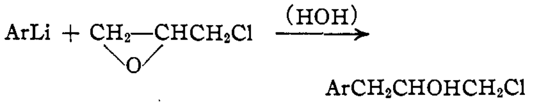
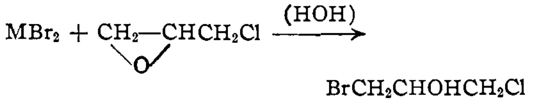
aryllithium reagents upon epichlorohydrin.[2] Accordingly, phenyl-, *p*-tolyl-, 1-naphthyl- and *p*-dimethylaminophenyllithium were treated with epichlorohydrin to give satisfactory yields of the corresponding arylpropylene chlorohydrins.


(1)

The reaction of 9-fluorenyllithium under like conditions did not produce an isolable product.

Similar reactions employing Grignard reagents have been carried out with epichlorohydrin to give generally unsatisfactory conversions to the desired products. The best yield of 1-chloro-3-phenyl-2-propanol prepared from phenylmagnesium bromide was 18.2%.[3] Yield data were not given in reports of authors employing *p*-tolylmagnesium bromide[4] and 1-naphthylmagnesium bromide.[3c] The product, 1-chloro-3-(*p*-dimethylaminophenyl)-2-propanol, which was prepared from *p*-dimethylaminophenyllithium has not been reported.

It has been shown previously[5] that the low yields of substituted chlorohydrins prepared from the less reactive organometallic compounds resulted from competition between reaction (1) and reaction (2) where M is a metallic cation capable of coordination with ether oxygen.


(2)

With phenylcadmium chloride,[6] for example, the only material isolated after 13 hours of reaction at room temperature was a dense liquid believed to be a mixture of glycerol bromochlorohydrin and glycerol dichlorohydrin.

The opening of the oxide ring by lithium bromide present in phenyllithium solutions may be responsible for the low yields obtained under ordinary conditions, since equivalent quantities of phenyllithium and epichlorohydrin at ether-reflux temperature gave only 9.8% of 1-chloro-3-phenyl-2-propanol. When initially lower temperatures and longer reaction periods were employed the yield was raised to 67%.

Experimental

All boiling points are uncorrected. The following example is typical of the procedures used to prepare three other chlorohydrins, the properties of which are reported in Table I.

1-Chloro-3-phenyl-2-propanol.—Epichlorohydrin (0.44 mole) in 60 ml. of anhydrous ether was placed in a 500-ml. three-necked flask fitted with a nitrogen inlet tube, mechanical stirrer and dropping funnel. The flask and contents were cooled to −78° in a Dry Ice–trichloroethylene-bath and 290 ml. (0.44 mole) of phenyllithium were added during a period of one-half hour. The mixture was stirred at −78° for 1.5 hours and then the bath was allowed to warm slowly to 0°.

TABLE I

SOME 3-ARYL-1-CHLORO-2-PROPANOLS

Ar–	Yield, %	B.p., uncor. °C.	Mm.	n^{20}_D	d^{20}_{20}	Chlorine, % Calcd.	Found
p-$CH_3C_6H_4$–	42	140–143	12	1.5366	1.126	19.22	19.30
1-$C_{10}H_7$–	43	180–182	0.2	1.6189	1.236	16.09	15.86
p-$(CH_3)_2NC_6H_4$–	38	36–38	0.13	1.5208	1.023	17.78	17.99

The hydrolysis[7] was carried out in dilute sulfuric acid containing crushed ice. The ether layer was separated and washed successively with water, sodium carbonate solution and water. Subsequent to the drying of the extract over anhydrous sodium sulfate, the ether was removed by distillation. The product was distilled at 132–142° (13–17 mm.) to yield 50.5 g. (67.4%) of distillate having n^{20}_D 1.5426. The 3,5-dinitrobenzoate melted at 119.5–120.5°. The reported n^{25}_D and m.p. are 1.5470 and 120–121°, respectively.[3a]

In another preparation 0.18 mole of phenyllithium was treated with 0.18 mole of epichlorohydrin under similar conditions. The yield was 36.6 g. (66.2%) of product having b.p. 125–127° (11–12 mm.), n^{20}_D 1.5420 and d^{20}_4 1.155.

Anal. Calcd. for $C_9H_{11}ClO$: Cl, 20.80. Found: Cl, 20.70.

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[2] For a discussion of the mechanism of the opening of oxide rings, see S. Winstein and R. B. Henderson in R. C. Elderfield, "Heterocyclic Compounds," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 27–42.

[3] (a) C. F. Koelsch and S. M. McElvain, THIS JOURNAL, **52**, 1164 (1930); see also (b) E. Fourneau and M. Tiffeneau, *Bull. soc. chim. France*, [4] **1**, 1227 (1907), and (c) E. Fourneau, J. Tréfouel and J. Tréfouel, *ibid.*, [4] **43**, 454 (1928).

[4] R. R. Read, H. Lathrop and H. L. Chandler, THIS JOURNAL, **49**, 3118 (1927).

[5] (a) I. Ribas and E. Tapia, *Anales soc. españ. fís. quím.*, **28**, 636, 691 (1930) [*C. A.*, **24**, 4265 (1930)] and (b) J. K. Magrane and D. L. Cottle, THIS JOURNAL, **64**, 484 (1942).

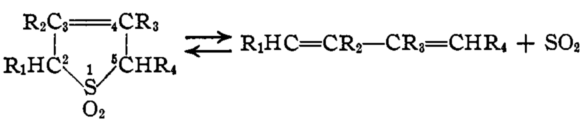
[6] Prepared by the addition of a small excess of fused and pulverized cadmium chloride to a solution of phenylmagnesium bromide.

[7] Color Test I should be negative before hydrolysis. See H. Gilman and F. Schulze, THIS JOURNAL, **47**, 2002 (1925).

Thermal Dissociation of 3-Phenyldihydrothiophene-1-dioxide

BY OLIVER GRUMMITT AND HELEN LEAVER

A comparison of the rates of thermal dissociation of the cyclic sulfones of butadiene, piperylene, isoprene, 1,3-dimethylbutadiene and 2,3-dimethylbutadiene to the diolefin and sulfur dioxide has



shown that this reaction is facilitated by 2-methyl substitution and is hindered to a smaller degree by 3-methyl substitution.[1] In extending this study to sulfones of arylbutadienes it was found that *cis*- and *trans*-1-phenyl-1,3-butadiene did not add sulfur dioxide to give either a cyclic sulfone or a polysulfone.[2] The sulfone of 2-phenyl-1,3-butadiene[3] was selected next.

While undertaking to prepare 2-phenyl-1,3-butadiene from methylethylphenylcarbinol by dehydration, bromination and debromination according to Backer and Strating,[3] the more convenient synthesis of Price, *et al.*, based on the condensation of α-methylstyrene, formaldehyde and acetic acid to 2-phenyl-4-acetoxy-1-butene and thermal de-

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[1] O. Grummitt, A. E. Ardis and J. Fick, THIS JOURNAL, **72**, 5167 (1950).

[2] (a) O. Grummitt and F. J. Christoph, *ibid.*, **73**, 3479 (1951); (b) O. Grummitt and J. Splitter, Organic Division, A.C.S. Meeting, Chicago, Illinois, September 5, 1950.

[3] H. J. Backer and J. Strating, *Rec. trav. chim.*, **53**, 525 (1934).

TABLE I

SPECIFIC REACTION VELOCITY CONSTANTS AND DERIVED DATA

Sulfone of	Temp., ± 0.02°	Av. k min.$^{-1}$ × 10^3	Detns.	Av. % dev.	Temp. for equal dissociation rates,[a] °C.	$\Delta E^{\ddagger b}$	$\Delta S^{\ddagger c}$	$\Delta F^{\ddagger d}$	Freq. fac.[e]
2-Phenyl-1,3-butadiene	138.8	3.72	2	0.5	150.4	43.5 ± 2.0	27 ± 4.9	32.1	7 × 10^{18}
	142.8	5.74	2	0.8					
	146.4	9.70	2	4.1					
Butadiene	115.1	6.26	4	2.7	124.7	33.6 ± 0.5	8.9 ± 1.2	30.1	7 × 10^{14}
	125.2	16.7	2	1.0					
	129.1	24.2	2	1.0					
Isoprene	108.8	1.35	1		131.2	34.6 ± 0.5	9.9 ± 1.2	30.6	1 × 10^{15}
	115.7	2.81	2	1.6					
	125.0	8.70	2	2.4					
	135.5	23.6	2	0.5					

[a] k = 15.8 × 10^{-3} min.$^{-1}$. [b,d] kcal./g. mole. [c] Entropy units. [e] Sec.$^{-1}$.

composition of this ester became available.[4] This readily gave the hydrocarbon in 34% yield and from this the sulfone was obtained in 50% yield, m.p. 131.3–131.8° (cor.).

The technique of carrying out the thermal dissociations and the calculation of the results were the same as used earlier.[1] The specific reaction velocity constants, heats of activation, etc., are summarized in Table I. The plot of the log of the undissociated sulfone *vs.* time at the various temperatures and the plot of log k *vs.* the reciprocal of the absolute temperature gave satisfactory straight lines. For comparison the corresponding data for butadiene and isoprene are included.

The greater stability of the sulfone of 2-phenyl-1,3-butadiene, as indicated by the higher values for $\Delta E^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta F^{\ddagger}$, compared to isoprene sulfone which in turn is somewhat more stable than butadiene sulfone, shows the stabilizing influence of the 3-phenyl group. While a reasonable explanation was offered for the facilitated dissociation of the sulfone due to the 2-methyl group,[1] there is no apparent explanation for the stabilizing influence of the 3-methyl group and the even greater effect of the 3-phenyl group in terms of the conventional strain theory or of inductive or electromeric effects.

These results suggest that related cyclic compounds containing the C_6H_5—C=C grouping should be stabilized and should form more readily. For example, phenylmaleic acid should more readily dehydrate to the anhydride than does maleic acid to maleic anhydride. This has already been observed in case of the methyl- and dimethylmaleic anhydrides, but there does not appear to be published information on phenylmaleic anhydride. A point of difference between the dissociation of the 2-phenylbutadiene sulfone and the other sulfones is the presence of liquid phenylbutadiene which does not distil rapidly from the unreacted sulfone, as do the more volatile butadiene and isoprene. This liquid phenylbutadiene might exert a solvent effect on the undissociated sulfone. The effect seemed to be a minor one however since the changing concentration of sulfone with time should alter the rate of dissociation. This was not observed.

From our work on the Backer and Strating synthesis of 2-phenyl-1,3-butadiene[3] two points are noteworthy: (1) the intermediate methylethylphenylcarbinol is more efficiently dehydrated in the presence of phosphoric acid than with alum, (2) the dehydrobromination of the intermediate phenylbromobutene, which had been done earlier over barium chloride at 380°, cannot be done with molten potassium hydroxide at 180° or with sodium amide.

Experimental

2-Phenyl-1,3-butadiene Sulfone.—The preparation of the hydrocarbon[4] started with purified Dow α-methylstyrene, b.p. 69–71° at 27 mm., n^{24}D 1.5368. The condensation with formaldehyde and acetic acid of 284 g. (2.5 moles) of α-methylstyrene gave 273 g. (1.44 moles) of 2-phenyl-4-acetoxy-1-butene, b.p. 149–154° at 15 mm., n^{25}D 1.5221, 57.5% yield. Pyrolysis through a tube 70 cm. long and 20 mm. inside diameter packed with 1/4" Berl saddles at 500–550° gave a 34% yield of 2-phenyl-1,3-butadiene, b.p. 55–64° at 15 mm., n^{20}D 1.5489. The maleic anhydride adduct melted 105–105.2°; lit. gives 105–105.5°.[3]

A mixture of 70 g. (1.1 moles) of liquid sulfur dioxide, 22 g. (0.17 mole) of 2-phenyl-1,3-butadiene and 1.1 g. of phenyl-β-naphthylamine was allowed to stand in a pressure bottle at room temperature for 36 hours and then heated on the steam-bath for 15 hours. After the excess sulfur dioxide had evaporated the crude sulfone was crystallized twice from a 1–1 mixture of 95% ethanol and water to give 16.8 g. (49%), m.p. 131.3–131.8°; lit. gives 132.5–133.5°.[3]

Addendum to Backer and Strating.[3]—Methylethylphenylcarbinol, b.p. 85.5–87.8° at 4 mm., n^{25}D 1.5173, d^{24}_4 0.9844, was prepared from ethylmagnesium bromide and acetophenone. The physical constants checked closely with the literature values.[5] Dehydration to 2-phenyl-2-butene in the presence of alum gave 40–50% yields, lit. gives 64%.[3] With phosphoric acid the yield was increased to 81%: to 27 g. of 85% phosphoric acid in a 100-ml. three-necked flask fitted with a thermometer, dropping funnel and condenser set for distillation was added 101 g. of carbinol at about one drop per second so that the temperature of the reaction mixture was held at 205–210°.[6] The mixture was heated for one hour after the addition. The distillate was dried and redistilled to give 72 g., 81% of product boiling 60.2–66° at 4–5 mm., n^{25}D 1.5327.

Bromine analyses were run on the intermediates for 2-phenyl-1,3-butadiene since these were not reported. Addition of bromine to the 2-phenyl-2-butene by the method described[3] gave a 97% yield of crude dried dibromide.

Anal. Calcd. for $C_{10}H_{12}Br_2$: Br, 54.7. Found: Br, 56.3.

Dehydrobromination with alcoholic potassium hydroxide as described gave an 89% yield of crude dried product; n^{25}D 1.5454.

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[4] C. C. Price, F. L. Benton and C. J. Schmidle, THIS JOURNAL, **71**, 2860 (1949); H. O. Mottern, U. S. Patent 2,335,691 (Nov. 30, 1943). We are grateful to Dr. Price and his co-workers for allowing us to use this method before its publication.

[5] A. Klages, *Ber.*, **35**, 3507 (1902).

[6] Patterned after the dehydration of cyclohexanol to cyclohexene of W. M. Dehn and K. E. Jackson, THIS JOURNAL, **55**, 4285 (1933).

Anal. Calcd. for $C_{10}H_{11}Br$: Br, 37.8. Found: Br, 31.1.

A second treatment with base reduced the bromine content to 27.4%. One more step did not change this.

The removal of more than the one atom of bromine in the first step, as indicated by the analysis, might arise from the mixture of products starting with the presence of some 2-phenyl-1-butene along with 2-phenyl-2-butene in the original olefin[6] which in turn would lead to mixtures of dibromides and monobromides in which the ease of hydrogen bromide removal would vary with structure.

When the monobromide of 31.1% bromine content was treated with molten potassium hydroxide under the conditions used for the preparation of phenylacetylene from β-bromostyrene,[7] the product failed to give the expected adduct with maleic anhydride. With excess sodium amide in liquid ammonia or ether solution for reaction times as long as 6.5 hours the removal of bromine from the monobromide was incomplete. The greatest dehydrobromination obtained in several experiments was about 20% of the calculated. The product contained no phenylbutadiene according to a reaction with maleic anhydride.

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[7] J. C. Hessler, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 438.

Addition of Hydrogen Chloride to 1-Phenyl-2-methyl-1-propene

BY ROSS H. HALL, R. G. PYKE AND GEORGE F WRIGHT

It is well-known that the addition of hydrogen chloride to styrene forms exclusively 1-phenyl-1-chloroethane. In the same manner 1-phenylpropene-1 is converted to 1-phenyl-1-chloropropane[1] in high purity. Since the homologous 1-phenyl-2-methyl-1-propene had not been examined in this manner we treated it with hydrogen chloride and were able to isolate only one product, 1-phenyl-2-methyl-2-chloropropane. The mode of addition is thus opposite to those characteristic of the lower homologs and is similar to the hydrohalogenation of 2-methyl-2-butene. No presently-known theory of bond polarization or polarizability seems adequate to explain these several modes of orientation, especially since mixtures of structural isomers have not been observed during addition to the phenylalkenes.

The characterization of 2-methyl-1-phenyl-2-chloropropane was accomplished in two ways. Firstly, it was hydrolyzed to 2-methyl-1-phenylpropanol-2 which was identified as its phenylurethane by comparison with an authentic sample. Secondly, the halide was converted to its Grignard reagent which, upon treatment with phenylisocyanate, was converted to the known anilide of 2,2-dimethyl-3-phenylpropanoic acid.[2]

Experimental[3]

2-Methyl-1-phenyl-2-chloropropane.—Ten grams (0.076 mole) of freshly-distilled 2-methyl-1-phenyl-1-propene (prepared by dehydration of 2-methyl-1-phenylpropanol-2,[4] $n^{20}D$ 1.5376, d^{20}_4 0.903, washed with dilute ferrous sulfate) was cooled in an ice-water-bath while dry hydrogen chloride was bubbled through it slowly during six hours. Water and ether were then added. The non-aqueous layer was washed with dilute aqueous sodium carbonate, then dried and distilled, yielding 12.0 g. (94%), b.p. 95–97° (10 mm.), $n^{20}D$ 1.5155.

2-Methyl-1-phenylpropanol-2.—A mixture of 5.0 g. (0.029 mole) of the halide just described with 16 g. (0.137 mole) of potassium carbonate in 100 ml. of water was stirred on the steam-bath for 11 hours. The cooled mixture was twice extracted with ether. This etherous solution was dried with magnesium sulfate and distilled, yield 3.5 g. (78%), b.p. 97–102° (10 mm.), $n^{20}D$ 1.5170. A 0.6-g. portion (0.004 mole) was treated with 0.35 ml. (0.003 mole) of phenyl isocyanate and 0.2 ml. of dry pyridine. This mixture yielded 0.5 g. (64%) of the phenylurethan melting at 86–88°, and contaminated with carbanilide. Six crystallizations from 95% ethanol (1 ml. per g.) raised this melting point to 93.0–93.7°. A mixed melting point with an authentic sample prepared from dimethylbenzylcarbinol (Eastman Kodak Co.) was not lowered.

Anal. Calcd. for $C_{17}H_{19}NO_2$: C, 75.8; H, 7.12; N, 5.20. Found: C, 75.6; H, 7.23; N, 5.28.

2,2-Dimethyl-3-phenylpropanoyl Anilide.—The preparation was identical with that reported by Whitmore.[2] The product melted at 106.5–107.5° whereas Whitmore reported 107–108°.

Anal. Calcd. for $C_{17}H_{19}ON$: C, 80.6; H, 7.55. Found: C, 79.8; H, 7.45.

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[1] A. A. Shamshurin, *Trudy Uzbekskogo Gosudarst Univ. Sbornik Rabot Khim*, **15**, 75 (1939); *C. A.*, **35**, 3984 (1941).

[2] F. C. Whitmore, *et al.*, THIS JOURNAL, **65**, 1469 (1943).

[3] All melting points have been corrected against reliable standards.

[4] M. Tiffeneau and A. Orekoff, *Bull. soc. chim.*, **29**, 816 (1921).

Absence of Exchange of Sulfur between Sulfide and Thiocyanate Ions in Aqueous Solution

BY G. B. HEISIG AND R. HOLT

We have found that little or no exchange of sulfur occurs between 0.1 *M* sulfide and 0.1 *M* thiocyanate ions in slightly alkaline aqueous solutions after 23 hours at 25 or 50° or in 47 hours at 100°.

The experiments were made by using S^{35} as a tracer. In some runs $S^{*=}$ prepared by bubbling H_2S^* into the calculated volume of sodium hydroxide was used, while in others S^*CN^- from KSCN[1] contained the tracer. The KCNS was prepared by digesting a mixture of K_2S^*, KCN and S. The H_2S^* was obtained from BaS^* prepared by reducing $BaSO_4$ with carbon.[2] The S^* was obtained from the A.E.C. as the $S^{*=}$ but was actually present as $S^*O_4^=$.

The reaction mixtures were heated for the desired time in glass-stoppered bottles or sealed tubes from which the air had been displaced by nitrogen. Following the reaction period the $S^=$ ions were removed from the reaction mixtures by treating with freshly precipitated cadmium carbonate. The precipitated cadmium salts were separated from the solution by centrifugation and the sulfide was oxidized to $SO_4^=$ by bromine. The activity of the $BaSO_4$ was determined.[3]

The centrifugate was freed of any traces of $SO_4^=$ by adding more of these ions as a carrier and precipitating with Ba^{++}. The SCN^- were then oxidized with bromine, the $SO_4^=$ precipitated with Ba^{++} and the activity of the precipitate determined.[3]

In two runs made at 100°, one at 50° and four at 25°, the greatest transfer of activity from the active to the inactive form was 5% and this was accounted for by the small amount of thiosulfate ions or possibly the polythionate ions present in the active thiocyanate reagent. The per cent. of exchange at 100° was essentially the same for 23 hours as for 47 hours.

We wish to acknowledge the aid of Dr. Armstrong in determining the activity of the samples.

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[1] I. M. Kolthoff and J. J. Lingane, THIS JOURNAL, **57**, 2126 (1935).

[2] A. E. Wells, *J. Ind. Eng. Chem.*, **8**, 770 (1916).

[3] W. D. Armstrong and J. Schubert, *Anal. Chem.*, **20**, 270 (1948).