sure 14.0 g., b.p. 115–133°, of a mixture of *trans*-olefin and acetylene, and 21.6 g. (51%) of crude I, b.p. 138–142°, n^{20}_{D} 1.4242.

The products from five runs were combined and redistilled through a 2.5 × 60 cm. glass helices-packed column to give 30 g., b.p. 143.0–143.6°, n^{20}_{D} 1.4263. To obtain samples for thermodynamic measurements, this fraction was redistilled on a spinning band column of 30-plate efficiency. This material had a practically constant boiling point at 143.0° on redistillation, and the mid-cut had n^{20}_{D} 1.4266. Its infrared spectrum was identical with that in the National Bureau of Standards file. Reported[5] physical constants are b.p. 144.2–144.4°, n^{20}_{D} 1.4271.

Gas chromatographic analysis of the sample of I sent to Dr. Rossini showed it to be essentially homogeneous. However, the sample of I sent to Dr. Turner had about 5% of impurity judged to be 2,2,5,5-tetramethylhexane. For the heat of hydrogenation experiments, Dr. Turner used I which had been purified by gas chromatography by Dr. W. Doering, Yale University.

Attempted isomerization by refluxing 1.5 g. of I with 0.075 g. of *p*-toluenesulfonic acid in 17 ml. of glacial acetic acid for 14 hours gave recovered material which was identical in refractive index and infrared spectrum. However, refluxing 1.5 g. of I with 0.8 g. of 5% palladium-on-alumina resulted in 80% isomerization to II after 2 hours, as estimated by refractive index and infrared spectra.

Various attempts to cause I, II and di-*t*-butylacetylene to undergo Diels-Alder reactions with 2,3-dimethylbutadiene and hexachlorocyclopentadiene[23] were unsuccessful.

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(23) We are indebted to Hooker Electrochemical Corp., Niagara Falls, N. Y., for a generous sample of this material.

COLUMBUS 10, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

Hydrogen Bonding of Phenols to Olefins[1]

BY ROBERT WEST

RECEIVED SEPTEMBER 8, 1958

Evidence for the formation of weak intermolecular hydrogen bonds between phenols and olefins in solution has been obtained by infrared spectral studies in the 3400–3800 cm.$^{-1}$ region. A new O–H absorption band characteristic of the hydrogen bonded complex appears at 60–130 cm.$^{-1}$ lower frequency than the absorption due to unassociated phenol hydroxyl groups. The relative basicities of some olefins have been measured by determining the frequency shift on hydrogen bonding. The basicities of olefins are increased by increasing alkyl substitution at the double bond, and decreased by conjugation. Olefins are stronger hydrogen bonding bases than simple aromatic hydrocarbons. Intramolecular hydrogen bonding to ethylenic π-electrons has also been observed in the compound *o*-allylphenol.

Both olefins and aromatic hydrocarbons behave as bases toward electrophilic reagents such as certain transition metal ions.[1a–4] The work of Jones and Badger[5] and of Tamres[6] on mixtures of aromatic hydrocarbons with alcohols and chloroform, and that of Brown[7] on hydrogen chloride–arene systems, has established that the π-electron systems of aromatic rings can serve as hydrogen-bonding bases, toward both strong and weak acids. However, little evidence has been presented for hydrogen bond formation involving olefinic π-electrons as bases. Olefins are known to form complexes with hydrogen chloride at low temperatures,[7,8] but no other examples of hydrogen bonding to olefins seem to have been reported.

This paper reports infrared studies of hydrogen bonding between hydroxyl compounds and olefins in carbon tetrachloride solution. The infrared absorption was observed in the 3000–3800 cm.$^{-1}$ region, near the fundamental O–H stretching frequency for the alcohols. In the presence of olefins the sharp absorption band due to non-bonded hydroxyl groups is diminished in intensity, and a broad new band at lower frequency appears, indicating that a hydrogen-bonded complex is formed. The hydroxyl association bands observed with olefins are generally of low intensity, which may account for the fact that this type of hydrogen bonding has not been reported previously.

In this work phenol, as suggested by Kuhn,[9] was used as the principal hydroxyl compound, along with the slightly more acidic compound *p*-fluorophenol. Phenols have many advantages as reference acids in hydrogen bonding studies. In particular they are superior to methanol-*d* used by earlier workers[1,2] for the following reasons: 1, the greater acidity of phenols leads to larger shifts of absorption position on hydrogen bonding; 2, phenols have a higher absorbency for the O–H vibration, so that the bands in question can be observed conveniently; and 3, phenols have less tendency to self-association than do aliphatic alcohols, and hence complications resulting from intermolecular association of hydroxyl groups with one another are minimized. At 0.020 *M* or less in carbon tetrachloride the self-association of the phenols which we used was negligible.

Experimental

Materials.—The phenol was Merck reagent grade material, fractionally crystallized and distilled in vacuum. *p*-Fluorophenol was used as obtained from the Pierce Chemical Co. The Pennsalt Chemicals Co. kindly donated a sample of 2,2,2-trifluoroethanol which was redistilled before use. 1-Methylcyclohexene and *o*-allylphenol were obtained from the Aldrich Chemical Co. Cyclohexene, isoprene and the aromatic hydrocarbons were from the Eastman Kodak Co., and all other olefins were from Matheson, Coleman and Bell Co. All of the olefin materials were dried and fractionally distilled through a short helix-packed column

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(1) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF 49(638)-285. Reproduction in whole or part is permitted for any purpose of the United States Government.

(1a) S. Winstein and H. J. Lucas, THIS JOURNAL, **60**, 836 (1938).

(2) H. J. Lucas, R. S. Moore and D. Pressman, *ibid.*, **65**, 227 (1943).

(3) L. J. Andrews and R. M. Keefer, *ibid.*, **71**, 3644 (1949); **72**, 3113, 5034 (1950); and **74**, 640 (1952).

(4) T. Moeller, "Inorganic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1952, p. 840.

(5) L. H. Jones and R. M. Badger, *ibid.*, **73**, 3132 (1951).

(6) (a) S. Searles and M. Tamres, *ibid.*, **73**, 3704 (1951); (b) M. Tamres, *ibid.*, **74**, 3375 (1952).

(7) H. C. Brown and J. D. Brady, *ibid.*, **74**, 3570 (1952).

(8) D. Cook, Y. Lupien and W. G. Schneider, *Can. J. Chem.*, **34**, 957 (1956).

(9) L. P. Kuhn, THIS JOURNAL, **74**, 2492 (1952).

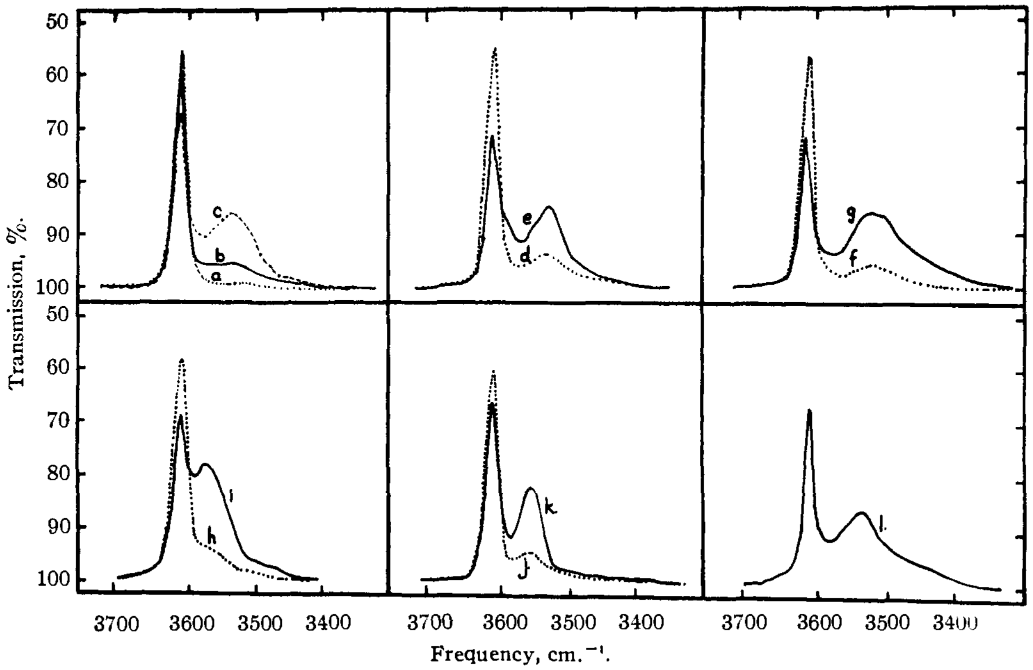

Fig. 1.—Difference plots showing spectrum of hydroxyl component in mixtures of phenol with hydrocarbons: a, 1.0 *M* *n*-heptane; b, 1.0 *M* 2-pentene; c, 4.7 *M* 2-pentene; d, 1.0 *M* cyclohexene; e, 5.0 *M* cyclohexene; f, 1.0 *M* 2-CH_3-2-butene; g, 4.8 *M* 2-CH_3-2-butene; h, 1.0 *M* isoprene; i, 5.0 *M* isoprene; j, 0.33 *M* *p*-xylene; k, 1.0 *M* *p*-xylene; l, 1.0 *M* 1-hexyne.

immediately before use. This precaution proved necessary because of the rapid development of basic impurities in the olefins when they were allowed to stand in contact with air.

Merck reagent grade carbon tetrachloride from freshly opened bottles was used as solvent. This material was free of hydroxylic or other basic impurities and gave results identical to those obtained with dried, fractionated carbon tetrachloride. Transfers of solvent and solutions were carried out in a room maintained at low humidity, using hypodermic syringes.

TABLE I

SHIFTS IN CM.$^{-1}$ OF O–H BAND IN MIXTURES OF ALCOHOLS AND HYDROCARBONS

Hydrocarbon	C_6H_5OH	*p*-FC_6H_4OH	CF_3CH_2OH	CH_3OD
1-Hexene	69	74		
1-Octene	62	69	66	
2-Pentene	86	95		
2-Hexene	85			
Cyclohexene	95	99		
2-CH_3-1-butene	104	106		
2-CH_3-1-pentene	100	114		
2-CH_3-2-butene	108	116	95	
1-CH_3-cyclohexene	113			
Benzene	47	49		24[a]
Toluene	58	61		26[a]
p-Xylene	66	69	58	30[a,b]
Mesitylene	73	78		34[a]
Isoprene	52	59		
1-Hexyne	92	96		

[a] Data from reference 6b. [b] Shift given is for *o*-xylene.

Spectra were measured using a Perkin–Elmer model 112 single-beam infrared spectrophotometer with a calcium fluoride prism, calibrated with ammonia gas. A slit width of 70 μ was used. Most of the hydrocarbons were run at two concentrations: 1.0 and 4.5–5.0 *M*, in carbon tetrachloride solvent. (The aromatic hydrocarbons and 1-hexyne were run only at 1.0 *M*.) Phenols or trifluoroethanol, when present, were always 0.020 *M*. For each concentration of each hydrocarbon, spectra were run both with and without hydroxyl compound. Point-by-point difference plots then were made to subtract out any olefin contribution in the hydroxyl region. Typical OH spectra resulting from this operation are shown in Fig. 1. Good agreement was observed between peak positions and shifts found at both olefin concentrations, indicating that the effect of the (rather small) change in dielectric constant on the spectrum is minor.

Association band positions were reproducible to ±6 cm.$^{-1}$ or better for olefins and isoprene, and ±3 cm.$^{-1}$ for aromatic hydrocarbons and 1-hexyne. The band shift data given in Table I are believed to be generally accurate within the same limits. Strongly basic oxygen-containing impurities, when present in hydrocarbons in appreciable amounts, led to hydrogen-bonded peaks at much lower frequencies. Traces of such materials probably were present even in the purified hydrocarbons, and led to a "tailing off" of the hydrocarbon hydrogen-bond peak on the low-frequency side.

Discussion

The shift in wave numbers from the non-bonded to the hydrogen bonded hydroxyl peak is a measure of the strength of the hydrogen bond, or more specifically of its enthalpy.[10a,10b] The shifts can therefore be used to measure quantitatively the acidity or basicity of molecules as hydrogen bond donors or acceptors. Observed shifts are listed in Table I. For a given hydrocarbon base, the band shift for phenol is always slightly less than for *p*-fluorophenol, indicating that the latter is a stronger hydrogen-bonding acid. On the basis of fragmentary data obtained with trifluoroethanol, it seems to be nearly as strong an acid as phenol.

Tamres[6b] observed that the H-bond basicity of aromatic hydrocarbons is increased by alkyl substitution, as would be predicted from the known positive inductive effect of alkyl groups. Tamres' data for mixtures of methanol-*d* with arenes is in-

(10) (a) R. F. Badger, *J. Chem. Phys.*, **8**, 288 (1940); (b) M. L. Huggins and G. C. Pimentel, *J. Phys. Chem.*, **60**, 1615 (1956).

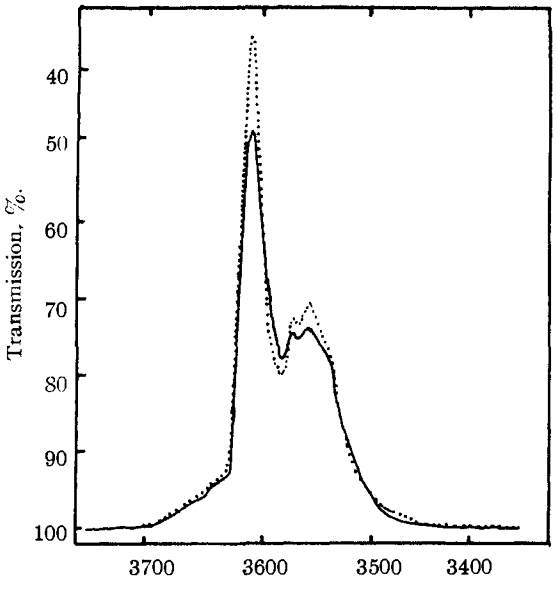

Fig. 2.—Spectrum of *o*-allylphenol in the hydroxyl region: solid line, 0.005 *M*; dotted line, 0.05 *M*.

cluded in Table I for comparison. As can be seen from Table I, our results confirm Tamres' conclusion in that we find the same trend of increasing hydroxyl shift with increasing alkyl substitution. The shifts are much larger for the phenols because of their higher acidity.

Data in Table I show that toward phenols, the basicity of olefins also increases with increasing alkyl substitution at the double bond. Thus the weakest bases are the 1-olefins, 1-hexene and 1-octene. The disubstituted olefins are intermediate in basicity, while the greatest shifts are observed for the trisubstituted compounds (2-methyl-2-butene and 1-methylcyclohexene). This is the same type of basicity order for olefins found by Brown and Brady[7] in their measurements of Henry's law constants for olefin–HCl mixtures at −78°. On the other hand, the basicity of olefins toward silver ion, as measured by the equilibrium constant for complex formation, decreases with increasing alkyl substitution.[1] As Winstein and Lucas suggest, this decrease in olefin basicity with alkyl substitution probably is due to steric hindrance to the approach of the large silver ion to the olefinic π-electrons.[1] A partial explanation for the opposite order of basicity toward phenols is that hydrogen bonding probably is much less sensitive to steric hindrance at the double bond, so that electron availability, rather than steric effects, determines the order of basicity. In addition, the infrared bands shifts, according to Badger's rule[10a,b] should be a measure of the enthalpy of hydrogen bonding. The free energy of complex formation, as measured by Winstein and Lucas' equilibrium constants, may be more influenced by steric effects than is the enthalpy.

While steric factors do not seem to be of primary importance in determining band shifts, they may play a secondary role. For instance, disubstituted olefins of type RHC=CHR appear to be significantly weaker bases toward phenols than those of type $R_2C=CH_2$. Another possible explanation for this difference is that the hydrogen bond to an olefin may involve significant polarization of the double bond in the direction of one of the carbon atoms, which could take place more easily in the unsymmetrically disubstituted olefins.[11]

Olefins generally are stronger hydrogen-bonding bases than are simple aromatic compounds. The least basic olefins, the 1-alkenes, are about as basic as *p*-xylene, while benzene and toluene are weaker bases than any of the olefins studied. That the basicity of the ethylenic π-electrons is weakened by conjugation with another carbon–carbon double bond is shown by the data for isoprene, which is also a weaker base toward phenol than any of the olefins. On the other hand, the single acetylenic compound which was studied, 1-hexyne, is about comparable to cyclohexene in basic strength, and much more strongly basic than the 1-olefins.

Comparing curve *k* in Fig. 1 with curves b, d and f, it appears that the hydrogen-bonded OH peaks for the phenol–arene complexes are more intense than those for phenol–olefin complexes, at the same hydrocarbon concentration. This is unexpected, since Huggins and Pimentel have shown that intensity of H-bonded bands is ordinarily proportional to basicity.[10b] Furthermore, the decrease in the height of the unbonded phenol peak is greater for a given concentration of arene than for the same concentration of olefin (Table II). Both of these facts suggest that the extent of hydrogen bond formation and the equilibrium constant for H-bonding must be greater for the aromatic compounds than for the olefins. This may be a steric, or statistical, effect resulting from the greater volume of the π-molecular orbitals in the aromatic compounds. When the concentration of *p*-xylene is cut down by a factor of 3, to 0.33 *M*, both the bonded peak intensity and the effect on the non-bonded OH peak become more nearly comparable to those observed with 1.0 *M* olefins (see curve j in Fig. 1, and Table II). Research is in progress on determination of the equilibrium constants for these and other hydrogen-bonded systems.

TABLE II

RELATIVE APPARENT INTENSITY OF NON-BONDED HYDROXYL BAND IN MIXTURES OF PHENOLS WITH 1.0 *M* HYDROCARBONS

Hydrocarbon	I_0	Hydrocarbon	I_0
n-Heptane	1.00	1-Hexyne	0.80
1-Hexene	0.93	Benzene	.85
2-Pentene	.94	*p*-Xylene	.80
Cyclohexene	.95	*p*-Xylene, 0.33 *M*	.90
2-CH_3-2-butene	.95		

TABLE III

RELATIVE APPARENT INTENSITIES OF NON-BONDED AND ASSOCIATED HYDROXYL PEAKS IN *o*-ALLYLPHENOL

Concn., *M*	I_H/I_0[a]
0.050	0.47
.025	.40
.0050	.43
.0025	.39
.0010	.37

[a] I_H = apparent intensity of H-bonded peak; I_0 = apparent intensity of non-bonded peak.

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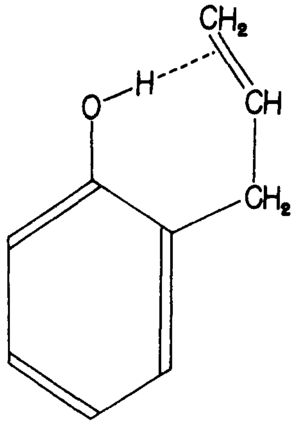
[11] The author is indebted to Dr. Paul Wigler for this suggestion.

Intramolecular Hydrogen Bonding.[11a]—An intramolecular analog is generally to be found for each known type of intermolecular hydrogen bonding. Recent notes have reported infrared evidence for intramolecular hydrogen bonding to aromatic rings in such compounds as 2-phenylethanol.[12,13] In a molecule with suitable geometry, it should be possible to observe intramolecular hydrogen bonding to ethylenic π-electrons also. Such a molecule is *o*-allylphenol, whose infrared spectrum in the hydroxyl region is shown in Fig. 2. In addition to the sharp non-bonded peak at 3600 cm.$^{-1}$ a broad hydrogen-bonded band appears at 3530 cm.$^{-1}$. The shift of 70 cm.$^{-1}$ between these bands corresponds well with those observed for intermolecular hydrogen bonds from phenols to olefins (Table I). As the data in Table III show, the relative heights of the two peaks are essentially independent of concentration from 0.205 down to 0.0010 *M*, the lowest concentration at which the spectrum could be conveniently measured. This concentration-independent hydrogen bonded peak provides strong evidence for the existence of the intramolecularly hydrogen bonded *cis*[14] form I, in equilibrium with the non-hydrogen bonded *trans* form in *o*-allylphenol.



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(11a) Added in proof.—Since the submission of this article, two papers have appeared demonstrating intramolecular hydrogen bonding to olefins: see A. W. Baker and A. T. Shulgin, THIS JOURNAL, **80**, 5358 (1958), and P. von R. Schleyer, D. S. Trifan and R. Backskai, *ibid.*, **80**, 6991 (1958).

(12) D. S. Trifan, J. L. Weinmann and L. P. Kuhn, *ibid.*, **79**, 6566 (1957); *cf.* W. H. Rodebush and R. Feldman, *ibid.*, **69**, 770 (1947).

(13) I. M. Goldman and R. O. Crister, *J. Org. Chem.*, **23**, 751 (1958).

(14) L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., 2nd ed., 1948, pp. 320–327.

MADISON 6, WIS.

[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

Cleavage of Alkoxides. Reversal of Grignard-Type Addition to Ketones[1]

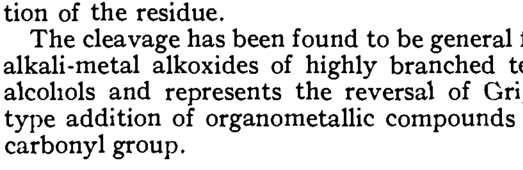
BY H. D. ZOOK, J. MARCH AND D. F. SMITH

RECEIVED AUGUST 6, 1958

Alkali-metal salts of highly branched tertiary alcohols are cleaved thermally in the dry state or in excess tertiary carbinol to give mixtures of ketones and paraffins. The eliminated carbanions are converted to the hydrocarbons by the excess alcohol or enolizable ketonic product. Phenyl, *t*-butyl and primary alkyl groups are eliminated in preference to isopropyl groups. Among the primary groups, ease of elimination increases in the order *n*-propyl < isobutyl < neopentyl. Variation of the cation does not affect the direction of cleavage, but ease of fission decreases significantly in the order K > Na > Li.

In an attempt to prepare a sodium alcoholate from di-*t*-butylneopentylcarbinol and sodium hydride, extensive cleavage occurred. The evolved gas consisted of hydrogen, isobutane and neopentane. Hexamethylacetone and *t*-butyl neopentyl ketone were obtained upon hydrolysis and distillation of the residue.

The cleavage has been found to be general for the alkali-metal alkoxides of highly branched tertiary alcohols and represents the reversal of Grignard-type addition of organometallic compounds to the carbonyl group.



$$\mathrm{R}\underset{\mathrm{R}}{\overset{\mathrm{O^-M^+}}{\overset{|}{\underset{|}{\mathrm{C}}}}}\mathrm{CH_2R} \rightleftharpoons \mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_2R} + \mathrm{R{:}^-M^+} \tag{1}$$

$$\mathrm{R}\underset{\mathrm{R}}{\overset{\mathrm{OH}}{\overset{|}{\underset{|}{\mathrm{C}}}}}\mathrm{CH_2R} + \mathrm{R{:}^-M^+} \longrightarrow \mathrm{R}\underset{\mathrm{R}}{\overset{\mathrm{O^-M^+}}{\overset{|}{\underset{|}{\mathrm{C}}}}}\mathrm{CH_2R} + \mathrm{RH} \tag{2}$$

$$\mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_2R} + \mathrm{R{:}^-M^+} \longrightarrow (\mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\underset{\cdot\cdot}{\mathrm{C}}\mathrm{HR})^-\mathrm{M^+} + \mathrm{RH} \tag{3}$$

Although the literature on the pyrolysis of metallic alkoxides is extensive, only the simpler organic skeletons have been studied, and these decompose at high temperatures to give carbon, hydrogen and olefins.[2,3]

In this study, several alkoxides were cleaved below the boiling points of the corresponding alcohols. Thus, the cleavage of the alcohols could be accomplished in the presence of a relatively small amount of alkoxide. The eliminated carbanion converted more alcohol to alkoxide (equation 2). The yields of cleavage products from several alcohols were much greater than the amount of alkali metal present. The major products in every case were par-

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(1) Presented at the 133rd Meeting of the American Chemical Society, San Francisco, Calif., April 14–18, 1958.

(2) W. A. Beatty, *Am. Chem. J.*, **30**, 224 (1903); J. F. Durand, *Compt. rend.*, **172**, 1504 (1921); G. Thomas, *Ann. chim.*, [12] **6**, 387 (1951); D. Ivanov, *Compt. rend.*, **188**, 1259 (1929); C. A. Bischoff, *Ber.*, **32**, 1761 (1899); J. U. Nef, *Ann.*, **318**, 137 (1901); P. G. Stevens, THIS JOURNAL, **54**, 3732 (1932).

(3) Ramart-Lucas, *Ann. chim.*, [8] **30**, 349 (1913), and V. Grignard, *ibid.*, [10] **2**, 282 (1924); *Compt. rend.*, **176**, 1860 (1923), **182**, 299 (1926), report ketonic cleavage of several tertiary alcohols at 600°. These fissions may well have occurred in anions formed from alkali in the glass. Also, Mosher, Fairbanks and Prucino, Abstracts of Papers, 126th Meeting of the American Chemical Society, New York, N. Y., p. O-91, obtained acetophenone and triphenylmethane in an attempt to prepare an alcoholate from benzopinacolone and methylmagnesium bromide.