

Nuclear Magnetic Resonance Spectrum of IX.—The sample used had been prepared by Lagidze's method, and the determination was carried out by Professor W. von E. Doering and Dr. Martin Saunders, Yale University, on a Varian model V-4300B high resolution nuclear magnetic resonance spectrometer. There were clearly four types of hydrogen: using benzene as a reference, there was one peak at -20 cycles corresponding to hydrogens attached to an aromatic ring, one smaller peak at 130 cycles (tertiary allylic hydrogen) and two of essentially equal area at 210 and 240 cycles, which appear to be due to the hydrogens in the methyl groups, two of which in models jut out in the plane of the molecule; the two remaining ones are essentially perpendicular to the latter, using a model with a *cis* ring junction in the center.

Acknowledgments.—We wish to thank several people for their most useful assistance: Professor W. von E. Doering, Dr. Horst Prinzbach and Dr. Martin Saunders, Yale University, and Mr. W. J.

Potts, Spectroscopy Laboratories, The Dow Chemical Co., Midland, Mich., kindly determined the nuclear magnetic resonance spectra and the infrared spectra; we also thank them for discussions regarding this material. Professor R. M. Lagidze, Tbilisi State University, Georgia, U.S.S.R. has most kindly made several manuscripts available to us, including the ultraviolet absorption spectrum of the 83° hydrocarbon. The Air Reduction Chemical Co. of New York generously donated a large quantity of 2,5-dimethyl-3-hexyne-2,5-diol and a sample of the diacetate prepared according to reference 7. The project has been financially supported by the Research Corporation of New York, to whom we are greatly indebted.

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[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, TENNESSEE A. AND I. STATE UNIVERSITY]

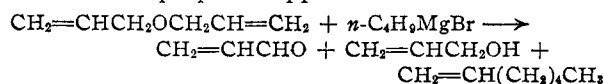
Grignard Reagents and Unsaturated Ethers. VI. The Cleavage of Diallyl Ethers by Aliphatic and Aromatic Grignard Reagents

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The behavior of several diallyl ethers toward aliphatic and aryl Grignard reagents has been investigated. Ethyl-, *n*-butyl- and phenylmagnesium bromides cleave allyl 2-allylphenyl ether and γ -phenyl- γ' -methyl diallyl ether to yield normal cleavage products. *n*-Butyl-, *t*-butyl- and phenylmagnesium bromides cleave diallyl ether to give both normal and abnormal cleavage products.

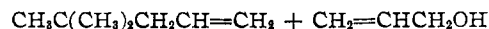
Previous papers^{1,2} have shown that Grignard reagents at the reflux temperature of diethyl ether react with unsubstituted and alkyl and aryl substituted allyl ethers to yield olefins, alcohols and phenols. Formation of these products might be explained on basis of 1,2- and 1,4-addition or various combinations of the SN_2 , SN_2' and SN_1 mechanisms. Because of the relatively high reactivity of the allyl system, it was postulated that the presence of two allyl groups might impart to the ether molecule additional reactivity. Further, it was anticipated that the reaction of such an ether molecule with tertiary and primary alkyl and aryl Grignard reagents might yield products unlike those obtained from unsaturated ethers which contain only one allyl group. This prediction has been borne out by experiment. When diallyl ether was allowed to react with *n*-butylmagnesium bromide, the reaction products were propenal (8%), allyl alcohol (55%) and 1-heptene (24%). The two latter products would be expected if the Grignard reagent cleaved the ether by a 1,2-addition mechanism. The propenal appears to be an abnormal



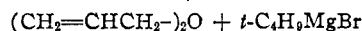
cleavage product. An obvious source of the propenal would be the allyl alcohol. However, the fact that the reaction of diallyl ether with phenylmagnesium bromide gave a 16% yield of propenal and that all reactions were carried out

under an atmosphere of nitrogen suggest propenal to be a product resulting from interaction of the ether and the Grignard reagent. Moreover, when a freshly distilled sample (30 g.) of allyl alcohol was dissolved in 150 ml. of dry diethyl ether and treated under experimental conditions similar to those used in the reaction of diallyl ether with *n*-butylmagnesium bromide, only 0.5 ml. of propenal was isolated.

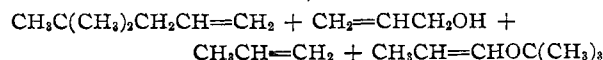
From the reaction of *t*-butylmagnesium bromide with diallyl ether various products were obtained. The nature and number of the reaction products seem to depend upon length of the heating period. For example, when the reaction was heated two hours, 4,4-dimethyl-1-pentene (7.5%), allyl alcohol (56%), 1-*t*-butoxy-1-propene (5%) and propylene were isolated; when heated 24 hours, 4,4-dimethyl-1-pentene (10%) and allyl alcohol (60%) were the reaction products.



↑ 24 hr.



↓ 2 hr.



Formation of the propylene and *t*-butoxy-1-propene could result from an abnormal reaction of *t*-butylmagnesium bromide with diallyl ether. Displacement of the π -pair of electrons from the olefinic bond during or after cleavage of the ether, accompanied by reductive action of the Grignard

(1) C. M. Hill, L. Haynes, D. E. Simmons and M. E. Hill, *THIS JOURNAL*, **75**, 5408 (1953).

(2) C. M. Hill, D. E. Simmons and M. E. Hill, *ibid.*, **77**, 3889 (1955).

TABLE I
 CLEAVAGE PRODUCTS OF DIALLYL ETHERS BY GRIGNARD REAGENTS

Grignard reagent, R	Products	°C.	B.p., mm.	d_4^{20}	n_D^{20}	Yield ^a , %
	Diallyl ether					
<i>n</i> -C ₄ H ₉ -	Propenal ^b	51-52	750	0.7480 ²¹	1.3633	8
	Allyl alcohol ^c	90-91	750	.8478 ²¹	1.4150	55
	1-Heptene ^d	95-96	750	.7000	1.4003	24
<i>t</i> -C ₄ H ₉	Propylene ^e
	4,4-Dimethyl-1-pentene ^f	72-74	737	0.6802	1.3910	7.5
	Allyl alcohol ^c	87-89	737	.8250	1.4160	56
	1- <i>t</i> -Butoxy-1-propene ^g	185-187	746	.8800	1.440	5
C ₆ H ₅	Propenal ^b	50-52	744	.7686	1.3733	16
	Allyl alcohol ^c	89-90	744	.8635	1.4265	40
	Allylbenzene ^h	154-155	744	.8992	1.5163	38
	Allyl 2-allylphenyl ether					
<i>n</i> -C ₄ H ₉	1-Heptene ^d	93-95	745	.6888	1.3994	22
	<i>o</i> -Allylphenol ⁱ	116-118	4	1.023	1.5400	55
C ₆ H ₅ -	Allyl benzene ^h	154-157	747	0.8990	1.5075	42
	<i>o</i> -Allylphenol ⁱ	117-118	4	1.033	1.5424	66
	γ -Phenyl- γ' -methyl diallyl ether					
C ₂ H ₅	2-Buten-1-ol ^j	89-91	749	0.8950	1.4565	31
	1-Phenyl-1-pentene ^k	180-183	10	1.038	1.5590	30

^a Yields are based on the amount of unrecovered allyl ether. ^b Observed m.p. of the 2,4-dinitrophenylhydrazone was 165-166°; reported m.p. of the hydrazone of propenal is 165° by S. M. McElvain, "Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1953, p. 207. *Anal.* Calcd. for C₉H₉O₄N₄: N, 23.70. Found: N, 23.40. ^c Observed m.p. of the 3,5-dinitrobenzoate was 49°; reported m.p. is 50° by footnote a, p. 201. Mixed m.p. with the 3,5-dinitrobenzoate prepared from authentic allyl alcohol was 49-50°. ^d This compound was converted to 1,2-dibromoheptane. *Anal.* Calcd. for C₇H₁₄Br₂: Br, 62.01. Found: Br, 62.31. ^e Molecular weight was determined on a vacuum line by the Regnault method; average of five determinations was 43; theoretical, 42. This hydrocarbon gave positive reactions with bromine-carbon tetrachloride solution and aqueous potassium permanganate. ^f Ozonolysis products were formaldehyde and 3,3-dimethylbutanal; their 2,4-dinitrophenylhydrazones melted at 165-166° (lit. value 166° by footnote a) and 141-142° (lit. value 141-142.5° by F. C. Whitmore, *et al.*, THIS JOURNAL, **63**, 652 (1941)). *Anal.* Calcd. for C₇H₁₄O₄N₄: N, 26.60. Found: N, 26.12, and *Anal.* Calcd. for C₁₂H₁₆O₄N₄: N, 20.00. Found: N, 19.68, respectively. ^g *Anal.* Calcd. for C₇H₁₄O: C, 73.70; H, 12.40. Found: C, 74.07; H, 12.80. Treatment of this ether with ozone followed by decomposition with water-zinc mixture gave acetaldehyde and a colorless liquid, presumably *t*-butyl formate, b.p. 88° (750 mm.), d_4^{20} 0.822, n_D^{20} 1.4200. The 2,4-dinitrophenylhydrazone of acetaldehyde melted at 171-172° (lit. value 168° by footnote a). *Anal.* Calcd. for C₉H₉O₄N₄: N, 25.00. Found: N, 24.86. ^h Treatment with ozone and decomposition of the ozonide with water-zinc mixture yielded formaldehyde and phenylacetaldehyde. The 2,4-dinitrophenylhydrazone of formaldehyde melted at 167-168° (lit. value 168° by footnote a); mixed m.p. with an authentic hydrazone was not depressed. The hydrazone of phenylacetaldehyde melted at 121° (lit. value 121° by footnote a). *Anal.* Calcd. for C₁₄H₁₂O₄N₄: N, 18.67. Found: N, 18.52. ⁱ M.p. of the phenylurethan was 116° (lit. value 116° by H. Normant, *Compt. rend.*, **218**, 683 (1944)); mixed m.p. with the urethan prepared from authentic *o*-allylphenol was 116°. *Anal.* Calcd. for C₁₆H₁₈O₂N₂: N, 5.53. Found: N, 5.34. ^j Reported b.p. is 112-120° (760 mm.) by M. S. Newman and W. M. Edwards, THIS JOURNAL, **76**, 1840 (1954). Observed m.p. of the 3,5-dinitrobenzoate was 70-71°. *Anal.* Calcd. for C₁₁H₁₀O₆N₂: N, 10.52. Found: N, 10.33. ^k This compound was treated with ozone. Decomposition of the ozonide with zinc-water mixture gave benzaldehyde and butanal whose 2,4-dinitrophenylhydrazones melted at 233-234° and 123-124°, respectively. Reported melting points are 237° and 123°, respectively, by footnote a.

reagent, could account for the formation of these abnormal products. Reduction has been observed as an abnormal reaction during addition of *t*-butylmagnesium bromide to certain unsaturated compounds.³

The reaction of allyl 2-allylphenyl ether with *n*-butyl- and phenylmagnesium bromides gave 1-heptene (22) and *o*-allylphenol (55%), and allylbenzene (42%) and *o*-allylphenol (66%), respectively. When ethylmagnesium bromide was allowed to react with γ -phenyl- γ' -methylallyl ether, 2-buten-1-ol (31%) and 1-phenyl-1-pentene (30%) were isolated. In these reactions, cleavage of the diallyl ether by the Grignard reagent is similar to the cleavage of alkoxy allyl ethers.^{1,2} A phenyl group between the ether oxygen and the second allyl group (as in allyl 2-allylphenyl ether)

does not change the mode of cleavage by the Grignard reagent.

All reactions were carried out in an excess of Grignard reagent over unsaturated ether. A quantity of unreacted diallyl ether was recovered from each experiment. The reaction of γ -phenyl- γ' -methylallyl ether with ethylmagnesium bromide gave, in addition to the normal cleavage products, a considerable amount of undistillable residue, presumably polymerized olefinic substances.

Experimental¹

Diallyl Ethers.—Diallyl and allyl 2-allylphenyl ethers were purchased from Peninsular Chemresearch, Inc. The γ -phenyl- γ' -methylallyl ether was synthesized by condensation of the sodium salt of 2-buten-1-ol with cinnamyl chloride.

Reaction of Diallyl Ethers with Grignard Reagents.—All reactions of the unsaturated ethers with the Grignard re-

(3) F. L. Greenwood, F. C. Whitmore and H. M. Crooks, THIS JOURNAL, **60**, 2028 (1938); F. C. Whitmore, *et al.*, *ibid.*, **63**, 643 (1941).

(4) All melting points are corrected.

agents were carried out under the same experimental conditions. Details of the procedure are described for the reaction of diallyl ether with *t*-butylmagnesium bromide. One and two-tenths moles of *t*-butylmagnesium bromide (prepared in diethyl ether) was placed into a flask. The first of two tubes connected in series was attached to the flask through the head of a condenser. The first tube was surrounded by a frozen carbon tetrachloride bath; the second by a Dry Ice-chloroform bath (-45°). The outlet to the second tube was attached to a vacuum line equipped with three traps; the first two were surrounded by Dry Ice-chloroform and the third by liquid nitrogen. The reaction flask was flushed with dry nitrogen. Stirring was started and one mole (98 g.) of diallyl ether dissolved in an equal volume of dry diethyl ether was added dropwise. The reaction was heated 2 hours and then hydrolyzed with saturated ammonium chloride. The ether layer of the hydrolyzed mixture was separated and the aqueous layer extracted continuously. The ether extracts were combined and dried over anhydrous magnesium sulfate. Removal of the ether and fractional distillation of the residue through a Todd column (60 theoretical plates) gave 4,4-dimethyl-1-pentene (7.5%), b.p. $72-74^{\circ}$ (737 mm.); allyl alcohol (56%), b.p. $87-89^{\circ}$ (737 mm.); and *t*-butoxy-1-propene (5%), b.p. $185-187^{\circ}$ (746 mm.).

The gaseous hydrocarbon was trapped in the third tube on the vacuum line and identified as propylene. Its molecular weight was determined by the Regnault method. The observed molecular weight (average of five determinations) was 43. The gaseous hydrocarbon gave positive tests for unsaturation when bubbled into bromine-carbon tetrachloride and potassium permanganate solutions.

Physical constants, yields and identification information for reaction products obtained from the several reactions are shown in Table I.

Preparation of 1,2-Dibromoheptane.—A solution of 2 g. of 1-heptene in 15 ml. of carbon tetrachloride was chilled in an ice-water-bath. To the chilled solution was added dropwise a dilute solution of bromine in carbon tetrachloride; the addition was continued until a light brown color persisted. The reaction mixture was allowed to warm to room temperature, and the solvent removed by distillation. Dis-

tillation of the residue gave 1,2-dibromoheptane, b.p. 120° (28 mm.). Bromine analysis of the dibromide was made according to the Pregl catalytic combustion method.⁵ *Anal.* Calcd. for $C_7H_{14}Br_2$: Br, 62.01. Found: Br, 62.31.

Identification of Unsaturated Products.—The olefinic hydrocarbons, except 1-heptene, were identified by ozonization. One- to four-gram samples of the olefins were dissolved in 50–75 ml. of petroleum ether or *n*-hexane, and the solution treated with an oxygen-ozone stream for 5–12 hours. The solvent was then removed by distillation. The ozonide was then added dropwise to a warm mixture of zinc dust and water contained in a flask. A trap containing 2,4-dinitrophenylhydrazine reagent was attached to the flask through the head of a condenser. After addition of the ozonide, the reaction mixture was heated 30 minutes and cooled. The mixture was filtered and the filtrate extracted several times with small portions of diethyl ether. The extracts were combined, dried, and the solvent removed. Distillation of the residue separated the liquid aldehydes, which were identified by preparation of their 2,4-dinitrophenylhydrazones. The formaldehyde which formed during decomposition of the ozonides of 4,4-dimethyl-1-pentene and allylbenzene was collected as the 2,4-dinitrophenylhydrazone in the hydrazone trap.

Identification of γ -Phenyl γ' -Methyldiallyl Ether.—The observed physical constants of this ether are: b.p. $120-123^{\circ}$ (6 mm.), d_4^{20} 0.982, n_D^{20} 1.5418; M_R 59.34 (calcd.), 60.37 (found). The compound gave positive tests for unsaturation and for the ether linkage. A 4-g. sample was dissolved in 150 ml. of petroleum ether and treated with ozone as described above. Ozonolysis products isolated were benzaldehyde and acetaldehyde; melting points of their 2,4-dinitrophenylhydrazones were 237° and 168° , respectively; reported melting points are 168° and 237° by footnote *a* of Table I.

Anal. Calcd. for $C_{13}H_{16}N_4O_4$: N, 19.60. Found: N, 19.90. Calcd. for $C_8H_8N_4O_4$: N, 25.00. Found: N, 25.70.

(5) A. Steyermark, "Quantitative Organic Microanalysis," The Blakiston Co., New York, N. Y., 1951, p. 184.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Rearrangements of Aryl Sulfones. I. The Metalation and Rearrangement of Mesityl Phenyl Sulfone¹

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The *n*-butyllithium-induced rearrangement of mesityl phenyl sulfone (I) to 2-benzyl-4,6-dimethylbenzenesulfonic acid (III) is reported. A mechanism is proposed for the rearrangement analogous to the base-catalyzed Smiles rearrangement.²

During the course of an investigation of the substituent group effect in the metalation of diaryl sulfones^{3a,b} the reaction of *n*-butyllithium with mesityl phenyl sulfone (I) was studied. When a solution of sulfone I in refluxing ether was treated with a slight excess of *n*-butyllithium, the initially deep red solution became light orange and a flocculent precipitate developed over a period of a few minutes. On hydrolysis, essentially the entire product was base soluble, and, on acidifying the resulting basic solution, a solid, almost colorless acid, having a neutral equivalent equal to the

molecular weight of the starting sulfone, was obtained in 98% yield.

An intramolecular rearrangement, similar to the base-induced Smiles rearrangement² of 2-hydroxy-2'-nitrodiphenyl sulfone to 2-(2-nitrophenoxy)-benzenesulfonic acid, and involving metalation of I at an *o*-methyl group, as outlined, is suggested. The Smiles rearrangement² also includes the intramolecular displacement of the arylsulfonfyl group of an appropriate sulfone by $-S^{\ominus}$ and $-NHR$ ($R = -H, -COR', -SO_2Ar$). However, our example appears to be the first such displacement involving a carbanion or its equivalent.

An indication of the structure of III was first obtained by oxidation and subsequent desulfonation to 3,5-dimethyldiphenylmethane. This hydrocarbon was synthesized by the Wolff-Kishner reduction of 3,5-dimethylbenzophenone, and was

(1) This paper was presented in part at the Symposium on Aromatic Substitution, American Chemical Society Meeting, Atlantic City, N. J., September, 1956. Abstracted in part from the Ph.D. Theses of William J. Ray, Jr., Oscar L. Norman and Daniel B. Eickemeyer.

(2) J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 362 (1951).

(3) (a) W. E. Truce and M. F. Amos, *THIS JOURNAL*, **73**, 3013 (1951); (b) W. E. Truce and O. Norman, *ibid.*, **75**, 6023 (1953).