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SULFONES. II.* ALKENES, DIENES, α,β-UNSATURATED SULFONES, AND MONOSULFONES FROM β-DISULFONES[1]

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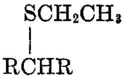
In our recent investigation of the behavior of β-disulfones when hydrogenated over Raney nickel and in reaction with lithium aluminum hydride several types of cleavage and reduction reactions were encountered (2). In order to elucidate the behavior of the β-disulfones more completely and to improve the usefulness of these reactions for synthetic purposes the effects of other basic reagents have been examined. The results which have been obtained are summarized in Tables I, II, and III.

TABLE I

CLEAVAGE OF BIS-(ALKYLSULFONYL)ALKANES WITH BASIC REAGENTS

SULFONE	REAGENT	CONDITIONS	$R_2C=CHCH_3$, %	OTHER PRODUCTS	UNREACTED,[c] %
Ib[a]	NaOH, 10%	24 hrs., 250°	33		
Ib[a]	$LiAlH_4$ ether	24 hrs. 25°	61		10
Ia[a]	$LiAlH_4$ tetrahydrofuran 3:1	24 hrs., 25°	63		
Ia[a]	$LiAlH_4$ ether 4:1	24 hrs., 25°	50	 $\underset{RCHR}{\overset{SCH_2CH_3}{\vert}}$ 13%	
Ia	$NaOC_2H_5$ ethanol	48 hrs., reflux	8	50% III	21
Ia	$KOC(CH_3)_3$ tert-butyl alcohol	16 hrs., reflux	89	[b]	
Ia	KOH ethylene glycol	17 hrs., 160–165°	12	39% III, 9% IV	
Ia	$NaNH_2$ ether	20 hrs., 25°	32		42
Ia	$NaNH_2$ NH_3	5 hrs.	—		97
Ia	Sodiopiperidide	3 hrs., 100°	30[d]		
Ia	Sodium dispersion[e]	25–40°, several hrs.	49	14% *n*-nonane	

[a] Previously reported, *cf.* ref. (2) [b] 82% $C_2H_5SO_2H$ was recovered as ethyl *p*-nitrobenzyl sulfone; [c] The percent of unreacted starting material was not determined in all cases; [d] Estimated, the alkene was contaminated; [e] *Cf.* Table II.

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[1] While common usage in the naming of disulfones, *cf.* ref (1a) applies the term α-disulfone to $RSO_2—SO_2R$, β-disulfone to $RSO_2—C—SO_2R$, and γ-disulfone to $RSO_2—C—C—SO_2R$, this nomenclature is somewhat confusing since it does not conform to the usual implications of α, β, and γ as generally used in organic nomenclature.

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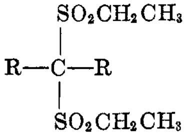
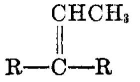
A comparison of the products obtained in the cleavage of the β-disulfones with reagents of different basicity indicates that the reaction path followed is somewhat dependent on the base strength of the reagent used. For example, potassium *tert*-butoxide with 5,5-bis-(ethylsulfonyl)nonane (Ia) gives an 89% yield of 3-*n*-butyl-2-heptene (IIa) while sodium ethoxide gives 8% of the same alkene and 50% of 5-ethylsulfonyl-4-nonene (III) and potassium hydroxide in ethylene glycol gives 12% of the alkene (IIa), 39% of the unsaturated sulfone (III), and 9% of ethylsulfonylpentane (IV). This last sulfone arises from III by way of a retrogressive aldol reaction (3, 4).



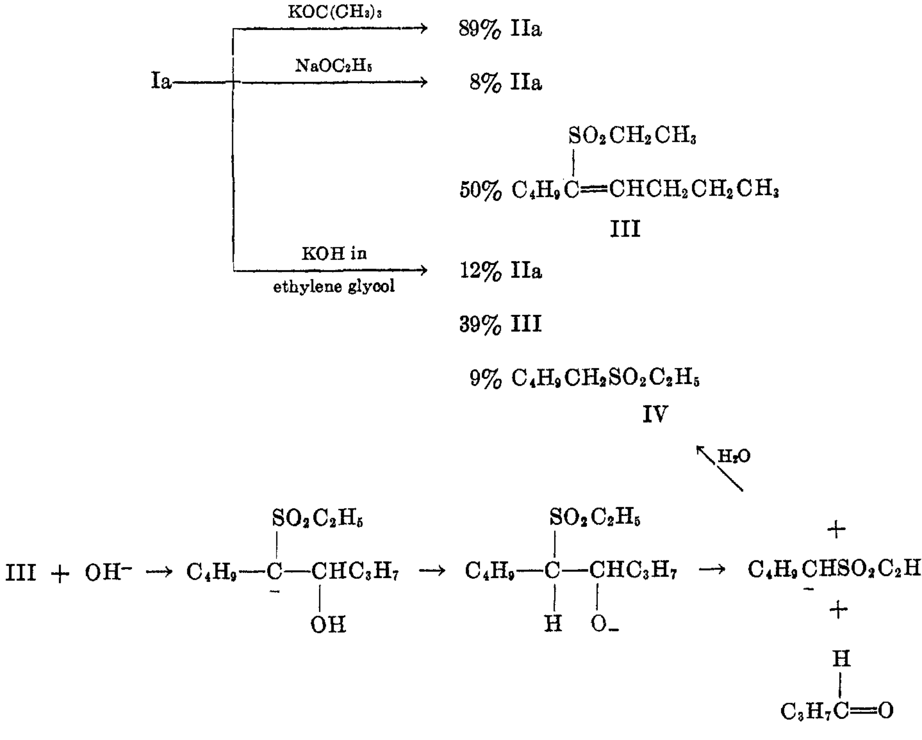
$R{-}C(SO_2CH_2CH_3)_2{-}R$

Ia, R = *n*-butyl
b, R = isoamyl

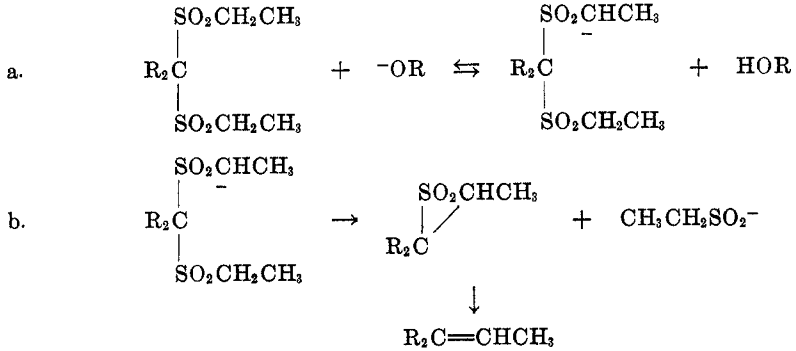


$R_2C{=}CHCH_3$

IIa, R = *n*-butyl
b, R = isoamyl



It is evident from a consideration of Bordwell and Cooper's mechanism (5) for alkene formation from α-halosulfones as applied to the similar reaction of the β-disulfones (2) that the character of the basic reagent used in the reaction should have a pronounced effect on the rate of alkene formation. A more basic reagent



which is capable of shifting the equilibrium in reaction (a) so as to increase the concentration of the α-methylene carbanion will increase the rate of formation of the 3-membered ring sulfone as indicated by reaction (b). In the case of the α-halo sulfones the formation of the 3-membered ring sulfone is the rate determining step (5) and this should also be true for the disulfones since the rate of ionization of the α-hydrogen should not be influenced greatly by the presence of the other sulfone group. This shift in the equilibrium expressed in (a) is responsible for the apparent reversal of the usual observation that in a competition between E2 elimination and S_N2 displacement the more basic the reagent the greater is the proportion of the E2 reaction (6a).

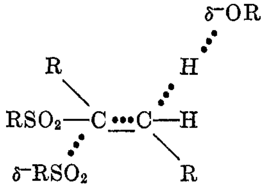
That the *tert*-butoxide is responsible for a considerable increase in the rate of alkene formation compared to ethoxide was indicated by a rough estimate of the half-lives of the reaction with the two reagents. With 2.5 *N* potassium *tert*-butoxide in refluxing *tert*-butyl alcohol the reaction responsible for the formation of IIa from Ia has a half-life of about 24 min.; while the same reaction has a half-life of eight to ten days with nearly the same concentration of sodium ethoxide in refluxing ethanol. With 2.5 *N* sodium ethoxide in ethanol the half-life of the reaction producing the α,β-unsaturated sulfone (III) is about 18–24 hours.

Other reagents apparently follow a similar pattern. With aqueous sodium hydroxide at 250° the yield of IIb was low. Though the yield of alkene with the sodiopiperidide cleavage of Ia was only about 30% there was little or no α,β-unsaturated sulfone isolated and with sodamide in ether the amount of unreacted sulfone recovered indicated a 55% conversion to the alkene. The appearance of 5-ethylthiononane in the reaction of lithium aluminum hydride with 5,5-bis-(ethylsulfonyl)nonane indicates that both types of attack may have occurred in this case, although direct reductive cleavage could also account for the same result (2).

The relative ease of elimination of the sulfone group from the β-disulfones compared to the drastic conditions necessary for an elimination reaction of a monosulfone (7) indicates clearly that the second sulfone group has a pronounced activating influence. In order to make a direct comparison, using the same carbon structure, of the influence of a second sulfone on the elimination reaction, 5-ethylsulfonylnonane was treated with sodium ethoxide in refluxing ethanol and with potassium *tert*-butoxide in refluxing *tert*-butyl alcohol. In each case titration of the reaction mixture after 48 hours indicated no elimination of the sulfone group.

This difference in the ease of elimination of a β-disulfone compared to a monosulfone is probably due in most part to a lower energy barrier provided by no-bond resonance in the transition state and conjugation of the double bond with the remaining sulfone group (8–11) as indicated by the transition state (V). This is analogous to the effect of an α-phenyl group on halide eliminations of the E2 type (6b).

The instability to alkali of the γ-disulfones and the β-sulfonyl esters (1b) is an indication of the effectiveness of combining both the transition state conjugative effect with an activation of the β-hydrogen which is, in this case, α to the remaining sulfone or ester group. Recently another type of structure has been found in which a similar combination of these effects gives rise to an alkali labile sulfone (12).



V

Qualitatively the difference in ease of elimination of a sulfone from a β-di sulfone compared to a monosulfone seems to be much greater than the corresponding difference between elimination from mono- and di-chloro compounds (13). Although other factors undoubtedly contribute it is most likely the conjugative effect which is primarily responsible for the magnitude of this difference.

The absorption spectrum of the α,β-unsaturated sulfone (III) is given in Fig. 1. With a maximum at 242 mμ and a log ϵ of 2.37 the maximum has shifted relative to ethyl vinyl sulfone (208–212 mμ) (9) in the same manner that the absorption maximum is shifted by the addition of alkyl groups to alkyl vinyl ketones (14–16).[3]

When the β-disulfone (Ia) was treated with sodium in liquid ammonia reductive cleavage occurred to give 86% of 5-ethylsulfonylnonane (VI). This is the same type of reaction which occurred upon hydrogenation of a β-disulfone over Raney nickel at 225° (2) and is a further indication of the susceptibility of the carbon-sulfone bond to reductive cleavage without reduction of the sulfone group (17). The addition of excess sodium followed by the addition of only enough ammonium chloride to discharge the blue color of the excess sodium

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[3] There is a rather interesting difference in the absorption spectra of methyl vinyl sulfone (16) and ethyl vinyl sulfone (9). The absorption spectra of several α,β-unsaturated sulfones is being investigated in order to determine whether there are any correlations in the maxima similar to those for the α,β-unsaturated ketones.

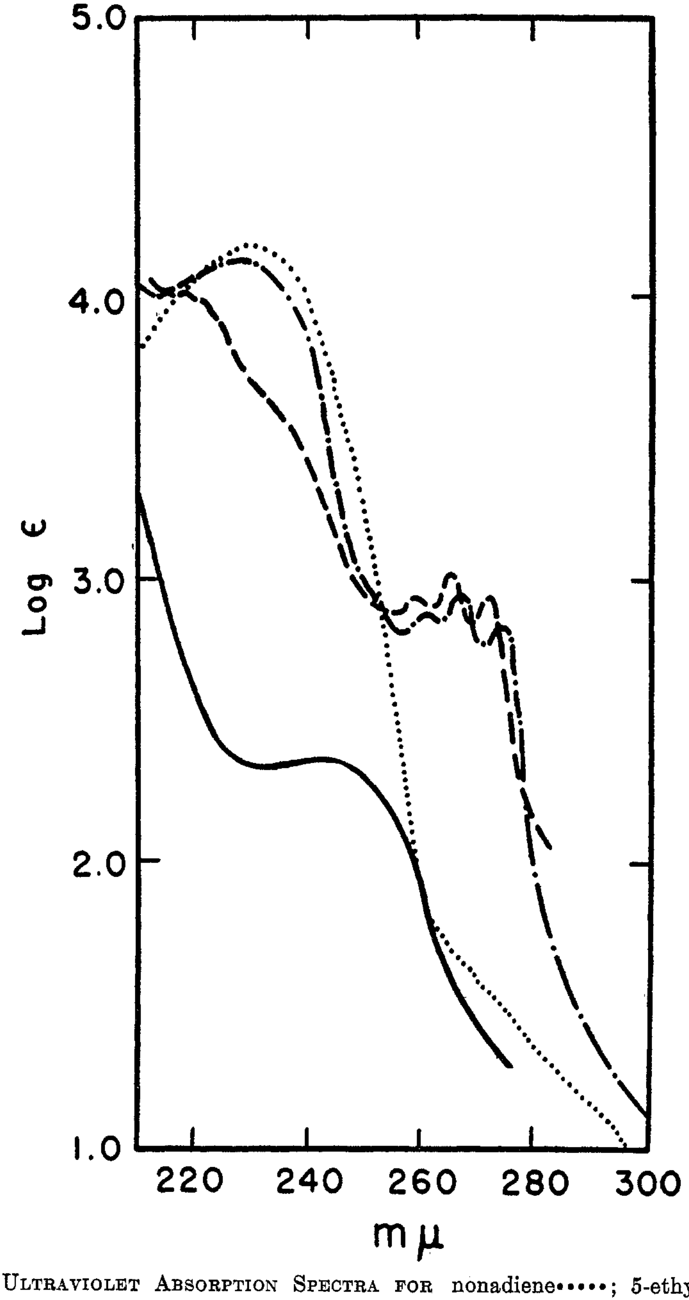
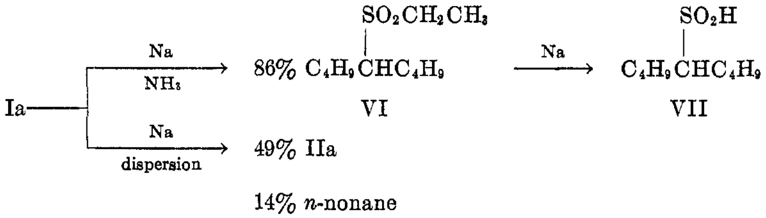


FIG. 1. ULTRAVIOLET ABSORPTION SPECTRA FOR nonadiene•••••; 5-ethylsulfonyl-4-nonene (III)————; 5-phenylsulfonyl-4-nonene (X)—•—•; 5-phenylsulfonylnonane (XII)——.

after the reaction gave some cleavage of the monosulfone (VI) to nonane-5-sulfinic acid (VII) so that a mixture of 53% of VI and 25% of VII was obtained.

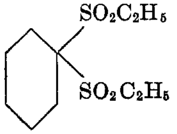
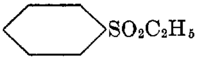
Sodium dispersion in toluene gave an exothermic reaction upon being mixed with the β-disulfone (Ia) and from the reaction mixture there was isolated 14% of *n*-nonane and 49% of the alkene (IIa).



In order to test the effect of the phenyl group on the lability of the β-sulfones toward elimination and reduction, 5,5-bis-(phenylsulfonyl)nonane (IX) was prepared and studied. Since this sulfone cannot give alkenes such as II it should show either elimination or reductive cleavage. Upon treatment of (IX) with excess potassium *tert*-butoxide in refluxing *tert*-butyl alcohol there was obtained an unsaturated hydrocarbon whose elemental analysis, quantitative catalytic hydrogenation, and ultraviolet absorption spectrum (Fig. 1) indicate that it must be a diene. The ultraviolet absorption maximum at 229 mμ with a log ε of 4.18 agrees quite well with the expected value of 227 mμ with a log ε of about 4.35 (18). The diene was oxidized with potassium permanganate in aqueous alkali and the resulting acids were identified by a paper chromatographic proce-

TABLE II

REDUCTIVE CLEAVAGE OF BIS-(ALKYLSULFONYL)ALKANES

SULFONE	REAGENT	CONDITIONS	PRODUCTS
Ib[a]	Ni, H_2[b], cyclohexane	8 hrs., 220°	72% VI, 8% RCH_2R (VIII)
Ib[a]	Ni, H_2[b], cyclohexane	36 hrs., 250°	78% VIII
Ib[a]	Ni, H_2[b], 10% NaOH	36 hrs., 250°	14% IIb, 14% VIII, 55% $RCH{=}CHCH_2CH(CH_3)_2$
Ia	Na, NH_3, 2½:1	1 hr.[c]	86% VI
Ib	Na, NH_3, 2½:1	1 hr.	73% $R_2CHSO_2C_2H_5$
Ia	Na, NH_3, 3½:1	1 hr.	53% VI, 24% VII[d]
	Na, NH_3	1 hr.	61% 
Ia	Na dispersion	Several hrs., 25-40°	35% IIa, 14% *n*-nonane 49% IIa, 14% *n*-nonane

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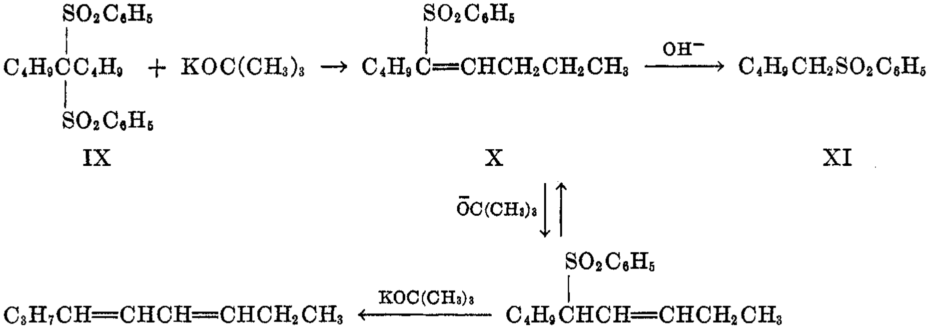
[a] Reported previously, *cf.* ref. (2); [b] 2500 lbs. pressure; [c] The reaction appeared to be nearly instantaneous, 1 hr. was the time allowed between the last addition of sodium and the addition of ammonium chloride; [d] Assuming the monohydrate.

dure. Acetic, propionic, butyric, and valeric acids were found but there were no indications of formic or caproic acids. Thus it would seem that the diene is a mixture of 3,5-nonadiene and 2,4-nonadiene.

The 3,5-nonadiene could result from an α,β- to β,γ-shift of the double bond in 5-phenylsulfonyl-4-nonene (X) followed by elimination of the second phenylsulfonyl group. Although the elimination of this second sulfone group requires a base attack on the hydrogen β to the sulfone which is less acidic than the α-hydrogen there are other examples of elimination reactions occurring under similar circumstances; *i.e.*, the formation of alkenes from monosulfones and the formation of α,β-unsaturated esters from α-halogen esters. These reactions are possible because the removal of the α-hydrogen is a reversible process while the competing reaction, the simultaneous removal of the β-hydrogen and expulsion of the group being eliminated, is an irreversible process.

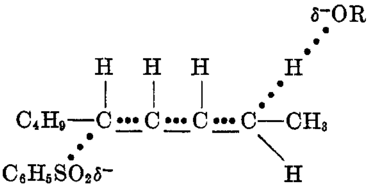


$$C_4H_9\overset{SO_2C_6H_5}{\underset{SO_2C_6H_5}{C}}C_4H_9 + KOC(CH_3)_3 \rightarrow C_4H_9\overset{SO_2C_6H_5}{C}{=}CHCH_2CH_2CH_3 \xrightarrow{OH^-} C_4H_9CH_2SO_2C_6H_5$$

IX X XI

$$\text{X} \underset{\bar{O}C(CH_3)_3}{\rightleftarrows} C_4H_9\overset{SO_2C_6H_5}{C}HCH{=}CHCH_2CH_3 \xrightarrow{KOC(CH_3)_3} C_3H_7CH{=}CHCH{=}CHCH_2CH_3$$

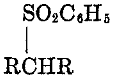
Since there are apparently no examples of a base-catalyzed β,γ- to γ,δ-shift of a double bond without the influence of a second activating group, and since there is no obvious path for such a shift, the 2,4-nonadiene may result from a direct elimination process which might be termed an E_4 elimination since it would resemble an E_2 elimination occurring across a double bond in the α,β-unsaturated sulfone. While there seem to be no well established examples of the occurrence of an elimination process of this type there is a possibility that such a mechanism may be operating in the formation of other dienes (19b).



The diene gives an adduct with maleic anhydride which is not the 1:1 product but, judging from the neutral equivalent, it is a mixture of adducts from dimers and trimers of the diene with the maleic anhydride. Esafov and Molchanova (19a) have reported similar results with long chain dienes. In addition to the diene there was obtained 19% of 1-phenylsulfonylpentane (XI). This would have been produced by a retrogressive aldol reaction as described for 1-ethyl-

TABLE III

REACTIONS OF 5,5-BIS-(PHENYLSULFONYL)NONANE (IX)

REAGENT	CONDITIONS	PRODUCTS
$KOC(CH_3)_3$, 5½:1 *tert*-butyl alcohol	48 hrs. reflux	56% Nonadiene[a], 18% XI
$KOC(CH_3)_3$, 1½:1 *tert*-butyl alcohol	44 hrs. reflux	22% Nonadiene,[a] 30% XI, 32% unreacted IX
Na, NH_3	3-4 hrs.	29% *n*-Nonane[b], 30% benzene
Na dispersion	5.5 hrs. reflux in benzene	29%  $\overset{SO_2C_6H_5}{\overset{\vert}{RCHR}}$ (XII)

[a] Mixture of 2,4- and 3,5-isomers; [b] Estimated from refractive index.

sulfonylpentane (IV). Only the slightest trace of water in the system could have given the observed result since the aldehyde produced would have undergone aldol polymerization with regeneration of some of the water initially used. That this may have occurred was indicated by the darkening of the solution as the reaction proceeded.

Upon treatment of 5,5-bis-(phenylsulfonyl)nonane (IX) with sodium in liquid ammonia there was obtained about 29% of *n*-nonane with some benzene and biphenyl. The appearance of the benzene and biphenyl indicates that some cleavage of the sulfone-phenyl bond occurred with formation of sodium phenyl. This is similar to the cleavage of phenyl sulfone by sodium in xylene (20).

The products obtained by treatment of IX with sodium in liquid ammonia and sodium dispersion are given in Table III. It is apparent (*Cf.* Table II) that these two reagents give opposite results with Ia and IX. During the fractionation of the products from the reaction of sodium dispersion with IX considerable decomposition was observed and some material with nearly the same boiling point as XII was obtained; its refractive index indicated that it might be the unsaturated sulfone. Since no starting material was recovered it seemed that the observed decomposition may have been a thermal decomposition of the sulfone (IX).

When 5,5-bis-(phenylsulfonyl)nonane (IX) was heated to 200–250° considerable charring occurred, (decomposition of benzene-sulfinic acid) and there was obtained a 90–95% yield of 5-phenylsulfonyl-4-nonene (X) whose ultraviolet absorption spectrum is given in Fig. 1. The slight bathochromic shift of the benzenoid absorption is the same as that observed for phenyl sulfone (9). The thermal decomposition of 5,5-bis-(ethylsulfonyl)nonane (Ia) gave 64% of 5-ethylsulfonyl-4-nonene (III).

A rough comparison was made of the relative ease of thermal decomposition of 5,5-bis-(ethylsulfonyl)nonane (Ia) and 5,5-bis-(phenylsulfonyl)nonane (IX) and these results are summarized in Table IV. The difference in ease of elimination between the two β-disulfones is understandable in terms of a combination of no-bond resonance with the conjugative interaction of the double bond in the transition state, not only with the remaining sulfone group (8–11), but through this sulfone to the benzene ring (9, 21). In addition to the driving force

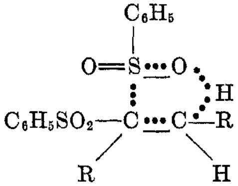
TABLE IV

PYROLYSIS OF β-DISULFONES

SULFONE	TEMP., °C.	TIME, min.	PRODUCT, %	UNREACTED, %
Ia	255–265	33	III, 64	
Ia	220–260	15	III, 68	8
Ia	228	20		82
IX	228	20		10
IX	255	20	X, 90	
IX	200–250, 20 mm.[a]	15–20	X, 96	

[a] With simultaneous distillation of the product.

provided by this conjugative interaction there is also, in both cases, an opportunity for some contribution from the hydrogen bonding interaction in the transition state between the β-hydrogen and an oxygen of the sulfone group being eliminated in much the same manner as for the acetate (22) and Chugaev (23) pyrolyses. The evidence from infrared studies (24) indicates that there is about as much hydrogen bonding strength in a sulfone as in an ester group.



Since the α,β-unsaturated sulfones III and X were readily prepared by the thermal decomposition reaction it was expected that they should be useful intermediates for the preparation of dienes if the assumption of X as an intermediate in the formation of the nonadiene was correct. When 5-ethylsulfonyl-4-nonene (III) and 5-phenylsulfonyl-4-nonene (X) were treated with potassium *tert*-butoxide in refluxing *tert*-butyl alcohol titration indicated, in each case, the consumption of somewhat less than one equivalent of the base in less than ten hours. The sulfone III gave 64% of the diene while X gave a 65% yield.

Previous methods of preparation of bis-(phenylsulfonyl)methane have used the condensation of methylene bromide or chloride with sodium thiophenoxide followed by oxidation of the mercaptal with either permanganate (25) or chromic acid (26). The β-disulfone is most readily prepared by condensation of formaldehyde with thiophenol followed by oxidation with hydrogen peroxide using the same procedure as for the bis-(ethylsulfonyl)methane (2).

EXPERIMENTAL[4]

The 5,5-bis-(ethylsulfonyl)nonane used in the following experiments was prepared by the alkylation of bis-(ethylsulfonyl)methane with butyl bromide as previously described (2).

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[4] Analyses by the Microanalytical Laboratory of the Department of Chemistry, University of California. The ultraviolet absorption spectra were taken in 95% ethanol using a Beckman Model DU spectrophotometer. All melting points are corrected.

REACTIONS OF 5,5-BIS-(ETHYLSULFONYL)NONANE (Ia)

a. With potassium tert-butoxide. To a suspension of potassium *tert*-butoxide from the solution of 7.0 (0.18 mole) of potassium in 75 ml. of *tert*-butyl alcohol was added 12.8 g. (0.09 mole) of 5,5-bis-(ethylsulfonyl)nonane and the mixture was allowed to reflux for 16 hrs. protected from moisture. The solution was diluted with water and extracted with pentane. The pentane extract was washed thoroughly with water and after drying over calcium chloride and removal of the solvent, fractionation of the residue through the 60 × 0.6 cm. wire gauze column (27) gave 5.6 g. (89%) of *3-n-butyl-2-heptene* (IIa) (2), b.p. 76–77° (17 mm.), n_D^{23} 1.4329. The 2,4-dinitrosulfonyl chloride adduct (28) melts at 127.5–130° after recrystallization from ethanol.

Anal. Calc'd for $C_{17}H_{25}ClN_2O_4S$: C, 52.50; H, 6.43; S, 8.24.

Found: C, 52.80; H, 6.64; S, 8.06.

In one experiment the aqueous solution after the pentane extraction was evaporated to dryness on the steam-bath and the residual salts were extracted with hot ethanol. Removal of the ethanol left the sodium salt of ethyl sulfinic acid, one gram of which was allowed to reflux in ethanol with 0.5 g. of *p*-nitrobenzyl chloride to give 0.55 g. (82%) of ethyl *p*-nitrobenzyl sulfone, m.p. 139–143° with previous softening. Recrystallization from chloroform gave a sample melting at 141–143.5° [lit. (29) 133–134°].

Anal. Calc'd for $C_9H_{11}NO_4S$: C, 47.15; H, 4.84; S, 13.98.

Found: C, 47.52; H, 4.78; S, 14.26.

b. With sodium ethoxide. A solution of 5.8 g. (0.252 mole) of sodium and 15.0 g. (0.048 mole) of Ia in 100 ml. of absolute ethanol was allowed to reflux for 48 hrs. protected from moisture. Dilution of the mixture with water, extraction with methylene chloride, and removal of most of the solvent through a short Vigreux column left a mixture which was cooled in an ice-salt bath to give 3.2 g. (21%) of Ia, m.p. 127–131°. The remainder of the reaction product was fractionated to give 0.6 g. (8%) of 3-*n*-butyl-2-heptene (IIa), b.p. 77–78° (17 mm.), n_D^{22} 1.4343 and 5.3 g. (50%) of *5-ethylsulfonyl-4-nonene* (III), b.p. 142–143° (4 mm.), n_D^{21} 1.4697.

Anal. Calc'd for $C_{11}H_{22}O_2S$: C, 60.50; H, 10.16; S, 14.68

Found: C, 60.67; H, 10.31; S, 14.36.

Ultraviolet absorption, λ_{max} 242 mμ, log ϵ 2.37.

A solution of 0.1362 g. of III in 20 ml. of acetic acid with 0.17 g. of 5% palladium on charcoal[5] took up 15 ml. of hydrogen (14 ml. calc'd) in six hours. The reduced sulfone, 5-ethylsulfonylnonane (VI), was recovered by evaporative distillation, n_D^{24} 1.4597 (from the sodium in liquid ammonia reaction, n_D^{24} 1.4598).

c. With potassium hydroxide in ethylene glycol. To a hot solution of 17 g. (0.257 mole) of potassium hydroxide in 150 ml. of ethylene glycol was added 10.0 g. (0.032 mole) of Ia and the mixture was heated at 160–165°. About 3 hrs. was required for solution of the sulfone and the mixture was heated a total of 17 hrs. After dilution with water and extraction with petroleum ether 0.9 g. (9%) of unreacted sulfone was recovered by filtration of both the organic and aqeuous solutions. After drying the petroleum ether solution and removing the solvent, the residual oil was fractionated to give 0.6 g. (12%) of impure IIa, b.p. 55–61° (10 mm.), n_D^{25} 1.4434, 2,4-dinitrosulfenyl chloride adduct, m.p. 123–126°, undepressed on admixture with an authentic sample and 2.7 g. (39%) of 5-ethylsulfonyl-4-nonene (III), b.p. 144–146° (2.5–3.0 mm.), n_D^{23} 1.4646 and about 0.5 g. (9%) of an intermediate fraction, b.p. 134–135° (2–3 mm.) which solidified on cooling, m.p. 35–48°. Recrystallization of this solid from pentane-ether by cooling in Dry Ice-acetone gave 1-ethylsulfonylpentane (IV) with m.p. 56–57°.

Anal. Calc'd for $C_7H_{16}O_2S$: C, 51.18; H, 9.82; S, 19.52.

Found: C, 50.88; H, 9.63; S, 19.53.

d. With sodium in liquid ammonia. To a suspension of 15.0 g. (0.048 mole) of Ia in 60 ml. of ammonia in a Dewar flask was added 2.7 g. (0.117 mole) of sodium in small pieces until

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[5] American Platinum Works, Newark, N. J.

the colorless solution became blue. After standing 1 hr., 10 g. of ammonium chloride was added to the solution in portions and the colorless solution was allowed to evaporate to dryness. After the addition of water to the residue chloroform extraction and fractionation gave 9.1 g. (86%) of *5-ethylsulfonylnonane* (VI), b.p. 140–141° (2.5 mm.), n_D^{24} 1.4598.

Anal. Calc'd for $C_{11}H_{24}O_2S$: C, 59.95; H, 10.98; S, 14.55.
Found: C, 59.88; H, 11.01; S, 14.29.

In the region from 219 mμ to 350 mμ the 5-ethylsulfonylnonane was transparent.

In another experiment with 30.0 g. (0.096 mole) of Ia and 7.6 g. (0.33 mole) of sodium the amount of ammonium chloride added was just sufficient to remove the blue color before evaporation of the ammonia. Treatment of the residue (which was quite sensitive to contact with air) as above gave 11.2 g. (53%) of 5-ethylsulfonylnonane (VI). The aqueous extract was acidified with hydrochloric acid, extracted with ether, and the ether was then dried and removed in a water-bath at 40°. The residual acids were titrated to the phenolphthalein end point with 0.5 *N* sodium hydroxide and, after removal of the water, the residue was dried *in vacuo* over barium perchlorate to leave about 5.5 g. (24% assuming the monohydrate) of the sodium salt of *5-nonanesulfinic acid* (VII). One gram of the salt was allowed to reflux for 18 hrs. with 0.8 g. of *p*-nitrobenzyl chloride in 10 ml. of ethanol. Removal of the alcohol and excess *p*-nitrobenzyl chloride by steam-distillation left 0.8 g. of material, m.p. 60–65°. Recrystallization of the solid from alcohol-water gave 0.6 g. (42%) of 5-nonyl *p*-nitrobenzyl sulfone, m.p. 82–83°. An analytical sample was prepared by recrystallization from carbon tetrachloride-ligroin, m.p. 86.5–87°, resolidifies and remelts at 90–90.5°.

Anal. Calc'd for $C_{16}H_{25}NO_4S$: C, 58.69; H, 7.70; S, 9.79.
Found: C, 58.51; H, 7.71; S, 9.35.

e. With sodamide. To a suspension in 75 ml. of ether of sodamide from 6.0 g. (0.26 mole) of sodium in liquid ammonia (30) was added 15.0 g. (0.048 mole) of Ia. The mixture was stirred for 20 hrs. and then 20 ml. of ammonia was distilled into the mixture which was then neutralized by the addition of 13 g. of ammonium chloride and stirred for 3 hrs. After the ammonia had evaporated from the solution the residue was taken up in water and 3.6 g. of starting material, m.p. 131–133°, was recovered by filtration of the ether and water. The ether was dried and evaporated and the residue was taken up in petroleum ether to leave another 3.2 g. of starting sulfone, m.p. 130–132°, total recovery, 6.8 g. (42%). Fractionation of the petroleum ether-soluble material gave 2.35 g. (32%) of the alkene IIa, b.p. 80° (20 mm.), n_D^{25} 1.4316, 2,4-dinitrosulfenyl chloride derivative, m.p. 127.5–130°.

There is apparently little reaction at liquid ammonia temperature as 14.5 g. out of 15.0 g. of Ia was recovered after treatment with 5.8 g. of sodium as sodamide for 5 hrs. in liquid ammonia.

f. With sodium dispersion. Within 10 min. after mixing 15.0 g. (0.048 mole) of Ia with 10 ml. of 50% sodium dispersion in toluene[6] in 25 ml. of dry benzene under a nitrogen atmosphere, the temperature had risen spontaneously to 40°. After 2¼ hrs. another 10 ml. of the dispersion was added and again the reaction was exothermic. A third addition of sodium was also exothermic but the fourth was not so the solution was then heated to refluxing in the oil-bath for 1 hr. To the stirred and cooled mixture there was slowly added 45 ml. of alcohol followed by 50 ml. of water. A pentane extract was dried and the pentane was removed. Fractionation of the residue at 20 mm. gave three fractions, (a) 0.4 g., b.p. 52–55°, n_D^{20} 1.4090; (b) 1.0 g., b.p. 55–79°, n_D^{20} 1.4228; (c) 2.3 g., b.p. 79–81°, n_D^{20} 1.4349. Fraction (a) did not react with bromine while fraction (c) did react. The atmospheric b.p.'s were (a) 150–153°, (c) 182–185°. Thus, from the refractive indices it can be calculated that the product consisted of about 0.87 g. (14%) of nonane [lit. (31) b.p. 150.8°, n_D^{20} 1.4055] and 2.83 g. (35%) of IIa. In another experiment, from 5 g. of starting sulfone there was obtained 1.3 g. (49%) of IIa and 0.3 g. (14%) of nonane.

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[6] Obtained through the courtesy of the National Distillers Chemical Co., Ashtabula, Ohio.

g. With sodamide in piperidine. To a solution of sodamide prepared from 6.0 g. (0.26 mole) of sodium in liquid ammonia was added 50 ml. of piperidine and the ammonia was removed by heating on the steam-bath. To the residual dark viscous liquid was added 10.0 g. (0.032 mole) of Ia and the mixture was heated for 3 hrs. on the steam-bath. After the addition of water and ether the ether extract was washed with dilute hydrochloric acid and with dilute potassium hydroxide and it was then dried and the solvent was removed. Fractionation of the residue gave 4.0 g. of liquid, b.p. 95–96° (40 mm.), n_D^{25} 1.4423. Refractionation of 3.5 g. at 30–33 mm. gave (a) 0.6 g., b.p. 88–89°, n_D^{23} 1.4350; (b) 0.3 g., b.p. 89–90.5°, n_D^{23} 1.4358; (c) 0.8 g., b.p. 90.5–91°, n_D^{23} 1.4371; (d) 1.0 g., 91–95°, n_D^{23} 1.4478. While the first three fractions are chiefly 3-*n*-butyl-2-heptene (IIa), the last fraction obviously contains some other material. An elementary analysis indicates that it is an oxygen-containing material. It was not further investigated. Judging from the refractive indices the yield of II was about 30%.

Sodium in Ammonia Reduction

a. 2,8-Dimethyl-5,5-bis-(ethylsulfonyl)nonane. Using the same procedure described above for the reduction of Ia, 15.0 g. of 2,8-dimethyl-5,5-bis-(ethylsulfonyl)nonane (Ib) (2) was treated with 3 g. of sodium in portions and there was obtained 8.0 g. (73%) of *2,8-dimethyl-5-ethylsulfonylnonane* (2), b.p. 141–143° (1–2 mm.), n_D^{25} 1.4564.

b. 1,1-bis-(ethylsulfonyl)cyclohexane. From 10.0 g. (0.037 mole) of 1,1-bis-(ethylsulfonyl) cyclohexane (2) and 3.0 g. (0.013 mole) of sodium in 40 ml. of ammonia there was obtained 4.0 g. (61%) of *1-ethylsulfonylcyclohexane*, b.p. 124–131° (1–1.5 mm.) which solidified upon standing, m.p. 25.5–26.5°. Recrystallization of this solid from carbon tetrachloride-ligroin followed by sublimation gave a sample which melted at 32–34°, $n_D^{33.5}$ 1.4838.

Anal. Calc'd for $C_8H_{16}O_2S$: C, 54.51; H, 9.15; S, 18.19.
Found: C, 54.67; H, 8.95; S, 17.96.

REACTIONS OF 5,5-BIS-(PHENYLSULFONYL)NONANE (IX)

a. With potassium tert-butoxide. To a solution of 8.0 g. (0.205 mole) of potassium in 135 ml. of *tert*-butyl alcohol was added 15.0 g. (0.0367 mole) of 5,5-bis-(phenylsulfonyl)nonane and the mixture was allowed to reflux. The reaction was followed by titration of aliquots of the solution. The half-life was about 3 hrs. but the heating was continued for two days. About 2.4 moles of potassium *tert*-butoxide were consumed per mole of disulfone. After the addition of water and extraction with methylene chloride, the organic extract was dried, the solvent was removed, and the residue was fractionated to give (a) 5 ml., b.p. 82–83°, n_D^{25} 1.3849; (b) 0.4 g., 83–156°, n_D^{25} 1.4281; (c) 1.35 g., 156–158°, n_D^{25} 1.4608; (d) 1.0 g., 59–60° (22 mm.), n_D^{25} 1.4620; (e) 0.5 g., 169–184° (5 mm.), n_D^{24} 1.5117; (f) 1.5 g., 184–205° (5 mm.), n_D^{24} 1.5124. Judging from the refractive indices of fractions (b), (c), and (d) there was present in the reaction product about 2.5 g. (56%) of *nonadiene*. Fraction 3 was analyzed.

Anal. Calc'd for C_9H_{16}: C, 87.02; H, 12.98.
Found: C, 86.60; H, 13.08.

Ultraviolet absorption spectrum $\lambda_{\max}$ 229 mμ, log ϵ 4.18. Calc'd (18) $\lambda_{\max}$ 227 mμ, log ϵ 4.35.

From 1.1 g. of fractions (e) and (f) by treatment with pentane-ether and cooling in Dry Ice-acetone there was obtained 0.74 g. of 1-phenylsulfonylpentane (XI), m.p. 28.7–31.6°. This represents 1.45 g. (18%) in the original distillate.

Anal. Calc'd for $C_{11}H_{16}O_2S$: C, 62.23; H, 7.60; S, 15.10.
Found: C, 62.53; H, 7.69; S, 14.85.

The aqueous extract was acidified and extracted with methylene chloride. Evaporation of the methylene chloride and crystallization of the residue from carbon tetrachloride gave 3.2 g. of crude benzenesulfinic acid which was identified by means of its quinone addition produce, m.p. 200–203° [lit. (32) 196°].

The disulfone (IX) (15 g.) was added to a solution of 1.7 g. (0.0435 mole) of potassium in 35 ml. of *tert*-butyl alcohol. After 44 hrs. 0.001 mole of base remained. When pentane was added to the residue remaining after the removal of the methylene chloride as described above, there was obtained 4.8 g. (32%) of starting sulfone (IX). Fractionation of the remainder of the product gave 0.7 g. (22%) of nonadiene, b.p. 54–55° (14 mm.), n_D^{23} 1.4624 and 2.33 g. (30%) of 1-phenylsulfonylpentane (XI), b.p. 169–171° (5 mm.), n_D^{23} 1.5178.

Reactions of the nonadiene. (A) *Polymerization.* A 0.95-g. sample of the diene (n_D^{19} 1.4712) which had stood for a month and a half in a cork-stoppered test tube was evaporatively distilled. A distillate of 0.52 g. was obtained, n_D^{19} 1.4634 and 0.4 g. of polymerized residue did not distill up to a bath temperature of 200°.

(B) *Diels-Alder reaction.* A 0.5-g. sample of the diene and 0.64 g. of maleic anhydride were dissolved in toluene and allowed to stand 20 hrs. at room temperature followed by a 3 hr. reflux period. After steam-distillation of the toluene the residue was heated in 20 ml. of refluxing 5% potassium hydroxide. Acidification and extraction with ether followed by filtration and removal of the ether left 0.32 g. of a viscous oil, N.E. 221. About 0.5 g. of resinous material was obtained by filtration of the ether, N.E. 267. Both of these products were alkali-soluble and would seem, therefore, to be mixtures of the adducts obtained by the addition of maleic anhydride to dimeric or trimeric material (19).

(C) *Hydrogenation.* Catalytic hydrogenation of 0.247 g. of the diene in 5 ml. of acetic acid with 0.03 g. of Adams' platinum catalyst[5] indicated an absorption of 82.5 ml. (86%) of hydrogen, calc'd 95.8 ml. The saturated hydrocarbon recovered from the hydrogenation had a b.p. (micro) of 150.5–150.8°, n_D^{20} 1.4054, which agrees with nonane (31).

(D) *Oxidation.* The nonadiene (0.302 g.) was added to a mixture of 3.0 g. (0.019 mole) of potassium permanganate in 50 ml. of water with 6 drops of 12 *N* sodium hydroxide. After the mixture had been shaken for 10 minutes it was allowed to stand for two weeks. The excess permanganate was removed with sodium sulfite, the manganese dioxide was filtered off, and the aqueous solution was evaporated to dryness. It was acidified with conc'd HCl and extracted with ether over anhydrous magnesium sulfate. The acids in the ether were neutralized with aqueous ammonia and, after evaporation of the ether, the residue was diluted to 10 ml. Blanks were prepared with acetic, propionic, butyric, and valeric acids in 10 ml. of ammonia solution. A descending chromatographic technique (33) was used with a solvent made by shaking 75 parts of *n*-butyl alcohol, 20 parts of water, and 5 parts of concentrated ammonia and using the organic phase. The spots were made visible by spraying the paper with an acidified solution of 1% Bromcresol Green in 50% alcohol.

The following R_f values were obtained:

LITERATURE (33)	BLANK	FROM DIENE	ACID REPRESENTED
0.11	0.12	0.13	Acetic
.19	.19	.18	Propionic
.29	.30	.29	Butyric
.41	.42	.43	Valeric

No other spots corresponding to formic or caproic acids were visible.

(*b*) *With sodium in ammonia.* To 10 g. (0.0245 mole) of the sulfone (IX) in 60 ml. of ammonia in a Dewar flask was added 4.4 g. (0.191 mole) of sodium in portions over a period of 2–3 hrs. The reaction was slower than in the case of Ia and the solution passed through a series of color changes from yellow to red to green to blue. The blue solution was allowed to stand for 1 hr. and then 15 g. (0.28 mole) of ammonium chloride was added in portions. The color changes occurred in reverse order during the addition of the ammonium chloride. Water and ether were added and the ammonia was allowed to evaporate. After separating and drying the ether it was carefully fractionated and there was obtained (a) 1.3 g., b.p. 60–80°, n_D^{18} 1.4728; (b) 0.1 g., 80–140°, n_D^{18} 1.4770; (c) 0.9 g., 40–70° (majority at 63°) (20 mm.), n_D^{18} 1.4098. The residue was evaporatively distilled to give 0.3 g. Fraction (a) was refractionated and most of it had b.p. 78–81°, n_D^{19} 1.5005 (benzene n_D^{20} 1.5014). Fraction (c) had an atmospheric b.p. of 150–151° and is probably chiefly *n*-nonane and would represent a 29% yield.

(*c*) *With sodium dispersion.* To 15.0 g. of 5,5-bis-(phenylsulfonyl)nonane stirred in 25 ml. of benzene was added 10.0 g. of 50% sodium dispersion in toluene.[6] After an initially slightly exothermic reaction the mixture was heated to refluxing for 5½ hrs. and then absolute ethanol was added slowly with cooling until all of the sodium had been destroyed. Water was added and the benzene was separated, washed with water, and dried. After removing the solvent the residue was evaporatively distilled at 200° (1.5 mm.) with much decomposition to give 6.2 g. of a dark oil. Redistillation gave 6.0 g. of product and subsequent fractionation of 2.0 g. of this material at 1.6 mm. gave (a) 0.45 g., 167–169°, n_D^{20} 1.5446; (b) 0.95 g., 169–170°, n_D^{20} 1.5174. Analysis of fraction (b) indicates that it is primarily *5-phenylsulfonylnonane* (XII) and represents a yield of about 29%.

Anal. Calc'd for $C_{15}H_{24}O_2S$: C, 67.12; H, 9.01; S, 11.94.

Found: C, 67.45; H, 9.00; S, 12.15.

The ultraviolet absorption spectrum showed typical benzene peaks at λ_{max} 259 mμ, log ϵ 2.94; λ_{max} 265 mμ, log ϵ 3.03; λ_{max} 272 mμ, log ϵ 2.94. In addition there was a broad band in the 215–220 mμ region, with slight peaks at 215 mμ, log ϵ 4.00, and 218 mμ, log ϵ 4.02.

After the following pyrolysis experiments fraction (a) was identified as 5-phenylsufonyl-4-nonene (X), resulting from thermal decomposition of the unreacted starting material (IX). The material responsible for the high refractive index was removed by treatment with Raney nickel.

(*d*) *Pyrolysis.* Compound IX (2 g.) was heated in a horizontal sublimer under 20 mm. pressure. Between 200–250° extensive decomposition occurred and a dark liquid distilled. The distillate was treated with charcoal in ether and, after removal of the ether, the residue was taken up in ethanol and treated with Raney nickel. The nickel and solvent were removed and the residue was evaporatively distilled at 200° (2.5 mm.) to give 1.25 g. (96%) of *5-phenylsulfonyl-4-nonene* (X) as a colorless viscous oil, n_D^{24} 1.5224.

Anal. Calc'd for $C_{15}H_{22}O_2S$: C, 67.65; H, 8.32; S, 12.02.

Found: C, 67.28; H, 8.33; S, 11.63.

Ultraviolet absorption spectrum, λ_{max} 227 mμ, log ϵ 4.13; λ_{max} 260 mμ, log ϵ 2.88; λ_{max} 266 mμ, log ϵ 3.0; λ_{max} 274 mμ, log ϵ 2.8; minima at 214 mμ, log ϵ 4.03; 256 mμ, log ϵ 2.82; 263 mμ, log ϵ 2.86, and 270 mμ, log ϵ 2.78.

On a larger scale 7.5 g. of the disulfone gave 4.4 g. (90%) of X after heating at 255° for 20 min.

Pyrolysis of 5,5-bis-(ethylsulfonyl)nonane (Ia) The disulfone (Ia) (10 g.) was heated in an oil-bath at 255–265° for 33 min. The product was treated as described above and there was obtained 4.5 g. (64%) of *5-ethylsulfonyl-4-nonene* (III) n_D^{24} 1.4729. In another experiment with heating for 15 min. at 220–260° there was obtained from 2.0 g. of the disulfone, 0.95 g. (68 %) of the unsaturated sulfone (III), n_D^{25} 1.4688 and 8% of unreacted starting material.

A rough comparison of the rates of decomposition was made at 228°. After 20 min. there was recovered from 1.0 g. of 5,5-bis-(phenylsulfonyl)nonane (IX) 0.1 g. of unreacted disulfone. From 10 g. of the 5,5-bis-(ethylsulfonyl)nonane (Ia) there was recovered 8.2 g. of unreacted starting material.

REACTION OF POTASSIUM *tert*-BUTOXIDE WITH α,β-UNSATURATED SULFONES

(*a*) *With 5-ethylsulfonyl-4-nonene* (III). To a solution of 2.4 g. (0.061 mole) of potassium in 100 ml. of *tert*-butyl alcohol was added 3.9 g. (0.0179 mole) of III and the alcohol was heated to refluxing for 24 hrs. Titration of an aliquot indicated that 0.0135 mole of base had been consumed after ten hours and that there was no appreciable uptake of base after that time. From the reaction mixture there was isolated 1.42 g. (64%, b.p. 62–63° (23 mm.), n_D^{22} 1.4622 of nonadiene and about 0.2 g. (7%) of 1-ethylsulfonylpentane (IV).

(*b*) *With 5-phenylsulfonyl-4-nonene* (X). Application of the same procedure to 7.1 g. (0.0267 mole) of X with 6.4 g. (0.164 mole) of potassium in 100 ml. of *tert*-butyl alcohol gave 2.14 g. (65%) of nonadiene, b.p. 62–63° (23 mm.), n_D^{27} 1.4603.

Bis-(phenylsulfonyl)methane.[7] A mixture of 42.7 g. (0.39 mole) of thiophenol, 5.83 g. (0.195 mole) of paraformaldehyde, and 0.5 g. of *p*-toluenesulfonic acid was heated on the steam-bath. After a vigorous exothermic reaction the solution was heated 4 hrs. and then

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[7] We are indebted to Mr. Peter Lim for the preparation of a quantity of this material.

dissolved in 125 ml. of glacial acetic acid. To the stirred, cooled solution there was added 150 ml. (1.54 moles) of 35% hydrogen peroxide[8] dropwise at such a rate that the temperature was maintained between 45° and 60°. The addition required about an hour and the solution was then stirred an additional 73 hrs. at room temperature. Permanganate titration indicated about 40% of the theoretical amount of peroxide consumed at the end of the addition and 110% after the 73 hrs. The solution was cooled in an ice-bath and the crystalline product was filtered. After being washed with water it was dissolved in 250 ml. of 15% sodium hydroxide. Filtration from a little insoluble material, acidification, and recrystallization of the product from ethanol gave 51 g. (89%) of material melting 118.5–120.5° [lit. (25) 118–119°].

1,1-Bis-(phenylsulfonyl)pentane. To a cooled and stirred suspension of 2.7 g. (0.112 mole) of sodium hydride in 100 ml. of dimethylformamide was added 36 g. (0.111 mole) of bis-(phenylsulfonyl)methane. After the initial vigorous reaction had subsided the solution was stirred at room temperature until all of the sodium hydride had dissolved. After the addition of 23 g. (0.167 mole) of *n*-butyl bromide the mixture was heated to 80–90°. Titration indicated that the reaction apparently has a half-life of less than a minute. The mixture was diluted with water and the product was filtered and triturated with 5% sodium hydroxide. Recrystallization from ethanol gave 40.8 g. (94%), m.p. 103–105°. An analytical sample was prepared by recrystallization from ethanol, m.p. 103.5–105.5°.

Anal. Calc'd for $C_{17}H_{20}O_4S_2$: C, 57.95; H, 5.71; S, 18.19.

Found: C, 57.56; H, 5.72; S, 17.94.

5,5-Bis-(phenylsulfonyl)nonane. The second alkylation was carried out without isolation of the monoalkyl product which was prepared as described above from 80 g. of bis-(phenylsulfonyl)methane, 6.5 g. of sodium hydride, and 37 g. of butyl bromide in 160 ml. of dimethylformamide. Another 6.5 g. of sodium hydride was added and after 6 hrs. stirring at room temperature it had reacted and 40 g. of *n*-butyl bromide was added. After 18 hrs. at 95° the solution was diluted with water but the crude product was apparently a mixture of mono- and di-sulfone and it was dried and redissolved in dimethylformamide and treated with 3.5 g. of sodium hydride as above followed by 25 g. of *n*-butyl bromide. The mixture was then heated for 3 days at 85–100°. Water was added and the precipitated solid was washed with ethanol and then recrystallized from glacial acetic acid to give a first crop of 50 g., m.p. 105–107°. A second crop of 27 g. melted at 86–97° and after recrystallization from ethanol gave 15.3 g., m.p. 103–105°. The total recovery was about 65 g. (61%) of the disulfone and 20 g. of a mixture of mono- and di-sulfone.

An analytical sample was prepared by recrystallization from ethanol, m.p. 105–107°.

Anal. Calc'd for $C_{21}H_{28}O_4S_2$: C, 61.85; H, 6.92; S, 15.68.

Found: C, 61.72; H, 6.91; S, 15.44.

SUMMARY

The reactions of 5,5-bis-(ethylsulfonyl)nonane (Ia) with various basic reagents have been investigated. Potassium *tert*-butoxide gives an 89% yield of 3-*n*-butyl-2-heptene while sodium ethoxide gives 50% of 5-ethylsulfonyl-4-nonene. The principal reaction products obtained with Ia and potassium hydroxide in ethylene glycol, sodamide in ether, sodiopiperidide and sodium dispersion in benzene have also been determined. Sodium in liquid ammonia with Ia gives 86% of 5-ethylsulfonylnonane (VI). The reaction of potassium *tert*-butoxide with 5,5-bis-(phenylsulfonyl)nonane (IX) gives a mixture which appears to be 2,4- and 3,5-nonadiene. The behavior of sodium in liquid ammonia and sodium dispersion with IX has also been determined.

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[8] Albone "35" from the Electrochemicals Department of E. I. du Pont de Nemours and Co., Inc.

Pyrolysis of IX at 225–250° gives 90–96% of 5-phenylsulfonyl-4-nonene (X) while pyrolysis of Ia gives 64% of III. Potassium *tert*-butoxide with either X or III gives about 65% of the nonadiene.

The various factors affecting these elimination reactions have been discussed.

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