1.018, 1.048, 0.985, 1.006, 1.017 and 1.015×10^{-2}) and for the deuterated compound (k_D) ($0.867 \pm 0.010) \times 10^{-2}$ (mean of 0.891, 0.877, 0.844, 0.877 and 0.844×10^{-2}) sec.$^{-1}$ mole^{-1} l. (0.008 and 0.010 are standard deviations of the mean).

Numerous examples of α-deuterium isotope effect in a carbonium ion solvolysis reaction have been reported,[5] but not in a bimolecular elimination (E_2). The effect is explained in terms of the reduction in the force constant for the bending of the C–H bond in the sp^2-bonded activated complex.[6]

The difference in the α-deuterium effects between 2-phenylethyl bromide and the corresponding sulfonium ion most probably results from the same reason as the old established difference in bimolecular eliminations between alkyl halides and alkyl sulfonium or ammonium ions governed by Saytzeff and Hofmann rules. A larger electron transfer from carbon to halogen is needed to give the transition state than in C–S heterolysis. Thus there should be more unsaturation in the transition state and the α-carbon should be closer to sp^2 hybridization.

The authors thank Sir Christopher Ingold and Professor W. H. Saunders for helpful discussions.

(5) V. J. Shiner, Jr., H. R. Mahler, R. H. Baker, Jr., and R. R. Hiatt, *Annals New York Acad. Sci.*, **84**, 583 (1960); A. Streitwieser, Jr., *ibid.*, **84**, 576 (1960).

(6) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey and S. Suzuki, *J. Am. Chem. Soc.*, **80**, 2326 (1958).

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A NEW COÖRDINATION TYPE AROUND FLUORINE ATOM

Sir:

In connection with the studies carried on from a long time in our Institute on metalloörganic complexes containing bridge bonds,[1,2,3] we have undertaken the X-ray structural study of the compound $KF \cdot 2Al(C_2H_5)_3$ (I), for the first time synthesized and studied by Ziegler *et al.*[4]

A $KF \cdot 2Al(C_2H_5)_2$ solution is obtained by reaction of finely ground KF with a stoichiometric quantity of $Al(C_2H_5)_3$ dissolved in toluene, at about 60°. We then have obtained good crystals of (I) by slow evaporation of toluene from the solution at room temperature.

Our X-ray analysis has confirmed that the complex (I) has the ionic structure $K^+[(C_2H_5)_3Al\text{-}F\text{-}Al(C_2H_5)_3]^-$;[5] moreover we have surprisingly obtained definite evidence of colinearity among Al–F–Al atoms. In fact, the ordinary Patterson analysis led us to the conclusion that the rhombo-

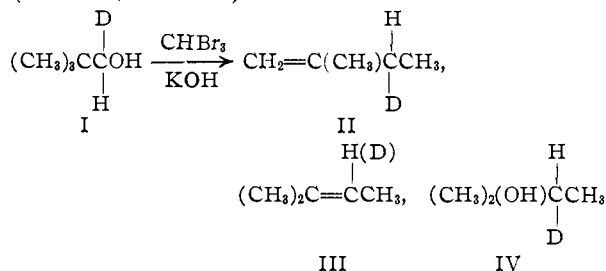(1) G. Natta, P. Corradini and I. W. Bassi, *J. Am. Chem. Soc.*, **80**, 775 (1958).

(2) G. Natta, G. Mazzanti, P. Corradini, U. Giannini, S. Cesca, *Rend. Acc. Naz. Lincei* **26**, 150 (1959).

(3) P. Corradini and G. Allegra, *J. Am. Chem. Soc.*, **81**, 5510 (1959).

(4) K. Ziegler, R. Köster, H. Lehmkuhl and K. Reinert, *Liebigs Ann. Chem.*, **629**, 33 (1960).

(5) K. Ziegler, "International Conference on Co-ordination Chemistry." The Chemical Society, London, April 6–11 (1959).

hedral unit cell of (I), containing only one molecule, is centrosymmetrical, so that K^+ ion and F atom are bound to lay on two crystallographic centers of symmetry, while the Al–F distance, successively determined by Fourier methods (1.80 ± 0.06 Å.), clearly indicates that the atoms are bonded together.

The unit cell of (I) has the constants: $a = b = c = 8.95 \pm 0.05$ Å.; $\alpha = \beta = \gamma = 55° 20' \pm 1°$, space group R$\bar{3}$; $N = 1$.

At this point of the refinement, we can assign fractional coördinates of first approximation to all the atoms (excepting hydrogen atoms). The present satisfying accordance between observed and calculated structure factors on the (1$\bar{1}$1) and (1$\bar{1}$0) projections ($R = 0.17$) allows us to conclude that: (1) the Al–F–Al axis is a threefold axis, with inversion center, for the $[(C_2H_5)_3Al\text{-}F\text{-}Al(C_2H_5)_3]^-$ ion; (2) the coördination type around the aluminum atom is tetrahedral, with normal Al–C^6 and C–C distances, while the Al–F distance appears to be close to that observed for instance in Na$_3$-AlF$_6$.[7] It is to be noted that this datum is in contrast with the fact that usual bridge bond distances are somewhat longer (0.20 ÷ 0.30 A.) than the corresponding single bond distances.[1,6,8]

If we suppose a sp hybridization for the fluorine atom, a partial π-bond character on the Al–F bond may arise from a certain overlap between the 2p$_y$ and 2p$_z$ filled fluorine orbitals and the 3d empty aluminum orbitals. This hypothesis seems to us particularly supported by recent studies, which demonstrate the ability of F^9 and C^{10} coördinated atoms to reduce the size of the 3d orbitals of second row elements.

(6) P. H. Lewis and R. E. Rundle, *J. Chem. Phys.*, **21**, 986 (1953).

(7) G. Menzer, *Fortsch. Min. Kryst. Petrog.*, **13**, 56 (1929).

(8) G. Natta, P. Corradini and G. Allegra, *J. Pol. Science*, **51**, 399 (1961).

(9) D. P. Craig and C. Zauli, *Gazz. Chim. Ital.*, **90**, 1700 (1960).

(10) D. P. Craig, private communication, 1961.

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STEREOSPECIFIC REARRANGEMENT OF NEOPENTYL ALCOHOL-1-$d^{1,2}$

Sir:

Neopentyl alcohol-1-d (I, 9.0 g.; acid phthalate, $[\alpha]^{28}$D -1.10, $C = 12$, acetone), which was optically active by virtue of isotopic substitution and which was obtained *via* asymmetric reduction of trimethylacetaldehyde-1-d by actively fermenting yeast,[3] has been rearranged by treatment with bromoform (200 g.) and aqueous potassium hydroxide (412 g., 56%) for four hours under reflux by the method for dehydration of alcohols investigated by

(1) Presented in part at the 140th meeting of the American Chemical Society, Chicago, September 4, 1961.

(2) We wish to acknowledge with gratitude, support of this research by Grant 5248 from the U. S. Public Health Service and Grant 495 from the Petroleum Research Fund.

(3) V. E. Althouse, E. Kaufmann, P. Loeffler, K. Ueda and H. S. Mosher, *J. Am. Chem. Soc.*, **83**, 3138 (1961).

(4) A. J. Hine, E. L. Pollitzer and H. Wagner, *ibid.*, **75**, 5607 (1953); A. J. Hine, A. D. Ketley and K. Tanabe, *ibid.*, **82**, 1398 (1960), and previous papers in this series and references therein.

Hine and co-workers[4] and applied to neopentyl alcohol by Skell, Starer and Krapcho.[5] From this reaction was isolated a mixture of 2-methyl-1-butene-3-d (II, 31% yield), 2-methyl-2-butene-3-d (III, 14% yield), 2-methyl-2-butanol-3-d (IV, 3% yield) and unreacted neopentyl alcohol-1-d (2.2 g., 24% recovery), acid phthalate $[\alpha]^{25}_D$ -1.10 ($C = 9$, acetone). The rotation of the rear-

$$(CH_3)_3C\overset{D}{\underset{H}{C}}OH \xrightarrow[\text{KOH}]{CHBr_3} CH_2=C(CH_3)\overset{H}{\underset{D}{C}}CH_3,$$

$$\text{I} \qquad\qquad\qquad\qquad \text{II}$$

$$(CH_3)_2C=\overset{H(D)}{\underset{}{C}}CH_3, \quad (CH_3)_2(OH)\overset{H}{\underset{D}{C}}CH_3$$

$$\text{III} \qquad\qquad\qquad \text{IV}$$

ranged 2-methyl-1-butene-3-d (II) was α^{25}_D $+1.22$ $\pm$ 0.02 ($l = 2$, neat), after purification by gas chromatography on a 300-cm. Ucon polar column in a Megachrome. Its retention time, infrared spectrum and n.m.r. spectrum were as expected for 2-methyl-1-butene-3-d.

Integration of the n.m.r. spectrum of the starting neopentyl alcohol-1-d indicated 1.00 $\pm$ 0.05 deuterium atoms per molecule in the one position; that of the 2-methyl-1-butene-3-d indicated 0.97 $\pm$ 0.05 deuterium atoms per molecule in the three position. There can be no doubt that this material owes its optical activity to a stereospecific rearrangement resulting in optically active olefin by virtue of isotopic substitution. The mechanism proposed for this reaction[6] postulates the formation of an intermediate carbonium ion, VIII, resulting from the decomposition of VII, which in turn is formed by the reaction of the alkoxide ion and dibromocarbene. From our

$$RO^- + :CBr_2 \longrightarrow ROC^-Br_2 \xrightarrow{-Br^-}$$
$$\text{V} \qquad\qquad \text{VI}$$

$$ROCBr \longrightarrow R^+ + CO + Br^-$$
$$\text{VII} \qquad \text{VIII}$$
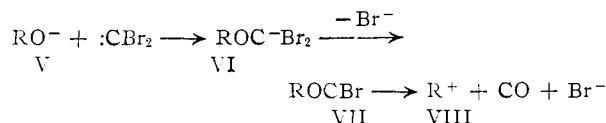
results it is quite apparent that under these basic conditions a carbonium ion, as a free entity, is not formed as the sole intermediate.[7] Previous evidence[5,8] has discounted the formation of a protonated cyclopropane intermediate in this rearrangement and the present evidence is also incompatible with such an interpretation. It was suggested[4] that some of the steps represented by V → VIII might be concerted and our results support this view. A proposed concerted transition state is represented by IX for the formation of 2-methyl-1-butene-3-d. This represents the decomposition of VII; it might be represented just as readily for VI with the simultaneous loss of two bromide ions. This concerted transition state not only would explain the stereospecificity of the

(5) P. S. Skell, I. Starer and A. P. Krapcho, J. Am. Chem. Soc., 82, 5257 (1960).

(6) P. S. Skell and I. Starer, ibid., 81, 4117 (1959).

(7) This does not exclude such an open carbonium ion under neutral or acid conditions. Preliminary experiments indicate that the t-amyl alcohol obtained from treatment of optically active neopentyl iodide-1-d with aqueous silver nitrate is optically inactive.

(8) G. F. Karabatsos and J. D. Graham, J. Am. Chem. Soc., 82, 5250 (1960).
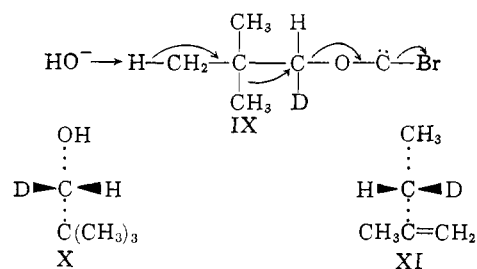
reaction but also the isomer ratio of about 2.3:1 in favor of the thermodynamically less stable olefin, 2-methyl-1-butene, as compared to a ratio of about 1:7 in favor of 2-methyl-2-butene in the acid catalyzed dehydration of t-amyl alcohol.[9] Not only are there nine equivalent hydrogens on the gamma carbon atoms versus two on the alpha, but the approach of the hydroxide ion to the position farthest removed from the leaving bromide ion would be the pathway of lowest energy.

The S absolute configuration,[10] X, has been assigned to the starting neopentyl alcohol-1-d^3. The mechanism represented by IX presumes that inversion occurs on the isotopically substituted carbon atom during the rearrangement. On this basis we predict that the (+)-2-methyl-1-butene-3-d will have the absolute S configuration XI. Synthesis of XI by a method which will independently establish its absolute configuration and that of the related t-amyl alcohol is in progress.

(9) F. C. Whitmore, C. S. Rowland, S. N. Wrenn and G. W. Kilmer, ibid., 64, 2970 (1942).

(10) Designation of R. S. Cahn, C. K. Ingold and V. Prelog, Experientia, 12, 81 (1956).

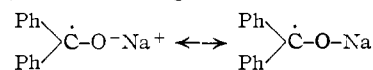DEPARTMENT OF CHEMISTRY
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STANFORD, CALIFORNIA   HARRY S. MOSHER

THE SOLVENT EFFECT ON SPECIFIC CATION-ANION INTERACTION. SPECTRA OF THE ALKALI KETYLS.

Sir:

We have found that the position of the visible band of the spectrum of sodium benzophenone (ketyl) (I) varies among a series of non-polar sol-

$$\underset{Ph}{\overset{Ph}{\diagdown}}\dot{C}-O^-Na^+ \longleftrightarrow \underset{Ph}{\overset{Ph}{\diagdown}}\dot{C}-O-Na$$

vents in a pronounced fashion. Carter, McClelland, and Warhurst[1] recently have reported the same observation for a single pair of solvents, as well as the observation, which we confirm, that there is also a large effect of the nature of the cation on the position of the same band. The variations are considerably more pronounced than the variations of the n→pi* transition of cyclohexanone among the same solvents. The table contains the pertinent data. The ketyl band under consideration is a broad, structureless band, centered in the neighborhood of 6500 A. The shape of the band and the width at half height, 11.1 $\pm$ 0.3 kcal./mole, are invariant with solvent.

On the basis of considerations of the shifts due to changes in the metal ion, the effects of substituents,

(1) H. V. Carter, B. J. McClelland, and E. Warhurst, Trans. Faraday Soc., 56, 455, (1960); see also B. J. McClelland, ibid., 57, 1458 (1961).