

*Anal.* Calcd. for  $C_{16}H_{18}O_4NS$ : C, 58.01; H, 3.96; N, 4.23; S, 9.66. Found: C, 57.90; H, 4.03; N, 4.25; S, 9.74.

**Independent Synthesis of IX.**—To a stirred, cooled solution of 4 g. (0.0247 mole) of benzoylacetone in 120 ml. of 0.25 *N* sodium hydroxide was added slowly a cold solution of 3.7 g. (0.0231 mole) of bromine and 10 g. of sodium bromide in 40 ml. of water, followed by 5 ml. of 1 *N* hydrobromic acid. The resulting oil was taken up in ether. The ether solution was washed with water and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure at room temperature to leave 5.93 g. (99%) of crude 3-bromobenzoylacetone as a pale yellow oil.<sup>29</sup> Addition of a drop of this product to a solution of potassium iodide in 2 ml. of water and 5 ml. of acetic acid under nitrogen produced immediately the dark brown color of iodine.

To a solution of 1.5 g. of crude 3-bromobenzoylacetone in 5 ml. of glacial acetic acid was added 5 ml. of 30–32% acetic acid–hydrogen bromide solution (Eastman Kodak Co). After stirring for 5 hr. at room temperature, the reaction mixture was poured into water, and the resulting mixture was extracted with ether. The ether extract was washed with water and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure at room temperature to leave 9–10 g. of an acetic acid solution of 1-bromobenzoylacetone, the maximum yield of which would be 1.5 g.<sup>30</sup> A negative test<sup>31</sup> for active halogen was obtained with a few drops of this solution (see above). The remainder of the solution was placed under reduced pressure until most of the acetic acid was removed. The residue was taken up in 5 ml. of dry acetonitrile, and 1 ml. of dry pyridine was added. After adding dry ether to produce cloudiness, the mixture was cooled in a refrigerator for 3 days to give 0.65 g. (35%) of 1-benzoylacetone pyridinium bromide, m.p. 177–182° dec. and at 181.5–183° dec. after recrystallization from a minimum of hot anhydrous ethanol, reported<sup>25</sup> m.p. 181° dec. The infrared spectrum of the pyridinium bromide showed peaks at 3.32, 5.77, 5.94, 6.12, 6.26, 6.35, 6.70, 7.52 and 8.26  $\mu$ .

The isomerization of 1.5 g. of crude 3-bromobenzoyl-

(29) Krohnke and Timmler<sup>25</sup> reported that this product could not be distilled.

(30) An attempt to distil this solution at 0.2 mm. led to decomposition with foaming near 100°, leaving in the flask an acetone-insoluble black gum.

(31) In this test only a yellow color was produced like that observed with chloroacetone under similar conditions.

tone was repeated to give the acetic acid solution of 1-bromobenzoylacetone (maximum yield 1.5 g., 0.0062 mole). This solution and 1.35 g. (0.0065 mole) of sodium benzenesulfinate dihydrate were dissolved in 50 ml. of 95% ethanol and the solution was refluxed for 24 hr. Most of the alcohol was removed under reduced pressure and cold water was added to the residue. The resulting precipitate was collected on a funnel and washed with water to give 1.05 g. (56%, based on crude 3-bromobenzoylacetone) of sulfone- $\beta$ -diketone IX, m.p. 143–145° after recrystallization from hexane–ethyl acetate. This m.p. was not depressed on admixture with a sample of IX obtained as described above; the infrared spectra of the two samples were identical.

**Treatment of 3-Bromobenzoylacetone with Sodium Benzenesulfinate.**—A solution of 1.0 g. (0.0041 mole) of crude 3-bromobenzoylacetone and 0.90 g. (0.0043 mole) of sodium benzenesulfinate dihydrate in 100 ml. of 95% ethanol was refluxed for 24 hr. The ethanol was evaporated, and the residue was triturated with dry ether, only part of the residue dissolving. The ether-insoluble material (0.679 g.) evidently contained sodium benzenesulfonate, not sodium benzenesulfinate, since its infrared spectrum (in KBr) was identical with that of the former salt and quite different from that of the latter salt. The ether-insoluble solid also appeared to contain some sodium bromide, since treatment of it with aqueous silver nitrate gave a precipitate that was insoluble in concentrated nitric acid. Silver benzenesulfonate (or benzenesulfinate) is soluble in this acid.

The ether solution obtained as described above was washed with sodium bicarbonate solution, then with water, and dried over anhydrous magnesium sulfate. The solvent was removed, and the residue (which did not give a test for active halogen) was recrystallized from benzene–hexane to give 0.191 g. (18%) of benzenesulfonylacetophenone, m.p. 70–80° and at 94–95° after recrystallization from methanol. This product was identified by the mixed melting method and by comparison of infrared spectra employing an authentic sample (m.p. 93–94°) prepared from sodium benzenesulfinate and  $\alpha$ -chloroacetophenone.<sup>32</sup>

The benzene–hexane filtrate (see above), on standing and evaporation of some of the solvent, gave a precipitate of 0.148 g. (22%) of benzoylacetone, m.p. 50–53° (identified by infrared spectrum).

The experiment was repeated with 0.001 mole each of crude 3-bromobenzoylacetone and sodium benzenesulfinate, and the reaction mixture (after 24 hr.) was poured into ice-water to precipitate benzoylacetone, m.p. 53–55°, in 25% yield.

(32) See J. Troger and O. Beck, *J. prakt. Chem.*, [2] **87**, 295 (1913).

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, UNION CARBIDE CHEMICALS CO., SOUTH CHARLESTON 3, W. VA.]

## A New Reaction of Allylic Sulfones<sup>1</sup>

BY EDWARD M. LA COMBE AND BYRON STEWART

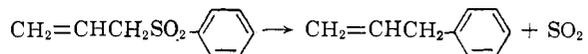
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Allylic sulfones have been found to undergo a thermal rearrangement accompanied by loss of sulfur dioxide to give olefinic products. Thus, when allyl benzyl sulfone is heated at a temperature of 215°, 4-phenyl-1-butene and sulfur dioxide are obtained as products. This reaction provides a novel method for lengthening carbon chains. The mechanism of the reaction is discussed.

Although there is considerable information on thermal reactions and rearrangements of allylic compounds in general, relatively little can be found regarding allylic sulfones. Allylic sulfones were the subject of one earlier study<sup>2</sup> to determine whether thermal rearrangement to the corresponding sulfinic esters occurred. No rearrangement was detected and in fact it was noted that one of

the sulfones studied, allyl phenyl sulfone, was stable up to about 250°.

We have found that allylic sulfones, including allyl phenyl sulfone at higher temperatures, undergo a thermal rearrangement to give olefinic compounds and sulfur dioxide. For example, allyl phenyl sulfone, when heated to 300–400°, yields allylbenzene and sulfur dioxide as



The reaction has been found to be general, but the temperature required to cause the pyrolysis is

(1) Presented in part before the Division of Organic Chemistry, 135th Meeting of the American Chemical Society, Boston, Mass., April 5–10, 1959.

(2) A. C. Cope, D. E. Morrison and I. Field, *J. Am. Chem. Soc.*, **72**, 59 (1950).

TABLE I  
PYROLYSIS OF ALLYLIC SULFONES OF THE GENERAL FORMULA  $RSC_2R'$ , WHERE  $R =$  UNSUBSTITUTED OR SUBSTITUTED ALLYL AND  $R' =$  UNSUBSTITUTED OR SUBSTITUTED ALKYL OR ARYL

R	R'	Method	Temp., °C.	Press., Mm.	Product	B.p., °C.		n <sub>D</sub> <sup>20</sup>	Yield, %	Analyses, %			Calcd. H	Other		
						°C.	Mm.			Found C	Found H	Found Cl				
$CH_2=CClCH_2$	$CH_2CH_2OAc$	Batch	170-190	100	$CH_2=CCl(CH_2)_2OAc$	74	10	1.4410	56	51.8	7.0	21.6	51.7	6.77	21.85	Cl
$CH_2=CClCH_2$	$n-C_4H_9$	Batch	175-200	100	$CH_2=CCl(CH_2)_6CH_3$	79	20	1.4355-1.4357	65	65.3	10.7	22.1	67.3	10.6	22.1	Cl
$CH_2=CHCH_2$	$CH_3CH_2-C_2H_5$	Batch	190-245	Atm.	$CH_2=CHCH_2CH_2CH=CH_2$	58	Atm.	1.3976	28	87.2	12.4		87.8	12.2		
$CH_2=CHCH_2$	$CH_3C_6H_5$	Batch	200-215	50	$CH_2=CHCH_2CH_2C_6H_5$	73.5	20	1.5020	35	90.8	9.4		90.9	9.1		
$CH_2=CHCH(CH_3)$	$CH_2C_6H_5$	Batch	210	50	$CH_2CH=CHCH_2CH_2C_6H_5$	63-65	5	1.5028-1.5032	32	90.2	9.8		90.4	9.6		
$CH_2=CHCH_2$	$CH_3$	Batch	200	Atm.	$CH_2=CHCH_2CH_3$	(Gas)		....	..							
$CH_2=CHCH_2$	$CH_3CH=CH_2$	Continuous	340-387	Atm.	$CH_2=CHCH_2CH_2CH=CH_2$	60	Atm.	1.3980	79							
$CH_2=C(CH_3)CH_2$	$CH_2C(CH_3)=CH_2$	Continuous	374-383	Atm.	$CH_2=C(CH_3)CH_2CH_2C(CH_3)=CH_2$	57.5	100	1.4238	58							
$CH_2=CHCH_2$	$CH_3COOC_2H_5$	Continuous	380-387	Atm.	$CH_2=CHCH_2CH_2COOC_2H_5$	68-69	50	1.4106-1.4110	24	64.9	9.7		65.7	9.4		
$CH_2=CHCH_2$	$i-C_3H_7$	Batch	190-245	150	$CH_2=CHCH_2-C_3H_7$	71-75	50	1.4235-1.4250	25							
$CH_2=C(CN)CH_2$	$CH_3$	Batch	190-240	90	$CH_2=C(CN)CH_2CN$	56	100	1.4065	47	72.7	9.7	16.8	N	74.1	8.6	17.3
$CH_2=CHCH_2$	$CH_3COCH_3$	Batch	220-240	200	$CH_2=CHCH_2CH_2COCH_3$	71-71.5	100	1.4161-1.4162	46	71.7	10.6		73.4	10.2		
$CH_2=C(F)CH_2$	$CH_3C_6H_5$	Batch	210-240	200	$CH_2=CFCH_2CH_2C_6H_5$	86	20	1.4873	45				13.08	F		12.7

<sup>a</sup> M.p. 2,4-dinitrophenylhydrazine 107-108° (lit. 107-108°).

dependent on the structure of the sulfone. For example, although allyl phenyl sulfone requires the high temperatures mentioned above, 2-(2-chloroallylsulfonyl)-ethyl acetate can be successfully converted to 4-chloro-4-pentenyl acetate at temperatures as low as 170-190°.

The data in Table I demonstrate the diversity of structure possible for the starting sulfone. Thus, in the equation where R represents the allylic radical, the following hydrocarbon groups were found to be satisfactory: allyl, methallyl, 1-methylallyl, and crotyl. Where R' represents the second radical, methyl, *n*-alkyl, *t*-alkyl, benzyl, phenyl and substituted phenyl groups were operable. In addition, many functional groups are unaffected by the conditions of the pyrolysis, making it possible to prepare many olefinic chloro and fluoro compounds, nitriles, esters, alcohols, acids, ketones and others. Further, these functional groups can be substituted on either of the radicals attached to the sulfone group. The following olefinic compounds which are not listed in Table I were prepared in a similar manner and in the following yields: 4-pentenyl acetate, 16%; allylbenzene, 6%; methyl 6-heptenoate, 9%; 4,4-dimethyl-1-pentene, 13%; 2,4,4-trimethyl-1-pentene, 16%; 3-butenylbenzene, 5%; *o*-allyltoluene, 2%; 4,4-dimethyl-1-hexene, 14%;  $CH_2=CHCH_2-C_6H_{13}$ -*t*, 13%; ethyl 2-pentenoate, 4%; isobutylbenzene, 2%; *p*-allylchlorobenzene, 2%; 1,9-decadiene, 15%.

Pyrolysis of diallyl sulfones and diallyl disulfones was successful and, in fact, the best yields were obtained when the radicals attached to the sulfone group were identical. Thus, 1,5-hexadiene was obtained in 79% yield from allyl sulfone.

By way of contrast, the saturated sulfone, *n*-butyl sulfone, when subjected to pyrolytic conditions in a hot tube showed no evidence of decomposition at 400°, the starting material being recovered in good yield. In another experiment, an equimolar mixture of *n*-butyl sulfone and allyl sulfone was passed through a hot tube at 375°. The only isolable products were 1,5-hexadiene, sulfur dioxide and recovered *n*-butyl sulfone, indicating no participation of the saturated sulfone.

Furthermore, vinyl sulfones<sup>3</sup> are prepared at temperatures of 350° demonstrating their good thermal stability and contrasting the behavior of the two types of unsaturated sulfones.

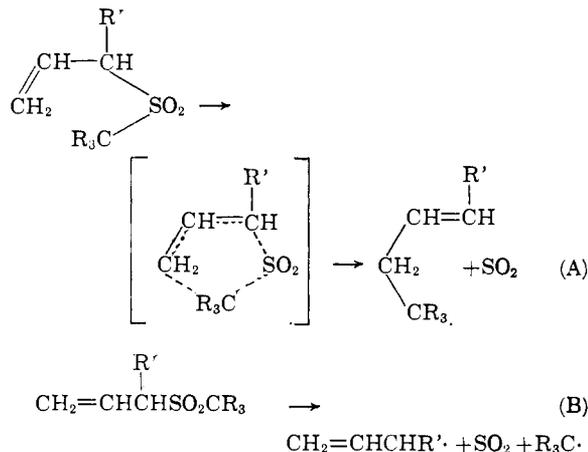
The question as to which position of the benzene ring the allylic group becomes attached was investigated by pyrolyzing allyl *o*-tolyl sulfone and allyl *p*-chlorophenyl sulfone. *o*-Allyltoluene was formed in the first pyrolysis and *p*-allylchlorobenzene in the second. However, the yields were very low (about 2%) and it seems likely from the distillation data that other isomeric disubstituted benzenes also were formed.

Allyl esters of sulfinic acids also can be expected to yield olefinic compounds by thermal treatment, probably by first rearranging to the allyl sulfone as an intermediate step. For example, it was demonstrated by Cope and co-workers<sup>2</sup> that allyl benzenesulfinate rearranged to allyl phenyl sul-

(3) U. S. Patent 2,474,808; D. L. Schoene to U. S. Rubber Co.

fone on heating at 100–175°. Further heating at elevated temperatures (300–400°), as shown above, would of course convert the allyl phenyl sulfone to allylbenzene.

Two mechanisms seem to be operative, one an intramolecular, four-center, cyclic mechanism (A) which predominates at lower temperatures and a free radical mechanism (B) encountered at higher temperatures. Evidence for mechanism A was



the formation of 5-phenyl-2-pentene (32% yield) from benzyl 1-methylallyl sulfone at 210°, and the apparent lack of catalysis by acidic or basic materials. To be sure, this result could be explained also by mechanism B but such an explanation would require RR' radicals R and R' from RSO<sub>2</sub>R' to form RR' exclusively without forming RR or R'R'. Although radical reactions become more specific at lower temperatures, this result would hardly be expected. No 1,5-hexadiene or 3,3,4,4-tetramethylhexane were observed.

Evidence for mechanism B was the formation from allyl *t*-pentyl sulfone at 350° of propylene, 1,5-hexadiene, 2-methyl-1-butene, isopentane and 4,4-dimethyl-1-hexene, all of which are best explained *via* radicals by coupling, hydrogen abstraction or disproportionation. As would be expected, the ratio (3.5 to 1) of 4,4-dimethyl-1-hexene to by-products at 200° (Table II) is considerably greater than at 350° (0.6 to 1) since at 200° this is the only product to be expected by mechanism A.

TABLE II  
EFFECT OF TEMPERATURE ON PYROLYSIS OF ALLYL *t*-PENTYL SULFONE

Temp., °C.	Product yield, % <sup>a</sup>				
	Propylene	2-Methyl-1-butene	1,5-Hexadiene	Iso-pentane	4,4-Dimethyl-1-hexene
205–250	5	7	0.2	3.3	54
300	3.0	4.5	1.5	0.8	42.0
300	..	7.6	3.5	.9	44.2
325	10.0	10.5	6	.1	32.6
325	..	9.5	6.0	3.6	37.0
350	24	16	7.7	3.6	30.2

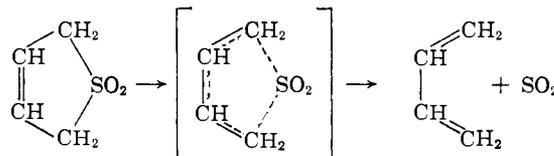
<sup>a</sup> Identified by boiling points, refractive indexes and mass spectrometric and infrared analyses.

The pyrolysis of two cyclic sulfones containing allylic unsaturation should be mentioned also, namely, 2,5-dihydrothiophene 1,1-dioxide<sup>4</sup> and

(4) H. Staudinger and B. Ritzenthaler, *Ber.*, **68**, 465 (1935).



1,3-dihydrobenzo[*c*]thiophene 2,2-dioxide.<sup>5</sup> In agreement with our results on acyclic sulfones, these cyclic sulfones also lose sulfur dioxide on heating. A comparable four-center, cyclic mechanism would appear to account for the initial products realized



It was found that benzyl sulfones also undergo this pyrolysis reaction. This had been predicted on the basis of the analogy commonly drawn between reactivities of allyl and benzyl compounds. Although the temperature required to pyrolyze benzyl isopropyl sulfone was high (384°) the expected isobutylbenzene and sulfur dioxide were obtained. In addition appreciable quantities of bibenzyl, propylene and toluene were isolated. The isolation of bibenzyl from this reaction mixture would be unexpected in light of some early pyrolysis experiments with benzyl sulfone.<sup>6</sup> Fromm and co-workers found that the destructive distillation at 290° of benzyl sulfone yielded stilbene, toluene and sulfur dioxide but no bibenzyl. This apparent discrepancy may be a consequence of the different contact times, the longer heating periods employed by Fromm possibly allowing the bibenzyl first formed to be dehydrogenated by benzyl free radicals to form stilbene and toluene.

During the course of this study several new allylic sulfides and sulfones were prepared and their properties and analyses appear in Table III.

### Experimental

The allylic sulfones were pyrolyzed at various temperatures ranging from about 170° in a batch process to about 400° in a continuous process as shown in Table I. In the batch process, a quantity of an allylic sulfone was heated at pressures and temperatures sufficient to cause rearrangement, loss of sulfur dioxide and distillation of the product. The reaction flask was attached to a modified Claisen distilling head leading through a condenser and receiver to a Dry Ice-acetone cold trap and vacuum pump. The pressure in the system was adjusted so that the products could be condensed readily and distilled somewhere between 50° and 100°. In this manner, generally, the unsaturated product was collected in the receiver while the predominant product in the trap was sulfur dioxide. The sulfur dioxide then was scrubbed from the product using dilute sodium hydroxide or sodium bicarbonate as demanded by the product involved. The products were purified by fractionation in an efficient column and confirmed in most cases by elemental, infrared and mass spectrometric analyses.

The continuous process comprised feeding the allylic sulfone through a metering pump to the top of a Filtropacked, Dowtherm jacketed, stainless steel tube at temperatures above 300° at atmospheric pressure. The effluent from the tube was condensed in a water-cooled condenser allowing most of the sulfur dioxide and any low boiling products to pass to a Dry Ice-acetone cold trap. The products were isolated and purified as described above.

Most of the allylic sulfones used in the rearrangement study were prepared by first treating commercially avail-

(5) M. P. Cava and A. A. Deana, *J. Am. Chem. Soc.*, **81**, 4266 (1959).

(6) E. Fromm and O. Achert, *Ber.*, **36**, 534 (1903).

TABLE III

Compound	M.p., °C., or b.p. (mm.)	$n_D^{20}$	Analyses, %					
			Found			Calculated		
			C	H	Other	C	H	Other
$\text{CH}_2=\text{C}(\text{CN})\text{CH}_2\text{SCH}_3$	67 (5)	1.4986-1.4993	..	..	27.8 S	..	..	28.3 S
$\text{CH}_2=\text{C}(\text{CN})\text{CH}_2\text{SO}_2\text{CH}_3$	158 (1.5)	1.4932	..	..	22.26 S 9.37 N	..	..	22.1 S 9.65 N
$\text{CH}_2=\text{C}(\text{Cl})\text{CH}_2\text{S}(\text{CH}_2)_5\text{CH}_3$	95 (1.5)	1.4811	..	..	....	..	..	....
$\text{CH}_2=\text{C}(\text{Cl})\text{CH}_2\text{SO}_2(\text{CH}_2)_5\text{CH}_3$	134 (1)	1.4799	48.2	7.8	14.3 S	48.1	7.57	14.26 S
$\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_2\text{SO}_2\text{CH}_3$	122-123	....	61.2	6.3	....	61.2	6.1	....
$\text{CH}_2=\text{CHCH}_2\text{SO}_2\text{CH}_2\text{COOC}_2\text{H}_5$	118 (0.5)	1.4681	43.7	6.4	17.0 S	43.7	6.25	16.7 S
$\text{CH}_2=\text{CHCH}_2\text{SO}_2(\text{CH}_2)_3\text{COOCH}_3$	146 (0.6)	1.4756-1.4761	46.6	6.9	15.1 S	46.6	6.8	15.5 S
$\text{CH}_2=\text{CHCH}_2\text{S}(\text{CH}_2)_3\text{COOCH}_3$	93.5 (5)	1.4765-1.4770	55.5	8.2	17.4 S	55.2	8.05	18.4 S
$\text{CH}_2=\text{C}(\text{Cl})\text{CH}_2\text{SCH}_2\text{CH}_2\text{OAc}$	105-108 (5)	1.4932	..	..	....	..	..	....
$\text{CH}_2=\text{CHCH}_2\text{SO}_2\text{CH}_2\text{CH}_2\text{OAc}$	128-130 (0.5)	1.4727	42.3	6.6	16.7 S	43.8	6.3	16.7 S
$\text{CH}_2=\text{CHCH}_2\text{SCH}_2\text{COCH}_3$	70 (10)	1.4867	55.6	8.2	24.25 S	55.3	7.7	24.6 S
$\text{CH}_2=\text{CHCH}_2\text{SO}_2\text{CH}_2\text{COCH}_3$	112-118 (12)	1.4820	44.3	6.5	20.07 S	44.5	6.2	19.7 S

able allylic chlorides with the sodium salts of mercaptan in aqueous media to give allylic sulfides which were then oxidized with peracetic acid in ethyl acetate to the corresponding sulfones. Several of the less obvious preparations are described.

**2-Chloroallyl *n*-Hexyl Sulfide and Sulfone.**—1,2,3-Trichloropropane, b.p. 58° (20 mm.),  $n_D^{20}$  1.477, was converted in 72% yield to 2,3-dichloropropene, b.p. 91°,  $n_D^{20}$  1.4552, on treatment with 30% aqueous sodium hydroxide.<sup>7</sup>

The sodium salt of *n*-hexyl mercaptan (200 g., 1.7 moles) was prepared by reaction with one equivalent of sodium hydroxide in aqueous medium at room temperature. The resulting solution was stirred vigorously at about 40° and 198 g. (1.8 moles) of 2,4-dichloropropene was added during 45 minutes. The reaction was exothermic and the kettle temperature rose to 60° during the addition. The reaction mixture was heated to 90° for 30 minutes, cooled and separated. The water layer was discarded and the organic layer was fractionated in an efficient column to give 280 g. (85% yield) of 2-chloroallyl *n*-hexyl sulfide, b.p. 95° (5 mm.),  $n_D^{20}$  1.4811.

2-Chloroallyl *n*-hexyl sulfone was prepared by oxidation of the corresponding sulfide with a 25% solution of peracetic acid in ethyl acetate. To the stirred peracetic acid solution (880 g., 2.9 moles) was added 280 g. (1.45 moles) of 2-chloroallyl *n*-hexyl sulfide dropwise during about 1 hour with vigorous stirring while the temperature was maintained at 20-30°. The stirring was continued for 2 hours at room temperature to ensure complete reaction. The product was transferred to a distilling flask equipped with a Claisen head and then freed of acetic acid and solvent under reduced pressure while keeping the kettle temperature below 70°. The residue product then was distilled through the same apparatus to give 278 g. (85% yield) of 2-chloroallyl *n*-hexyl sulfone, b.p. 133-134° (1.0 mm.),  $n_D^{20}$  1.4798.

*Anal.* Calcd. for  $\text{C}_8\text{H}_{17}\text{ClO}_2\text{S}$ : C, 48.1; H, 7.6; S, 14.3. Found: C, 48.2; H, 7.8; S, 14.3.

**Methyl 4-Allylsulfonylbutyrate.**—4-Mercaptobutyric lactone (1020 g., 10 moles) in 3000 ml. of methanol was saturated with dry hydrogen chloride during about 2 hours which caused the temperature to rise to 60°, and was then refluxed gently for about 18 hours. Two liters of the methanol was then removed under reduced pressure and the residual product was poured into 2 l. of wet ice. The oil layer weighed 1200 g. and was fractionated in an efficient column to give several fractions (996 g., 73% yield) of methyl 4-mercaptobutyrate, b.p. 59° (5 mm.),  $n_D^{20}$  1.4674.

Methyl 4-mercaptobutyrate (550 g., 4.1 moles) and allyl chloride (306 g., 4.0 moles) were stirred together in a reaction flask. Then, during 2.5 hours, 160 g. (4 moles) of sodium hydroxide dissolved in 2000 ml. of methanol was fed dropwise to the stirred reaction mixture while maintaining the temperature at 20-30° with a cold water-bath. The reaction mixture was stirred for 2 hours at room temperature, cooled to 5° and filtered to remove the salt. The filtrate was distilled in an efficient column to give 556 g. (80% yield) of methyl 4-allylthiobutyrate, b.p. 93.5° (5 mm.),  $n_D^{20}$  1.4769.

(7) A. L. Henne and F. W. Haackl, *J. Am. Chem. Soc.*, **63**, 2692 (1941).

The methyl 4-allylthiobutyrate was treated with a 25% solution of peracetic acid in ethyl acetate, as described above, to give a 69% yield of methyl 4-allylsulfonylbutyrate, b.p. 146° (0.6 mm.),  $n_D^{20}$  1.4761.

*Anal.* Calcd. for  $\text{C}_8\text{H}_{14}\text{O}_4\text{S}$ : C, 46.6; H, 6.8; S, 15.15. Found: C, 46.6; H, 6.9; S, 15.14.

**2-(Methylsulfonylmethyl)-acrylonitrile.**—A mixture of isomeric chloromethylacrylonitriles, [2-(chloromethyl)-acrylonitrile and 3-chloro-2-methylacrylonitrile from pyrolysis of 2-acetoxy-3-chloro-2-methylpropionitrile], was treated with a 25% solution of the sodium salt of methyl mercaptan at 15-20° to give 166 g. of 2-(methylthiomethyl)-acrylonitrile, b.p. 67° (5 mm.),  $n_D^{20}$  1.4993, and recovered 3-chloro-2-methylacrylonitrile, b.p. 58-61° (20 mm.),  $n_D^{20}$  1.4550-1.4560.

The 2-(methylthiomethyl)-acrylonitrile was oxidized as described above with 25% peracetic acid in ethyl acetate to give 112 g. (52% yield) of 2-(methylsulfonylmethyl)-acrylonitrile, b.p. 158° (1.5 mm.),  $n_D^{20}$  1.4932, and which was a low melting solid.

*Anal.* Calcd. for  $\text{C}_8\text{H}_7\text{NO}_2\text{S}$ : N, 9.65; S, 22.1. Found: N, 9.4; S, 22.3.

**Ethyl 4-Methylsulfonylcrotonate.**—Ethyl crotonate (1140 g., 10 moles) was treated with 890 g. (5 moles) of *N*-bromosuccinimide in 1500 ml. of carbon tetrachloride<sup>8</sup> and refluxed for 7 hours at 88-90°. The product was allowed to cool and the succinimide (509 g.) was removed by filtration. The filtrate was distilled through a short packed column to give 668 g. (69% yield) of ethyl 4-bromocrotonate, b.p. 65-66° (2 mm.), 55° (1.25 mm.),  $n_D^{20}$  1.4878.

*Anal.* Calcd. for  $\text{C}_8\text{H}_9\text{BrO}_2$ : C, 37.3; H, 4.7; Br, 41.5. Found: C, 36.5; H, 4.7; Br, 43.1.

The ethyl 4-bromocrotonate (925 g., 4.8 moles) was treated with a slight excess of 25% solution of the sodium salt of methyl mercaptan at 30-40°, as described above, separated and distilled in an efficient column to give 352 g. (46% yield) of ethyl 4-methylthiocrotonate, b.p. 71-74° (2 mm.),  $n_D^{20}$  1.4900.

*Anal.* Calcd. for  $\text{C}_7\text{H}_{12}\text{O}_2\text{S}$ : C, 52.5; H, 7.5; S, 20.0. Found: C, 52.4; H, 7.6; S, 19.8.

Ethyl 4-methylthiocrotonate (300 g., 1.875 moles) was oxidized to ethyl 4-methylsulfonylcrotonate as described above using a 25% solution of peracetic acid in ethyl acetate. The ethyl 4-methylsulfonylcrotonate thus obtained was distilled to yield 270 g. (75% yield) of product, b.p. 150° (1.2 mm.),  $n_D^{20}$  1.4837.

*Anal.* Calcd. for  $\text{C}_7\text{H}_{12}\text{O}_4\text{S}$ : C, 43.75; H, 6.25; S, 16.65. Found: C, 43.4; H, 6.7; S, 16.7.

**Allylsulfonylacetone.**—Chloroacetone (370 g., 4 moles, b.p. 65-65° (100 mm.),  $n_D^{20}$  1.4279), obtained by the low temperature reaction of chlorine with isopropenyl acetate, was treated at 20-30° with 384 g. (4 moles) of the sodium salt of allyl mercaptan in aqueous solution as described above. There was obtained from this reaction, upon fractionation in an efficient column, 382 g. (83% yield) of allylthioacetone, b.p. 70° (10 mm.),  $n_D^{20}$  1.4867.

(8) K. Ziegler, A. Späth, E. Schaaf, W. Schumann and E. Winkelman, *Ann.*, **551**, 118 (1942).

*Anal.* for  $C_8H_{10}OS$ : C, 55.3; H, 7.7; S, 24.6. Found: C, 55.6; H, 8.2; S, 24.25.

The allylthioacetone (324 g., 2.5 moles) was converted to allylsulfonylacetone by oxidation with peracetic acid as described above. The product was fractionated to give 330 g. (82% yield) of allylsulfonylacetone, b.p.  $115^\circ$  (1.2 mm.),  $n_D^{20}$  1.4820.

*Anal.* Calcd. for  $C_8H_{10}O_3S$ : C, 44.5; H, 6.2; S, 19.7. Found: C, 44.3; H, 6.5; S, 20.07.

**5-Phenyl-2-pentene.**—To a flask equipped for a batch pyrolysis was added 193 g. (0.96 mole) of 3-benzylsulfonyl-1-butene. The pressure in the system was reduced to 50 mm. and the temperature of the sulfone in the reaction flask was raised to  $210^\circ$ . Heating was continued for 5 hours, during which time 85 g. of distillate was collected in the receiver and 5 g. of trap material after the sulfur dioxide had been evaporated. The two distillates were combined, washed with a 5% sodium hydroxide solution, and fractionally distilled. There was obtained 43 g. (32% yield) of material, b.p.  $63-65^\circ$  (5 mm.),  $n_D^{20}$  1.5028–1.5032. The product, 5-phenyl-2-pentene, was identified by elemental analyses (Found: C, 90.2; H, 9.8. Calcd.: C, 90.4; H, 9.6), mass spectrometric and infrared analyses.

***o*-Allyltoluene.**—This experiment was conducted using the equipment for the continuous process. A total of 360 g. (1.83 moles) of allyl *o*-tolyl sulfone was passed through the tube (maintained at  $380-388^\circ$ ) at a rate of about 110 ml./hour. Approximately 288 g. of material was collected in the receiver and 45 g. in the cold trap. The receiver material was distilled and a fraction weighing 89 g. and having a boiling range of  $40^\circ$  (50 mm.) to  $105^\circ$  (10 mm) was collected. This fraction plus 24 g. of trap material from this distillation were combined, washed with 0.5 *N* sodium hydroxide and water, and then fractionally distilled. A 5-g. (2% yield) fraction, boiling range  $64-66^\circ$  (10 mm.) and  $n_D^{20}$  1.5138, was identified as *o*-allyltoluene. Infrared spectra showed  $CH_2=$  absorption at  $3.25\mu$ ,  $\begin{array}{c} | \\ -C=C- \\ | \end{array}$  at

$6.1\mu$ , aromatic unsaturation at  $6.23$ ,  $6.3$ ,  $6.67\mu$ , and *ortho* disubstitution at  $5.15$ ,  $5.25$ ,  $5.57$ ,  $13.47\mu$ . *Anal.* Calcd. for  $C_{10}H_{12}$ : C, 90.9; H, 9.1. Found: C, 89.9; H, 9.6.

***p*-Allylchlorobenzene.**—*p*-Allylchlorophenyl sulfone (795 g., 3.68 moles) was pyrolyzed in three equal batches at  $265-285^\circ$  at 200 mm. for about 2 hours at which time no more distillate could be obtained. The distillates were combined (318 g.) and washed with 1 liter of 10% sodium hydroxide solution to yield 225 g. of material. The organic material was fractionally distilled to yield products boiling from  $54^\circ$  at 2 mm. to  $126^\circ$  at 1 mm. A 5-g. fraction, boiling at  $56-57^\circ$  at 2 mm.,  $n_D^{20}$  1.5263, was analyzed.

*Anal.* Calcd. for  $C_8H_9Cl$ : C, 70.8; H, 5.9; Cl, 23.3. Found: C, 70.3; H, 5.89; Cl, 21.6. Infrared absorption peaks  $3.24$ ,  $3.3$ ,  $5.28$  and  $5.65\mu$  (assigned to *p*-disubstitution)  $5.48$ ,  $6.1$ ,  $6.25$ ,  $6.33$ ,  $6.68$ ,  $11.95$ ,  $12.5\mu$ . Mass spectrometric analyses were consistent with an allylchlorobenzene.

**1,9-Decadiene.**—This reaction was conducted in a batch type reaction in equipment similar to that described in Example 1. A total of 552 g. (2.07 moles) of 1,4-di-(allylsulfonyl)-butane was heated in the range of  $195^\circ$  (250 mm.) to  $260^\circ$  (150 mm.) for most of the reaction and finally at  $180^\circ$  (2 mm.). The trap material weighing 227 g. and the receiver material weighing 99 g. were combined and washed with dilute sodium hydroxide solution to yield 120 g. of oily layer which was fractionally distilled. There was obtained 41 g. (15% yield) of distillate, boiling range  $50-54^\circ$  (10 mm.),  $n_D^{20}$  1.4436–1.4450. Infrared spectra and mass spectrometric analysis indicated the material was predominantly the terminally unsaturated diolefin, 1,9-decadiene, with a small amount of an internally unsaturated compound.

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## Diacyl Peroxide-Olefin Reactions. Evidence for a Direct Reaction<sup>1</sup>

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*m,m'*-Dibromobenzoyl peroxide and *p,p'*-dimethoxy-*trans*-stilbene react in benzene solution at  $45^\circ$  to afford two 1:1 adducts, shown to be *meso*-dihydroanisoin bis-*m*-bromobenzoate (28%) and the *dl*-diester (57%), in a process that is first order in each reactant. In the presence of the free radical, galvinoxyl, the rate of the peroxide-olefin reaction is reduced by 25%. Evidence of the efficiency of galvinoxyl as a radical scavenger and of its unreactivity toward the dimethoxystilbenes and toward the peroxides employed is presented. It is concluded that the major course of the reaction proceeds by direct reaction between peroxide and olefin, on which is superimposed a radical chain reaction of short chain length. From the increase in consumption of galvinoxyl in the presence of both peroxide and olefin, it has been determined that scavengable radicals are formed in 10% efficiency by the direct reaction of peroxide with olefin. The effect of substituents and solvents on rate indicates a weak response to ionic factors.

Reaction between peroxygen compounds and carbon-carbon unsaturation has long been known in the epoxidation of olefins with peracids.<sup>3</sup> Examination of direct reaction between diacyl peroxides and olefins generally is precluded by the facility with which such reactants lead to free radical polymerization, although acyl peroxides and vinyl ethers<sup>4,5</sup> have been reported to yield diesters in addition to polymers. Evidence for a

direct reaction between acyl peroxides and unsaturation is found in the reaction of the cyclic diacyl peroxide, phthaloyl peroxide, with olefins<sup>6</sup> and in the recent demonstration by Martin and Drew<sup>7</sup> of a lack of equivalence in the oxygen-18 distribution between aryl and alkyl oxygen in the cyclohexyl acetate formed from acetyl peroxide-carbonyl-oxygen-18 and cyclohexene. The object of the present study has been the examination of mechanisms in olefin-acyclic diacyl peroxide reactions.

### Results

From the effect of substituents on peracid and on olefin in the epoxidation reaction<sup>8</sup> it was ex-

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(2) General Electric Fellow 1960-1961.

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