The Reaction of Triisobutylaluminum with Carbon Tetrachloride. A Novel Preparation of Diisobutylaluminum Chloride

J. W. COLLETTE

Contribution No. 124 from E. I. du Pont de Nemours and Company, Inc., Elastomer Chemicals Department, Wilmington 98, Delaware

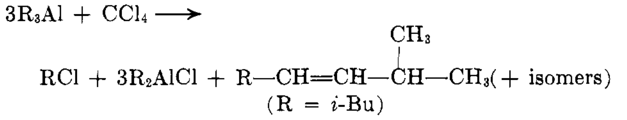
Received February 25, 1963

Trialkylaluminums have been reported to react violently with carbon tetrachloride.[1,2] Baker[1] reported that hydrolysis of the reaction product of triethylaluminum and carbon tetrachloride showed the presence of free chloride ion indicating that some of the chlorines on the carbon tetrachloride had been removed.

We wish to report evidence that this reaction proceeds with the intermediate formation of dichlorocarbene and that, under suitably dilute conditions, the reaction can be controlled to yield, as a major product, the corresponding dialkylaluminum chloride.

The main features of the reaction of a 1.0 *M* solution of triisobutylaluminum with carbon tetrachloride can be summarized as follows: (1) Triisobutylaluminum is converted essentially quantitatively to diisobutylaluminum chloride; (2) diisobutylaluminum chloride is stable to further reaction with carbon tetrachloride; (3) one mole of carbon tetrachloride converts three moles of triisobutylaluminum to diisobutylaluminum chloride; and (4) isobutyl chloride is one of the reaction products.

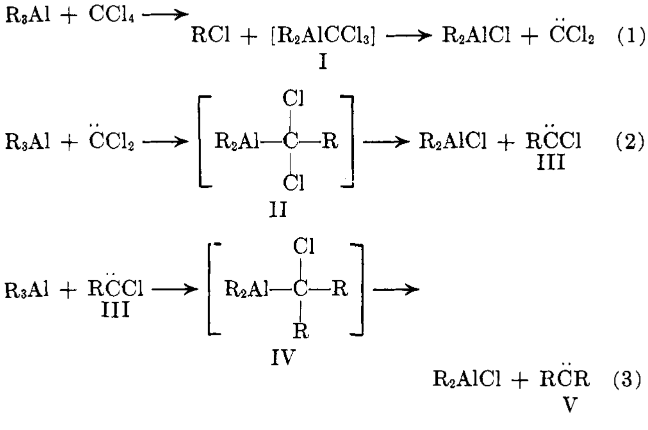
The over-all reaction is proposed to be the following.



$$3R_3Al + CCl_4 \longrightarrow RCl + 3R_2AlCl + R{-}CH{=}CH{-}\overset{CH_3}{\overset{|}{C}H}{-}CH_3(+\text{ isomers})$$

$$(R = i\text{-Bu})$$

The mechanism can be pictured as shown.



$$R_3Al + CCl_4 \longrightarrow RCl + \underset{\text{I}}{[R_2AlCCl_3]} \longrightarrow R_2AlCl + \ddot{C}Cl_2 \quad (1)$$

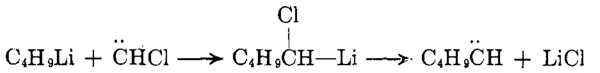
$$R_3Al + \ddot{C}Cl_2 \longrightarrow \underset{\text{II}}{\left[R_2Al{-}\overset{Cl}{\underset{Cl}{C}}{-}R\right]} \longrightarrow R_2AlCl + \underset{\text{III}}{R\ddot{C}Cl} \quad (2)$$

$$R_3Al + \underset{\text{III}}{R\ddot{C}Cl} \longrightarrow \underset{\text{IV}}{\left[R_2Al{-}\overset{Cl}{\underset{R}{C}}{-}R\right]} \longrightarrow R_2AlCl + \underset{\text{V}}{R\ddot{C}R} \quad (3)$$

The first step can be conceived as attack of the trialkylaluminum on carbon tetrachloride to yield isobutyl chloride and an unstable trichloromethyldialkylaluminum I. This compound decomposes to yield the dialkylaluminum chloride and free dichlorocarbene (equation 1).

The dichlorocarbene can react further in a variety of ways. If the reaction is carried out so that the trialkylaluminum is present in excess, the carbene will react with the electron-rich metal alkyl bonds.[3] The insertion product II is unstable and decomposes to yield a second mole of dialkylaluminum chloride and an alkylchlorocarbene III (equation 2). Carbene III will attack more of the original trialkylaluminum to form a new insertion product IV which again decomposes yielding a third mole of dialkylaluminum chloride and a dialkylcarbene V. The dialkylcarbene V may rearrange to olefin,[3] cyclize to a cyclopropane,[3] or attack yet another mole of trialkylaluminum.

Support for this mechanism is available from the work of Miller and Kim who demonstrated that the reaction of carbon tetrachloride with butyllithium proceeds with the intermediate formation of dichlorocarbene; when these components are allowed to react in the presence of cyclohexene, dichloronorcarane is the main product.[4] The sequence of carbene insertion into metal alkyl bonds followed by elimination of a new carbene and a metal halide, as postulated in equations 2 and 3, is analogous to the reaction of chlorocarbene with butyllithium.[3]



$$C_4H_9Li + \ddot{C}HCl \longrightarrow C_4H_9\overset{Cl}{\overset{|}{C}}H{-}Li \longrightarrow C_4H_9\ddot{C}H + LiCl$$

The α-haloaluminum alkyl, $(C_2H_5)_2AlCH_2I$, analogous to intermediates I, II, and III, has been characterized by Hoberg[5]; this compound decomposes above −10° to yield $(C_2H_5)_2AlI$ and products resulting from carbene.[6] Haszeldine[7] has made the generalization that any compound with halogen on a carbon alpha to a metal atom will tend to decompose to yield a metal–halogen bond and a carbene.

According to the prosposed mechanism, one mole of carbon tetrachloride should react with three moles of triisobutylaluminum chloride. This was demonstrated on a preparative scale where a 92% yield of diisobutylaluminum chloride was isolated. The low boiling fraction from this reaction was shown to contain isobutylchloride by vapor phase chromatography. The yield of isobutyl chloride was 25% of the theoretical amount based on the postulated mechanism. This will be a minimum value inasmuch as the low boiling fraction was not quantitatively removed from the main product.

As a further test, the two components were allowed to react on a smaller scale; in one case the $R_3Al:CCl_4$ ratio was 3:1 and in a second case the $R_3Al:CCl_4$ ratio was 1:1. Hydrolysis of the product indicated that in both cases the reaction was essentially complete at the end of the addition of carbon tetrachloride and that all the trialkylaluminum had been converted to dialkylaluminum chloride. When the ratio was 1:1, the reaction proceeded much more violently; however, only one aluminum–chlorine bond was formed per aluminum atom. Therefore, the carbon tetrachloride

---

(1) E. B. Baker, Ph.D. dissertation, Ohio State University, 1953.

(2) Ethyl Corporation Technical Data Sheet on Aluminum Alkyls and Alkylaluminum Halides, November, 1959.

(3) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **81**, 4996 (1959); **82**, 5725 (1960).

(4) W. T. Miller and C. S. Y. Kim, *ibid.*, **81**, 5009 (1959).

(5) H. Hoberg, *Angew Chem.*, **73**, 114 (1961).

(6) H. Hoberg, *Ann.*, **656**, 1, 15 (1962), recently has suggested that this and similar reactions proceed *via* addition–elimination reactions rather than by formation of free carbenes.

(7) W. I. Bevan, R. N. Haszeldine, and J. C. Young, *Chem. Ind.*, 789 (1961).

in excess of that required to convert the trialkylaluminum to dialkylaluminum chloride did not react further with the products.

To confirm this result, a solution of diisobutylaluminum chloride in cyclohexane was allowed to react with carbon tetrachloride. Periodic analysis of the hydrolyzable chloride showed no increase over seventy-two hours indicating that no isobutylaluminum dichloride, $RAlCl_2$, was formed.[8]

Experimental

Reaction of Triisobutylaluminum with Carbon Tetrachloride.—To a mixture of 50 ml. of triisobutylaluminum (0.2 mole) and 100 ml. of heptane in a flame-dried 250 ml. three-necked flask equipped with a magnetic stirrer, a dropping funnel, a Vigreux column, and a thermometer, was added a solution of 6.45 ml. of carbon tetrachloride (0.067 mole) in 50 ml. of heptane. The solution was added dropwise over 2.5 hr., while the temperature was maintained at 30°. The solution was allowed to stir overnight, then distilled. Material boiling up to 40° (100 mm.), fraction A, 93 g., was collected in a Dry Ice–acetone cooled receiver. The remaining solvent was then removed *in vacuo* and the product distilled to yield, after a small forerun, 32.5 g. (92%), b.p. 93° (0.3 mm.) [lit.[9] b.p. 108° (1 mm.)].

Anal. Calcd. for $C_8H_{18}AlCl$: C, 54.4; H, 10.3; Cl, 20.1. Found: C, 54.1; H, 9.9; Cl, 19.4.

Fraction A, analyzed by g.l.c., was found to contain 1.65% isobutyl chloride, or 1.5 g. (25%).

Effect of the Ratio of Triisobutylaluminum to Carbon Tetrachloride.—In a 250 ml. three-necked flask, equipped as previously described, was placed 50 ml. of dry tetrachloroethylene. Then 25 ml. (0.1 mole) of triisobutylaluminum was added by means of a hypodermic syringe. A solution of 3.2 ml. (0.33 mole) of carbon tetrachloride in tetrachloroethylene (total volume, 25 ml.) was added at room temperature over 1 hr. The final solution was 0.1 *M* in aluminum.

Similarly, 9.7 ml. (0.1 mole) of carbon tetrachloride in tetrachloroethylene (total volume 25 ml.) was added to 0.1 mole of triisobutylaluminum in 50 ml. of tetrachloroethylene. The temperature of this reaction rose rapidly to over 100° during the early addition; the addition was, therefore, stopped and the reaction mixture cooled before continuing. The addition was completed over a period of 1 hr.

Both solutions were analyzed immediately after the addition was complete and then after several hours as follows. A 4-ml. aliquot was removed with a hypodermic syringe and added to 10-ml. of a 9:1 cyclohexane–1-butanol mixture. The resultant solution was extracted with 40 ml. of 5% sulfuric acid. The acid was washed twice with 10 ml. of ether, heated briefly on a steam bath to remove the traces of ether, transferred quantitatively to a 50-ml. volumetric flask, and diluted to volume with 5% sulfuric acid. The solution was analyzed for Cl^- potentiometrically. The results are in Table I.

Stability of Isobutylaluminum Dichloride to Carbon Tetrachloride.—A mixture of 19.4 ml. of diisobutylaluminum chloride (0.1 mole) and 75 ml. of cyclohexane was allowed to react with 4.9 ml. (0.05 mole) of carbon tetrachloride. Aliquots (4 ml.) of the mixture were analyzed for hydrolyzable chlorine periodically. No change in this value was observed over a period of 72 hr.

TABLE I

EFFECT OF RATIO OF TRIISOBUTYLALUMINUM TO CARBON TETRACHLORIDE ON FORMATION OF DIISOBUTYLALUMINUM CHLORIDE

		Chloride concn., mmole/ml.[a]	
Ratio i-$Bu_3Al:CCl_4$		3:1	1:1
Time, hr.,	0	0.960	0.93
	2	.960	.96
	3	.960	1.01

[a] Theory for complete conversion of R_3Al to R_2AlCl is 1.00 mmole/ml.

---

(8) C. Eden and H. Feilchenfeld, *J. Phys. Chem.*, **66**, 1355 (1962), recently have suggested that triethylaluminum does not react with carbon tetrachloride. The small heat of reaction which they noted on *mixing these two components* and which they ascribed to impurities is probably due to the formation of diethylaluminum chloride; the effect is small because of the dilute solutions being used (3.5 mmoles/100 ml.). It seems improbable that there would be such a great difference in reactivity between triisobutylaluminum and triethylaluminum. It further would be a serious error to conclude from their results that triethylaluminum can be safely mixed in all proportions with carbon tetrachloride.

(9) J. E. Knap, R. E. Leech, A. J. Reid, and W. S. Tamplin, *Ind. Eng. Chem.*, **49**, 879 (1957).

A Reinvestigation of the Structure of "Cordycepic Acid"[1a]

MILON SPRECHER AND DAVID B. SPRINSON[1b]

Department of Biochemistry,
College of Physicians and Surgeons, Columbia University,
New York, New York

Received March 1, 1963

In 1957, Chatterjee, Srinivasan, and Maiti[2] reported the isolation of a new compound from the fungus *Cordyceps sinensis* (Berkeley) Saccardo. It was named "cordycepic acid," and was assigned the structure of a 1,3,4,5-tetrahydroxycyclohexanoic acid, isomeric with quinic acid, in which the hydroxyl groups in positions 3, 4, and 5 are all *trans* to the carboxyl group.

Since quinic acid can be formed enzymically[3] from 5-dehydroquinic acid, an intermediate in the biosynthesis of the aromatic amino acids, it was of interest to investigate the possible relation of "cordycepic acid" to this biosynthetic pathway.

The data presented by Chatterjee, *et al.*,[2] clearly ruled out the stereochemical configuration suggested for "cordycepic acid." Optical rotations were reported for both "cordycepic acid" and for the product of its acetylation, whereas the proposed structure has a plane of symmetry and is incapable of being optically active.

Authentic samples of *Cordyceps sinensis* (Berkeley) Saccardo were easily obtained with the aid of the detailed description given by Chatterjee, *et al.*[2] The ethanolic extract[2] of the fungus afforded a single compound, the highly water-soluble "cordycepic acid," as colorless needles, m.p. 166–168°. The yield was approximately 7%, as reported.[2] Acetylation of the product gave a compound having m.p. 122–123° and $[\alpha]^{26}D$ +29.7° (*c* 0.46, EtOH); [lit.[2] m.p. 126° and $[\alpha]^{26}D$ +29.2° (EtOH)]. It also was possible to prepare an isopropylidene derivative which was soluble in petroleum ether.[2,4]

Further investigation showed, however, that the structural assignment reported previously is completely erroneous. "Cordycepic acid" is neither a new compound nor an acid. It is in fact D-mannitol, considerable amounts of which are known to occur in various

---

(1) (a) This work was supported by grants from the American Cancer Society, the American Heart Association, and the National Institutes of Health of the U. S. Public Health Service; (b) Career Investigator of the American Heart Association.

(2) R. Chatterjee, K. S. Srinivasan, and P. C. Maiti, *J. Am. Pharm. Assoc.*, **46**, 114 (1957); M. W. Miller, "The Pfizer Handbook of Microbial Metabolites," McGraw-Hill Book Co., Inc., New York, N. Y., 1961, p. 147.

(3) S. Mitsuhashi and B. D. Davis, *Biochem. Biophys. Acta*, **15**, 268 (1954); D. B. Sprinson, *Advan. Carbohydrate Chem.*, **16**, 235 (1960).

(4) This solubility characteristic is incompatible with the proposed[2] structure. Shikimic acid, which has one less hydroxyl group than quinic acid, yields an isopropylidene derivative which is insoluble in petroleum ether.