Allylic Halogenation of α-Methylstyrene. Preparation of α-Chloromethylstyrene[1a]

SAMUEL F. REED, JR.[1b]

Rohm and Haas Company, Redstone Arsenal Research Division, Huntsville, Alabama

Received April 16, 1965

N-Bromosuccinimide[2] (NBS) has been used extensively in allylic bromination reactions while N-chlorosuccinimide (NCS) has been employed to a much lesser extent. Very few studies have been reported which compare the relative effectiveness of these reagents in allylic halogenation reactions. Ucciani and Naudet[3] have shown that in the reaction of these reagents with methyl oleate the allylic bromide was obtained in an 87% yield compared with a 9% yield of the allylic chloride. Other comparative studies[4] have been concerned mainly with halogenation in aromatic or heterocyclic side chains and in saturated hydrocarbons. As a part of another program the need for both α-bromomethylstyrene and α-chloromethylstyrene arose and prompted the present study.

α-Bromomethylstyrene has been prepared by reacting α-methylstyrene with NBS[5] in a reaction yielding α-methyl-β-bromostyrene as a secondary reaction product. The reaction of NCS with α-methylstyrene has not been reported, although α-chloromethylstyrene has been prepared by other methods.[6] Conditions employed in the present reactions with either NBS or NCS were similar to those described by Pines[5] with the exception that the refluxing mixtures were not cooled immediately in an ice-water bath, but rather, cooled slightly below the reflux temperature and then allowed to cool slowly to ambient temperature. After removal of the succinimide by filtration, the reaction products were isolated by distillation. In the reaction with NBS the allylic and vinyl bromides were obtained in yields of 73 and 5%, respectively, whereas, in the earlier study[5] the corresponding yields were 47 and 17%. In contrast the NCS reaction gave the allylic and vinyl chlorides in yields of 57 and 19%, respectively, along with 2% of an unidentified product.

It would appear from the results of the present study that there is little difference in the total halogenating efficiency of these reagents on α-methylstyrene. The ease and convenience of the halogenation reactions present an attractive method for the laboratory preparation of the allylic halides.

Experimental[7]

α-Methylstyrene. A. NBS Reaction.—A mixture of 94.4 g. (0.8 mole) of α-methylstyrene, 90.0 g. (0.5 mole) of NBS, and 50.0 ml. of carbon tetrachloride contained in a flask fitted with a reflux condenser and magnetic stirrer was heated in an oil bath at 160–170° until the mixture was refluxing and the NBS was dissolving at which point a very vigorous exothermic reaction was noted. The reaction was moderated by intermittent cooling in an ice-water bath in order to maintain a gentle reflux until the NBS had completely dissolved (approximately 3–4 min.). As the exothermic reaction subsided, the temperature dropped below the reflux temperature and the mixture was allowed to cool slowly over a period of 3 hr. The precipitated succinimide was separated by filtration and the carbon tetrachloride and the excess α-methylstyrene were removed under reduced pressure. The residue was examined by gas chromatography and found to contain a small quantity of α-methylstyrene and two unidentified components. Distillation of the mixture yielded 84.8 g. of bromides, b.p. 56–64° (1 mm.). Separation of the bromides was accomplished by fractional distillation on an 18-in. spinning-band column to give 5.1 g. (5%) of α-methyl-β-bromostyrene, b.p. 60–61° (0.9 mm.), $n^{20}\text{D}$ 1.5892 [lit.[5] b.p. 98° (10 mm.), $n^{20}\text{D}$ 1.5891], and 71.6 g. (73%) of α-bromomethylstyrene, b.p. 66–67° (0.9 mm.), $n^{20}\text{D}$ 1.5924 [lit.[5] b.p. 104–105° (10 mm.), $n^{20}\text{D}$ 1.5925].

B. NCS Reaction.—A mixture of 94.4 g. (0.8 mole) of α-methylstyrene, 66.8 g. (0.5 mole) of NCS, and 50 ml. of carbon tetrachloride contained in a flask fitted with a reflux condenser and magnetic stirrer was heated to reflux in an oil bath at 160–170°. An exothermic reaction occurred which required intermittent cooling to maintain gentle reflux conditions. These conditions were maintained until the NCS had completely dissolved (approximately 10–12 min.) at which point the mixture was cooled slightly below reflux with the ice-water bath and then allowed to cool slowly over the next 3 hr. The mixture of chlorides, b.p. 46–54° (0.6 mm.), was isolated as described for the bromides. Gas chromatography showed the presence (2%) of a third component, which was not separated sufficiently pure for characterization. From this mixture 14.5 g. (19%) of α-methyl-β-chlorostyrene, b.p. 76° (4.0 mm.), $n^{20}\text{D}$ 1.5623 [lit.[8] b.p. 102–105° (14 mm.)], and 43.5 g. (57%) of α-chloromethylstyrene, b.p. 53° (0.65 mm.), $n^{20}\text{D}$ 1.5633 [lit.[6a] b.p. 87–88° (5 mm.)], were obtained by fractional distillation on an 18-in. spinning-band column. The proton n.m.r. spectra were obtained in carbon tetrachloride solution using a Varian Associates A-60 n.m.r. spectrometer employing tetramethylsilane as an internal standard. The proton n.m.r. spectrum of α-chloromethylstyrene showed signals for the methylene group (τ 5.66), the proton *trans* to the methylene group (τ 4.63), and the proton *cis* to the methylene group (τ 4.53). The coupling constants were $J_{\text{CH}_2-\text{H}\ trans} = 1.09 \pm 0.1$ c.p.s., $J_{\text{CH}_2-\text{H}\ cis} = <0.1$ c.p.s., and $J_{\text{H}-\text{H}} = 0.94 \pm 0.01$ c.p.s. In the n.m.r. spectrum of α-methyl-β-chlorostyrene the methyl group appeared at τ 7.85 and the vinyl proton at τ 3.76 with a coupling constant of $J_{\text{CH}_3-\text{H}} = 1.51 \pm 0.02$ c.p.s. These data are in agreement with that expected of the two isomers.

---

(1) (a) This work was performed under the sponsorship of the U. S. Army under Contract No. DA-01-021-ORD-11878. (b) I. I. I. Research Institute, 10 West 35th St., Chicago, Ill.

(2) C. Djerassi, *Chem. Rev.*, **43**, 271 (1948).

(3) E. Ucciani and M. Naudet, *Bull. soc. chim. France*, 1151 (1960).

(4) (a) M. F. Hebbellynck and R. H. Martin, *Bull. soc. chim. Belges*, **59**, 193 (1953); (b) N. P. Buu-Hoï and P. Demerseman, *J. Org. Chem.*, **18**, 649 (1953); (c) N. P. Buu-Hoï, *Rec. trav. chim.*, **73**, 197 (1954).

(5) H. Pines, H. Alul, and M. Kolobielski, *J. Org. Chem.*, **22**, 1113 (1957).

(6) (a) L. F. Hatch and T. L. Patton, *J. Am. Chem. Soc.*, **76**, 2705 (1954); (b) K. A. Ogloblin and V. P. Semenov, *Zh. Obschch. Khim.*, **29**, 2006 (1959); *Chem. Abstr.*, **54**, 86796 (1960); (c) R. Huttel, J. Kratzer, and M. Bechter, *Chem. Ber.*, **94**, 766 (1961).

(7) All boiling points are uncorrected.

(8) D. Seyferth, S. O. Grim, and T. O. Read, *J. Am. Chem. Soc.*, **82**, 1510 (1960).

Reaction Products Formed by the Pyrolysis of Substituted Dibenzyl Sulfones

E. C. LEONARD

Union Carbide Corporation, Plastics Division, Bound Brook, New Jersey

Received March 19, 1965

A previous paper in this series[1] described the pyrolysis of dibenzyl sulfone and a number of *para*-disubstituted dibenzyl sulfones. These pyrolyses led to 35–90% yields of the corresponding diarylethanes. The present paper reports the extension of sulfone

---

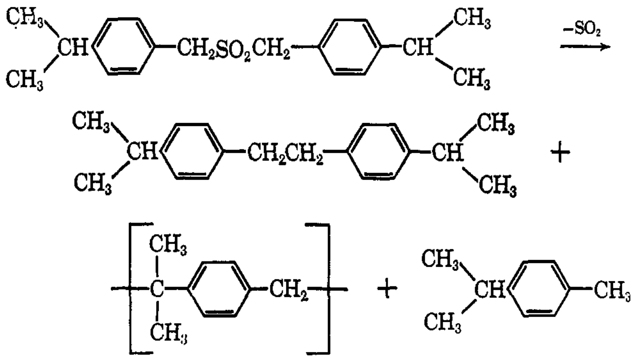
(1) E. C. Leonard, Jr., *J. Org. Chem.*, **27**, 1921 (1962).

pyrolyses to cover the preparation of poly-*p*-xylylenes, styrenes, and acetylenes.

The earlier paper suggested that dibenzyl sulfones undergo homolytic cleavage to form benzyl radicals and sulfur dioxide. In the case of dibenzyl sulfone itself there is essentially a quantitative yield of the product of the coupling reaction—1,2-diphenylethane. However, in three instances in which dibenzyl sulfone was substituted in the *para* positions, it was noted that disproportionation as well as coupling products occurred during the pyrolysis, and that one of the disproportionation products was high molecular weight poly-*p*-xylylene. In the work which will be described here, poly-*p*-xylylenes have been produced as by-products in the pyrolysis of di-*p*-xylyl sulfone, from bis(4-isopropylbenzyl) sulfone, and from bis(4-benzylbenzyl) sulfone.

The pyrolysis of di-*p*-xylyl sulfone was carried out in the temperature range 600–700°, at a pressure of less than 10 mm. The yield of poly-*p*-xylylene has varied from 5 to 20%, with the yield of *p*-xylene being approximately equivalent to that of polymer and the yield of 1,2-di-*p*-tolylethane invariably being in excess of 50%. The infrared spectrum of poly-*p*-xylylene prepared by sulfone pyrolysis and that of poly-*p*-xylylene prepared by the pyrolysis of cyclodi-*p*-xylylene[2] are identical. The polymer is soluble in benzyl benzoate at elevated temperatures. There was a possibility that the poly-*p*-xylylene obtained in the reaction just described was the product, not of the sulfone cleavage, but of the cleavage of a carbon–carbon bond in 1,2-di-*p*-tolylethane. It has been demonstrated by us, however, that, under the conditions of our experiment, the carbon–carbon bond in 1,2-di-*p*-tolylethane does not rupture and that poly-*p*-xylylene cannot be formed in the 600–700° temperature range by the pyrolysis of this compound.

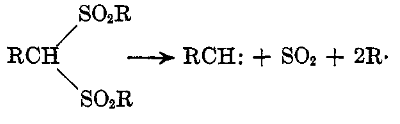
The second sulfone which was found to yield a poly-*p*-xylylene on pyrolysis was bis(4-isopropylbenzyl) sulfone. The major product of the vacuum pyrolysis of this sulfone in the temperature range 600–700° was 1,2-bis(4-isopropylphenyl)ethane. The pyrolysis has also yielded small amounts of poly(α,α-dimethyl-*p*-xylylene), along with *p*-cymene.



Poly(α,α-dimethyl-*p*-xylylene), unlike other members of the poly-*p*-xylylene family, is soluble in aromatic hydrocarbons at 80°. The reduced viscosity of the polymer was 1.5 and the softening temperature was 235–245°.

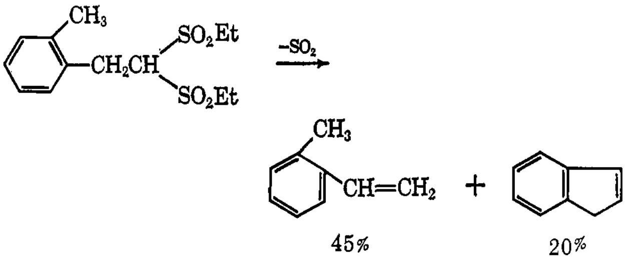
A third poly-*p*-xylylene, poly(α-phenyl-*p*-xylylene), has been prepared by the pyrolysis of bis(α-benzylbenzyl) sulfone. Poly(α-phenyl-*p*-xylylene) apparently is easily oxidized and during or subsequent to its formation becomes cross linked. Only in one instance, in which extreme care was used in opening the pyrolysis tube, was a soluble sample (in toluene at 80°) of polymer obtained and in this case the reduced viscosity was 1.2. It is suspected, although not proved, that in this case the oxidation and cross linking take place at the tertiary carbon atom.

In addition to the work which led to the isolation of poly-*p*-xylylene, some other aspects of sulfone pyrolysis have been examined. Since the pyrolysis of single sulfone systems led to radicals, it was felt that there was a possibility that the pyrolysis of disulfones, in which both sulfone groups were attached to the same carbon atom, would lead to carbenes.



$$RCH(SO_2R)_2 \longrightarrow RCH\colon + SO_2 + 2R\cdot$$

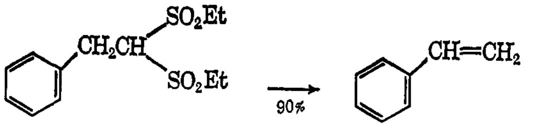
Dissulfones of the type shown are readily available by a variation of the malonic ester synthesis which was developed by Cronyn.[3] The vacuum pyrolysis of 1,1-bis(ethylsulfonyl)-2-(2-methylphenyl)ethane was carried out at 650°. The fate of the disulfone is shown below.



At 400° there was no evidence of decomposition of the sulfone under our experimental conditions.

The results which were obtained can be explained by a simple series of radical reactions. The formation of indene, for example, can be explained by a ring closure involving radical coupling and the subsequent dehydrogenation of indan.

In a less complicated system than 1,1-bis(ethylsulfonyl)-2-(2-methylphenyl)ethane, the reaction is much more straightforward. The pyrolysis of 1,1-bis(ethylsulfonyl)-2-phenylethane at 650° gave a 90% yield of styrene.

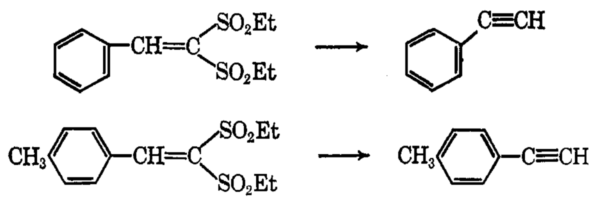


In a new synthetic method related in a general way to the Knoevenagel reaction, the previously unreported bis(ethylsulfonyl)ethylenes have been prepared, in each case in about 50% yield, by the base-catalyzed reaction of the appropriate aldehyde and bis(ethylsulfonyl)methane. These two compounds have been pyrolyzed at 650° and are found, like their saturated

---

[2] The preparation of poly-*p*-xylylene by the pyrolysis of cyclodi-*p*-xylylene is described, *inter alia*, in two Canadian patents issued to Union Carbide Corp.: Canadian Patent 637,507 (March 6, 1962); Canadian Patent 638,335 (March 20, 1962).

(3) M. Cronyn, *J. Am. Chem. Soc.*, **74**, 1228 (1954).



analogs, to eliminate sulfur dioxide. One organic product, formed in approximately 40% yield, is the corresponding acetylene.

Experimental

The apparatus and experimental conditions used for the pyrolysis of the sulfones are described in the previous paper.[1] The preparation and physical properties of the sulfones are also described in that paper.

Pyrolysis of *p*-Xylyl Sulfone.—The pyrolysis of *p*-xylyl sulfone, which is described in the previous paper as yielding 86% 1,2-di-*p*-tolylethane at 600–700°, also yielded 5% *p*-xylene, which was identified by the refractive index and infrared spectrum and a 5% yield of poly-*p*-xylylene which was identified by comparing the infrared spectrum of the polymer film with that of an authentic sample of poly-*p*-xylylene prepared by another route. The polymer was completely soluble in benzyl benzoate at 305° and could be isolated as a tough pliable film in the exit tube of the pyrolysis furnace.

Pyrolysis of Bis(4-isopropylbenzyl) Sulfone.—The pyrolysis of bis(4-isopropylbenzyl) sulfone which resulted in the 66% yield of 1,2-bis-(4-isopropylphenyl)ethane described in the earlier paper[1] resulted also in a 10% yield of *p*-cymene, which was identified by its infrared spectrum and refractive index, and a 10% yield of a polymeric material, which had a reduced viscosity of 1.5 (80°, 0.2% concentration) and a softening range of 235–245°. The infrared spectrum of films of this polymer had bands characteristic of poly-*p*-xylylenes with additional bands characteristic of the methyl group.

Anal. Calcd. for $(C_{10}H_{12})_x$: C, 90.90; H, 9.10. Found: C, 90.76; H, 8.98.

Pyrolysis of Bis(4-benzylbenzyl) Sulfone.—The pyrolysis of bis(4-benzylbenzyl) sulfone resulted in a 90% yield of bis(4-benzylphenyl)ethane and a 5% yield of poly(α-phenyl-*p*-xylylene), which, when isolated very carefully, had a reduced viscosity of 1.2 in toluene at 80°. Unless the reduced viscosity of the solution was measured very rapidly, cross linking occurred and the polymer precipitated.

Anal. Calcd. for $(C_{14}H_{12})_x$: C, 93.33; H, 6.67. Found: C, 93.24; H, 6.36.

Preparation of 1,1-Bis(ethylsulfonyl)-2-phenylethane.—Potassium hydroxide (20 g., (0.35 moles) was dissolved in 250 ml. of Diethyl Carbitol with heating. Bis(ethylsulfonyl)methane[3] (68 g., 0.33 mole) was added to the cooled solution which was then heated to 150–160° for 1 hr. with the removal of 6 ml. of water. The mixture was cooled to 110° and 60 g. (0.35 mole) of benzyl bromide was added. The mixture was held at 170° for 2 hr. and then poured over ice. The solid was recrystallized from ethanol. The yield was 42 g. (44%). The melting point was 129–132° (lit.[3] m.p. 133–135°).

Preparation of Styrene by the Pyrolysis of 1,1-Bis(ethylsulfonyl)-2-phenylethane.—1,1-Bis(ethylsulfonyl)-2-phenylethane (13 g., 0.044 mole) was distilled through the pyrolysis furnace at pressures ranging from 0.5 to 15 mm. in 1 hr. The temperature of the pyrolysis furnace was 600°. The 4 g. of liquid isolated from the trap was identified by its infrared spectrum and refractive index as styrene. The yield was 90%.

Preparation of 1,1-Bis(ethylsulfonyl)-2-(2-methylphenyl)ethane.—Potassium hydroxide (12 g., 0.21 mole) was suspended in 150 ml. of Diethyl Carbitol and the mixture was heated to 180°. The solution was cooled to room temperature and 40 g. (0.20 mole) of bis(ethylsulfonyl)methane[3] was added. The mixture was heated at 150–165° until 4 ml. of water was distilled over. The temperature was allowed to fall to 110° and 37 g. (0.20 mole) of *o*-tolyl bromide was added. The mixture was heated at 160° for 1 hr. The contents of the flask were then poured over ice and the solid was removed by filtration. The crude product was recrystallized from ethanol. The yield was 48 g. (80%) of material, m.p. 138–140°C. The analysis showed it to be the previously unknown 1,1-bis(ethylsulfonyl)-2-(2-methylphenyl)ethane.

Anal. Calcd. for $C_{13}H_{20}O_4S_2$: C, 51.32; H, 6.58; S, 21.05. Found: C, 51.69; H, 6.62; S, 21.12.

Preparation of *ortho*-Methylstyrene by the Pyrolysis of 1,1-Bis(ethylsulfonyl)-2-(2-methylphenyl)ethane.—Pyrolysis of 1,1-bis(ethylsulfonyl)-2-(2-methylphenyl)ethane was carried out in the standard apparatus at 650° and 0.3-mm. pressure. Analysis of the pyrolysate by vapor phase chromatography showed a 45% yield of *o*-methylstyrene and a 20% yield of indene.

Preparation of 1,1-Bis(ethylsulfonyl)-2-phenylethylene.—A mixture of 66 g. (0.33 mole) of bis(ethylsulfonyl)methane, 80 g. (0.66 mole) of benzaldehyde, 150 ml. of benzene, and 5 ml. of piperidine was refluxed for 72 hr., most of the benzene was then removed, and the solid material [excess bis(ethylsulfonyl)methane] was filtered off. The filtrate was steam distilled to remove benzaldehyde and the solid residue was recrystallized twice from ethanol to give 1,1-bis(ethylsulfonyl)-2-phenylethylene, m.p. 93–95°, yield 43 g. (45%).

Anal. Calcd. for $C_{12}H_{16}O_4S_2$: C, 50.00; H, 5.55; S, 22.22. Found: C, 49.97; H, 5.75; S, 22.04.

Pyrolysis of 1,1-Bis(ethylsulfonyl)-2-phenylethylene.—1,1-Bis(ethylsulfonyl)-2-phenylethylene (1.54 g., 0.0053 mole) was distilled through the pyrolysis furnace at a pressure of 40–80 μ and a furnace temperature of 650°. The amount of liquid product was 0.43 g. A vapor phase chromatographic analysis showed that the material contained 70% phenylacetylene (52% yield).

Preparation of 1,1-Bis(ethylsulfonyl)-2-(4-methylphenyl)ethylene.—A mixture of 66 g. (0.33 mole) of bis(ethylsulfonyl)methane, 56 g. (0.48 mole) of tolualdehyde, 150 ml. of benzene, and 5 ml. of piperidine was refluxed for 18 hr. The procedure for isolating the product was exactly the same as was the case for the benzaldehyde derivative. The yield of recrystallized 1,1-bis(ethylsulfonyl)-2-(4-methylphenyl)ethylene (m.p. 105–107°) was 25 g. (42%).

Anal. Calcd. for $C_{13}H_{18}O_4S_2$: C, 51.66; H, 5.99; S, 21.05. Found: C, 51.66; H, 6.07; S, 20.99.

Pyrolysis of 1,1-Bis(ethylsulfonyl)-2-(4-methylphenyl)ethylene.—Under the same conditions described in the previous pyrolysis experiment, 15 g. of 1,1-bis(ethylsulfonyl)-2-(4-methylphenyl)ethylene was distilled through the pyrolysis unit. Four grams of liquid product was isolated which was redistilled, giving 3 g. (50%) of product: b.p. 83–84 (210 mm.); v.p.c. showed 96.4% purity; $n^{25}{}_D$ 1.5432 (lit. $n^{25}{}_D$ 1.5447).

Anal. Calcd. for C_9H_8: C, 93.10; H, 6.90. Found: C, 93.32; H, 7.08.