Sulfonation at 20° gave a product which was about 56% 8-sulfonic acid and 44% the 4-isomer; at 80° the composition was 33% of 8- and 67% 5-acid.

A control experiment without boron trifluoride at 75–80° indicated 52% sulfonation based on recovered β-naphthylamine.

Sulfonation of β-Naphthol.—Twenty-nine grams was sifted into 116 g. of sulfuric acid previously saturated with boron trifluoride. The naphthol was added during ten minutes and the treatment with boron trifluoride continued for two hours at 80–90° when 22 g. had been absorbed. Dilution with water gave a clear orange-red solution. Examination of the sodium, barium and β-naphthylamine[5] salts indicated that the chief material is the 3,6-disulfonic acid.

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[5] Forster and Keyworth, *J. Soc. Chem. Ind.*, **46**, 26T (1927).

DEPARTMENT OF CHEMISTRY
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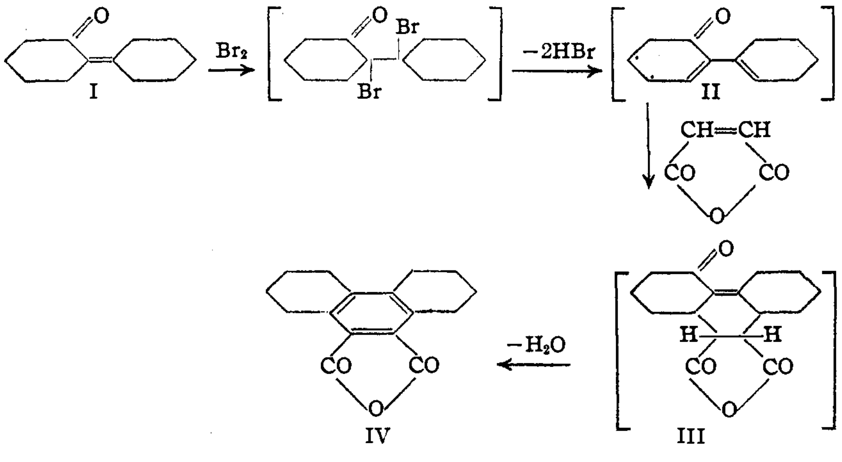
A Novel Preparation of *sym*-Octahydrophenanthrene-9,10-dicarboxylic Anhydride

BY CHARLES C. PRICE, MARTIN KNELL AND JAMES P. WEST

The ready availability of 2-cyclohexylidenecyclohexanone (I) through the hydrogen chloride-catalyzed condensation of cyclohexanone with itself[1] suggested the possibility that this compound might be a useful raw material for the synthesis of hydrophenanthrene derivatives. For example, the addition of bromine to the double bond[2] followed by dehydrohalogenation[3] should form 2-ketobicyclohexenyl (II).



Since the diene system of bicyclohexenyl itself is capable of undergoing a normal Diels–Alder condensation with maleic anhydride,[4] it was anticipated that treatment of II with maleic anhydride should yield 4-keto-*sym*-dodecahydro-9,10-phenanthrenedicarboxylic anhydride (III).

All attempts to isolate 2-ketobicyclohexenyl from the bromination and dehydrohalogenation of 2-cyclohexylidenecyclohexanone have failed. Evidently the compound is susceptible to polymerization, even at room temperature, since the only product obtainable was a non-volatile, pale tan, thermoplastic resin.

It was possible to carry out the Diels–Alder reaction with II only as formed in the reaction mixture. 2-Cyclohexylidenecyclohexanone was brominated in the cold (dry ice–acetone bath), maleic anhydride was then added and the mixture was allowed to warm slowly to room temperature. By this procedure, 2-cyclohexylidinecyclohexanone was converted to *sym*-octahydrophenanthrene-9,10-dicarboxylic anhydride (IV, 16% yield) identical with the material reported by Weidlich.[5]

A blank experiment showed the bromine to be essential since, in its absence, the starting materials, 2-cyclohexylidenecyclohexanone and maleic anhydride, were recovered unchanged.

Since the expected keto-anhydride III was not isolated, the initial addition of maleic anhydride to II may well have followed some other course than that indicated in the equations.

Experimental

2-Cyclohexylidenecyclohexanone (I).—Dry hydrogen chloride was passed into freshly distilled cyclohexanone (320 g.) cooled in an ice-bath and the resulting crystalline mass was shaken with 10% sodium hydroxide according to Rapson's directions.[1b] Ether extraction and vacuum distillation yielded 200 g. (70%) of 2-cyclohexylidenecyclohexanone, b. p. 149–150° (22 mm.). The semicarbazone melted at 187–188° (lit., 189–190°).[1a]

Addition of Halogen.—Attempts to add bromine or chlorine, directly or by means of sulfuryl chloride, at temperatures ranging from 25 to −78° under air or nitrogen atmosphere and in chloroform or ether solution gave essentially the same results. Hydrogen halide was eliminated spontaneously and a viscous, deep purple-red oil was formed. On addition of a base such as piperidine or aqueous alkali, the color faded to pale tan but acidification with aqueous hydrochloric acid regenerated the deep purple-red color. The material, either before or after treatment with a base, was non-volatile; even attempts at molecular distillation under 10^{-3} mm. pressure failed. The residue from all attempted distillations was a pale tan, red-green fluorescent, thermoplastic resin. This resin was insoluble in water, phosphoric acid, hydrochloric acid and alkali, sparingly soluble in alcohol and ether and soluble in sulfuric acid. It was essentially halogen-free; one sample was found to contain 0.67% chlorine.

***sym*-Octahydrophenanthrene-9,10-dicarboxylic Anhydride (IV).**—A solution of 13 ml. (0.25 mole) of bromine in 100 ml. of anhydrous ether was added slowly to a stirred solution of 50 ml. (0.25 mole) of 2-cyclohexylidenecyclohexanone in 200 ml. of anhydrous ether. The solution was stirred vigorously and cooled by means of a dry ice–methanol bath. The color of the bromine was discharged instantly, even at this temperature. After the addition of

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[1] (a) Zelinsky, Schuikin and Fatejew, *J. Gen. Chem.*, U. S. S. R., **2**, 671 (1932). (b) Rapson, *J. Chem. Soc.*, 15 (1941).

[2] See, *e. g.*, Claisen and Claparete, *Ber.*, **14**, 2460 (1881).

[3] See, *e. g.*, Zelinsky and Gorsley, *ibid.*, **41**, 2479 (1908).

[4] Gruber and Adams, THIS JOURNAL, **57**, 2555 (1935).

[5] Weidlich, *Ber.*, **71**, 1208 (1938).

bromine was completed, 49 g. (0.50 mole) of maleic anhydride was added and the stirring was continued for one hour while the mixture was still immersed in the dry ice-methanol bath. The flask was then removed and, as the solution warmed to room temperature, it turned dark red. After two hours of boiling under reflux, the ether was evaporated, leaving a gummy red solid. Recrystallization removed the heavy red oil that resulted from decomposition of the bromination product. From acetic anhydride, the solid product, ***sym*-octahydrophenanthrene-9,10-dicarboxylic anhydride (IV)**, separated as long colorless needles; from ethyl acetate as colorless platelets, m. p. 312° (Maquenne block) (lit., 310°).[5] The over-all yield was 10 g. (16%).

Anal. Calcd. for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29; mol. wt., 256; sap. eq., 128. Found: C, 75.12; H, 6.45; mol. wt., 285; sap. eq., 130.

The identity of the anhydride (IV) was further established by decarboxylation with soda lime followed by dehydrogenation with selenium to yield phenanthrene, which was identified by melting point and mixed melting point.

From an experiment identical with the above except that the bromine was omitted, the starting materials, 2-cyclohexylidenecyclohexanone and maleic anhydride, were recovered.

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Identification of Alkylbenzenes. III. The Acetamino and Benzamino Derivatives of Isobutylbenzene

BY V. N. IPATIEFF AND LOUIS SCHMERLING

In previous papers[1] the characterization of all but one of the monoalkylbenzenes from toluene through the eight amylbenzenes was described. The mono- and diacetamino and monobenzamino derivatives of the exception, isobutylbenzene, have since been prepared and are reported here in order to make the series complete.

TABLE I

PREPARATION OF ISOBUTYLBENZENE

Method	Reactants, g.	Conditions: Temp.	Conditions: Time, hr	Isobutylbenzene: Yield, g.	Isobutylbenzene: B. p., °C.	Isobutylbenzene: $n^{20}D$
A	C_6H_5Br,[a] 31; i-C_4H_9-Br, 27; Na, 9	Room	24	8	164–170	1.4912
B	$C_6H_5CH_2MgCl$,[b] 75; i-C_3H_7Br, 62	Reflux	120	7	166–170	1.4891

[a] Dissolved in 50 cc. benzene. [b] Dissolved in 275 cc. ether.

TABLE II

DERIVATIVES OF ISOBUTYLBENZENE

Derivative	M. p., °C. (uncor.)	Crystalline appearance	Nitrogen, %: Calcd.	Nitrogen, %: Found
i-$C_4H_9C_6H_4NHCOCH_3$[a]	127–128[b]	Pearly flakes	7.33	7.23
i-$C_4H_9C_6H_3(NHCOCH_3)_2$	210–211[c]	White	11.29	11.54
i-$C_4H_9C_6H_4NHCOC_6H_5$	128–129[d]	Pearly flakes	5.53	5.52

[a] Hickinbottom and Preston, *J. Chem. Soc.* 1566 (1930); see, also, Hennion and Auspos, THIS JOURNAL, **65**, 1605 (1943). [b] Mixed m. p. (1:1 mixture) with monoacetamino-*s*-butylbenzene (m. p. 126°), 108–112°. [c] Mixed m. p. (1:1 mixture) with diacetamino-*t*-butylbenzene (m. p. 210°) 190–195°; with diacetamino-*n*-butylbenzene (m. p. 214°), 204–206°. [d] After recrystallization from hexane. The crude derivative was rather difficultly purified. Recrystallization from alcohol usually yielded material melting at about 118–122°.

Isobutylbenzene was prepared in 30% yield by the Fittig reaction between phenyl bromide and isobutyl bromide and in 10% yield by the reaction between benzylmagnesium chloride and isopropyl bromide (Table I). That very little or no isomerization occurred during the reactions was shown by the fact that both preparations yielded identical derivatives.

The derivatives were prepared by the procedure described in the previous papers. Their properties are given in Table II. Both the mono- and the diaminoisobutylbenzene could be isolated from a single nitration product, separation being effected as usual by extracting the tin salt of the monoamine with ether.

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[1] Ipatieff and Schmerling, THIS JOURNAL, **59**, 1056 (1937); **60**, 1476 (1938).

The Preparation of 4'-Aminobenzanilide

BY CARL E. SPENCER

During recent synthetic work, 4'-aminobenzanilide was required. Methods previously described for its preparation using tin and hydrochloric acid[1] or iron and acetic acid[2] proved unsatisfactory because of undesirable by-products. It was found that it could be prepared readily in excellent yield and high purity from 4'-nitrobenzanilide by reduction with hydrogen using platinum black as a catalyst.

The 4'-nitrobenzanilide was prepared from *p*-nitroaniline (Eastman Practical grade) by the method of Lettré and Barnbeck[3] with a yield of 72%, m. p. 197–198°. Twenty-four grams of it in 100 ml. of ethanol with 1 ml. of 0.1 *M* ferrous sulfate was added to platinum black prepared by the reduction of 0.1 g. of platinum oxide in 100 ml. of ethanol by hydrogen at 50 lb. pressure. The reaction

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[1] Hübner, *Ann.*, **208**, 295 (1881); Rivier and Zeltner, *Helv. Chim. Acta*, **20**, 691–704 (1937).

[2] Morgan and Micklethwait, *J. Chem. Soc.*, **87**, 933 (1905).

[3] Lettré and Barnbeck, *Ber.*, **71**, 1227 (1938).