Recently Davies, Hey and Williams[5] have investigated the very interesting formation of binaphthyls (among other products) from the reaction of benzoyl peroxide with naphthalene. A possible alternative to their mechanism is the formation of the dibenzoate of a dihydroxytetrahydrobinaphthyl (III), a close analog of the tetrahydroquaterphenyl (I). Such a compound could easily give a

$$C_6H_5COOC_{10}H_8\cdot \longrightarrow \underset{\text{III}}{C_6H_5COOC_{10}H_8C_{10}H_8OCOC_6H_5}$$

binaphthyl by various routes, *e.g.*, by attack of radicals or during the alkaline hydrolysis step used in the isolation procedure.

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[5] D. I. Davies, D. H. Hey and G. H. Williams, *J. Chem. Soc.*, 1878 (1958).

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RECEIVED JUNE 20, 1958

OXYGEN FUNCTION REARRANGEMENT IN BENZOPINACOLONE[1]

Sir:

Acid catalyzed ketone rearrangements,[2] aldehyde–ketone interconversions[2,3] and closely related pinacol rearrangements[3,4] have received much attention recently. The reversibility of the ketone forming step in the pinacol rearrangement has been considered frequently and there is excellent experimental evidence that it is not reversible under many conditions.[3,5–7] However, under conditions of high acidity the reversibility of certain aliphatic ketone–ketone interconversions is well established, and Rothrock and Fry[2] have pointed out that the carbonium ion intermediates involved in the sulfuric acid catalyzed rearrangement of 3,3-dimethyl-2-butanone-1-C^{14} are identical, except for the label, with those usually proposed in the rearrangement of pinacol to pinacolone.

A further step in this reversibility of ketone rearrangements, with the concurrent pinacol rearrangement implications, has now been demonstrated. Upon treatment with strong acids under certain conditions, 1,2,2,2-tetraphenyl-1-oxoethane-1-C^{14} (benzopinacolone), is converted into a mixture of the 1- and 2-labelled ketones. Thus the oxygen function in benzopinacolone has rearranged[8] from one of the central carbon atoms to the other.

The labelled ketone was prepared by treating benzoyl-α-C^{14} chloride with triphenylmethylsodium. After rearrangement, the recovered ketone was cleaved to benzoic acid and triphenylmethane with alcoholic sodium hydroxide, and the activities of the reactants and degradation products were determined by standard methods.[2] The reaction conditions and experimental results are summarized in Table I.

The demonstration by Barton and Porter[9] that the main path for the acid catalyzed rearrangement of 2,2,4,4-tetramethyl-3-pentanone-3-C^{14} did not involve oxygen function rearrangement perhaps may be explained by the facile cleavage of the product 3,3,4,4-tetramethyl-2-pentanone.

Three of the mechanisms[2] which have been considered for ketone rearrangements would account for the oxygen function rearrangement. (1) The conjugate acid of the ketone, by a concerted or stepwise process, may form the conjugate acid of the symmetrical oxide, which upon reversal, would give equal quantities of the 1- and 2-labelled compounds. (2) In the intermediate carbonium ion, the conjugate acid hydroxyl group may migrate to the adjacent position. (3) The intermediate carbonium ion may react reversibly with water or solvent to give a pinacol or pinacol ester.[2,3,5]

TABLE I

OXYGEN FUNCTION REARRANGEMENT IN BENZOPINACOLONE

Reaction medium	Temp., °C.	Time, hr.	Relative molar activities[a] Benzoic acid	Triphenyl-methane	Benzoic acid + triphenyl-methane	Isomerization[b] %
Aluminum chloride–water (1:1) in benzene	25	12	99.3	0.8	100.1	1.6
Iodine in acetic acid	Reflux	1/4	99.0	0.06	99.1	0.1
Zinc chloride in acetic anhydride	Reflux	5	99.5	4.2	103.7	8.4
Dilute sulfuric acid in acetic acid	Reflux	26	98.1	0.0	98.1	0.0
Concd. sulfuric acid	10	1/2	97.4	1.7	99.1	3.4
92.8% sulfuric acid	50	3	90.9	9.2	100.1	18.4
Concd. sulfuric acid in acetic acid	Reflux	1	75.6	23.4	99.0	46.8
Perchloric acid in acetic acid	50	24	84.8	16.8	101.6	33.6

[a] Relative to an initial activity of benzopinacolone of 100.0; actual benzopinacolone activity = 0.04111 mc./mole. [b] Calculated from triphenylmethane activities; 100% isomerization corresponds to complete randomization of the activity between the two central carbon atoms.

These results point up the necessity for keeping the possibility of oxygen function migration clearly in mind in interpreting results of studies of the

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[1] This work was supported by the Atomic Energy Commission.

[2] For a recent review, see T. S. Rothrock and A. Fry, THIS JOURNAL, **80**, 4349 (1958).

[3] V. F. Raaen and C. J. Collins, *ibid.*, **80**, 1409 (1958), and previous work cited there.

[4] H. J. Gebhart, Jr., and K. H. Adams, *ibid.*, **76**, 3925 (1954).

[5] C. A. Bunton, T. Hadwick, D. R. Llewellyn and Y. Pocker, *J. Chem. Soc.*, 403 (1958).

[6] D. N. Kursanov and Z. N. Parnes, *Zhur. Obshchei Khim.*, **27**, 668 (1957).

[7] J. F. Duncan and K. R. Lynn, *J. Chem. Soc.*, 3512 (1956).

[8] Oxygen function rearrangement does not necessarily imply oxygen migration (see mechanism 3 below).

[9] S. Barton and C. R. Porter, *J. Chem. Soc.*, 2483 (1956).

pinacol rearrangement and related rearrangements of aldehydes and ketones.

DEPARTMENT OF CHEMISTRY — ARTHUR FRY
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RECEIVED JUNE 27, 1958

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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RECEIVED JULY 10, 1958

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, K. 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).