pinacol rearrangement and related rearrangements of aldehydes and ketones.

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CYCLOPENTADIENYLTITANIUM TRICHLORIDE

Sir:

Previously no redistribution reaction between a "sandwich" compound of a transition metal, *i.e.*, a molecule having delocalized bonds involving d-orbitals or their hybrids, and a corresponding metal halide, has been described for the preparation of a mixed cyclopentadienyl metal halide derivative.

We now wish to report the synthesis of a novel organotitanium compound, cyclopentadienyltitanium trichloride (I), by a redistribution reaction between bis-(cyclopentadienyl)-titanium dichloride (II) and titanium tetrachloride either with or without a solvent present. A higher yield of product is obtained and work-up of the reaction mixture is more facile with a solvent. It is also preferable to employ an excess of the metal halide.

Thus, heating (II) with an excess of titanium tetrachloride between 115–120° for approximately 24 hours in *p*-xylene affords an 84% yield of yellow prisms which can be crystallized conveniently either from a minimum of methylene chloride or a mixture of ethyl acetate and *n*-pentane. Freshly crystallized I melts at about 185° (uncorrected) with some decomposition.

Anal. Calcd. for $C_5H_5Cl_3Ti$: C, 27.37; H, 2.30; Cl, 48.49; Ti, 21.84; mol. wt., 219.4. Found: C, 27.63; H, 2.38; Cl, 47.96; Ti, 22.1; mol. wt., 231.

Another unique method by which I can be derived is *via* the preferential cleavage of II by chlorine. This reaction is reminiscent of the chlorine cleavage of ferrocene[1] to give 1,2,3,4,5-pentachlorocyclopentane, but it is unique in that the reaction can be controlled so as to cleave only one cyclopentadienyl ring from II.

Continuous gassing of II by chlorine in carbon tetrachloride at 55–60° until II is consumed yields both I and 1,2,3,4,5-pentachlorocyclopentane. Ultraviolet irradiation accelerates the reaction, but prolonged exposure of the product to chlorine results in decreased yields.

The infrared absorption spectrum of I as a KBr pellet shows a single C–H stretching frequency at 3.3 μ. Also, the compound fails to react with maleic anhydride. This indicates the bonding of the cyclopentadienyl ring to titanium to be similar to that in II, which has been shown to have the "sandwich" structure.[2]

Chemical evidence is compatible with I. When I is treated with an equivalent amount of cyclopentadienylsodium, an 85% yield of II is obtained. Moreover, I is cleaved by chlorine at room temperature to give pentachlorocyclopentane and titanium tetrachloride.

I is relatively stable in air and the crystals appear to react very slowly with water. In solution, *e.g.*, in acetone, hydrolysis by aqueous NaOH is rapid with all three Ti–Cl bonds being ruptured. I is soluble in ethers, ketones and aromatics, as well as in concentrated sulfuric acid.[3]

The author is grateful to Dr. R. P. Curry for his assistance in the interpretation of the infrared data.

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[1] A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya, T. V. Nikitina and N. A. Simukova, *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.*, 749 (1956); *C.A.*, **51**, 1945 (1957)).

[2] G. Wilkinson and J. M. Birmingham, THIS JOURNAL, **76**, 4281 (1954).

[3] The physical properties of I, particularly the melting point, are in sharp disagreement with those described in an earlier publication (British Patent, 793,354 (April 16, 1958)), in which it is claimed that I is a yellow oil boiling at 29–34° at 1 mm.[3] The method of preparation is stated to involve the reaction of cyclopentadienyllithium with titanium tetrachloride in benzene in a 1:1 molar ratio.

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THE PREPARATION OF DIBORON TETRACHLORIDE

Sir:

In a recent communication Frazer and Holzmann[1] have described the production of diboron tetrachloride (B_2Cl_4) by microwave excitation of boron trichloride, the yields being comparable to those of Schlesinger, Wartik and Moore,[2] and also of Apple,[3] obtained by the passage of an a.c. discharge through boron trichloride vapor using mercury electrodes. This latter method gave diboron tetrachloride at the rate of *ca.* 0.008 g. per hr. per discharge cell.

We have found that by using a d.c. discharge in a cell similar to those described by Schlesinger and by Apple, the rate of production of diboron tetrachloride can be increased more than ten-fold to about 0.1 g. per hr. The boron trichloride vapor was pumped from a trap, held at −78.5°, through a water-cooled cell across which a d.c. arc was maintained at 100 volts/cm. of arc path and 500 ma. current. The diboron tetrachloride was condensed in a second trap at −78.5° from which excess boron trichloride was recirculated. The diboron tetrachloride was fractionated from boron trichloride and small amounts of tetraboron tetrachloride (B_4Cl_4) and identified by vapor pressure–temperature measurements and the formation of a 1:1 compound with ethylene.[4] Considerable amounts of mercurous chloride were deposited in the cell; the interconnecting tubes were colored light brown by deposition of boron subchlorides.

During earlier work Schlesinger[4] had noted that cell temperatures below 12° gave no yield of diboron tetrachloride, suggesting the need for mercury vapor to be present to ensure the reduction

$$2\ BCl_3 + 2\ Hg \longrightarrow Hg_2Cl_2 + B_2Cl_4$$

In the d.c. arc the negative end of the discharge is stationary and causes local superheating of the mercury resulting in the presence of much mercury vapor inside the cell. This, together with the

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[1] J. W. Frazer and R. T. Holzmann, THIS JOURNAL, **80**, 2907 (1958).

[2] H. I. Schlesinger, T. Wartik, R. E. Moore and G. Urry, *ibid.* **76**, 5293 (1954).

[3] E. Apple, private communication.

[4] G. Urry, J. Kerrigan, T. D. Parson and H. I. Schlesinger, THIS JOURNAL, **76**, 5299 (1954).

continuous nature of the discharge, may account for the increased rate of production of diboron tetrachloride in a d.c. arc.

Work is in progress to increase the yield still further, and an investigation of electrode materials other than mercury is planned.

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RECEIVED JULY 14, 1958

THE ACTION OF POTASSIUM AMIDE IN AMMONIA ON *o*-CHLOROPHENYLACETONE: CORRECTION.[1]

Sir:

We recently reported a new principle of ring closure, the essence of which is the intramolecular addition of a nucleophilic center to a benzyne structure.[2]

Amongst examples of the new principle, the conversion of *o*-chlorophenylacetone to indan-2-one, through the action of potassium amide in liquid ammonia, was described. We have now discovered an error: the compound reported as indan-2-one (m.p. 60–61°)[3] is actually 2-methylindole (m.p. 62°).[4] The compound obtained, in 25% yield in recent experiments, strongly depresses the mixed melting point with authentic indan-2-one, but does not alter the mixed melting point with authentic 2-methylindole. Also, the compound gives a positive sodium fusion test for nitrogen. All our efforts to isolate authentic indan-2-one from the reaction in question have been fruitless.

It is of theoretical interest that 2-methylindole is formed in this reaction; the matter will be discussed in a future publication.

[1] Research supported in part by the Office of Ordnance Research, U. S. Army.

[2] B. F. Hrutfiord and J. F. Bunnett, THIS JOURNAL, **80**, 2021 (1958).

[3] H. D. Porter and C. M. Suter, *ibid.*, **57**, 2022 (1935).

[4] L. Marion and C. W. Oldfield, *Can. J. Research*, **25B**, 1 (1947).

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RECEIVED AUGUST 4, 1958

1,2;5,6-DI-*O*-ISOPROPYLIDENE 3-DEOXY-3-AMINO-α-D-ALLOSE

Sir:

Hydrolysis of the new antibiotic kanamycin has been found[1] to yield 3-deoxy-3-amino-D-glucose (I).[2]

The crystalline amine which is formed[3] on the aminolysis of 1,2;5,6-di-*O*-isopropylidene α-D-glucofuranose tosylate (II) has been characterized[2,3] as 1,2;5,6-di-*O*-isopropylidene-3-deoxy-3-amino-α-D-glucose. These reactions therefore appear to provide a convenient route for the preparation of I.

This communication is to report that, as suspected by Cope and Shen,[4] the aminolysis actually proceeds with inversion of carbon-3 to form 1,2,5,6-di-*O*-isopropylidene-3-deoxy-3-amino-D-allose (III).

Compound III can be prepared in 83% yield by hydrogenolysis of the 1,2;5,6-di-*O*-isopropylidene-3-deoxy-3-hydrazino-D-hexose (IV) of Freudenberg and Brauns[5] in ethanol at 80° using Raney nickel catalyst and 40 p.s.i. of hydrogen. The advantage of this route is that, whereas the aminolysis of II proceeds in 16% yield,[3] the hydrazinolysis proceeds in 60% yield.[5] Acid hydrolysis of III produced an aminosugar of different paper-chromatographic properties than that obtained on the hydrolysis of methyl 4,6-benzylidene-3-deoxy-3-amino-α-D-glucoside diacetate.[2]

The N-acetyl derivative of III (V), m.p. 127–128°, $[\alpha]_D$ +71.3° (*c*, 2 in chloroform), [calcd. for $C_{14}H_{23}O_6N$: C, 55.80; H, 7.69; N, 4.65. Found: C, 55.87; H, 7.73; N, 4.85.] was hydrolyzed for two hours at 100° in 0.2 *N* hydrochloric acid. N-Acetylation was then accomplished by the addition of acetic anhydride to the neutralized hydrolyzate. Evaporation of the solvent and extraction of the residue with ethanol gave a 1,2-*O*-isopropylidene-3-deoxy-3-acetamido-α-D-hexose (VI), m.p. 154–156°. Calcd. for $C_{11}H_{19}O_6N$: C, 50.56; H, 7.33; N, 5.36. Found: C, 50.25; H, 7.44; N, 5.29.

Periodate oxidation of VI, reduction of the product with sodium borohydride and acetylation of the reduced product gave a crystalline substance which was hydrolyzed to aminosugar using *N* hydrochloric acid at 100°. On evaporation, a crystalline product was isolated whose infrared spectrum (KBr disc) and X-ray powder diagram were identical to those obtained with an authentic sample of 3-deoxy-3-amino-D-ribose hydrochloride (VII).[6] These results establish the *allo*-configuration for III-VI and provide a new synthesis of VII which is a constituent of the antibiotic puromycin.[7]

Acknowledgments.—The authors wish to thank Dr. M. Przybylska for the X-ray analyses.

[1] M. J. Cron, D. L. Evans, F. M. Palermiti, D. F. Whitehead, I. R. Hooper, P. Chu and R. U. Lemieux, THIS JOURNAL, **80**, 4741 (1958).

[2] S. Peat and L. F. Wiggins, *J. Chem. Soc.*, 1810 (1938).

[3] K. Freudenberg, O. Burkhart and E. Braun, *Ber.*, **59**, 714 (1926).

[4] A. C. Cope and T. Y. Shen, THIS JOURNAL, **78**, 3177 (1956).

[5] K. Freudenberg and F. Brauns, *Ber.*, **55**, 3233 (1922).

[6] B. R. Baker and R. E. Schaub, *J. Org. Chem.*, **19**, 646 (1954).

[7] P. W. Fryth, C. W. Waller, B. L. Hutchings and J. H. Williams, THIS JOURNAL, **80**, 2736 (1958).

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RECEIVED JULY 21, 1958

STRUCTURE OF THE Ag^+ (CYCLOÖCTATETRAENE) COMPLEX

Sir:

Complexes between metal ions and organic π bonding systems have been of interest for some time[1,2] and are germane to general discussions[3] of weak complexes and their reactivities.[1,2,4] Aside from the Ag^+ (Benzene) complex,[5,6] few such com-

[1] S. Winstein and H. J. Lucas, THIS JOURNAL, **60**, 836 (1938); **79**, 4339 (1957).

[2] L. J. Andrews, *Chem. Revs.* **54**, 713 (1954).

[3] R. S. Mulliken, *J. Chem. Phys.*, **19**, 514 (1951); THIS JOURNAL, **72**, 600 (1950); **74**, 811 (1952).

[4] R. E. Rundle and J. D. Corbett, *ibid.*, **79**, 757 (1957).

[5] R. Rundle and J. Goring, *ibid.*, **72**, 5337 (1950); for a structural study of the styrene–$PdCl_2$ complex see J. Holden and N. Baenziger, *ibid.*, **77**, 4987 (1955).

[6] H. G. Smith and R. E. Rundle, Abstracts, American Crystallographic Society Meeting, Milwaukee, Wisconsin, June 23–27 (1958).