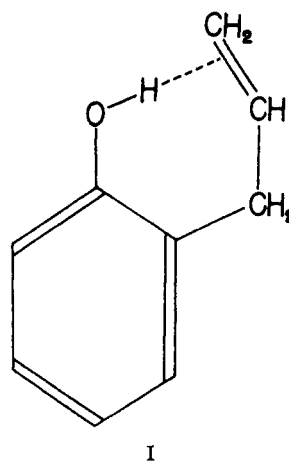


Intramolecular Hydrogen Bonding.^{11a}—An intramolecular analog is generally to be found for each known type of intermolecular hydrogen bonding. Recent notes have reported infrared evidence for intramolecular hydrogen bonding to aromatic rings in such compounds as 2-phenylethanol.^{12,13} In a molecule 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

(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).



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.

(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 Ketones¹

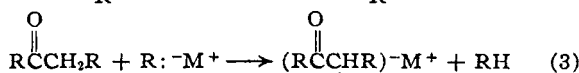
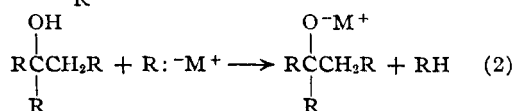
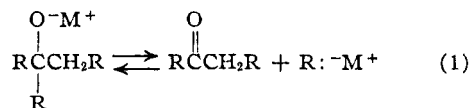
BY H. D. ZOOK, J. MARCH AND D. F. SMITH

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 $\text{K} > \text{Na} > \text{Li}$.

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.



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

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-

(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.

TABLE I
 CLEAVAGE OF SODIUM ALKOXIDES $R_1R_2R_3CO^-Na^+$

Reactants, carbinol				NaNH ₂ , mole	Temp., ^a °C.	Time, hr.	Products, mole %				
R ₁	R ₂	R ₃	Mole				R ₁ R ₂ R ₃ - COH	R ₁ COR ₂	R ₂ H	R ₁ COR ₃	R ₂ H
<i>i</i> -Pr	<i>i</i> -Pr	<i>n</i> -Pr	0.0243	0.0239	266-392	3.5	30	19	58	0	..
<i>i</i> -Pr	<i>i</i> -Pr	<i>i</i> -Bu	.0244	.0140	264-362	4.3	53	37	38	0	6
<i>i</i> -Pr	<i>i</i> -Pr	neo-P	.0205	.0044	222-240 ^b	6.0	26	35	36	0	0
<i>i</i> -Pr	<i>i</i> -Pr	Ph	.0345	.0060	242-276 ^b	5.5	13	72	70	3	3
<i>i</i> -Pr	<i>i</i> -Pr	<i>t</i> -Bu	.0327	.0101	199-215 ^b	2.0	7	52	31	32	23
<i>i</i> -Pr	<i>i</i> -Pr	<i>i</i> -Pr	.0143	.0079	300-312	1.5	21	20	24
<i>i</i> -Bu	<i>i</i> -Bu	neo-P	.0170	.0095	247-257	3.0	76	7	7	12	5
Ph	Ph	Ph	.0160	.0060	280-320 ^b	4.0	51	23	31		
Et	Et	Et			335	2.0	No cleavage				

^a The temperature range corresponds to the time of heating. When cleavage did not occur in the presence of excess carbinol, the excess distilled throughout the range and most cleavage occurred at the higher temperature. ^b Partly cleaved in the presence of excess carbinol.

affins corresponding to the groups eliminated and ketones corresponding to the remainder of the molecules. Even when excess alcohol was absent, the products were the same, for then the eliminated carbanions were converted to paraffins by removal of protons from the enolizable ketonic products (equation 3). The ketones were recovered from their salts by hydrolysis. The data are summarized in Tables I and II. When cleavage occurred at relatively low temperatures, as in the presence of excess carbinol, side reactions were insignificant. The ketones and corresponding paraffins were formed in stoichiometric amounts. When higher temperatures were required, some charring of the residue occurred, and appreciable quantities of methane were evolved.

 TABLE II
 CLEAVAGE OF DIISOPROPYLALKYL CARBINOLS $(i\text{-Pr})_2\text{RCOH}$.
 EFFECT OF CATION

R	Alkoxide Cation	Temp., °C.	Products, mole %			Ratio <i>i</i> -Pr/R
			Carbi- nol	$(i\text{-Pr})_2\text{CO}$	<i>i</i> -Pr- COR	
<i>t</i> -Bu	K	160-182	0	60	35	0.58
<i>t</i> -Bu	Na	199-215	7	52	32	0.61
<i>t</i> -Bu	Li	213-320	24	35	25	0.71
neo-P	K	192-254	7	64	0	0
neo-P	Na	222-240	26	35	0	0

The cleavage occurs at a reasonable rate when branching in the alkyl groups is sufficient to produce strain within the alkoxide. The most highly branched carbinols were cleaved under the mildest conditions. For example, the sodium salt of diisopropyl-*t*-butylcarbinol was cleaved in the presence of excess carbinol at 200°, whereas the corresponding salt of triisopropylcarbinol required a temperature of 300°, and triethylcarbinol could not be cleaved at 335°. Because primary groups are more readily eliminated than secondary or tertiary groups of similar size (see below), steric factors, therefore, are of considerable importance in the fission.

Many instances may be cited in which cleavages of analogous compounds result in the formation of the most stable anions. The reversal of the aldol condensation to give the resonance-stabilized enolate ion,⁴ the loss of cyanide ion from cyanohydrins,⁵ and the loss of trihalomethide ion from tri-

halo ketones⁶ are a few examples. By analogy with these reactions, the direction of cleavage of tertiary alkoxides might provide some measure of relative stabilities of the various alkyl carbanions.

A primary alkyl group was cleaved from several diisopropylalkylcarbinols in which the amount of β -branching in the primary group was varied. Again, the ease of cleavage increased with increasing bulkiness of the group: *n*-propyl < isobutyl < neopentyl. No trace of the primary alkyl isopropyl ketone could be detected by infrared analysis of the products. The greater stability of the primary carbanion parallels that reported for the addition of metal alkyls to ethylene.⁷ Addition of a secondary carbanion occurred readily, but the primary carbanion thus formed did not react further with ethylene.

The sodium salt of diisobutylneopentylcarbinol was the only compound studied in which all three groups were primary radicals. Both isobutyl and neopentyl anions were eliminated in approximately the statistical ratio of 2:1.

Preferential elimination of a *t*-butyl group over an isopropyl group definitely has been established. Even though a statistical factor of two favors elimination of an isopropyl anion from diisopropyl-*t*-butylcarbinol, the ratio of diisopropyl ketone to isopropyl-*t*-butyl ketone was 3:2 in the decomposition of lithium, sodium and potassium alkoxides. This ratio was confirmed by analysis of the hydrocarbon gases. The potassium alkoxide was easily and completely cleaved at 160-182°; 95% of the ketones and 99% of the paraffins were obtained.

The importance of the accompanying metallic cation in the transition state for the cleavage was indicated by the results obtained by variation of the metal. Significant differences in the ease of cleavage, as measured by the temperature and amount of recovered alcohol, were observed (Table II). The order of decreasing ease of cleavage is K > Na > Li. The least electronegative metal allows a greater negative charge on the anion of the ion

Tweed, *ibid.*, 2831 (1952); J. W. Baker and H. B. Hopkins, *ibid.*, 1089 (1949); G. Wittig, V. Todt and K. Nagel, *Chem. Ber.*, **83**, 110 (1950).

(6) A. G. Fishburn and H. B. Watson, *J. Am. Pharm. Assoc.*, **28**, 491 (1939); F. K. Cameron and H. A. Holby, *J. Phys. Chem.*, **2**, 322 (1898); C. Willgerodt and S. Schiff, *J. prakt. Chem.*, **41**, 515 (1890).

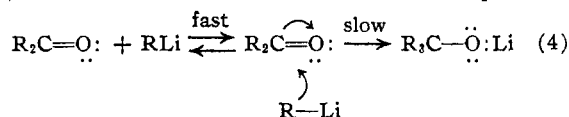
(7) P. D. Bartlett, S. Friedman and M. Stiles, *THIS JOURNAL*, **75**, 1771 (1953); H. Pines, J. A. Vesely and V. N. Ipatieff, *ibid.*, **77**, 554 (1955).

(4) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 283-297.

(5) A. Lapworth, *J. Chem. Soc.*, 995 (1903); D. P. Evans and J. R. Young, *ibid.*, 1310 (1954); J. W. Baker, G. F. C. Barrett and W. T.

pair. Increase in the electronegativity of the cation results in more covalent character to the bond between the ions, less defined charges on both anionic and cationic species, and greater stability for the alkoxide.

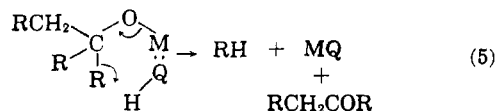
A mechanism for the addition of organolithium compounds to ketones has been proposed by Swain⁸ on the basis of second-order kinetics and the results of structural variations of both reactants (equation 4). Our work indicates that the over-all process is



reversible even though the position of the equilibrium is far toward the alcoholate. In the presence of excess tertiary alcohol or enolizable ketone, the equilibrium is disturbed by conversion of the organometallic compound to paraffin. It is interesting to compare the behavior of phenyl and isopropyl groups in both forward and reverse processes. Swain found that the rate of addition of isopropyl-lithium to Michler ketone was only one-tenth that for phenyllithium. Preferential elimination of phenyl over isopropyl groups in the reverse process is illustrated by the fission of diisopropylphenylcarbinol where the ratio of phenyl to isopropyl elimination is 70 to 3.

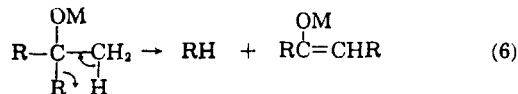
Isolation of small quantities of olefinic hydrocarbons corresponding to the eliminated groups also supports this mechanism. For example a 0.3% yield of isobutylene was obtained at 160–180° from the cleavage of the potassium salt of diisopropyl-*t*-butylcarbinol in the presence of excess carbinol. The main products of thermal decomposition of organoalkali compounds at these temperatures are olefins and metallic hydrides.⁹

A six-centered transition state proposed for similar cleavages of more complex alkoxides¹⁰ cannot be ruled out for the direct formation of at least a portion of the paraffinic product.



where $\text{HQ} = \text{R}_3\text{COH}$ or RCH_2COR .

The four-centered degradation of alkoxide directly to paraffin and enolate, proposed to explain the formation of acetophenone enolate from benzopinacolone and methylmagnesium bromide,³ cannot account for some of our products. Hexamethylacetone is formed from di-*t*-butylneopentylcarbinol



and benzophenone from triphenylcarbinol. Enolates of these ketones do not exist. Furthermore, the cleavage of the sodium salt of diisopropyl-*t*-butylcarbinol in the presence of excess deuterated carbinol, $\text{R}_2\text{R}'\text{COD}$, gave deuterated paraffin.

- (8) C. G. Swain and L. Kent, *THIS JOURNAL*, **72**, 518 (1950).
 (9) W. H. Carothers and D. D. Coffman, *ibid.*, **52**, 1254 (1930), **51**, 558 (1929); E. Wiberg and R. Bauer, *Ber.*, **85**, 593 (1952).
 (10) J. L. Greene and H. D. Zook, *THIS JOURNAL*, **80**, 3629 (1958).

Thus, even when α -hydrogen atoms are available in the alkoxide, at least some of the paraffin is formed from hydrogen atoms originally part of the solvent.

The preparation of diisopropylneopentylcarbinol in 71% yield from diisopropyl ketone and neopentyl-lithium provides an excellent example of the superiority of the lithium alkyl over the Grignard reagent in the preparation of highly hindered carbinols. A yield of only 4% is obtained by the Grignard process; the remainder of the ketone is converted to the magnesium enolate.¹¹ The preparation of tri-*t*-butylcarbinol¹² from di-*t*-butyl ketone illustrates the advantage of *t*-butyllithium over *t*-butyl Grignard reagent in giving addition rather than reduction; however, enolization is impossible in this case.

Experimental

Materials.—The usual Grignard methods were used to prepare triethylcarbinol (3-ethyl-3-pentanol),¹³ b.p. 141–142° at 731 mm., n_D^{20} 1.4272–1.4278; triphenylcarbinol,¹⁴ m.p. 162–163°; and diisopropylphenylcarbinol (α , α -diisopropylbenzyl alcohol),¹⁵ b.p. 77° at 1 mm., n_D^{20} 1.514–1.516. Lithium alkyls were employed in the preparations of triisopropylcarbinol (3-isopropyl-2,4-dimethyl-3-pentanol),¹² b.p. 190.5–192° at 721 mm., n_D^{20} 1.4456–1.4461; diisopropyl-*t*-butylcarbinol (3-isopropyl-2,4,4-trimethyl-3-pentanol),¹² b.p. 48° at 1 mm., n_D^{20} 1.4560–1.4561; and diisopropylisobutylcarbinol (3-isopropyl-2,5-dimethyl-3-hexanol),¹² b.p. 47–48° at 2 mm., n_D^{20} 1.4402.

n-Propyl isopropyl ketone was prepared by adding 8.4 g. of *n*-propylisopropylcarbinol in small portions to a solution of 7.5 g. of potassium dichromate, 6.5 ml. of sulfuric acid and 55 ml. of water. The mixture was shaken and cooled to room temperature after each addition. The product was steam distilled and fractionated to give 4.3 g. (52%) of *n*-propyl isopropyl ketone,¹⁶ b.p. 134° at 733 mm., n_D^{20} 1.4030–1.4032.

Isopropyl neopentyl ketone, b.p. 56–58° at 22 mm., n_D^{20} 1.4100, was made from ethyl *t*-butylacetate and isopropylmagnesium chloride.¹⁷ Diisopropyl ketone, b.p. 125° at 740 mm., n_D^{20} 1.3980; phenyl isopropyl ketone, b.p. 84° at 6.5 mm., n_D^{20} 1.5143; and diisobutyl ketone, b.p. 166° at 737 mm., n_D^{20} 1.4120, were obtained by fractional distillation of commercial products. The preparations of isopropyl *t*-butyl ketone,¹⁸ isobutyl neopentyl ketone,¹⁷ diisopropyl-*n*-propylcarbinol¹⁸ and diisobutylneopentylcarbinol¹⁷ have been described previously.

C.P. Matheson hydrocarbon gases were used as standards for infrared analyses.

Diisopropylneopentylcarbinol (3-Isopropyl-2,5,5-trimethyl-3-hexanol).—To a rapidly stirred suspension of 8.3 g., 1.19 moles, of finely divided lithium¹² in 200 ml. of dry ether at –40° was added over a period of 1.5 hr. 61 g., 0.58 mole, of neopentyl chloride in 75 ml. of ether. A nitrogen atmosphere was maintained throughout the reaction. After 40 minutes additional stirring, the concentration of neopentyl-lithium was 1.46 *M* (85% yield). To the solution of lithium alkyl at –78° was added slowly a solution of 52.5 g., 0.46 mole, of diisopropyl ketone. The lithium alkoxide was hydrolyzed by 400 ml. of water and fractionally distilled through a 16-cm. column packed with 1/8-inch, single-turn, glass helices. Eight fractions of carbinol were obtained, b.p. 52–54° at 1 mm., n_D^{20} 1.4459–1.4460. The yield, based on ketone, was 60.7 g., 71%.

- (11) F. C. Whitmore and R. S. George, *ibid.*, **64**, 1239 (1942).
 (12) P. D. Bartlett and E. B. Lefferts, *ibid.*, **77**, 2804 (1955); P. D. Bartlett and M. S. Swain, *ibid.*, **77**, 2801 (1955).
 (13) J. Boeseken and A. J. Wildschut, *Rec. trav. chim.*, **51**, 169 (1932).
 (14) W. E. Bachmann and H. P. Hetzner, *Org. Syntheses*, **23**, 98 (1943).
 (15) J. Stas, *Bull. soc. chim. Belg.*, **35**, 382 (1926); F. C. Whitmore and R. S. George, *THIS JOURNAL*, **64**, 1239 (1942).
 (16) H. Meerwein, *Ann.*, **419**, 140 (1919).
 (17) F. C. Whitmore and W. S. Forster, *THIS JOURNAL*, **64**, 2906 (1942).
 (18) H. D. Zook, W. E. Smith and J. L. Greene, *ibid.*, **79**, 4438 (1957).

Apparatus.—The preparations and cleavages of the alcoholates were carried out in a 1.8×8.5 -cm. cylindrical flask fitted to a 0.7×12 -cm. total-condensation variable-take-off column packed with $1/8$ -inch glass helices. Distillate was collected in a 15-ml. tube cooled in ice. Evolved gases were led to a 30-ml. trap cooled by liquid nitrogen. A slow stream of nitrogen gas was passed across a T-tube at the outlet of the trap to prevent condensation of air and moisture. Temperature was measured by an iron-constantan thermocouple placed in a well inside the flask. Condensed gases were expanded for measurement into a storage system consisting of a manifold to which was attached two 1-liter flasks, manometer, and stopcocks leading to a vacuum pump and a 10-cm. gas cell for infrared measurements.

Preparation of Alkoxides.—A weighed quantity of the tertiary alcohol was converted under nitrogen in the apparatus to the lithium, sodium or potassium alcoholate. Metallic potassium, powdered lithium hydride (Maywood Chemical Co.), ethereal sodium triphenylmethide and sodium amide (Farchan Research Laboratories) were employed as bases. The temperature was increased sufficiently to produce reaction. Ammonia or ether, when present, was removed by distillation into a separate trap.

Cleavage of Alkoxides.—The procedure is illustrated by one example, cleavage of the potassium salt of diisopropyl-*t*-butyl carbinol. The alkoxide was prepared from 6.406 g., 0.0372 mole, of carbinol and 0.658 g., 0.0168 mole, of potassium. Cleavage began at 180° in the presence of the excess carbinol. The temperature in the flask then fell to 160° during the next 8 hours even though that of the surrounding air-bath was increased from 185 to 250° . A few drops of distillate were collected during this period. Finally, distillation occurred rapidly at a flask temperature of 177 – 182° . The residue then was heated for 80 min. at 190 – 196° , but no additional distillate was collected.

The distillate, 2.146 g., was a clear, colorless liquid with a sweet odor. A 0.132-g. aliquot was diluted to 10.0 ml. with carbon tetrachloride for infrared analysis. The spectrum showed the presence of only diisopropyl ketone and isopropyl-*t*-butyl ketone; characteristic peaks for diisopropyl-*t*-

butylcarbinol at 2.80, 10.44 and 10.50μ were absent. Absorbances at 9.45 and 9.73μ were 0.424 and 0.471, respectively. Specific absorbances for diisopropyl ketone at these wave lengths are 0.11 and $1.35 \text{ l. g.}^{-1} \text{ cm.}^{-1}$. For isopropyl-*t*-butyl ketone, the values are 0.92 and $0.056 \text{ l. g.}^{-1} \text{ cm.}^{-1}$. Solution of simultaneous equations gave 0.0058 g./ml. for diisopropyl ketone and 0.0080 g./ml. for isopropyl-*t*-butyl ketone corresponding to 0.0082 and 0.0100 mole of each, respectively.

The residue, 3.033 g., was a cream-colored solid. After hydrolysis with 20 ml. of water, the mixture was extracted with 10-ml., 5-ml., 5-ml. and 3-ml. portions of carbon tetrachloride. The combined extract was washed with 7 ml. of water, diluted to 25.0 ml. with carbon tetrachloride and dried over Drierite. Again, the spectrum showed the presence of only the two ketones. The absorbances were 0.800 at 9.45μ and 4.98 at 9.73μ corresponding to 0.014 mole of diisopropyl ketone and 0.0031 mole of isopropyl-*t*-butyl ketone.

Expansion of the condensed gases gave 783 ml. of hydrocarbon gas at S.T.P. The following composition was obtained by infrared analysis: isobutane, 460 ml., 0.021 mole; propane, 270 ml., 0.016 mole; isobutylene, 3 ml., 0.00012 mole; and methane, 50 ml., 0.00022 mole. The over-all results are summarized in Table II.

Infrared Spectra and Analyses.—Spectra were measured with a Perkin-Elmer model-21 double-beam spectrophotometer equipped with sodium chloride optics. Analyses of liquid products in carbon tetrachloride solution were made by determination of a base line with solvent in two 0.52-mm. matched cells, then by substitution of the solution for the solvent in one cell. Absorbances were measured at frequencies characteristic of each product present, and concentrations were determined by solution of simultaneous equations. Spectra of all pure alcohols, ketones and hydrocarbon gases were measured separately at three or more concentrations and found to follow Beer's law at the wave lengths used for analysis. Benzene and neopentane were measured in both gas and distillate.

UNIVERSITY PARK, PENNA.

[CONTRIBUTION FROM THE COLGATE-PALMOLIVE CO.]

The Reaction of Lauric Acid Esters with Sulfuric Acid

By ROBERT A. BAUMAN AND IRVING J. KREMS¹

RECEIVED OCTOBER 2, 1958

Reversibility of the reaction of methyl laurate with sulfuric acid to form lauric acid and methyl sulfuric acid has been demonstrated, and concentration equilibrium constants have been calculated for the reaction at 30.5 and 40.7° . The effect of water and of sulfuric anhydride was observed. Diesters of lauric acid and ethylene, propylene, trimethylene and pentamethylene glycols were prepared and allowed to react with 100% sulfuric acid. The reactions of ethylene glycol monolaurate and of sodium lauroxyethyl sulfate with sulfuric acid also were studied. Stepwise rapid cleavage of lauric acid from the diesters was observed, and, except in the case of pentamethylene glycol dilaurate, one of the principal products obtained on quenching the reaction with water was the glycol monolaurate. A cyclic carbonium ion mechanism is suggested to account for the results.

Previous work on the reaction of simple esters with concentrated sulfuric acid has established that a product is formed which yields a carboxylic acid on dilution with water, and that the rate and extent of formation of this product varies with the structure of the ester.² The structure of this product has been given variously as RCO^+ (in the case of mesitoates and certain related esters),^{3,4} RCO-OH_2^+ ⁵ or RCOOSO_3H .⁶ Cryoscopic evidence for the instability of the acetyl and benzoyl cations in

sulfuric acid of concentration 100% or less has been obtained by Leisten.⁷ The postulation of the mixed anhydride RCOOSO_3H he shows to be unnecessary, leaving the protonated carboxylic acid as the most likely structure of the stable species from unhindered esters. The other product of the reaction is an alkyl sulfuric acid, which, at least for the methyl and ethyl esters, has been found to be completely stable in sulfuric acid.⁸

The only clear-cut evidence for a mechanism is that of Leisten⁹ who assigns the unimolecular acyl-oxygen fission mechanism (AAC1) to the solvolysis of methyl and ethyl benzoates and the corresponding alkyl-oxygen fission mechanism (AAL1)

(1) University of Vienna, Vienna, Austria.

(2) R. J. Gillespie and J. A. Leisten, *Quart. Revs.*, **8**, 40 (1954).

(3) H. P. Treffers and L. P. Hammett, *This Journal*, **59**, 1708 (1937).

(4) M. S. Newman, *ibid.*, **63**, 2341 (1941).

(5) M. S. Newman, R. A. Craig and A. B. Garrett, *ibid.*, **71**, 869 (1949).

(6) L. P. Kuhn and A. H. Corwin, *ibid.*, **70**, 3370 (1948).

(7) J. A. Leisten, *J. Chem. Soc.*, 298 (1955).

(8) R. J. Gillespie, *ibid.*, 2542 (1950).

(9) J. A. Leisten, *ibid.*, 1572 (1956).