XCIII.—*Influence of Poles and Polar Linkings on the Course pursued by Elimination Reactions. Part VII. A Generalised Form of the Olefinic Degradation of Sulphones.*

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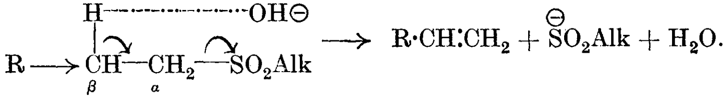
IT was shown in Parts III and IV (J., 1928, 3127; 1929, 2338) that sulphones in the presence of concentrated potassium hydroxide solution undergo a degradation the mechanism of which is almost certainly identical in type with that which was applied in Parts I and II (J., 1927, 997; 1928, 3125) to the decomposition of quaternary ammonium hydroxides. The normal products of the degradation of sulphones are an olefin and a sulphinic acid, and the facility with which the reaction proceeds depends on the extent to which the C_γ–C_ω part of the alkyl group ultimately eliminated as an olefin activates or de-activates the β-hydrogen atom attacked by hydroxide ion :



$$\overset{\displaystyle H\cdots\cdots\cdots\cdots OH^{\ominus}}{R \longrightarrow \underset{\beta}{CH}-\underset{\alpha}{CH_2}-SO_2Alk} \longrightarrow R{\cdot}CH{:}CH_2 + \overset{\ominus}{SO_2Alk} + H_2O.$$

The straight arrow in the formula represents a de-activating effect, because electron-repulsion towards C_β must diminish the tendency of the β-hydrogen atom to separate in the kationic form; and in this connexion it was observed that, under the conditions used, the reaction became sluggish or failed altogether when R was a higher alkyl group than methyl. It also failed if there were two de-activating groups attached to C_β, even when these were only methyl groups. Although substitution at C_α is not expected adversely to affect the degradation to any marked extent (the investigation of di*iso*propylsulphone supports this assumption), the reaction in the form in which we have described it is evidently far from being as general as the corresponding decomposition of quaternary ammonium hydroxides, and this is in agreement with the smaller electron-affinity of $-SO_2R$ than of $-\overset{\oplus}{N}R_3$ (see Parts III and IV).

Obviously, however, the sulphone degradation might be made general by the use of a more basic anion (*i.e.*, one with greater proton affinity) than hydroxide; and for this purpose the methoxide and ethoxide ions suggested themselves (Ingold and Shoppee, J., 1929, 447; Kon and Linstead, *ibid.*, p. 1269).

We find that the degradation can readily be generalised by the replacement of aqueous potassium hydroxide by alcoholic sodium ethoxide : all the sulphones which resisted the former reagent have been found to undergo the degradation in the presence of the latter.

No.	Sulphone.	Olefin.	KOH.	NaOEt.
1	Phenyl-β-phenylethyl*	Styrene	*	*
2	Diethyl	Ethylene	*	*
3	Ethyl-*n*-propyl	,,	*	—
4	Ethyl*iso*amyl	,,	*	—
5	Ethyl-*n*-octyl	,,	*	—
6	Di*iso*propyl	Propylene	*	—
7	Di-*n*-propyl	,,	*	*
8	Di-*n*-butyl	Δ^α-*n*-Butylene	Little action	*
9	Di-*n*-octyl	Δ^α-*n*-Octene	No action	*
10	Di*iso*amyl	Δ^α-*iso*Amylene	,,	*
11	Di*iso*butyl	*iso*Butylene	,,	*

* With potassium hydroxide the products were styrene, benzene, and sulphur dioxide, but when sodium ethoxide was used the benzenesulphinic acid formed was isolated as such. In all the other cases the sulphinic acid was obtained with either reagent.

The above is a tabular summary of the observations recorded in Parts III and IV and in this paper. The examples studied are arranged in order of the theoretically anticipated inhibition to the elimination of the olefin formed. A star indicates that degradation by the reagent indicated has been observed, and a line that the corresponding experiment was not tried.

EXPERIMENTAL.

Preliminary Experiments.—Di-*n*-octylsulphone (Part III) was used because the liquid olefin *n*-octene could scarcely be confused with any unsaturated substance which might arise from the sodium ethoxide. The sulphone (4 parts), freshly prepared sodium ethoxide (10 parts), and alcohol (1·5 parts) were heated in a metal bath and the products were passed through water and bromine and into a eudiometer. Reaction occurred at just below 200° (bath temperature) and an oily product, but no gas, was evolved. The liquid product was identified by its b. p. 122—123°, and by conversion into its dibromide, as Δ^{α}-*n*-octene. In a similar experiment the bath temperature was carried to 300° after the subsidence of the original reaction; and at this temperature both saturated and unsaturated gases were evolved. The unsaturated gas was represented by a small amount of oil which was obtained after destruction of the excess of bromine in the bromine trap. The gas collected in the eudiometer contained oxygen, nitrogen (which was used for sweeping), and hydrogen, but no hydrocarbons. The *n*-octene obtained in this experiment (yield, 50%; b. p. 120—125°) gave, on ozonolysis, formaldehyde as volatile product and an oil having the odour of heptaldehyde. We conclude that the gaseous products evolved at 300° come from the sodium ethoxide and that the Δ^{α}-*n*-octene, formed at 200°, has not undergone displacement of the double linking.

General Method.—The aliphatic sulphones were heated with sodium ethoxide as above, but only until the initial reaction ceased; in no case was the bath temperature raised above 235°. The volatile products were passed directly into bromine, the excess of which was afterwards destroyed with water and sulphur dioxide; the bromides were drawn off, dried and weighed, distilled, and in some cases analysed. The sulphinic acids were isolated in the form of their silver salts, as described in Part III. The treatment of phenyl-β-phenylethylsulphone was different. In order to avoid the risk of the nuclear bromination of styrene by an excess of bromine, the hydrocarbon was collected as such in a trap containing water at 0°, and then extracted with chloroform; the dried chloroform solution was treated with dry bromine in chloroform until coloured, and the styrene dibromide, obtained on evaporation, was identified and weighed. The benzenesulphinic acid was isolated, as such, from the residue by acidification of its aqueous solution and extraction with ether.

Results.—These are recorded in tabular form. The *silver* salts, the analytical data for which are italicised, are new. *αβ-Dibromo-n-octane* also is new, since, although it was prepared and analysed by Ingold and Vass in connexion with their work on quaternary ammonium hydroxides, the description and data were inadvertently omitted from the paper.

Sulphone.[§]	Olefin dibromide.						Silver sulphinate.				
			Found.		Calc.			Found.		Calc.	
	Yield %.	B. p.	C %.	H %.	C %.	H %.	Yield %.	C %.	H %.	C %.	H %.
1	91	—[*]	—	—	—	—	72[†]	—	—	—	—
2	77	130—132°	12·9	2·2	12·8	2·1	62	—	—	—	—
7	76	139—141	18·2	3·1	17·8	3·0	60	16·4	3·4	16·7	3·3
8	77	160—164	22·0	3·5	22·2	3·7	62	*20·9*	*3·9*	*20·9*	*3·9*
11	61	148—152	21·8	3·5	22·2	3·7	54	*20·7*	*4·0*	*20·9*	*3·9*
10	73	178—182	—	—	—	—	65	24·5	4·7	24·7	4·5
9	70	240—242[‡]	*35·3*	*5·8*	*35·3*	*5·9*	62	*33·4*	*6·2*	*33·7*	*6·0*

[*] M. p. and mixed m. p., 73—74°.

[†] Yield of free benzenesulphinic acid, m. p. and mixed m. p., 82—84°.

[‡] Very pale yellow oil when freshly distilled; darkens on keeping.

[§] The numbers denote the sulphones named in the first table.

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