yields with *n*-propyl, isopropyl and *n*-butyl alcohols were not made; but the corresponding alkyl 2,4-dinitrobenzene-sulfenates were readily obtained by direct reactions of I and excess of the dry alcohols, by procedures similar to the ones for the methyl and ethyl esters, above. Yields of products (without working up the mother liquors) were: *n*-propyl (m.p. 75–76°, 56%); isopropyl (m.p. 77–78°, 53%)—mixed melting point with the *n*-propyl ester, 56–60°; *n*-butyl (m.p. 53–54°, 68%). Attempts to obtain a similar ester from *t*-butyl alcohol (without using pyridine) were not successful.

Hydrogen Chloride-catalyzed Reactions of the Sulfenate Esters with an External Alcohol.—The methyl ester was recovered (85% yield) unchanged (m.p. and mixed m.p.) after refluxing 1 g. of the ester in 50 ml. of absolute ethanol for 3 hours. The isopropyl ester was similarly recovered after refluxing a solution in absolute methanol for ten hours.

With hydrogen chloride present, rapid alcohol interchange occurred. Thus, into a solution of 200 mg. of pure ethyl 2,4-dinitrobenzenesulfenate, in 25 ml. of absolute methanol at 30°, a gentle stream of dry hydrogen chloride was passed. The solution was refluxed for two minutes,

and most of the solvent distilled rapidly. The cooled residual mixture was filtered, yielding 11 mg. of methyl 2,4-dinitrobenzenesulfenate; yellow needles, m.p. 122–123°. The mixed m.p. with authentic methyl ester was not depressed; mixed m.p. with ethyl ester (m.p. 123–124°) was 110–115°. Dilution of the filtrate with water gave 48 mg. more of methyl ester; total yield 84%. The reverse conversion was effected in 83% yield. Similarly, isopropyl 2,4-dinitrobenzenesulfenate (m.p. 77–78°) yielded the methyl ester (m.p. 121–122°) by refluxing with excess methanol, saturated with hydrogen chloride.

Rearrangement of Benzyl Sulfides to Mercaptans and of Sulfonium Ions to Sulfides Involving the Aromatic Ring by Alkali Amides[1,2]

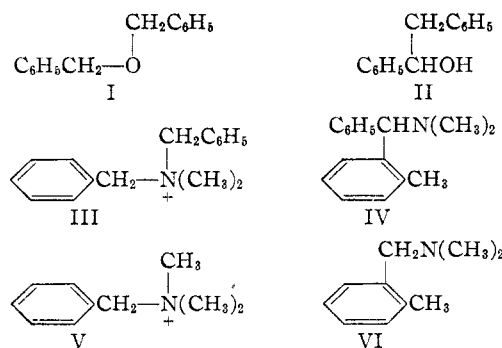By Charles R. Hauser, Simon W. Kantor and Wallace R. Brasen

Certain benzyl sulfides and sulfonium ions were rearranged by alkali amides to form mercaptans and sulfides, respectively. Determination of the structures of the products showed that the type of rearrangement realized involved substitution at the ortho position of the benzene ring like that observed previously with benzyl quaternary ammonium ions. The Stevens 1,2-shift observed with benzyl ethers was not realized. The generality of the ortho substitution type of rearrangement is pointed out.

In general benzyl ethers and benzyl quaternary ammonium ions have exhibited different types of rearrangement with alkali amides. For example, dibenzyl ether (I) undergoes the Stevens 1,2-shift to form carbinol II with potassium amide in refluxing ethyl ether[3] or with sodium amide in liquid ammonia,[4] whereas dibenzyldimethylammonium ion (III) undergoes a rearrangement involving substitution at the ortho position of the benzene ring to form tertiary amine IV with sodium amide in liquid ammonia.[5,6] An interesting series of the latter type of rearrangement has been realized starting with quaternary ammonium ion V and ending with the completely substituted product, the first product being tertiary amine VI.

In the present investigation a study was made of the possible rearrangement of certain benzyl sulfides and sulfonium ions with alkali amides. Since benzyl sulfides have more of a formal resem-

blance to benzyl ethers than to quaternary ammonium ions, the sulfides might be expected to exhibit the Stevens 1,2-shift especially with potassium amide in refluxing ether. However, dibenzyl sulfide (VII) was found to undergo with this reagent the type of rearrangement involving substitution at the ortho position of the benzene ring to form mercaptan VIII (79%). The structure of the product was established by independent synthesis from *o*-tolylmagnesium bromide and benzaldehyde. The 2,4-dinitrophenyl thioether of the mercaptan obtained from this synthesis was identical with that prepared from the rearranged mercaptan. The mechanism of the rearrangement involves presumably the isomerization of an intermediate carbanion in which the benzene ring functions as an acceptor, similar to that proposed for the analogous rearrangement of quaternary ammonium ions.[6]

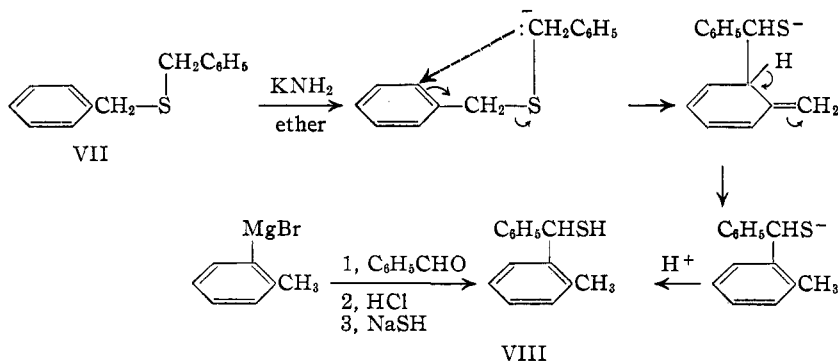(1) Supported by the Office of Naval Research.

(2) Paper III on Isomerization of Carbanions. Presented in part at Conference on Reaction Mechanism, Northwestern University, August, 1950.

(3) C. R. Hauser and S. W. Kantor, This Journal, **73**, 1437 (1951). For the use of lithium phenyl in this rearrangement see G. Wittig and co-workers, *Ann.*, **550**, 260 (1942); **557**, 205 (1947).

(4) A. J. Weinheimer and C. R. Hauser, unpublished result.

(5) S. W. Kantor and C. R. Hauser, This Journal, **73**, 4122 (1951).

(6) It should be mentioned that quaternary ammonium ion III has exhibited the Stevens 1,2-shift with fused sodium amide at 140–150°; T. Thomson and T. S. Stevens, *J. Chem. Soc.*, 1932 (1932). Certain quaternary ammonium ions also exhibit the 1,2-shift with other bases including lithium phenyl; G. Wittig, R. Mangold and G. Felletschin, *Ann.*, **560**, 116 (1948).

VII $\overset{CH_2C_6H_5}{\underset{|}{C_6H_5CH_2-S}}$ $\xrightarrow[\text{ether}]{KNH_2}$ (intermediate with $:CH_2C_6H_5$) $-CH_2-S$ $\longrightarrow$ $C_6H_5CHS^-$ ... $=CH_2$ (with H)

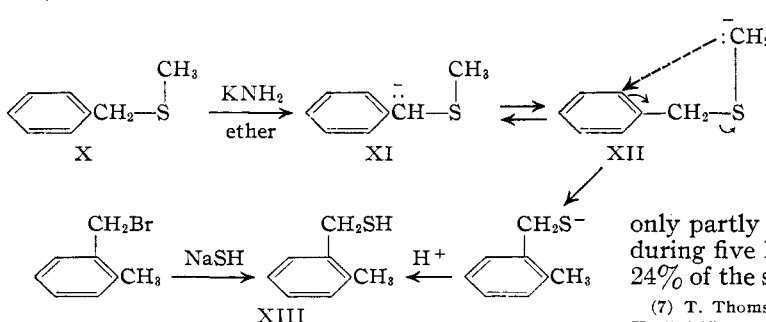$\overset{MgBr}{\underset{|}{C_6H_4CH_3}}$ $\xrightarrow[\substack{2, HCl \\ 3, NaSH}]{1, C_6H_5CHO}$ $\overset{C_6H_5CHSH}{\underset{|}{C_6H_4CH_3}}$ VIII $\overset{H^+}{\longleftarrow}$ $\overset{C_6H_5CHS^-}{\underset{|}{C_6H_4CH_3}}$

were methylated with dimethyl sulfate to form sulfide XIV which was oxidized to sulfone XV.

An attempt to effect the further rearrangement of sulfide XIV into the benzene ring to form the vicinal methyl derivative similar to that realized with the methiodide of VI was unsuccessful, the only products apparently being methyl mercaptan and polymeric material.

The mercaptan obtained from this rearrangement had first been shown not to have structure IX, which would have been formed had the Stevens 1,2-shift occurred. This was established by the synthesis of mercaptan IX from benzylphenylcarbinol. Contrary to the report of earlier workers, mercaptan IX distilled *in vacuo* without appreciable decomposition (see Experimental).

$\overset{CH_2C_6H_5}{\underset{|}{C_6H_5CHOH}}$ $\xrightarrow[\text{2, NaSH}]{\text{1, SOCl}_2}$ $\overset{CH_2C_6H_5}{\underset{|}{C_6H_5CHSH}}$
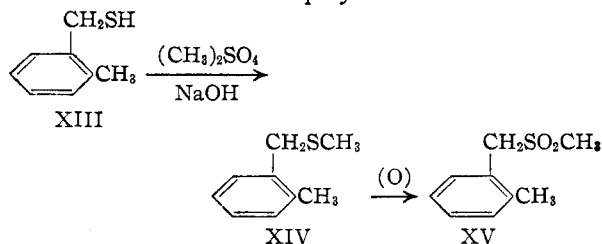
IX
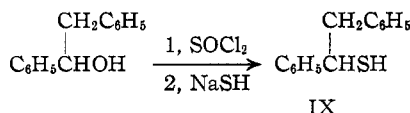
Similarly, benzylmethyl sulfide (X) was found to undergo with potassium amide in refluxing ether the rearrangement involving the benzene ring to form mercaptan XIII (74%). The structure of the product was established by desulfurization with Raney nickel alloy and sodium hydroxide to form *o*-xylene and by independent synthesis from *o*-xylyl bromide. The mechanism of the rearrangement is considered to be analogous to that represented above for dibenzyl sulfide except that the intermediate carbanion undergoing the isomerization is assumed to be XII which, presumably, would be present in the reaction mixture in lower concentrations than carbanion XI. Evidence for the isomerization of a less predominant carbanion was obtained for corresponding rearrangements of quaternary ammonium ions such as the further rearrangement of the methiodide of VI into the benzene ring.[5] It should be mentioned that, whereas quaternary ammonium ion V underwent the rearrangement readily with sodium amide in liquid ammonia, benzylmethyl sulfide (X) appeared to undergo little if any rearrangement with this reagent during three hours.
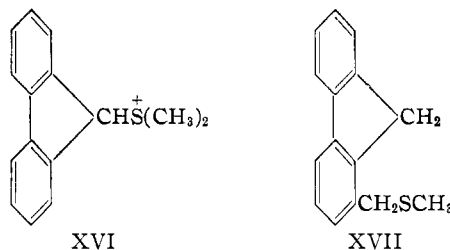
$\overset{CH_2SH}{\underset{|}{C_6H_4CH_3}}$ XIII $\xrightarrow[\text{NaOH}]{(CH_3)_2SO_4}$

$\overset{CH_2SCH_3}{\underset{|}{C_6H_4CH_3}}$ XIV $\xrightarrow{(O)}$ $\overset{CH_2SO_2CH_3}{\underset{|}{C_6H_4CH_3}}$ XV

Although sulfonium ions have generally exhibited the Stevens 1,2-shift with bases,[7] one such ion, XVI, has been observed to undergo the rearrangement involving the benzene ring to form sulfide XVII. The yield was 28% with sodium hydroxide, and 75% when the sulfonium ion was allowed to stand in liquid ammonia for two weeks at room temperature.[8]

(dibenzofuran-type structure) $CH\overset{+}{S}(CH_3)_2$ XVI

(dibenzofuran-type structure) CH_2 ... CH_2SCH_3 XVII

We have found that the more simple sulfonium ion, XVIII, readily undergoes this type of rearrangement with sodium amide in liquid ammonia to form sulfide XIV (51%), which was also obtained by the methylation of mercaptan XIII as described above. The structure of the product from this rearrangement was further established by oxidation to sulfone XV. The mechanism for the rearrangement is considered to be analogous to that represented above for benzylmethyl sulfide in which a less predominant carbanion (XIX) is the reactive intermediate.

Unsuccessful attempts were made to effect the rearrangement of dibenzyl disulfide,[9] dibenzyl sulfone, and dibenzyl sulfoxide under the conditions employed in the present investigation. The disulfide reacted only partly with sodium amide in liquid ammonia during five hours to form benzyl mercaptan (30%), 24% of the starting material being recovered. The

$\overset{CH_3}{\underset{|}{C_6H_4CH_2-S}}$ X $\xrightarrow[\text{ether}]{KNH_2}$ $\overset{CH_3}{\underset{|}{C_6H_4\ddot{C}H-S}}$ XI $\rightleftarrows$ $C_6H_4(-CH_2-S)(:CH_2)$ XII

$\overset{CH_2Br}{\underset{|}{C_6H_4CH_3}}$ $\xrightarrow{NaSH}$ $\overset{CH_2SH}{\underset{|}{C_6H_4CH_3}}$ XIII $\overset{H^+}{\longleftarrow}$ $\overset{CH_2S^-}{\underset{|}{C_6H_4CH_3}}$

Samples of mercaptan XIII obtained from both the rearrangement and the independent synthesis

(7) T. Thomson and T. S. Stevens, *J. Chem. Soc.*, 69 (1932); F. Krollpfeiffer and H. Hartman, *Ber.*, **83**, 90 (1950).

(8) L. A. Pinck and G. E. Hilbert, THIS JOURNAL, **68**, 751 (1946).

(9) We are indebted to the Dow Chemical Company for a sample of this compound.

XVIII

XIX
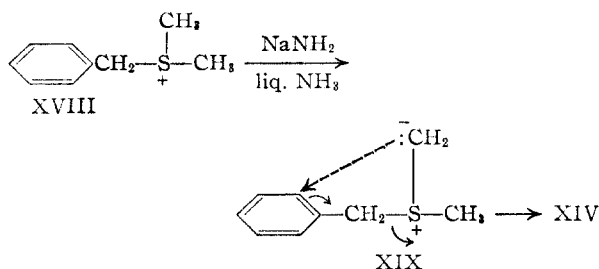
sulfone and sulfoxide were apparently converted to their sodium salts by sodium amide in liquid ammonia, but after replacing the ammonia by ether and refluxing 12 to 15 hours, the starting compounds were largely recovered. It is possible that under more drastic conditions rearrangement might be realized, although Bradley[10] observed no reaction on refluxing dibenzyl sulfone with sodium amide in piperidine for three hours.

Summarizing, the ortho substitution type of rearrangement has been realized with quaternary ammonium ions such as III and V, sulfides VII and X, and sulfonium ions XVI and XVIII. The general mechanism may be indicated by XX in which A is N$^+$, S and S$^+$, respectively. This type of rearrangement has usually been effected with sodium amide in liquid ammonia or potassium amide in ether. The Stevens 1,2-shift, which may be indicated by XXI, has also been observed with quaternary ammonium ions and sulfonium ions but bases other than alkali amides have usually been employed. Moreover certain of the compounds exhibiting this type of rearrangement are not capable of undergoing the other type. Thus far, only the ortho substitution type of rearrangement has been realized with benzyl sulfides, and only the 1,2-shift, with benzyl ethers, although both rearrangements are possible with each of these types of compounds.

XX   XXI
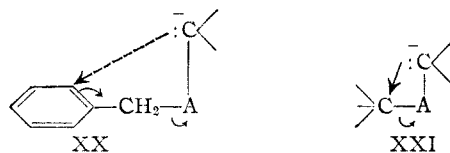
Experimental[11]

Rearrangement of Dibenzyl Sulfide (VII) to 2-Methylbenzohydryl Mercaptan (VIII).—To a stirred solution of 0.2 mole of potassium amide in 250 ml. of liquid ammonia[12] was added a solution of 21.4 g. (0.1 mole) of dibenzyl sulfide in 250 ml. of anhydrous diethyl ether. The reddish brown colored mixture was stirred until all the ammonia had evaporated (about 1.5 hours) and the resulting ethyl ether suspension was refluxed on a steam-bath for 16 hours. The mixture was cooled in an ice-bath and carefully decomposed with 200 ml. of water followed by acidification with hydrochloric acid. The ether layer was separated, washed with water, dried over sodium sulfate and the solvent distilled. The residue was distilled in vacuo to give 16.8 g. (79%) of 2-methylbenzohydryl mercaptan (VIII), boiling at 147–150° at 4 mm., and at 149–150° at 4 mm. on redistillation.

Anal. Calcd. for C$_{14}$H$_{14}$S: C, 78.45; H, 6.58; S, 14.96. Found: C, 78.92; H, 6.50; S, 14.66.

The product apparently contained traces of the corresponding thioketone since it was light blue during and imme-

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(10) W. Bradley, *J. Chem. Soc.*, 548 (1938).

(11) Melting points and boiling points are uncorrected. Analyses are by Clark Microanalytical Laboratory, Urbana, Ill.

(12) R. S. Yost and C. R. Hauser, THIS JOURNAL, **69**, 2325 (1947).

diately after distillation, slowly becoming colorless on standing. It was only sparingly soluble in dilute sodium hydroxide. The sodium salt of the mercaptan precipitated on treatment with 50% sodium hydroxide or on dissolving in benzene and adding sodium. The mercaptan dissolved in cold, concentrated sulfuric acid evolving hydrogen sulfide to form benzohydrol as indicated by the deep red color of the solution. The mercaptan failed to give solid derivatives on oxidation with permanganate.

The 2,4-dinitrophenyl thioether derivative[13] was prepared by adding a solution of 4.3 g. (0.02 mole) of the mercaptan and 0.8 g. (0.02 mole) of sodium hydroxide in 60 ml. of absolute ethanol and 6 ml. of water to a solution of 4.0 g. (0.02 mole) of 2,4-dinitrochlorobenzene in 20 ml. of absolute alcohol. The resulting mixture was refluxed for 10 minutes, filtered hot and allowed to cool. The crude yellow derivative melted at 100–102° and at 122–123° after three recrystallizations from 95% ethanol.

Anal. Calcd. for C$_{20}$H$_{16}$N$_2$O$_4$S: C, 63.14; H, 4.24. Found: C, 63.17; H, 4.42.

Independent synthesis of mercaptan VIII was effected with o-tolylmagnesium bromide and benzaldehyde. The resulting 2-methylbenzohydrol was converted to 2-methylbenzohydryl chloride as described previously.[5] To a stirred solution of 22.5 g. (0.4 mole) of anhydrous sodium hydrosulfide in 200 ml. of absolute ethanol was added 21.7 g. (0.1 mole) of 2-methylbenzohydryl chloride[5] and the resulting mixture was stirred for 6 hours at room temperature and for 12 hours under reflux. After removal of most of the alcohol by distillation the residue was acidified with dilute hydrochloric acid and extracted with ether. The ether extract was washed with water, dried over sodium sulfate and the solvent distilled. The residue was fractionated in vacuo giving, after removal of 2 g. of forerun, 10.8 g. (50%) of crude 2-methylbenzohydryl mercaptan, b.p. 138–146° at 3 mm. The crude product was stirred with 75 ml. of 50% sodium hydroxide solution, and the resulting sodium salt of the mercaptan was filtered off and washed several times with ether. This salt was acidified with dilute hydrochloric acid yielding 8.8 g. (41%) of pure 2-methylbenzohydryl mercaptan, b.p. 145–146° at 3 mm. Its 2,4-dinitrophenyl thioether prepared as described above melted at 122–123°. A mixed melting point with the thioether derivative of the mercaptan obtained from the rearrangement was the same.

α-Mercaptodibenzyl (IX).—A mixture of benzylphenylcarbinol (55.0 g., 0.277 mole) and thionyl chloride (99 g., 0.833 mole) was refluxed 4 hours, and the resulting solution distilled[14] to give an 81% yield of α-chlorodibenzyl, b.p. 127–129° at 0.5 mm. (reported b.p. 180–184° at 16 mm.).[15]

Anal. Calcd. for C$_{14}$H$_{13}$Cl: C, 77.60; H, 6.04; Cl, 16.36. Found: C, 77.90; H, 5.82; Cl, 16.50.

A mixture of 10.84 g. (0.05 mole) of α-chlorodibenzyl and 8.5 g. (0.15 mole) of anhydrous sodium hydrosulfide in 150 ml. of commercial absolute ethanol was allowed to stand for 2 hours and refluxed for 2 hours more. The mixture was poured into 300 ml. of cold water, acidified with dilute hydrochloric acid and extracted with ether. The ether layer was washed with water, dried over sodium sulfate, and the solvent distilled. The residue was fractionated in vacuo to give, after distilling 4.7 g. of material, b.p. 142–146° at 4 mm., 3.4 g. (32%), of α-mercaptodibenzyl (IX) b.p. 146–148° at 4 mm.[16]

The 2,4-dinitrophenyl thioether melted at 132.5–133° after two recrystallizations from ethanol.

Anal. Calcd. for C$_{20}$H$_{16}$N$_2$O$_4$S: C, 63.14; H, 4.24; S, 8.43. Found: C, 63.56; H, 4.25; S, 8.81.

A mixed melting point of this thioether with that prepared from mercaptan VIII was 101–110°.

Rearrangement of Benzylmethyl Sulfide (X) to 2-Methylbenzyl Mercaptan (XIII).—To a stirred solution of 1.3 moles of potassium amide in 1 l. of liquid ammonia was added 77.5 g. (0.56 mole) of benzylmethyl sulfide, and the resulting red-brown solution stirred for 10 minutes. After 600 ml. of

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(13) R. W. Bost, J. O. Turner and R. D. Norton, *ibid.*, **54**, 1985 (1932).

(14) P. A. Levene and L. A. Mikeska, *J. Biol. Chem.*, **65**, 512 (1925) reported this reaction but did not distil the product.

(15) W. Steinkopf and A. Wolfram, *Ann.*, **430**, 160 (1923).

(16) Levene and Mikeska (ref. 14) reported that their mercaptan, prepared by a similar procedure, decomposed above 50° to form hydrogen sulfide and stilbene.

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}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}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-methyl-

benzyl 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}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}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.

(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.

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

(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).

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.