutene* (VIII).—Finely divided toluene-*p*-sulphonyl chloride (200 mg., 1·0 equiv.) was added to 2-amino-1,3-dihydro-1,3-diphenylisoindole hydrochloride (270 mg.) in

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[11] Gabriel and Neumann, *Ber.*, 1893, **26**, 527.

[12] Fränkel, *Ber.*, 1900, **33**, 2812.

[13] Baker, Banks, Lyon, and Mann, *J.*, 1945, 27.

[14] Boyd and Ladhams, *J.*, 1928, 2093.

[15] Vogel, *J.*, 1927, 594.

pyridine (1·5 ml.) at room temperature. Slow evolution of nitrogen began at once, and, after it had ceased (6 hr.), the solution was boiled for ½ hr., poured into dilute hydrochloric acid, and extracted with ether (3 × 20 ml.). The extracts were shaken with aqueous sodium hydroxide to remove toluene-*p*-sulphinic acid, dried, and distilled, leaving a viscous, yellow oil (112 mg.), whose benzene solution was chromatographed on an alumina column. The final fraction (20 mg.) did not crystallise. The first fraction (77 mg.) solidified, and was crystallised from ethanol at 0°, giving 1,2-diphenylbenzocyclobutene (VIII) as colourless needles, m. p. 93—94°, $\lambda_{\text{max.}}$ at 261 (log ε 3·32), 266 (3·55), and 272·5 mμ (3·27); Jensen and Coleman [8] give m. p. 94·5—95·2° and $\lambda_{\text{max.}}$ 260 (log ε 3·24), 266 (3·36), and 272 mμ (3·32). The second fraction (22 mg.) also solidified and when crystallised from ethanol gave 9,10-dihydro-9-phenylanthracene, m. p. 85—86°.

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