

that a balance between further polymerization and varying degrees of sulfonation could occur so that the integral *i*-factors would be obtained for the compounds which did polymerize. Also the molecular weight determination of the polymer formed by 4-nitrobenzhydrol in sulfuric acid is evidence for the formation of a dimer. The elemental analysis suggests that the dimer is associated with one sulfur-containing group.

It should be noted that the absorption spectra were obtained on very dilute solutions, and in the cases of the 4-nitrobenzhydrol and bis-(3-nitrobenzhydryl) ether, these were produced by extraction from a carbon tetrachloride solution as the volatile solvent was removed. Neither the concentration nor the method of preparation was com-

parable with the product isolation or "*i*"-factor experiments. The extraction method has been used quite successfully for 3-methylbenzhydrol which gives polymers in the chemical runs, and quite typical carbonium ion spectra in solutions thus prepared. This same situation is found in the titration experiments. The carbinol (or ether) was in dilute solution in carbon tetrachloride, and the first end-point obtained should be due to carbonium ions rather than polymer formation. It should be further noted that even if dimers were formed when the spectra were being obtained or during titration studies, the carbonium ions thus produced should have spectra similar to their simpler counterparts.

KNOXVILLE, TENNESSEE

[CONTRIBUTION FROM CHEMICAL DEPARTMENT, NAGOYA UNIVERSITY]

## The Dipole Moments and Electronic Structures of Some Azulene Derivatives

BY YUKIO KURITA AND MASAJI KUBO

RECEIVED MARCH 29, 1957

The dielectric constants and densities of dilute solutions of six azulene derivatives, three azaazulene derivatives, oxazulene and azaazulene in benzene have been measured and used to calculate the dipole moments of the molecules. The moment of 2-chloroazulene affords the first experimental evidence in support of the correctness of prediction by the method of molecular orbitals on the direction of moment in an azulene molecule. The analysis of the moments of 2-aminoazulene and 6-bromo-2-aminoazulene leads to the conclusion that the imino form of 2-aminoazulene, as suggested from the chemical properties of 2- and 6-amino-1,3-diazaazulenes as well as from the considerable stability of an azulenium ion, cannot be reconciled with the experimental data. The large mesomeric moment of the amino group is attributed to guanidinium-type resonance. The moments of azaazulenes, oxazulene and azaazulene can be accounted for by the probable geometric structures of these molecules with due regard to resonance contributions from highly polar structures as well as to the formation of hydrogen bonds in solutions.

Although a number of theoretical investigations<sup>1-4</sup> based on the method of molecular orbitals have been carried out on azulene and its derivatives, experimental investigations providing evidences for the conclusions thereof are still meager, probably because suitable sets of compounds of this series have not been available. Samples of eleven azulene derivatives, however, were kindly furnished by Prof. Nozoe of Tohoku University for dipole moment measurements, which enabled us to draw important conclusions concerning the electronic structures of the molecules of these compounds. The results of analysis of the measurements comprise the following scope: the experimental determination of the direction of a moment in an azulene molecule, the problem of amino-imino isomerism in aminoazulene, the mesomeric moments of Cl, Br, NH<sub>2</sub>, NHCOCH<sub>3</sub> and CN groups attached to an azulene ring, the polarity of an azaazulene molecule as well as of 1-oxazulene-2-one and 1-azaazulene-2-one molecules, and so forth.

### Experimental Method and Results

Materials, listed in Table I, were synthesized and purified in Tohoku University. The measurements were carried out at 25, 30 or 35° on dilute solutions in benzene. The dielectric constants were measured by means of a heterodyne

beat apparatus provided with a platinum cell.<sup>5</sup> The molar polarization of the solute was calculated from the experimental data by a method similar to that introduced by Halverstadt and Kumler,<sup>6</sup> differing in that densities were used rather than the specific volumes. The deformation polarizations of these deeply colored compounds were calculated from that of azulene and the contributions from various

TABLE I

	Compounds	M.p., °C.	References
1	2-Chloroazulene	91	<sup>a</sup>
2	2-Aminoazulene	93-94	<sup>b</sup>
3	6-Bromo-2-aminoazulene	135	<sup>c</sup>
4	2-Acetylaminoazulene	168	<sup>b</sup>
5	2-Cyanoazulene	78	<sup>c</sup>
6	1,3-Diethoxycarbonylazulene	125	<sup>b</sup>
7	2-Chloro-1-azaazulene	73	<sup>d</sup>
8	2,6-Dichloro-1-azaazulene	179	<sup>e</sup>
9	1,3-Diazaazulene-H <sub>2</sub> O	120	<sup>f</sup>
10	1-Oxazulene-2-one	72-73	<sup>g</sup>
11	1-Azaazulene-2-one	163-164	<sup>h</sup>

<sup>a</sup> T. Nozoe, S. Seto, S. Matsumura and T. Asano, *Proc. Japan Acad.*, **32**, 339 (1956). <sup>b</sup> T. Nozoe, S. Matsumura, Y. Murase and S. Seto, *Chem. & Ind.*, 1257 (1955). <sup>c</sup> T. Nozoe, *et al.*, to be published shortly. <sup>d</sup> T. Nozoe, S. Seto, S. Matsumura and T. Terasawa, *Chem. & Ind.*, 1357 (1954). <sup>e</sup> T. Nozoe and T. Toda, to be published shortly. <sup>f</sup> T. Nozoe, T. Mukai and I. Murata, *This Journal*, **76**, 3352 (1954). <sup>g</sup> S. Seto, *Sci. Repts. Tohoku Univ.*, **1**, 37, 367 (1953). <sup>h</sup> T. Nozoe, S. Seto, S. Matsumura and T. Terasawa, *Chem. & Ind.*, 1356 (1954).

(5) Y. Kurita, M. Kubo, *et al.*, *Bull. Chem. Soc. Japan*, **24**, 10, 99 (1951); **26**, 192, 242, 272 (1953); **27**, 364 (1954).

(6) I. F. Halverstadt and W. D. Kumler, *This Journal*, **64**, 2988 (1912).

(1) G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, **17**, 264 (1949).

(2) B. Pullman and A. Pullman, "Théorie électronique de la chimie organique," Masson, Paris, 1952.

(3) C. Berthier and B. Pullman, *Bull. soc. chim. France*, D 457 (1949).

(4) A. Julg, *J. chim. phys.*, **52**, 378 (1955).

substituent atoms or groups. The former was approximated with the observed molar refraction of naphthalene, an isomer of azulene, for the  $D$  line. The latter were estimated from the differences between the molar refractions of the corresponding benzene derivatives and that of benzene. Since the values of moments were great, no serious errors were introduced by this assumption, probable errors being estimated to be less than 0.05 D.

The results are shown in Table II, in which  $\epsilon_1$  and  $d_1$  denote, respectively, the dielectric constant and density of the solvent;  $\alpha$  and  $\beta$  are, respectively, the changes of the dielectric constant and density of the solution with the weight fraction of the solute; other notations have their usual significances.

TABLE II  
DIPOLE MOMENTS OF SOME AZULENE DERIVATIVES IN BENZENE SOLUTION

Compd.	$t_1$ °C.	$\epsilon_1$	$d_1$ g./cc.	$\alpha$	$\beta$ g./cc.	$P_{2\infty}$ cc.	$R_D$ cc.	$\mu$ , D.
1	35	2.2525	0.86170	4.86	0.244	192.1	49.3	2.69
2	30	2.2630	.86687	3.65	.226	135.7	48.0	2.09
3	25	2.2731	.87147	7.12	.402	338.9	55.6	3.72
4	30	2.2629	.86670	6.28	.223	268.6	55.4	3.26
5	25	2.2729	.87177	23.23	.210	710.4	49.8	5.68
6	30	2.2630	.86679	1.30	.233	135.6	75.7	1.72
7	35	2.2526	.86166	12.82	.292	440.6	45.8	4.47
8	30	2.2599	.86675	5.98	.359	265.4	53.4	3.25
9	25	2.2726	.87116	14.45	.270	438.7	44.0	4.39
10	30	2.2653	.86672	23.34	.296	682	43.0	5.64
11	30	2.2628	.86668	5.68	.285	190.4	44.9	2.73

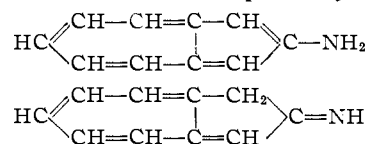
### Discussion of Results

The dipole moment of azulene has been measured by Wheland and Mann<sup>1</sup> as 1.0 D. The direction of the moment in the molecule, however, cannot be determined from this value alone, and although Wheland and Mann,<sup>1</sup> Pullman<sup>2,3</sup> and others<sup>4</sup> have predicted from theoretical calculations that the positive end of the dipole is on the side of the seven-membered ring whereas the negative end points toward the five-membered ring, no experimental confirmation has been made of this theoretical prediction as yet.

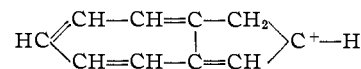
It is definitely established from investigations by electron diffraction on tropone<sup>7</sup> and tropolone<sup>8,9</sup> as well as by X-ray crystal analysis on tropolone derivatives<sup>10</sup> that a cycloheptatriene ring is planar. Therefore, from symmetry considerations, both the moment of azulene and the C-Cl moment of 2-chloroazulene are directed along the twofold axis of symmetry joining two carbon atoms at 2- and 6-positions. The C-Cl bond moment of 2-chloroazulene being presumed to be in the range between 1.6 D. for monochlorobenzene and 2.0 D. for alkyl chlorides, the moment of 2-chloroazulene is calculated as either 2.6-3.0 or 0.6-1.0 D., depending upon whether these two component moments are parallel or antiparallel to each other. The observed moment, 2.69 D., of this compound enables a choice between the two alternatives to be made. Thus one arrives at the conclusions that the electron transfer takes place from the seven-membered ring to the five-membered ring of an azulene molecule and that the C-Cl bond moment in 2-chloro-

azulene is 1.69 D. in its magnitude. The first conclusion ascertains the prediction from the method of molecular orbitals and substantiates the general view that an unsaturated seven-membered ring behaves as an electron donor while an unsaturated five-membered ring acts as an electron acceptor, thus approaching a stable configuration of an aromatic sextet, as in tropones, tropolones,<sup>11-13</sup> ferrocenes, etc. As to the second conclusion, it should be pointed out that the C-Cl bond moment of 2-chloroazulene is nearly equal in its magnitude to that of monochlorobenzene rather than to those of alkyl chlorides, indicating a striking resemblance of azulene to benzene in affecting the nature of a C-Cl bond attached to them.

The problem of the two alternative structures of 2-aminoazulene, *i.e.*, an amino-form and an imino-form resonating among various structures of which the representative ones are, respectively



cannot be settled from the chemical properties of this compound alone. It is known that aniline and amines take an amino-form, whereas 2- and 6-amino-1,3-diazaazulenes do not display properties characteristic of typical aromatic amines,<sup>14,15</sup> suggesting the presence of an imino-form. Azulene is basic to a considerable extent. With strong acids, it forms salts. The resulting azulonium ion, which exists as a resonance hybrid in



and a variety of other resonating forms, is stabilized by a greater resonance energy than that of azulene.<sup>16</sup> Accordingly, in the absence of any definite proof, it is not adequate to disregard the possibility of the imino-form. The dipole moment data afford a means of decision to be made for the presence or absence of the imino-form.

Let the component of the moment of 2-aminoazulene parallel to an axis joining two carbon atoms at 2- and 6-positions be denoted by  $\mu_{\parallel}$ , the component of the same moment perpendicular to the axis by  $\mu_{\perp}$  and the C-Br bond moment by  $\mu_{\text{Br}}$ . Then, one has the following equations for the moments of 2-aminoazulene and 6-bromo-2-aminoazulene, respectively.

$$\begin{aligned} \mu_{\parallel}^2 + \mu_{\perp}^2 &= 2.09^2 \\ (\mu_{\parallel} + \mu_{\text{Br}})^2 + \mu_{\perp}^2 &= 3.72^2 \end{aligned}$$

These simultaneous equations immediately lead to the conclusion that  $\mu_{\parallel}$  and  $\mu_{\text{Br}}$  are parallel rather than antiparallel to each other. The moment of

(7) K. Kimura, S. Suzuki, M. Kimura and M. Kubo, *J. Chem. Phys.*, **26**, 320 (1957).

(8) E. Heilbronner and K. Hedberg, *THIS JOURNAL*, **73**, 1386 (1951).

(9) M. Kimura and M. Kubo, *Bull. Chem. Soc. Japan*, **26**, 250 (1953); M. Kubo, M. Kimura and K. Kimura, *ibid.*, **27**, 455 (1954).

(10) Y. Sasada, K. Osaki and I. Nitta, *Acta Cryst.*, **7**, 113 (1954); Y. Sasada and I. Nitta, *ibid.*, **9**, 205 (1956).

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(12) Y. Kurita and M. Kubo, *ibid.*, **24**, 13 (1951).

(13) Y. Kurita, *Science Repts. Tohoku Univ.*, **1**, **38**, 85 (1954).

(14) T. Nozoe, T. Mukai, K. Takase, I. Kurata and K. Matsumoto, *Proc. Japan Acad.*, **29**, 452 (1953); T. Nozoe, M. Seto, S. Ito, K. Matsui and T. Matsuda, *ibid.*, **29**, 565 (1953); T. Nozoe, T. Mukai and I. Murata, *THIS JOURNAL*, **76**, 3352 (1954).

(15) H. Kon, *Science Repts. Tohoku Univ.*, **1**, **38**, 67 (1954).

(16) E. Heilbronner and M. Simonetta, *Helv. Chim. Acta*, **35**, 1049 (1952); H. M. Frey, *J. Chem. Phys.*, **25**, 600 (1956).

the imino-form can be calculated from reasonable numerical values for bond moments,  $H-C = 0.4$  D.,  $C=N = 1.44$  D. and  $H-N = 1.31$  D., and for a valency angle,  $\angle CNH = 120^\circ$ , the positive end of each bond moment being at the first one of bonded atoms. The calculation leads to the conclusion that  $\mu_{||} = 1.2$  D. and that  $\mu_{||}$  and  $\mu_{Br}$  are antiparallel to each other. (This gives a lower limit, because the absolute value becomes greater, if the transfer of  $\pi$ -electrons from the seven-membered ring to a nitrogen atom is taken into account.) This cannot be reconciled with the experimental data. On the other hand, the amino-form is consistent with experiments. Thus, introducing  $\mu_{\perp} = 1.13$  D.<sup>17,18</sup> evaluated from the moment of *p*-phenylenediamine into the simultaneous equations mentioned above, one obtains  $\mu_{||} = 1.76$  D. and  $\mu_{Br} = 1.79$  D. the former having the same direction as the latter. The value of  $\mu_{Br}$  is also of a right order of magnitude, since it falls in a range between 1.6 D. for monobromobenzene and 2.0 D. for alkyl bromides.

The absence of the imino-form could also be confirmed by means of infrared absorption spectra. In the frequency range of N-H and C-H stretching vibrations, two  $NH_2$ - stretching modes ( $3300-3500$   $cm^{-1}$ ) and one stretching mode of aromatic C-H bonds ( $3030$   $cm^{-1}$ ) will appear if only the amino-form is present, whereas one NH- stretching mode ( $3200-3400$   $cm^{-1}$ ), one CH- stretching mode ( $3030$   $cm^{-1}$ ) and two CH- stretching modes of a  $CH_2$ - group ( $2926 \pm 10$ ,  $2853 \pm 10$   $cm^{-1}$ ) are expected for the imino-form.<sup>19</sup> Actually, the infrared absorption of 2-aminoazulene studied by means of a Perkin-Elmer spectrometer with a rock salt prism showed three strong absorption bands at  $3470$ ,  $3380$  and  $3020$   $cm^{-1}$  in the wave number range in question ( $2000-4000$   $cm^{-1}$ ).

The interactions of an unsaturated ring system with a substituent atom or group attached to it can conveniently be expressed by the mesomeric moment of the substituent. It is defined as the difference between  $\mu_{ArX}$ , the moment of the substitution product, and  $\mu_{RX}$ , that of a corresponding alkyl compound. In the case when the unsaturated hydrocarbon itself is polar as in azulene, also its moment  $\mu_{ArH}$  must be subtracted from  $\mu_{ArX}$ , with due regard to its sign. Thus

$$\mu_{mes.} = \mu_{ArX} - \mu_{RX} - \mu_{ArH}$$

The values of some mesomeric moments calculated from the data of the present investigation are given in Table III, in which, as in the following paragraphs, the positive sign of moments indicates electrons being displaced from the ring system to the substituents. In Table IV, the mesomeric moments in azulene derivatives thus obtained are compared with those evaluated by Sutton<sup>17</sup> and others for benzene derivatives.

Although Sutton has pointed out that mesomeric moments increase or decrease progressively

(17) K. B. Everard, L. Kumar and L. E. Sutton, *J. Chem. Soc.*, 2807 (1951); K. B. Everard and L. E. Sutton, *ibid.*, 2818 (1951).

(18) Y. Kurita and M. Kubo, *Bull. Chem. Soc. Japan*, **27**, 361 (1954).

(19) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen, London, 1954, pp. 13, 54, 212.

TABLE III

MESOMERIC MOMENTS IN AZULENE DERIVATIVES				
Compounds	$\mu_{ArX}$	$\mu_{ArX} - \mu_{ArH}$	$\mu_{RX}$	$\mu_{mes.}$
2-Chloroazulene	2.69	1.69	2.01	-0.32
6-Bromoazulene <sup>a</sup>	...	1.79	2.00	-0.21
2-Aminoazulene <sup>b</sup>	-1.76	-2.76	0	-2.76
2-Cyanoazulene	5.69	4.69	3.60	+1.09

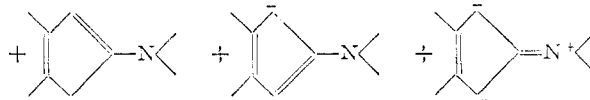
<sup>a</sup> Calculated from the moment of 6-bromo-2-aminoazulene. <sup>b</sup> Components along the C-N axis.

TABLE IV

MESOMERIC MOMENTS OF VARIOUS SUBSTITUENTS				
Unsaturated ring systems	$NH_2$	Cl	Br	CN
Benzene	-1.02	-0.41	-0.43	0.45
Biphenyl	-1.44	-0.37	-0.35	.73
Stilbene	-1.73	...	-0.33	.82
Azulene <sup>a</sup>	-2.76	-0.32	-0.21	1.09

<sup>a</sup> Bromine is substituted at the 6-position, while other substituents are at the 2-position.

with the linear dimension of conjugated systems, those in azulene derivatives do not obey this rule: azulene having a molecular dimension intermediate between those of benzene and biphenyl behaves as if it had a greater linear dimension than that of stilbene. The large mesomeric moment of the amino group is very likely the result of guanidinium-type resonance. Since azulene has a much greater



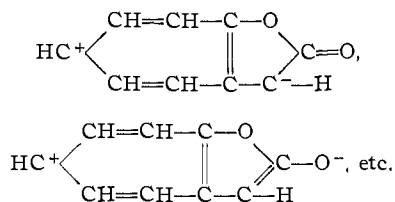
electron affinity than that of benzene, the migration of  $\pi$ -electrons from the lone pair orbital of an  $NH_2$ -group to the azulene ring plays an important role.

With the assumption of a regular pentagon form of the five-membered ring, the moments of 1-azaazulene and 1,3-diazaazulene can be calculated as 3.1 and 2.6 D., respectively, from the observed moment of azulene, 1.0 D., and the C-N bond moment, 2.2 D., evaluated from the moment of pyridine. Unfortunately, these two compounds have not been available in the present investigation. The moment of the former compound, however, may well be approximated with the observed moment of 2,6-dichloro-1-azaazulene, 3.25 D. The agreement of this value with the calculated moment for 1-azaazulene, 3.1 D., is good in view of the approximations made in the calculation. The direction of the moment of 1-azaazulene with respect to some reference line fixed in the plane of the molecule can also be determined from the observed moments of 2,6-dichloro-1-azaazulene and 2-chloro-1-azaazulene and the C-Cl bond moment, 1.6 D. It makes an angle of about  $49^\circ$  with the line joining two carbon atoms at the 2- and 6-positions. This value for the angle is consistent with  $54^\circ$  calculated by use of the assumptions mentioned above.

It is difficult to presuppose the behavior of 1,3-diazaazulene monohydrate in benzene solution. If the hydrate dissociates completely in the solution and each component part independently orients itself in the external field, the moment of 1,3-diazaazulene is calculated as  $(4.39^2 - 1.75^2)^{1/2} = 4.03$  D., which does not fit with the theoretical value, 2.6 D.

If the monohydrate complex persists in the solution with the moments of its component parts directed in parallel, its moment is calculated as  $2.60 + 1.75 = 4.35$  D. in good agreement with the observed value, 4.39 D. In this connection, it is desirable that X-ray crystal analysis be carried out on the monohydrate.

The large increase, about 1.52 D., in moment of 1-oxaazulan-2-one, 5.64 D., over those of  $\gamma$ -lactones represented by that of  $\gamma$ -butyrolactone,<sup>20</sup> 4.12 D., seems to indicate the contribution to resonance of polar structures such as



An analogous case already has been reported by

(20) R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.*, 1383 (1936).

Di Giacomo and Smyth,<sup>21</sup> who found a large increase, about 1.4 D., in the moment of cycloheptatrienone over those of other cyclic ketones. On the other hand, the increase in moment of 1-azaazulan-2-one, 2.73 D., over that of 2-pyrrolidone, 2.3 D.,<sup>22</sup> is not so great as that predicted by the same reasoning. This suggests the following explanation in terms of hydrogen bonding. Unlike 1-oxaazulan-2-one, 1-azaazulan-2-one has an NH group capable of forming a hydrogen bond with the oxygen atom of another molecule. The formation of dimers having an almost vanishing moment in dilute solutions would lead to the decrease of observed moment of 1-azaazulan-2-one below the true moment of a single molecule of this compound.

**Acknowledgment.**—We wish to express our cordial thanks to Prof. Nozoe and his collaborators for providing us with the purified materials used in the present investigation.

(21) A. Di Giacomo and C. P. Smyth, *THIS JOURNAL*, **74**, 4411 (1952).

(22) G. Devoto, *Gazz. chim. ital.*, **63**, 495 (1933); cf. E. Fischer, *J. Chem. Soc.*, 4525 (1952).

CHIKUSA, NAGOYA, JAPAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF BAYLOR UNIVERSITY]

## Hydrogenolysis by Metal Hydrides. I. Hydrogenolysis of Aryl Allyl Ethers by Lithium Aluminum Hydride<sup>1</sup>

BY VIRGIL L. TWEEDIE AND MICHAEL CUSCURIDA<sup>2</sup>

RECEIVED OCTOBER 8, 1956

Lithium aluminum hydride has been found to be an effective hydrogenolytic agent for aryl allyl ethers, the reaction products being phenols and alkenes. The hydrogenolyses were catalyzed by a number of salts and metallic oxides of which nickel(II) chloride was most frequently used. The extent of cleavage was markedly influenced by the nature of the solvent and by the type of substituent groups on the aryl ring and the allylic chain. Hydrogenolysis of phenyl allyl ether at 35° was 86% in tetrahydrofuran, 18% in ethyl ether and 59% in dioxane. Chloro groups in the *ortho* and *para* positions and phenyl and chloro groups on carbon three of the allylic system generally enhanced the hydrogenolysis reaction; methyl groups in the corresponding positions decreased the extent of cleavage compared to that of phenyl allyl ether. Phenyl *n*-propyl ether and phenyl 3-butenyl ether were not cleaved under the conditions employed.

### Introduction

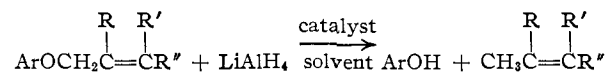
Although the hydrogenolysis of various types of organic compounds by complex metal hydrides has been reported frequently, there are relatively few reports of the hydrogenolysis of ethers by lithium aluminum hydride. Karrer and Ruttner<sup>3</sup> reported 26% cleavage of phenyl allyl ether and 10% cleavage of phenyl benzyl ether, using ethyl ether as a solvent and cobalt(II) chloride as a catalyst. Soffer and Parrotta<sup>4</sup> found that in the lithium aluminum hydride reduction of  $\beta$ -alkoxy- and  $\beta$ -aryloxypropionitriles to the corresponding amines, there was considerable cleavage of the alkoxy and aryloxy groups to give *n*-propylamine and alcohols or phenols. Other compounds containing ether linkages which undergo hydrogenolysis by lithium alumi-

num hydride are epoxides,<sup>5</sup> solasodine<sup>6</sup> and sapogenins.<sup>7</sup>

It was the purpose of this investigation to determine the general applicability of lithium aluminum hydride as a hydrogenolytic agent for aryl allyl ethers and to study the influence of catalysts, reaction conditions and molecular structure.

### Discussion

The work of Karrer and Ruttner was verified although with somewhat lower yields. Fourteen aryl allyl ethers have been cleaved in good yields by reaction in a solvent for 24 hr. with a catalyst and an excess of lithium aluminum hydride. All underwent hydrogenolysis at the alkyl oxygen bond to form a phenol and an alkene.



(5) L. W. Trevoy and W. G. Brown, *ibid.*, **71**, 1675 (1949).

(6) L. H. Briggs and R. H. Locker, *J. Chem. Soc.*, 3020 (1950).

(7) H. M. Doukas and T. D. Fontaine, *THIS JOURNAL*, **73**, 5917 (1951).

(1) Paper presented at March, 1954, A.C.S. Meeting, Kansas City, Mo.

(2) From the dissertation submitted by Michael Cuscurida in partial fulfillment of the requirements for the Ph.D. degree, Baylor University, 1955.

(3) P. Karrer and O. Ruttner, *Helv. Chem. Acta*, **33**, 812 (1950).

(4) L. M. Soffer and E. W. Parrotta, *THIS JOURNAL*, **76**, 3580 (1954).