222. Base-catalysed Reactions of Benzylic Sulphur Compounds.

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The decomposition of several benzyl-type sulphur compounds was studied in potassium *t*-butoxide–dimethylformamide solution at 80° ± 1°. Benzyl sulphide, benzyl disulphide, and benzyl sulphoxide yielded stilbene as the olefinic decomposition product. Studies on these and related sulphur compounds indicated that the expected products from α-elimination reactions were not formed. Steric factors and stability of the initially formed carbanion were also important in olefin formation. Competition and trapping experiments are consistent with an intramolecular reaction involving a 1,3-rearrangement to form an unstable anion which decomposes by a β-elimination sequence to produce the olefin. A comparison of these reactions with previous elimination studies has been made.

Previous studies here have been concerned with base-catalysed elimination and oxidation reactions of various types of sulphur compound. In potassium t-butoxide–dimethyl sulphoxide aliphatic sulphones, sulphoxides, sulphides, disulphides, and thiols are unstable at 55° and β-eliminate to produce olefins and sulphur anions.[1,2] Subsequent kinetic and tritium-exchange studies established that these reactions were E_2 in nature.[3] In related oxidation studies, it has been established that aliphatic and aromatic thiols and disulphides can be oxidized by molecular oxygen to their corresponding sulphonate salts in polar solvents.[4] However, toluene-α-thiol and benzyl disulphide yielded potassium toluene-α-sulphonate, benzoic acid, and stilbene as the oxidation products.[5] The formation of stilbene under these conditions was of interest and prompted us to investigate the stability and reactions of various benzyl-type sulphur compounds in the presence of potassium t-butoxide and a polar solvent, as now reported.[6]

Experimental

Reagents.—Potassium t-butoxide, from the Mine Safety Appliance Co. (Callery, Pa.) as the sublimed white powder in wax-sealed containers, was at least 98·5% pure, the impurity being potassium carbonate. Dimethyl sulphoxide (Crown Zellerbach) and dimethylformamide (Matheson, Coleman, and Bell) were distilled *in vacuo* over Linde-13X molecular sieves, calcined under nitrogen at 400° for 4 hr., to remove all traces of adsorbed water. The base and solvents were stored continuously in a nitrogen dry-box equipped with a moisture conductivity cell.

Benzyl disulphide (m. p. 70°) was prepared from toluene-α-thiol and iodine in aqueous sodium hydroxide, as described by Vogel.[7] Benzyl phenyl sulphoxide and benzyl methyl sulphoxide were prepared from the oxidation of their corresponding sulphides by hydrogen peroxide in acetic acid. 9-Fluorenyl sulphide was generously donated by Dr. P. M. G. Bavin of the Smith, Kline, and French laboratories. Potassium toluene-α-sulphonate was prepared from benzyl bromide and potassium sulphite.[8] All other starting compounds and those compounds employed as standards for product identification were purchased as reagent grade materials. Purity was established by gas chromatography.

General Procedure For Decomposition Studies.—In each decomposition, a general procedure was employed. The desired quantity of base and solvent were added to a three-necked flask in a nitrogen dry-box. The flask had a magnetic stirring bar, condenser, thermometer, and nitrogen bubbler. When the base was completely dissolved the reactant was added, and the

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[1] Hofmann, Wallace, Argabright, and Schriesheim, *Chem. and Ind.*, 1963, 1243.

[2] Wallace, Hofmann, and Schriesheim, *J. Amer. Chem. Soc.*, 1963, **85**, 2739.

[3] Hofmann, Wallace, and Schriesheim, *J. Amer. Chem. Soc.*, 1964, **86**, 1561.

[4] Wallace and Schriesheim, *Tetrahedron Letters*, 1963, No. 17, 1131.

[5] Wallace, Pobiner, and Schriesheim, *J. Org. Chem.*, 1964, **29**, 888, and references therein.

[6] For a preliminary communication, see Wallace, Pobiner, Hofmann, and Schriesheim, *Proc. Chem. Soc.*, 1963, 137.

[7] Vogel, " A Textbook of Practical Organic Chemistry," Longmans, Green and Co., London, England, 1959, chap. 3, pp. 496—498.

[8] Fromm and Parma, *Ber.*, 1906, **39**, 3312.

flask was sealed, removed from the dry-box, and placed in a constant-temperature bath (80° ± 1°), and nitrogen was bubbled through. After 22—24 hr., water (3 vol.) was added to deactivate the base and prevent air oxidation when the sample was exposed to the atmosphere for analysis.

Analysis.—The predominant olefin produced was stilbene. Quantitative data were obtained by the method of Pobiner, Wallace, and Hofmann.[9] Two techniques can be employed. One involves an extraction–ion-exchange–infrared procedure and the other an extraction–ultraviolet procedure. Both rely on initial homogenization of the reaction mixture with water and subsequent extraction with cyclohexane to remove starting material and non-acidic products. This removes spectral interference from acidic products. The olefin may then be determined directly by using standard ultraviolet curves. Where acids are formed, they are liberated from the aqueous polar solvent phase by acidification. If aromatic, the acid can be determined directly by ultraviolet analysis. If aliphatic, or presenting a weak ultraviolet absorption, the aqueous phase is treated with Amberlite LA-2 anion-exchange resin and the free acid is extracted by carbon tetrachloride and quantitatively determined by infrared spectroscopy. In addition to the characteristic spectra, stilbene (m. p. 124°) was further substantiated by isolation from several reaction mixtures.

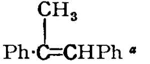
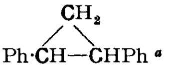
Other Analytical Methods.—In several experiments, qualitative analyses for stilbene, toluene-α-thiol, and α-methylstilbene were carried out by gas chromatography on an F and M model 609 Flame Ionization Gas Chromatograph equipped with a 3 ft. silicone rubber column (30% w/w silicone rubber on Chromosorb, 0·25 in. stainless steel tubing), operated at 150—250° and 15 lb./in.^{2} helium. Mass spectrography was used to determine the distribution of olefins from the co-reaction of benzyl sulphide with di-(α-methylbenzyl) sulphide and the presence or absence of 7-phenylnorcarane from the reaction of cyclohexene with benzyl sulpide, sulphoxide, and disulphide. A Consolidated Electrodynamic Corp. spectrophotometer (model 21-103) modified with a high-temperature inlet system, was used.

RESULTS AND DISCUSSION

Because of its high dielectric constant and general application as a solvent for carbanion reactions,[10] dimethyl sulphoxide was first employed as a solvent for our decomposition studies. Qualitative results on the decomposition of benzyl sulphide, toluene-α-thiol, and benzyl sulphoxide in potassium t-butoxide–dimethyl sulphoxide at 80° are summarized in Table 1. All three experiments indicated that the solvent was participating in side reactions with the reactants and the olefinic product, stilbene. Benzyl sulphoxide production from benzyl sulphide probably occurs by oxygen transfer from DMSO.[11] Disulphide

TABLE 1.

Decomposition studies in potassium t-butoxide–dimethyl sulphoxide at 80°.

Reactant (moles)	DMSO (ml.)	KOtBu (moles)	Probable products	Method of detection
$PhCH_2{\cdot}SCH_2Ph$ (0·05)	100	0·15	$Ph{\cdot}CH{=}CHPh$, 2·5%	uv, gc
			$Ph{\cdot}CH_2{\cdot}SO{\cdot}CH_2Ph$	gc, ir
			 $Ph{\cdot}\overset{CH_3}{C}{=}CHPh$ [a]	gc
			 [a]	ms
$Ph{\cdot}CH_2{\cdot}SH$ (0·05)	100	0·15	$Ph{\cdot}CH_2{\cdot}S{\cdot}S{\cdot}CH_2Ph$, 25%	Isolation
			$Ph{\cdot}CH{=}CHPh$, 2%	uv, gc
$Ph{\cdot}CH_2{\cdot}SO{\cdot}CH_2Ph$ (0·125)	100	0·075	$Ph{\cdot}CH{=}CHPh$, 8%	uv, gc
			$PhCMe{=}CHPh$ [a]	gc

[a] Structural assignment is tentative since only gc retention times or ms were employed.

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[9] Pobiner, Wallace, and Hofmann, *Analyt. Chem.*, 1963, **35**, 680.

[10] (*a*) Parker, *Quart. Rev.*, 1962, **16**, 163; (*b*) Cram, *Chem. Eng. News*, 1963, **41**, No. 33, 92 *et seq.*

[11] Searles and Hays, *J. Org. Chem.*, 1958, **23**, 2028.

production from toluene-α-thiol involves a reaction of the type shown which has been studied in detail.[12,13] α-Methylstilbene is produced by reaction of the methylsulphinyl carbanion

$$2RSH + R_2'SO \longrightarrow RSSR + R'_2S + H_2O \tag{1}$$

($CH_3{\cdot}SO{\cdot}CH_2^-$) with the initially formed stilbene. Product formation involves a series of addition, elimination, and isomerization reactions.[14,15] Detailed analyses of these products were not undertaken since we were primarily interested in dimethyl sulphoxide as a solvent. The fact that competing reactions were observed dictated the use of another solvent. Thus, dimethylformamide ($\varepsilon = 36$) was employed in all subsequent reactions.

The details of our decomposition studies in potassium t-butoxide–demethylformamide at 80° are summarized in Table 2. Qualitative and quantitative data on all products were

TABLE 2.

Base-catalysed decompositions in potassium t-butoxide–dimethylformamide, at 80°.

Reactant(s) (moles)	DMF (ml.)	KOBu^t (moles)	Product(s) Moles (%)	Yield [a]	Identification
$PhC{\cdot}H_2{\cdot}S{\cdot}CH_2Ph$ [b] (0·05)	75	0·15	$Ph{\cdot}CH{=}CHPh$ [d]	41	uv, ir, gc
			$Ph{\cdot}CH_2SH$	None	gc
$Ph{\cdot}CH_2{\cdot}S{\cdot}CH_2Ph$ [b] (0·05)	75	0·15	$Ph{\cdot}CH{=}CHPh$	45	uv, ir
$Ph{\cdot}CH_2{\cdot}SH$ (0·0125	75	0·15	$Ph{\cdot}CH{=}CHPh$	0·5	uv, Titratin
$Ph{\cdot}CH_2{\cdot}SPh$ (0·025)	75	0·075	No Stilbene		uv
$Ph{\cdot}CH_2{\cdot}SO{\cdot}CH_2Ph$ (0·0125)	37·5	0·075	$Ph{\cdot}CH{=}CHPh$ [d]	50	uv, ir, gc
$Ph{\cdot}CH_2{\cdot}SO{\cdot}CH_2Ph$ (0·025)	75	0·075	$Ph{\cdot}CH{=}CHPh$	24	uv
$Ph{\cdot}CH_2{\cdot}SO{\cdot}Ph$ (0·0023)	10	0·01	No Stilbene		uv
$Ph{\cdot}CH_2{\cdot}S{\cdot}SCH_2Ph$ [c] (0·025)	37·5	0·075	$Ph{\cdot}CH{=}CHPh$	13·2	uv, ir
			H_2S	8·4	Titration
$Ph{\cdot}CH_2{\cdot}S{\cdot}SCH_2Ph$ [c] (0·025)	37·5	0·075	$PhCH{=}CHPh$	17·2	uv
			H_2S	8·8	Titration
$PhCHMe{\cdot}S{\cdot}CHPhMe$ (0·05)	75	0·15	$CPhMe{=}CPhMe$	~18	ir,[e] ms, uv
			Polymer		
$PhCH_2{\cdot}S{\cdot}CH_2Ph$ (0·025)			$Ph{\cdot}CH{=}CHPh$	32	uv, ms
			$CPhMe{=}CPhMe$	8	ir,[e] ms
$PhCHMe{\cdot}S{\cdot}CHPhMe$ (0·025)	100	0·15	$PhCPhMe{=}CHPh$	None	ms, gc
9-Fluorenyl sulphide (0·0025)	10	0·01	No Bifluorenyl		uv
$Ph\text{-}CH_2{\cdot}SO{\cdot}Me$ (0·0032)	10	0·01	$Ph{\cdot}CH{=}CHPh$	1·5	uv, gc
$Ph{\cdot}CH_2{\cdot}SO_3K$ (0·05)	100	0·15	$Ph{\cdot}CH{=}CHPh$	0·2	uv

[a] Moles product/moles reactant × 100. [b] A positive test for hydrogen sulphide was observed with silver nitrate. [c] An additional product, possibly a thiol, was formed. [d] gc indicated that the ratio of *trans*-stilbene/*cis*-stilbene was 12. [e] See Jones, *J. Amer. Chem. Soc.*, 1943, **65**, 817.

obtained by the previously described experimental methods. In all cases, addition of the reactant to the potassium t-butoxide–dimethylformamide mixture was accompanied by the formation of dark red or blue colours, which is characteristic of carbanion formation. The compounds of primary interest were benzyl sulphide, disulphide, and sulphoxide. As indicated, stilbene was formed from these compounds in 13—50% yield depending on the reaction conditions employed. Hydrogen sulphide was also observed with the sulphide and disulphide. The latter suggested that olefin formation arose by a rearrangement–elimination sequence of the initially formed carbanion. An alternative, but less likely, possibility for the formation of stilbene was formation of phenylcarbene by an α-elimination. Subsequent dimerization of the carbenoid intermediate or addition to the initial carbanion followed by elimination could also lead to stilbene. To resolve this problem, the probable products from α-elimination reactions were sought and the decomposition of other pertinent sulphur compounds was investigated.

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[12] Wallace, *Chem. and Ind.*, 1964, **501**.

[13] Wallace, *J. Amer. Chem. Soc.*, 1964, **86**, 2018.

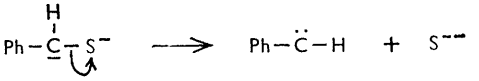
[14] Chaykovsky and Corey, *J. Org. Chem.*, 1962, **28**, 254.

[15] Walling and Bollyky, *J. Org. Chem.*, 1962, **28**, 256.

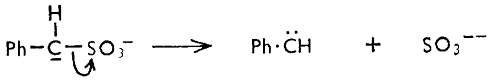
In the case of benzyl sulphide, no evidence for toluene-α-thiol formation could be obtained by gas chromatography. With benzyl sulphoxide, spectrophotometry indicated that benzyl disulphide and potassium toluene-α-sulphonate were absent. The latter are the most probable products if α-elimination from the sulphoxide occurred to produce an unstable toluene-α-sulphenate ion ($\mathrm{Ph{\cdot}CH_2{\cdot}SO^-}$). Sulphenate ions are capable of disproportionating to disulphides and sulphonate ions.[16] The absence of the above products

$$\mathrm{3Ph{\cdot}CH_2{\cdot}SO^- \longrightarrow Ph{\cdot}CH_2S{\cdot}SCH_2{\cdot}Ph + Ph{\cdot}CH_2{\cdot}SO_3^-} \qquad (2)$$

was inconsistent with an α-elimination reaction in the sulphide and sulphoxide. The possibility of toluene-α-thiol being unstable under these conditions was also discounted. After 24 hr. of reaction in potassium t-butoxide–dimethylformamide, 95% of the thiol could be accounted for by titration and only a 0·5% yield (maximum) of stilbene was observed. An identical result was obtained with potassium toluene-α-sulphonate. Hence the reactions

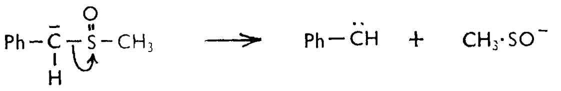


$$\mathrm{Ph{-}\underset{-}{\overset{H}{C}}{-}S^- \longrightarrow Ph{-}\ddot{C}{-}H + S^{--}} \qquad (3)$$



$$\mathrm{Ph{-}\underset{-}{\overset{H}{C}}{-}SO_3^- \longrightarrow Ph{\cdot}\ddot{C}H + SO_3^{--}} \qquad (4)$$

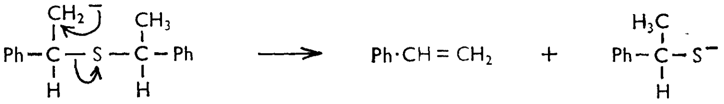
do not proceed to any major extent under the present conditions. The possibility of α-eliminations occurring in benzyl phenyl sulphide and sulphoxide was also investigated. No evidence for stilbene formation from either compound was found. This suggests that two reactive benzylic positions must be present for olefin formation to occur. This point was further established with methyl phenyl sulphoxide. The maximum yield of stilbene



$$\mathrm{Ph{-}\underset{H}{\overset{-}{C}}{-}\overset{O}{\overset{\|}{S}}{-}CH_3 \longrightarrow Ph{-}\ddot{C}H + CH_3{\cdot}SO^-} \qquad (5)$$

observed in 24 hr. was 1·5%. Thus, α-elimination of methylsulphenate ion is also negligible under these conditions. The last result is in contrast to the rapid, β-elimination of alkylsulphenate ions in potassium t-butoxide–dimethyl sulphoxide at 55°.[2,3]

Decomposition was studied with two other sulphides. 9-Fluorenyl sulphide was recovered unchanged after 24 hr. in potassium t-butoxide–dimethylformamide. Further, no spectral evidence for the presence of bifluorenyl was obtained. Di-(α-methylbenzyl) sulphide yielded 18% of 2,3-diphenylbut-2-ene and an undetermined amount of polymer which had



$$\mathrm{Ph{-}\underset{H}{\overset{CH_2^-}{C}}{-}S{-}\underset{H}{\overset{CH_3}{C}}{-}Ph \longrightarrow Ph{\cdot}CH{=}CH_2 + Ph{-}\underset{H}{\overset{H_3C}{C}}{-}S^-} \qquad (6)$$

many of the characteristic infrared bands of polystyrene. The latter probably arose from a competing β-elimination (eqn. 6). Such a reaction occurs with aliphatic sulphides and with 2-phenylethanethiol.[17] The above results with these two compounds would suggest that the ease of olefin formation depends on the stability of the initially formed carbanion and steric factors.

Final mechanistic studies were concerned with possible olefin addition reactions and cross-product formation. Benzyl sulphide, disulphide, and sulphoxide decompositions

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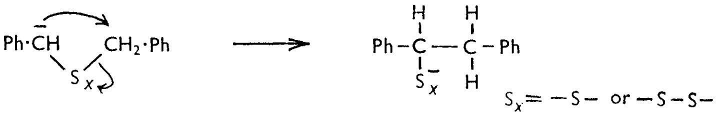
[16] Parker and Kharasch, *Chem. Rev.*, 1959, **59**, 583.

[17] Sontag, *Ann. Chim.* (*France*) *Ser. II*, 1934, **1**, 359.

were carried out in the presence of cyclohexene (equimolar). Water dilution, subsequent extraction by cyclohexane, and mass spectrography of each extract indicated stilbene was formed in each reaction. No parent ion corresponding to 7-phenylnorcarane [18] ($m/e = 168$) or its isomer, phenylcycloheptene, was observed. The cyclopropyl compound would be expected if Ph·$\ddot{\mathrm{C}}$H was present.[18] Cross-over experiments were carried out with an equimolar mixture of di-(α-methylbenzyl) sulphide and benzyl sulphide. Water dilution and cyclohexane extraction followed by gas chromatography, mass spectrometry, and infrared and ultraviolet spectroscopy indicated that stilbene and 2,3-diphenylbut-2-ene were formed in a 4 : 1 molar ratio. α-Methylstilbene was not observed. This result coupled with the previous lack of evidence for carbenoid addition and elimination products prompts us to suggest that these reactions are mainly intramolecular in nature. Specifically, the initial carbanion formed from the sulphide and disulphide rearrange to mercaptide and persulphide ions which, in the presence of excess of base, form unstable dianions that β-eliminate sulphide ion. In the case of the sulphoxide, a similar sequence would lead to an unstable sulphenate ion that eliminates the species SO^{--}. This last reaction is consistent with our results on tetramethylene sulphoxide which decomposes to butadiene and $[SO^{--}]$ by a double β-elimination sequence.[1,2] Although reactions (8) and (9) are written as E_1cb in nature, an E_2 elimination at this stage of reaction cannot be eliminated.[3]



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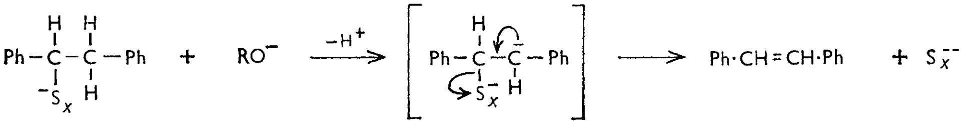

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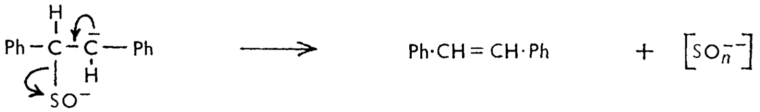

(9)

Although negative, our results on other benzyl derivatives should be mentioned. No evidence for olefin formation from phenylcyclopropane, toluene-α-cyclopropane, benzyl formate, benzyl acetate, or benzyl benzoate was observed under these conditions. This is in general agreement with our previous results.

Esso Research and Engineering Co., Process Research Division,
Exploratory Research Section, Linden, New Jersey, U.S.A. [*Received, May 14th,* 1964.]

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[18] Closs and Closs, *Tetrahedron Letters*, 1960, No. 24, 26.