anhydrous ether was added, the ammonia was allowed to evaporate (3 hours). The gray-brown ether suspension was refluxed for 24 hours and decomposed by dropwise addition of 200 ml. of water. The water layer, after washing with ether until the ether washes were no longer colored, was acidified, and the liberated oil taken up in ether. After drying over drierite the solvent was removed and the residue distilled to give 57.15 g. (74%) of 2-methylbenzyl mercaptan (XIII), b.p. 57–58° at 5 mm., $n^{25}{}_{\mathrm{D}}$ 1.5702. The characteristic mercaptan odor was particularly pronounced with this product.

Anal. Calcd. for $C_8H_{10}S$: C, 69.51; H, 7.29. Found: C, 69.65; H, 7.01.

When 1.2 moles of potassium amide (which is a 20% excess) was used with 1.0 mole of the sulfide (X) the yield of the mercaptan was only 18% (70% of the starting material being recovered) even though the reaction mixture was refluxed 48 hours. However, the yield of the mercaptan was 68% when the reaction was carried out in a mixture of five parts of toluene and one part of dioxane (refluxed 12 hours), with only a 10% excess of the potassium amide.

The 2,4-dinitrophenyl thioether of the mercaptan, prepared by the usual method, melted at 167–168° after recrystallization from a mixture of benzene and ethanol.

Anal. Calcd. for $C_{14}H_{12}O_4N_2S$: C, 55.75; H, 3.98. Found: C, 55.86; H, 4.09.

Desulfurization of the mercaptan (XIII) by the general method of Papa and co-workers[17] yielded *o*-xylene, b.p. 142–143°, which was further identified by its sulfonamide, m.p. 143–144°.[18] A mixed melting point with an authentic sample of 3,4-dimethylbenzenesulfonamide, m.p. 143–144°, was the same.

Independent synthesis of mercaptan XIII, b.p. 57–58° at 5 mm., $n^{25}{}_{\mathrm{D}}$ 1.5708, was effected in 40% yield by refluxing an alcoholic solution of *o*-xylyl bromide and sodium hydrosulfide (in 20% excess) for one hour. The 2,4-dinitrophenyl thioether of this product melted at 167–168°. A mixed melting point with a sample of the thioether prepared from mercaptan XIII obtained from the rearrangement was the same.

Conversion of Mercaptan XIII to Sulfide XIV and Sulfone XV.—To a stirred solution of 46 g. (0.33 mole) of 2-methylbenzyl mercaptan (XIII) in 240 ml. of 15% sodium hydroxide solution (25% excess) were added dropwise 50 g. (20% excess) of dimethyl sulfate, and the mixture refluxed for two hours. Considerable heat was evolved during the addition and the oily 2-methylbenzylmethyl sulfide soon began to separate. The mixture was cooled and the oil taken up in ether. After drying over drierite, the solvent was removed and the residue distilled *in vacuo* to yield 44.65 g. (88%) of strong smelling 2-methylbenzylmethyl sulfide (XIV), b.p. 67–68° at 1 mm., $n^{25}{}_{\mathrm{D}}$ 1.5599.

Anal. Calcd. for $C_9H_{12}S$: C, 71.00; H, 7.95. Found: C, 71.30; H, 7.67.

Oxidation of 2.65 g. of the sulfide (XIV) in 2 ml. of glacial acetic acid with 6 ml. 30% hydrogen peroxide (added cautiously) gave, after heating on the steam -bath for 30 minutes and standing at room temperature for two days, 2.12 g. (66%) of 2-methylbenzylmethyl sulfone (XV), m.p. 77–78° after two recrystallizations from a mixture of benzene and heptane.

Anal. Calcd. for $C_9H_{12}O_2S$: C, 58.86; H, 6.52. Found: C, 58.88; H, 6.28.

Rearrangement of Benzyldimethylsulfonium Ion (XVIII) to 2-Methylbenzylmethyl Sulfide (XIV).—To a stirred suspension of 0.413 mole of sodium amide in one liter of liquid ammonia[19] was added, over a period of 25 minutes, 87.5 g. (0.375 mole) of benzyldimethylsulfonium bromide.[20] During the first 5 minutes of the addition a green color developed which changed to a rich violet and finally a gray-brown after almost all of the salt had been added.

The resulting solution was stirred for one hour, 400 ml. of ether added, and stirring continued until the ammonia had evaporated. After adding water, the ether layer was separated, washed with water, and dried over drierite. The solvent was removed and the residue distilled *in vacuo* to yield 29.15 g. (51%) of 2-methylbenzylmethyl sulfide (XIV), b.p. 61–63° at 0.5 mm., $n^{25}{}_{\mathrm{D}}$ 1.5600.

Oxidation of a sample of this sulfide gave sulfone XV, melting at 76–78°. A mixed melting point with a sample of the sulfone prepared as described above was the same.

When the time of addition of the sulfonium salt to the sodium amide suspension was reduced to 15 minutes the yield of sulfide was 41%. When the addition time was 5 minutes no sulfide was obtained and no identifiable material was isolated.

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(17) D. Papa, E. Schwenk and H. F. Ginsberg, *J. Org. Chem.*, **14**, 723 (1949).

(18) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1940, p. 91.

(19) R. Levine and C. R. Hauser, THIS JOURNAL, **66**, 1770 (1944).

(20) F. E. Ray and J. L. Farmer, *J. Org. Chem.*, **8**, 391 (1943).

DURHAM, N. C.

[CONTRIBUTION FROM THE SCIENTIFIC DEPARTMENT, ISRAELI MINISTRY OF DEFENCE]

A New Synthesis of 4,5-Dimethylphenanthrene

BY ERNST D. BERGMANN AND ZVI PELCHOWICZ[1]

RECEIVED DECEMBER 15, 1952

The synthesis of 4,5-dimethylphenanthrene from 6,6′-dimethyldiphenic acid is described. The essential step is the reaction between phenyllithium and 2,2′-bis-(bromomethyl)-6,6′-dimethylbiphenyl (II).

The observation[2] that 2,2′-bis-(bromomethyl)-biphenyl is converted into 9,10-dihydrophenanthrene by reaction with phenyllithium opens a new and general route from the biphenyl into the phenanthrene series. As the method can be applied also to the synthesis of fairly complex phenanthrene derivatives, such as 3,4,5,6-dibenzophenanthrene,[3] it seemed interesting to investigate whether it could be utilized for the preparation of "sterically hindered" 4,5-disubstituted phenanthrene derivatives. Indeed, 4,5-dimethylphenanthrene could thus be prepared in an over-all yield of 47% from 2-nitro-3-methylbenzoic acid by the method indicated in the chart.

2-Amino-3-methylbenzoic acid, prepared from the nitro compound by catalytic hydrogenation, was converted *via* the diazonium salt into 6,6′-dimethyldiphenic acid (I), and the latter reduced by means of lithium aluminum hydride. Successive treatment of the dialcohol so obtained, with phosphorus tribromide (to give II) and lithium phenyl gave 4,5-dimethyl-9,10-dihydrophenanthrene (III) which was dehydrogenated by means of palladium to IV.

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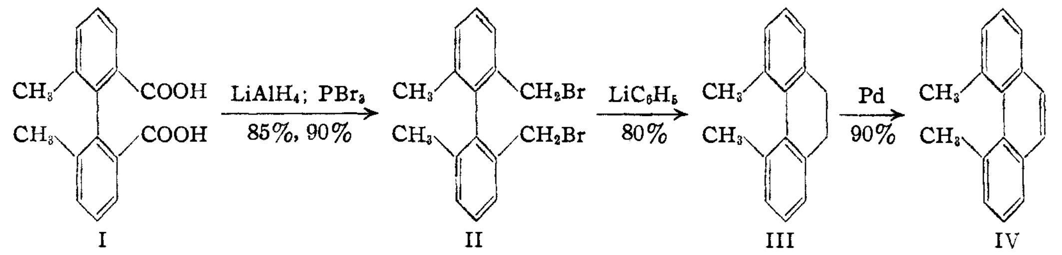
[1] Part of a thesis presented by Z. Pelchowicz to the Hebrew University, Jerusalem, in partial fulfillment of the requirements for the degree of Ph.D.

[2] D. M. Hall and E. E. Turner, *Nature*, **163**, 537 (1949); D. M. Hall, M. S. Lesslie and E. E. Turner, *J. Chem. Soc.*, 711 (1950); D. M. Hall and E. E. Turner, *ibid.*, 3072 (1951).

[3] E. Bergmann and J. Szmuszkovicz, THIS JOURNAL, **73**, 5153 (1951).



Newman and Whitehouse[4] have prepared IV by a five-step process from pyrene with an over-all yield of 35.5%.[5] A sample of the hydrocarbon, kindly supplied by Dr. Newman, proved identical with the end-product of the synthesis, the 2,4,7-trinitrofluorenone derivative had the expected melting point, and also the ultraviolet absorption spectrum was practically identical with that reported by Newman and Whitehouse.

Newman and Whitehouse		Present authors
λmax	log ε	log ε
224	3.91	4.14
230	3.98	4.13
235	3.84	4.00
255	4.56	4.67
285	3.73	3.86
301	3.91	4.02
307	3.82	3.93
313	3.92	4.03

Of theoretical interest is the spectrum of 4,5-dimethyl-9,10-dihydrophenanthrene (III) (Fig. 1), in comparison with that of 9,10-dihydrophenanthrene.[6] As recently pointed out,[6e] the band of the latter situated at 2635 Å. (ε 18,000) is the normal one of biphenyl, whilst the longer band at 2995 Å., but of lower intensity (ε 4,750), represents a biphenyl in which the central bond is sufficiently twisted[7] to impede coplanarity and to permit the unconjugated benzene rings an independent contribution to the absorption spectrum.

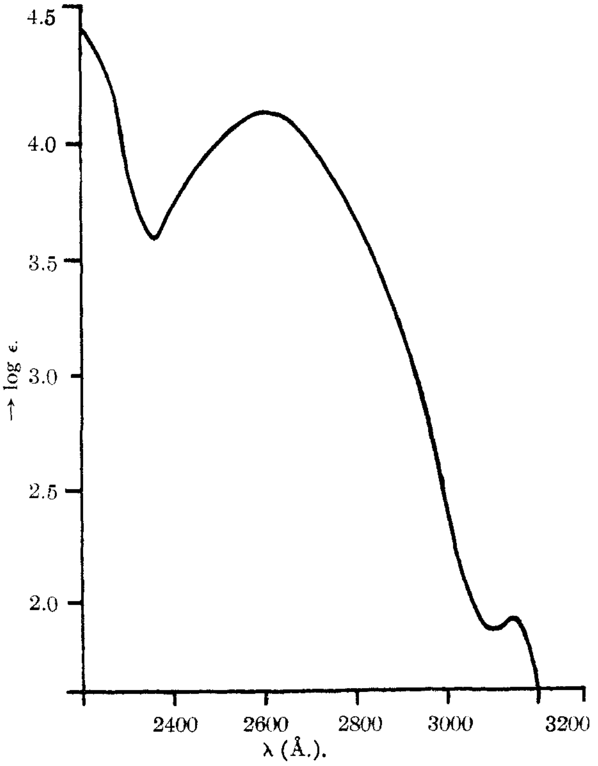


Fig. 1 —Ultraviolet spectrum of 4,5-dimethyl-9,10-dihydrophenanthrene (III) in alcohol.

Accordingly, in 4,5-dimethoxy-9,10-dihydrophenanthrene[6a]) in which the twisting effect is increased by the substituents in 4- and 5-position, the biphenyl band (2720 Å.) is of lower intensity (ε 13,500) whilst the second band (at 3045 Å.) shows increased intensity (ε 9,300), and fine structure (new band at 2930 Å., ε 8,650). In III, the band at 2610 Å. has ε 25,900, that at 3140 Å. the very low intensity of 156. This is not what one should expect from the greater bulk of the methyl, as compared with the methoxy group.[8]

Experimental

2-Amino-3-methylbenzoic Acid.—2-Nitro-3-methylbenzoic acid (from alcohol, m.p. 222–223°)[9] was catalytically hydrogenated in methanol solution at room temperature and under a pressure of 1–3 atm., over Raney nickel. The yield was the theoretical, and the colorless crystals had m.p. 176° (literature, 172°,[10–12] 168–169°[13]).

6,6'-Dimethyldiphenic Acid (I).—The foregoing amino acid was diazotized and reduced by the method described[14] for the preparation of diphenic from anthranilic acid. Recrystallized from alcohol, it formed slightly yellowish crystals of m.p. 237° (dec.) (literature[15] 230°).

Dimethyl 6,6'-Dimethyldiphenate.—A mixture of 16 g. of the preceding acid, 250 cc. of methanol and 10 cc. of concentrated sulfuric acid was refluxed for 4 hours. The ester, isolated in 80% yield, was an oil, b.p. 140–142° (0.2 mm.).

2,2'-Bis-(hydroxymethyl)-6,6'-dimethylbiphenyl.—It was found more convenient to prepare the dialcohol from the acid I than from the ester. A suspension of the acid (12 g.) in ether was added to the solution of 5 g. of lithium aluminum hydride (3 mole per mole of the acid) in 500 cc. of an-

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[4] M. S. Newman and H. S. Whitehouse, This Journal, 71, 3664 (1949).

[5] Assuming the highest possible yield (34%) in the ozonization of pyrene according to H. Vollmann, et al., Ann., 531, 1 (1937).

[6] (a) F. H. Askew, J. Chem. Soc., 509 (1935); (b) L. C. Craig, W. A. Jacobs and G. I. Lavin, J. Biol. Chem., 139, 277 (1941); (c) N. Jones, This Journal, 63, 1658 (1948); (d) E. A. Braude, J. Chem. Soc., 1902 (1949); (e) G. H. Beaven, D. M. Hall, M. S. Lesslie and E. E. Turner, ibid., 854 (1952).

[7] The angle of twist is about 20° according to Jones, ref. 6c.

[8] Compare the well-known fact that 6-methoxy substituted diphenic acids have a much higher rate of racemization than the corresponding methyl compounds. R. Adams and J. B. Hale, This Journal, 61, 2825 (1939); R. Adams and G. C. Finger, ibid., 61, 2828 (1939). Equally, 6,6'-dimethoxydiphenic acid is racemizable (E. McMahon and R. Adams, ibid., 55, 706 (1933)). 6,6'-diamino-2,2'-ditolyl is not (J. Meisenheimer and M. Hoering, Ber., 60, 1425 (1927)).

[9] E. Mueller, Ber., 42, 423 (1909).

[10] H. L. Wheeler and Ch. Hoffman, Am. Chem. J., 45, 445 (1910).

[11] O. Jacobson, Ber., 14, 2354 (1881).

[12] W. Findeklee, ibid., 38, 3555 (1905).

[13] P. Freundler, Bull. soc. chim. France, [4] 1, 222 (1895).

[14] "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., p. 222.

[15] F. Mayer, Ber., 44, 2298 (1911).

hydrous ether, and refluxed for four hours. The product was decomposed with ice and dilute sulfuric acid and the ethereal solution washed with sodium bicarbonate solution and water, dried and concentrated. The solid residue was recrystallized from benzene and melted at 125°; yield 85%.

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.3; H, 7.4. Found: C, 79.5; H, 7.5.

2,2′-Bis-(bromomethyl)-6,6′-dimethylbiphenyl (II).—To a suspension of 9 g. of the dialcohol in 300 cc. of anhydrous benzene, which contained a few drops of pyridine, there was added at room temperature 28 g. of phosphorus tribromide (2 mole per mole of the dialcohol). During the reaction, the dialcohol dissolves. The reaction was completed by heating at 60° for two hours; the solution was washed with water, and sodium bicarbonate solution and evaporated. Trituration with cold alcohol caused the oily residue to crystallize in analytically pure form, m.p. 69.5–70°; yield 90%.

Anal. Calcd. for $C_{16}H_{16}Br_2$: Br, 43.5. Found: Br, 43.3.

4,5-Dimethyl-9,10-dihydrophenanthrene (III).—From 0.3 g. of lithium metal and 3.7 g. of bromobenzene in 35 cc. of ether, a solution of lithium phenyl was prepared (nitrogen atmosphere) and added slowly to the solution of 5.5 g. of the dibromide II in 130 cc. of ether with vigorous agitation. After one hour at room temperature and a further hour of refluxing, ice and dilute sulfuric acid was added and the ethereal layer washed with bicarbonate solution and water, dried and evaporated. The residual oil (3 g., 98%) was fractionated in a vacuum of 0.2 mm.; b.p. 115–117°, yield 2.4 g. (80%).

Anal. Calcd. for $C_{16}H_{16}$: C, 92.3; H, 7.7. Found: C, 92.4; H, 7.7.

4,5-Dimethylphenanthrene (IV).—The mixture of 0.5 g. of the dihydro compound III, and 0.5 g. of 10% palladium–charcoal was heated for 4 hours at 300° in a current of nitrogen. In order to prevent losses of the hydrocarbon, the reaction vessel was mounted with a water-cooler of finger type.[16] The reaction product was isolated by extraction with ether and purified by slow distillation under 0.1 mm. pressure at 100°. The oil which was thus obtained (0.45 g., 95%), crystallized upon trituration with alcohol; from alcohol, m.p. 76.3–76.7° (literature[4] 76.3–76.9°); mixed m.p. with an authentic specimen no depression.

The 2,4,7-trinitrofluorenone complex was prepared in alcoholic solution and recrystallized from the same solvent. It formed glistening, red needles, m.p. 122° (literature[4] 120.7–121.3°).

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(16) L. F. Fieser, "Experiments in Organic Chemistry," 2nd Edition, D. C. Heath and Co., Boston, Mass., pp. 461–462.

TEL-AVIV, ISRAEL

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF WASHINGTON]

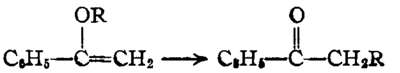
The Thermal Rearrangement of Methyl Benzoate

BY KENNETH B. WIBERG

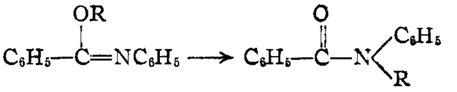
RECEIVED JANUARY 2, 1953

The possibility of observing a thermal rearrangement of methyl benzoate in which the methyl migrates from one oxygen to the other has been investigated using O^{18} as a tracer. No rearrangement was observed under 250°, but at 400° the reaction proceeds at a reasonable rate. A convenient preparation of O^{18}, labeled methanol is also given.

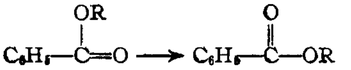
Current studies of the thermal rearrangement of vinyl ethers (A),[1] and of benzimido ethers (B),[2] have led to an investigation of the possibility of observing the corresponding rearrangement of an ester (C). Such a rearrangement, if facile, might effect partial racemization of esters of some optically active alcohols on distillation, and might have other similar consequences.



$$C_6H_5-C(OR)=CH_2 \longrightarrow C_6H_5-C(=O)-CH_2R \quad (A)$$



$$C_6H_5-C(OR)=NC_6H_5 \longrightarrow C_6H_5-C(=O)-N(C_6H_5)R \quad (B)$$



$$C_6H_5-C(OR)=O \longrightarrow C_6H_5-C(=O)-OR \quad (C)$$

It was desired to attempt this reaction using methyl benzoate (I) labeled with O^{18} on the ether oxygen,[3] since it was believed that an especially convenient method of following the reaction could be found, and since the ester is known to be quite stable toward thermal decomposition[4] thus eliminating undesirable side reactions. The most convenient method for the preparation of this ester would be the reaction of benzoyl chloride with O^{18}-enriched methanol. Methanol-O^{18} has been obtained by the fractional distillation of ordinary methanol,[5] and by the hydrolysis of methyl phosphate[6] in acid solution containing H_2O^{18}. The first of these methods is inconvenient and leads to only a small degree of enrichment under practical conditions, whereas in the latter method considerable dimethyl ether forms during the reaction and a product having considerably less O^{18} than the water used is obtained. Furthermore, the conversion of water to methanol is not too favorable unless the water is repeatedly recycled.

In order to find a more convenient method for the preparation of methanol-O^{18}, the reaction between methylmagnesium bromide with O_2^{18} was investigated. This reaction is known to be satisfactory for the preparation of aliphatic alcohols when an excess of oxygen is used.[7] The labeled oxygen was obtained by the electrolysis of H_2O^{18}-enriched water[8] with sulfuric acid. Under conditions employed, 50–70% of the theoretical amount of methanol was obtained, based on the water used. The methanol had only a slightly smaller O^{18}-content than the water, the loss of O^{18} probably being due to exchange with the sulfuric acid[9] during electrolysis. The composition of the methanol was determined from the cracking pattern obtained using a mass spectrometer.

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(1) L. Claisen, *Ber.*, **29**, 2931 (1896).

(2) A. W. Chapman, *J. Chem. Soc.*, 1743 (1927).

(3) As opposed to carbonyl labeled.

(4) E. M. Bilger and H. Hibbert, THIS JOURNAL, **58**, 823 (1936).

(5) I. Roberts and H. C. Urey, *ibid.*, **60**, 2391 (1938).

(6) E. Blumenthal and J. B. M. Herbert, *Trans. Faraday Soc.*, **41**, 611 (1945).

(7) F. Runge, "Organometallverbindungen," Wissenschaftliche Verlagsgesellschaft M. B. H., Stuttgart, 1944, p. 299.

(8) Obtained from the Stuart Oxygen Co. on allocation from the Atomic Energy Commission.

(9) J. Halperin and H. Taube, THIS JOURNAL, **74**, 375 (1952).