shown to be dependent upon enolization and the dissociation of enolic forms. Increasing dissociation occurs upon dilution for cyclic β-diketones, but does not occur for non-cyclic β-diketones. In both cases, however, dissociation does take place upon the addition of alkali and the absorption spectra are shifted toward longer wave lengths.

The spectra of several bromo derivatives of 5,5-dimethylcyclohexanedione-1,3 have been determined. Photochemical reduction of 2,2-dibromo derivatives of 5,5-dimethylcyclohexanedione-1,3 has been shown to occur with the formation of the corresponding 2-monobromo compounds.

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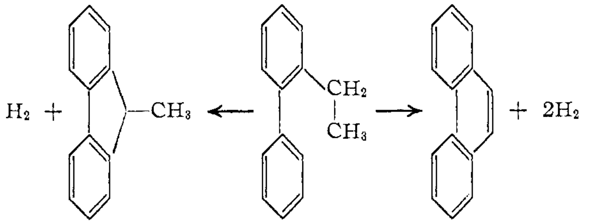
[CONTRIBUTION FROM THE CENTRAL EXPERIMENT STATION, BUREAU OF MINES]

Aromatic Cyclodehydrogenation. III. Experiments with 2-Ethylbiphenyl[1]

BY MILTON ORCHIN[2]

Previous communications[3] have dealt with the cyclodehydrogenation of 2-methylbiphenyl and 2,2′-dimethylbiphenyl and their conversion to the fluorene nucleus by vapor-phase treatment with a palladium catalyst. It was of interest to determine the fate of 2-ethylbiphenyl (I) under the same conditions. If cyclodehydrogenation proceeded without the loss of a carbon atom, either 9-methylfluorene (II) or phenanthrene (III) or both could be formed.



II I III

2-Ethylbiphenyl was synthesized by the reaction of ethylmagnesium bromide with 2-phenylcyclohexanone. The gas evolved in this reaction corresponded to about 10% enolization which is considerably less than the 50% reported[4] for this ketone in the Reformatsky reaction. The crude carbinol isolated from the Grignard reaction was dehydrated to 2-ethyltetrahydrobiphenyl (IV), and IV dehydrogenated to I by treatment with sulfur.

Treatment of ethylbiphenyl at about 480° with palladium-charcoal gave both 9-methylfluorene and phenanthrene, but the major product was fluorene (V). Similar treatment of the tetrahydro derivative, IV, likewise gave all three conversion products. Since both phenanthrene, III, and fluorene, V, were isolated after similar cyclodehydrogenation of 9-methylfluorene, there is a possibility that the latter may be an intermediate in the formation of III and V. Graebe[5] achieved the thermal conversion of 9-methylfluorene to phenanthrene by passing the former through a glowing tube but made no mention of the loss of a methyl group. The survival of 9-methylfluorene under the conditions of the present experiments and its presence in the conversion products from ethylbiphenyl and the ethyl-tetrahydrobiphenyl is probably a function of the contact time with the catalyst, a factor which is difficult to control with small quantities and the type of catalyst used in these experiments.

Experimental[6]

2-Ethyl-tetrahydrobiphenyl, IV.—To the Grignard solution prepared from 78 g. of ethyl bromide, 18 g. of magnesium and 440 cc. of dry ether, there was added dropwise with stirring, a solution of 118 g. of 2-phenyl-cyclohexanone[4] in 200 cc. of benzene and 50 cc. of ether. During the addition about 1.3 liters (N. T. P.) of gas was liberated. The mixture was refluxed eighteen hours. About 200 cc. of ether was then distilled from the mixture, whereupon it was decomposed with ammonium chloride solution. The organic fraction, on distillation through a Widmer column, gave 117.4 g. (85%) 1-ethyl-2-phenylcyclohexanol, b. p. 120–121° (5–6 mm.). The carbinol (101 g.) was refluxed with 350 cc. of 90% formic acid for three and one-half hours. The top layer was separated and combined with a benzene extract of the acid bottom layer. The benzene solution was washed, dried and evaporated and the residue distilled. There was obtained 65.6 g. (71%) ethyl-tetrahydrobiphenyl, colorless liquid, b. p. 103–105° (5–6 mm.). Analysis indicated the presence of a small quantity of an oxygenated compound. A second treatment with formic acid did not remove the oxygen. An ethanol solution of the material was then treated with semicarbazide hydrochloride and sodium acetate. The material recovered after this treatment had b. p. 93–93.5° (3–4 mm.), $n^{20}{}_D$ 1.5417, $d^{20}{}_4$ 0.961. *Anal.* Calcd. for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.1; H, 9.8. No attempt was made to prove the location of the double bond.

2-Ethylbiphenyl, I.—A mixture of 14.7 g. of IV and 5.05 g. of sulfur was heated at 210–240° for one and one-half hours and distilled *in vacuo.* The crude distillate (8.1 g.) was dissolved in petroleum ether and chromatographed on alumina. The first portion to come through was rejected. The balance of the hydrocarbon was recovered from the petroleum ether by distillation whereupon there was obtained 6.1 g. (42%) 2-ethylbiphenyl, b. p. 93–94° (2–3 mm.), $n^{20}{}_D$ 1.5808. *Anal.* Calcd. for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found[7]: C, 92.0; H, 8.0.

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[1] Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior. Not copyrighted.

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[3] (a) Orchin and Woolfolk, THIS JOURNAL, **67**, 122 (1945); (b) Orchin, *ibid.*, **67**, 499 (1945).

[4] Newman and Farbman, *ibid.*, **66**, 1550 (1944).

[5] Graebe, *Ber.*, **37**, 4146 (1904).

[6] All melting points corrected. Analyses by Dr. T. S. Ma, University of Chicago, unless otherwise noted.

[7] Bureau of Mines, Coal Analysis Section.

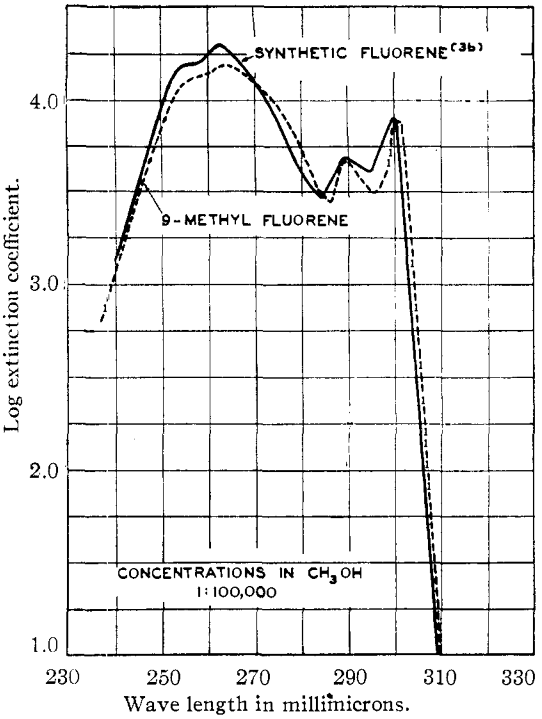

Fig. 1.—Ultraviolet absorption spectra.

9-Methylfluorene, II.—This compound was prepared from fluorenone and methylmagnesium iodide as described by Badger.[8] After recrystallization from methanol it had melting point 45–45.8°.

Cyclodehydrogenation Experiments.—The apparatus and catalyst used for the dehydrogenation of liquid compounds have been described previously.[3a] 2-Ethylbiphenyl (4.5 g.) was passed over the catalyst at 475–480° during the course of one hour. The product (3.3 g.) was a mixture of solids which fluoresced strongly in ultraviolet light. The mixture was dissolved in petroleum ether and chromatographed on a column of alumina. Three bands were obtained. The top, most strongly adsorbed band gave a light blue fluoresence; it contained the phenanthrene. The middle band gave a purple fluorescence and contained fluorene and 9-methylfluorene. The balance of the column did not fluoresce in ultraviolet light; it contained unchanged 2-ethylbiphenyl. The bands were eluted by washing with petroleum ether that was diluted with increasing quantities of benzene, the percolate receivers being changed to collect each band separately. Phenanthrene and 2-ethylbiphenyl were readily isolated in this way. The fluorene and 9-methylfluorene were collected together since some difficulty was anticipated[9] in their separation from each other by chromatographic adsorption. It was at first thought that the estimation of the quantities of each of these latter two substances in a mixture containing only the two of them could be accomplished by ultraviolet absorption spectrum measurements. However, the methyl group in the 9-position of fluorene produced such a small bathochromic shift (Fig. 1) that ultraviolet absorption analysis was impracticable.[10] The fraction containing the methylfluorene and fluorene was then rechromatographed. The first portion to come through the column contained pure 9-methylfluorene and the last portion, pure fluorene. The intermediate portion containing the mixture was then rechromatographed and the same procedure repeated several times. By chromatographic separation it was thus possible to isolate in a quite good state of purity the following compounds in the stated quantities: 0.59 g. of 2-ethylbiphenyl, 1.04 g. of fluorene, 0.20 g. of phenanthrene, and 0.61 g. of 9-methylfluorene. The last three compounds were compared with authentic specimens by melting point and mixed melting point determinations and the first by refractive index. Phenanthrene was characterized further by formation of its complex with *s*-trinitrobenzene. Preliminary runs indicated that the ratio of components of the reaction mixture varies with the time of passage over the catalyst. Too much importance, therefore, should not be attached to the various proportions of compounds found.

The cyclodehydrogenation of 2-ethyl-tetrahydrobiphenyl (9.5 g.) was performed at 490° during the course of four and one-half hours. From the product (8 g.) it was possible to isolate the following compounds in the approximate quantities indicated: 3.8 g. of 2-ethylbiphenyl, 2.5 g. of fluorene, 1.0 g. of phenanthrene, and 0.2 g. of 9-methylfluorene.

One and one-half grams of 9-methylfluorene was passed over the palladium–charcoal catalyst in a modified apparatus[11] at 485–490° during the course of one and one-half hours. The product (1 g.) was separated into 0.38 g. of pure fluorene and 0.47 g. of pure phenanthrene. A small quantity (about 5 mg.) of a high molecular weight material which formed a trinitrobenzene complex, m. p. 175–178°, was also obtained but was not further investigated. No 9-methylfluorene could be isolated.

Summary

Treatment of 2-ethylbiphenyl or 2-ethyl-tetrahydrobiphenyl in the vapor phase at 475–490° with a palladium catalyst gave a mixture of fluorene, 9-methylfluorene and phenanthrene. 9-Methylfluorene under similar conditions gave fluorene and phenanthrene.

PITTSBURGH, PA. RECEIVED NOVEMBER 28, 1945

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[8] Badger, *J. Chem. Soc.*, 535 (1941).

[9] Wieland and Probst, *Ann.*, **530**, 274 (1937).

[10] The author wishes to thank Dr. R. A. Friedel and Miss Lois Jean Lutz for the ultraviolet absorption measurements.

[11] Orchin, *Ind. Eng. Chem., Anal. Ed.*, **17**, 673 (1945).