744. *Action of Alkali Metals on Organic Sulphur Compounds. Part III.* The Cleavage of Benzyl Phenyl Sulphide and Dibenzyl Sulphide by Potassium in 1,2-Dimethoxyethane.*

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The cleavage of benzyl phenyl sulphide by potassium in dimethoxyethane occurs with approximately equal amounts of initial rupture of the benzyl–sulphur and phenyl–sulphur bonds. For the reaction with dibenzyl sulphide a considerable amount of 2-methyldiphenylmethane is formed; this arises from the attack of benzyl anions resulting from the normal cleavage reaction on unchanged starting material.

From stoicheiometric measurements and detailed examination of the reaction products we have shown [1] that the overall cleavage of sulphides is mainly anionic in 1,2-dimethoxyethane, although a small fraction of the reaction proceeds by a one-electron radical mechanism. A preliminary survey had, however, indicated that the cleavage of dibenzyl sulphide by potassium was more complex, and we report here the results of a detailed examination of this reaction and of the cleavage of the related benzyl phenyl sulphide.

Benzyl phenyl sulphide is easily cleaved between −20 and 0° in 1,2-dimethoxyethane. Dibenzyl sulphide, however, is more slowly decomposed by potassium than the other sulphides so far studied. At room temperature up to 6 days are necessary for complete reaction, and 20 hours at 80°. Dibenzyl sulphide is not decomposed by potassium in pure benzene although thioanisole [1a] and diphenyl sulphide [1b] are readily cleaved (addition of 1% of 1,2-dimethoxyethane to benzene does not induce the reaction).

Our qualitative and semiquantitative observations are in the Table. The amounts of the compounds formed were mainly determined by vapour-phase chromatography as previously described.[1b]

Reaction of potassium and the sulphides in 1,2-dimethoxyethane.

A. Benzyl phenyl sulphide.

Conditions	Products *						g.-atom K consumed
	C_6H_6	PhMe	$(Ph \cdot CH_2)_2$	PhSH	$Ph \cdot CH_2 \cdot SH$	H_2S	
21 hr. at −10° ...	†	0·66	0·02	0·40	0·25	0·28	2·2

B. Dibenzyl sulphide.

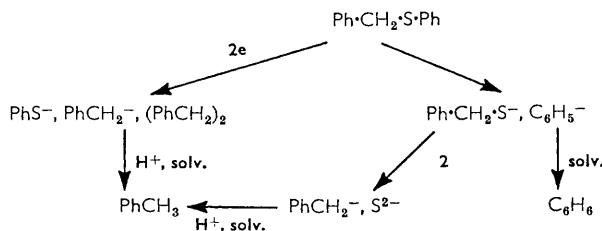| Conditions	Main products *					g.-atom K consumed
	$o\text{-Me} \cdot C_6H_4 \cdot CH_2Ph$	$(Ph \cdot CH_2)_2$	PhMe	$Ph \cdot CH_2 \cdot SH$	H_2S	
140 hr. at 20°	0·32	0·06	1·0	0·02	0·95	3·4
22 hr. at 20°	————0·18 ‡————		1·1	0·24	0·6	1·9
21 hr. at 80°	0·09	0·29	0·8	None	0·95	3·0

* The yields are in mole product per mole thioether consumed; they are averaged over a few separated experiments.   † Only qualitatively determined.   ‡ Ratio of both components was not determined.

Both carbon–sulphur bonds of the unsymmetrical sulphide benzyl phenyl sulphide are cleaved in about the same ratio by a two-electron process, to form phenyl and benzyl anions and the corresponding potassium aryl sulphide. A fraction of the potassium benzyl sulphide is further cleaved by the excess of potassium to give an almost quantitative yield of hydrogen sulphide and toluene as was demonstrated separately. The approximately symmetrical cleavage of benzyl phenyl sulphide is consistent with the empirical

* Part II, *J.*, 1963, 5444.

[1] Gerdil and Lucken. *J.*, (*a*) 1963, 2857; (*b*) 1963, 5444.

suggestion by Truce, Tate, and Burdge.[2] that cleavage occurs to produce the least basic anion of the pair having the greatest difference in basicities. The difference in pK_a of thiophenol and toluene-α-thiol is 3·5;[3] the difference in pK_a of phenyl and benzyl anions lies provably very close [4] to that value: therefore it is expected that there will be no preferred direction of cleavage for benzyl phenyl sulphide. Our results indicate that at least 92% of the benzyl phenyl suphide consumed can be accounted for by the two simultaneous reaction paths in Scheme A.

A.

$$Ph \cdot CH_2 \cdot S \cdot Ph$$

2e

$$PhS^-,\ PhCH_2^-,\ (PhCH_2)_2 \qquad\qquad Ph \cdot CH_2 \cdot S^-,\ C_6H_5^-$$

H^+, solv.   2   solv.

$$PhCH_3 \longleftarrow PhCH_2^-,\ S^{2-} \qquad\qquad C_6H_6$$
H^+, solv.

Dibenzyl sulphide is also likely to undergo a two-electron cleavage leading to benzyl-potassium and potassium benzyl sulphide in a first step; but the end products suggest that secondary reactions are involved in the overall process. Hauser *et al.* have reported [5] that dibenzyl sulphide undergoes with potassium amide an intramolecular rearrangement involving *ortho*-substitution of the benzene ring to form 2-methyldiphenylmethanethiol. The rearrangement is regarded as involving the isomerization of an intermediate carbanion with nucleophilic attack on the neighbouring benzene ring (see pathway *D* in Scheme B). It is attractive, to account for the formation of 2-methyldiphenylmethane in the present work, to assume that the benzyl anions have the same potent action on diphenyl sulphide as the amide ions and that the sulphide formed (pathway *D*) undergoes a fast desulphurization (similar to that of the potassium benzyl sulphide) with the excess of potassium to give 2-methyldiphenylmethane and potassium sulphide (pathway *E*). A similar desulphurization of potassium 1,2-diphenylethyl sulphide leading to bibenzyl also seems possible. A careful examination of the products of the reaction with potassium failed to demonstrate the presence of 2-methyldiphenylmethanethiol. More recently a new type of anionic rearrangement of benzyl sulphide with elimination of the sulphur portion to form stilbene was reported.[6]

We investigated the action of a solution of benzylpotassium, in 1,2-dimethoxyethane, on dibenzyl sulphide, and found, surprisingly that 2-methyldiphenylmethane and bibenzyl are formed in equimolar quantities (0·3 mole per mole of sulphide consumed), together with potassium sulphide, stilbene, and some unidentified products. Toluene was also detected but its quantitative determination is meaningless because its presence might arise from the very preparation of benzylpotassium. A careful analysis of the small fraction of acidic products isolated in this reaction failed to reveal 2-methyldiphenylmethanethiol or 1,2-diphenylethanethiol. The main process of the last reaction almost certainly does not involve a nucleophilic attack of a benzyl anion on the sulphide molecule because, if the reaction passed through a carbanion, rearranged potassium aryl sulphides or benzyl sulphide would be formed in appreciable quantities. None of these products was found. To make sure that the potassium aryl sulphides are not subsequently decomposed by the excess of benzylpotassium we also examined the action of benzylpotassium on potassium benzyl sulphide but found that less than 1% of bibenzyl and traces of unidentified compounds were formed in the neutral fraction after 5 days at room temperature. Although we observed that the action of benzylpotassium alone is sufficient to promote desulphurization and

² Truce, Tate, and Burdge, *J. Amer. Chem. Soc.*, 1960, **82**, 2872.
³ Maurin and Pâris, *Compt. rend.*, 1951, **232**, 2428.
⁴ Morton, *Chem. Rev.*, 1936, **35**, 1.
⁵ Hauser, Kantor, and Braten, *J. Amer. Chem. Soc.*, 1953, **75**, 2660.
⁶ Wallace, Pobiner, Hofmann, and Schriesheim, *Proc. Chem. Soc.*, 1963, 137.

intramolecular rearrangement * of dibenzyl sulphide (pathway *A*) we cannot conclude that the heterogeneous reaction with potassium (where benzylpotassium is generated *in situ* at the surface of the metal) will take the same course. Indeed the experimental details in the Table suggest that different simultaneous pathways must be considered. The paths in Scheme B are not intended to represent the only ones possible, but they are consistent with our experimental results and with observations made by others on the same reactant in similar conditions. All the end products shown were identified in the reaction mixtures.

B.
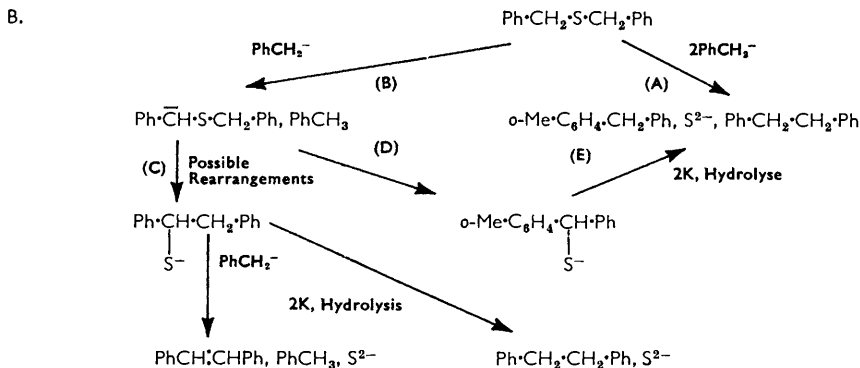
No phenylacetic acid was isolated after carbonation of the reaction mixture and this is probably due to the rapid reaction of the benzyl anions, generated *in situ*, with dibenzyl sulphide.

EXPERIMENTAL

Unless otherwise stated, the methods used are as previously described.[1]

1,2-Dimethoxyethane (Fluka purum) was distilled under nitrogen after having been re-fluxed over sodium. Benzyl phenyl sulphide (m. p. 42°) was recrystallized from ethanol and dibenzyl sulphide (m. p. 50°) in chloroform–light petroleum before use. Only typical experiments are reported.

(i) *Cleavage of Benzyl Phenyl Sulphide.*—A mixture of benzyl phenyl sulphide (0·070 mole) and finely divided potassium (0·15 g.-atom) in 1,2-dimethoxyethane (200 ml.) was stirred for 21 hr. between −20 and 0°. Practically all potassium had then reacted. The mixture was worked up and analysed as usual. Benzene, toluene (0·043 mole), bibenzyl (0·001 mole) and unchanged benzyl phenyl sulphide (0·005 mole) were identified in the neutral fraction. The thiols were ether-extracted after acidification of the aqueous layer. Gas chromatography showed thiophenol (0·026 mole) and toluene-α-thiol (0·016 mole). Potassium sulphide was determined in an aliquot portion of the aqueous solution. The sulphide was boiled out as hydrogen sulphide after acidification with diluted hydrochloric acid and collected in a known volume of aqueous 0·1N-iodine. The unconsumed iodine was then titrated with 0·1N-sodium thiosulphate (Found: 0·018 mole SH_2).

(ii) *Cleavage of Dibenzyl Sulphide.*—Dibenzyl sulphide (0·05 mole) and finely divided potassium (0·20 g.-atom) in 1,2-dimethoxyethane (200 ml.) was stirred for 140 hr. at room temperature. After 20 hr. the mixture was reddish-brown and faded upon subsequent de-composition of the excess of potassium (about 14%) with aqueous propan-2-ol. The final mixture was worked up as in (i) and the fractions were examined by gas–liquid chromatography: methanol, toluene (0·049 mole), 2-methyldiphenylmethane and bibenzyl (0·019 mole together, giving a single peak), toluene-α-thiol (0·001 mole), and minute amounts of unidentified compounds were present. No unchanged dibenzyl sulphide was detected. Potassium sulphide (0·045 mole) was determined in the aqueous layer as described in (i). 2-Methyldiphenylmethane

* To our knowledge, this particular type of reaction, the mechanism of which is not known, has never been mentioned and may deserve attention. However the related air-oxidation of benzyl anions to bibenzyl does occur.[7]

[7] Hopton and Hush, *Mol. Spectroscopy*, 1963, **6**, 209.

was identified as follows: the neutral fraction of the reaction mixture was fractionated after evaporation of the solvents. The fraction of b. p. 130—138°/11 mm. was redistilled to give an oil, b. p. 136—138°/11 mm. (Found: C, 92·14; H, 7·81. Calc. for $C_{14}H_{14}$: C, 92·26; H, 7·74%). The structure of 2-methyldiphenylmethane was determined from the nuclear magnetic resonance (n.m.r.) spectrum of the oil dissolved in deuterochloroform. The n.m.r. spectrum also showed that the sample contained about 7% of bibenzyl. In another experiment at 80° the neutral fraction solidified after evaporation of the solvents and on crystallization from methanol afforded bibenzyl, m. p. and mixed m. p. 52°. The ratio of concentration of 2-methyl-diphenylmethane and bibenzyl in unknown mixtures of both compounds was determined by comparing the intensities of the absorption bands at 1105 and 1050 cm.$^{-1}$ with those of synthetic mixtures of known composition. The intensity of the absorption band at 1030 cm.$^{-1}$ was used as unity standard.

After carbonation of the reaction mixture with solid carbon dioxide, fractional distillation of the neutral fraction yielded 5% of stilbene (calc. from the initial sulphide) apart from the expected hydrocarbons. The crude product afforded plates, m. p. and mixed m. p. 125°, on crystallization from ethanol. Infrared and n.m.r. spectra confirmed the structure. A resinous acid fraction was obtained (10% of initial dibenzyl sulphide) which slowly yielded a small crystalline fraction. Part of the crystals were water-soluble and had m. p. 183—185°; the water-insoluble crystals had m. p. 220—240°. These compounds are probably crude $(\pm)$- and *meso*-diphenylsuccinic acid, respectively. They are the expected carboxylation products of the di-potassium adduct of stilbene.[8] Phenylacetic acid was not found.

Reaction of Dibenzyl Sulphide with Benzylpotassium.—Benzylpotassium was prepared from chlorobenzene and potassium in toluene [9] in a vessel with sintered-glass disc. Toluene was filtered off and the mixture taken up in 1,2-dimethoxyethane. The deep red solution (45 ml.) of benzylpotassium (0·017 mole; determined on an aliquot portion by carboxylation with solid carbon dioxide and extraction of the phenylacetic acid) was filtered off under nitrogen, and dibenzyl sulphide (0·025 mole) added. The colour of the solution immediately turned lighter and an amorphous precipitate appeared. After 90 hr. the mixture was decomposed with water and worked up as usual. A mixture of 2-methyldiphenylmethane and bibenzyl (0·006 mole together), stilbene (0·0019 mole), unchanged dibenzyl sulphide (0·014 mole) and unidentified substances (6% of the neutral fraction) were found in the neutral fraction apart from toluene and 1,2-dimethoxyethane. The aqueous layer was acidified with diluted hydrochloric acid and ether-extracted after boiling out of the hydrogen sulphide. Evaporation of the ether left a residue (0·5 g.) of tiny crystals (thin colourless plates, m. p. 204—212° (decomp.), on crystallization from chloroform) mixed with an oil. Half of an ethanol solution of the residue was refluxed with NaOH and 1-chloro-2,4-dinitrobenzene. A yellow crystalline precipitate almost insoluble in ethanol was obtained upon cooling; the crude product had m. p. 185—190° (2,4-dinitrophenyl 2-methyldiphenylmethyl sulphide has m. p. 122—123°; the 1,2-diphenyl-ethyl derivative, m. p. 132—133° [5]). The remaining half of the solution decolourised 8·1 ml. of 0·1N-iodine.

[8] Wright, *J. Amer. Chem. Soc.*, 1939, **61**, 2106.
[9] Nobis and Moormeier, *Ind. Eng. Chem.*, 1954, **46**, 540.