

1.018, 1.048, 0.985, 1.006, 1.017 and  $1.015 \times 10^{-2}$ ) 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  $0.844 \times 10^{-2}$ )  $\text{sec.}^{-1} \text{mole}^{-1}$ . (0.008 and 0.010 are standard deviations of the mean).

Numerous examples of  $\alpha$ -deuterium isotope effect in a carbonium ion solvolysis reaction have been reported,<sup>5</sup> 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.<sup>6</sup>

The difference in the  $\alpha$ -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  $\alpha$ -carbon should be closer to  $sp^2$  hybridization.

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(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 metalloorganic complexes containing bridge bonds,<sup>1,2,3</sup> we have undertaken the X-ray structural study of the compound  $\text{KF} \cdot 2\text{Al}(\text{C}_2\text{H}_5)_3$  (I), for the first time synthesized and studied by Ziegler *et al.*<sup>4</sup>

A  $\text{KF} \cdot 2\text{Al}(\text{C}_2\text{H}_5)_2$  solution is obtained by reaction of finely ground KF with a stoichiometric quantity of  $\text{Al}(\text{C}_2\text{H}_5)_3$  dissolved in toluene, at about  $60^\circ$ . 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  $\text{K}^+[(\text{C}_2\text{H}_5)_3\text{Al-F-Al}(\text{C}_2\text{H}_5)_3]^-$ ; 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-

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

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

At this point of the refinement, we can assign fractional coordinates of first approximation to all the atoms (excepting hydrogen atoms). The present satisfying accordance between observed and calculated structure factors on the (111) and (110) projections ( $R = 0.17$ ) allows us to conclude that: (1) the Al-F-Al axis is a threefold axis, with inversion center, for the  $[(\text{C}_2\text{H}_5)_3\text{Al-F-Al}(\text{C}_2\text{H}_5)_3]^-$  ion; (2) the coordination type around the aluminum atom is tetrahedral, with normal Al-C<sup>6</sup> and C-C distances, while the Al-F distance appears to be close to that observed for instance in  $\text{Na}_3\text{-AlF}_6$ .<sup>7</sup> It is to be noted that this datum is in contrast with the fact that usual bridge bond distances are somewhat longer ( $0.20 \div 0.30 \text{ \AA.}$ ) than the corresponding single bond distances.<sup>1,6,8</sup>

If we suppose a  $sp$  hybridization for the fluorine atom, a partial  $\pi$ -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  $\text{F}^9$  and  $\text{C}^{10}$  coordinated 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,  $[\alpha]^{25}_D - 1.10$ ,  $C = 12$ , 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,<sup>3</sup> 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

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(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.

(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).