CRYSTAL STRUCTURE OF THE COMPLEX $(C_5H_5)_2$-TiCl$_2$Al(C$_2$H$_5$)$_2$

Sir:

In a preceding communication to THIS JOURNAL there was reported[1] the synthesis of a soluble crystallizable complex containing titanium and aluminum showing catalytic activity in the polymerization of ethylene. This fact was taken as supporting our opinion that Ziegler type catalysts are bimetallic complexes. It was also supposed that the two different metal atoms contained in the crystallizable complex were joined by bridges of the same type as the one present for instance in the monochlorodimethylaluminum dimer.[2]
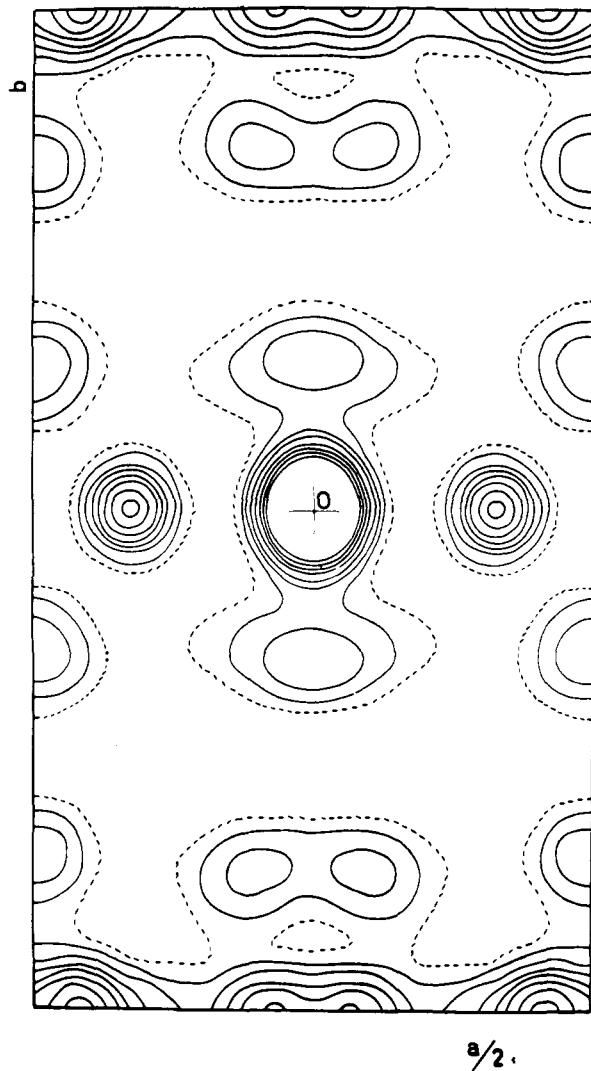

Fig. 1.—Patterson projection on the a-b plane.

To confirm the above reported hypothesis, we wish to communicate some preliminary results of an X-ray examination of single crystals of the complex $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$.

(1) G. Natta, P. Pino, G. Mazzanti and U. Giannini, THIS JOURNAL, **79**, 2975 (1957).

(2) G. Natta, P. Pino, G. Mazzanti, and U. Giannini, communication presented at the International Symposium on the Chemistry of Coordination Compounds, Roma, September 15–21, 1957.

The unit cell constants are

$$a = 15.77 \pm 0.08 \text{ Å}. \quad b = 14.24 \pm 0.07 \quad c = 7.54 \pm 0.04$$
$$\alpha = \beta = \gamma = 90°$$

The number of molecules contained in the unit cell is four, and possible space groups are Pnma or Pn2$_1$a ((0kl) reflections with $k + l = 2n + 1$ and (hk0) reflections with $h = 2n + 1$ being extinguished).

The space group Pnma requires that the molecule contains a mirror plane. In this case Ti and Al must necessarily lie in this plane ($y = 1/4$).

In fact, the Patterson projection on the a-b plane of the interatomic vectors (Fig. 1) showing a concentration of the highest peaks along the lines $y = 0$ and $y = 1/2$ supports the hypothesis that heavy atoms are contained in the $y = 1/4$ plane.

A complete interpretation of the Patterson projection confirms that: (1) Pnma must be chosen as the correct space group; (2) the position and the weight of the peaks appearing along the lines $y = 0$, $y = 1/2$ may be accounted for by supposing that

$$y_{Ti} = y_{CII} = y_{CIII} = y_{Al} = 1/4 \text{ and } x_{Ti} = x_{CII} = 0.021;$$
$$x_{CIII} = x_{Al} = 0.183 \text{ or } x_{Ti} = x_{CIII} = 0.271; \ x_{CIII} = x_{Al} = 0.433$$

Moreover, (1) from the pseudosystematic absence of the reflections $hk3$ with $h = 2n$ it follows, with other restrictions, that $z_{Ti} - z_{CII} = z_{CIII} - z_{Al} \sim 0.333$: (2) a Fourier synthesis (Fig. 2)
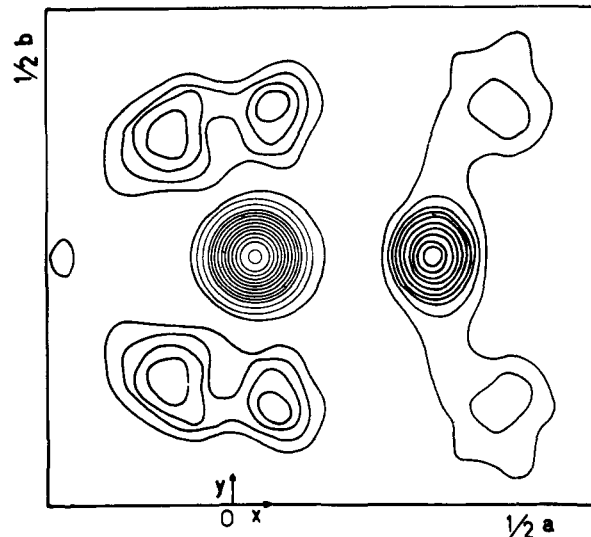

Fig. 2.—Fourier projection on the a-b plane (only half contours of the heavy atoms are drawn).

on the ab plane shows clearly images of the cyclopentadienyl and ethyl groups, which happen to be in suitable positions.

A model of the molecule is shown in Fig. 3.

From the model, we may conclude that: (1) both Ti and Al have a tetrahedral coördination and are joined by bridges of Cl atoms forming a square ring, the Ti–Cl and Al–Cl distances being about 2.5 Å. (2) The plane of a cyclopentadienyl group is perpendicular to the line joining titanium to the center of the group, the five Ti–C distances being all equal and of the order of 2.3 Å. (3) Ethyl groups are bonded to the Al atoms. The cyclopentadienyl groups in this sandwich $\sigma\pi$-bonded
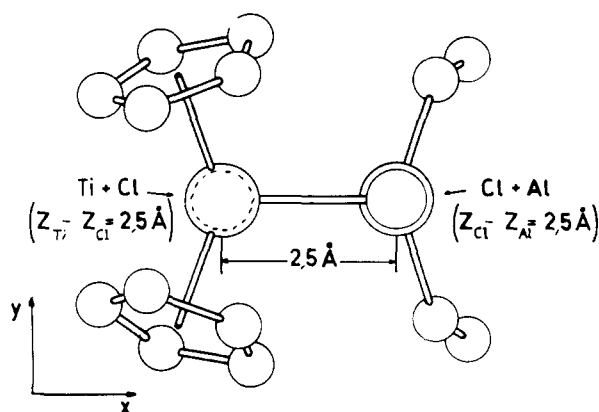
Fig. 3.—Model of the molecule corresponding to the Fourier projection.

complex are not parallel each other as in ferrocene. The orientation of these groups appears dependent on the type of the hybridization of the metal atom to which they are bonded. Further structural work for this and other similar compounds is going on in our laboratory.

INSTITUTE OF INDUSTRIAL CHEMISTRY   GIULIO NATTA
POLYTECHNIC OF MILAN   PAOLO CORRADINI
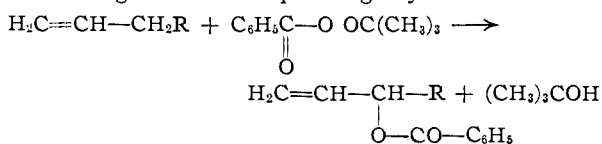MILAN, ITALY   IVANO W. BASSI
            RECEIVED DECEMBER 26, 1957

THE REACTIONS OF *t*-BUTYL PERBENZOATE AND OLEFINS—A STEREOSPECIFIC REACTION[1]

Sir:

Although the reactions of benzoyl peroxide have been studied in great detail by various workers during the past several decades,[2] the chemistry of a related substance, *t*-butyl perbenzoate,[3] except for several kinetic studies,[4] has received little attention. In view of the low reactivity of the perbenzoate and of the difficulties in isolating well-defined products from its reaction mixtures this fact is not surprising.

It has now been found that *t*-butyl perbenzoate in the presence of a transition metal salt catalyst (such as a cuprous halide, cupric 2-ethylhexoate or cobaltous 2-ethylhexoate), reacts with various olefins to give the corresponding allylic benzoates.

$$H_2C{=}CH{-}CH_2R + C_6H_5C{-}O\ OC(CH_3)_3 \longrightarrow$$
$$\overset{\|}{O}$$

$$H_2C{=}CH{-}CH{-}R + (CH_3)_3COH$$
$$\underset{O{-}CO{-}C_6H_5}{|}$$

Generally, olefins undergo radical reactions to give mixtures of isomeric allylic compounds[5]; but *t*-butyl perbenzoate under similar conditions gives only one allylic benzoate. It appears, therefore, that this reagent reacts stereospecifically, and can

(1) This investigation is supported by a grant from the Office of Naval Research.

(2) A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954, pp. 72-88.

(3) N. A. Milas and D. M. Surgenor, THIS JOURNAL, 68, 642 (1946).

(4) A. T. Blomquist, A. F. Ferris and I. A. Berstein, ibid., 73, 3408, 3412, 5546 (1951).

(5) M. S. Kharasch, R. Malec and N. C. Yang, J. Org. Chem., 22, 1443 (1957); M. S. Kharasch, P. L. Pauson and W. Nudenberg, J. Org. Chem., 18, 322 (1953); L. Bateman and J. I. Cunneen, J. Chem. Soc., 941 (1950).

thus in certain instances be utilized to advantage for preparative purposes.

The reaction of *t*-butyl perbenzoate and cyclohexene in the presence of cuprous bromide at 80° gives a 70% yield of cyclohex-1-en-3-yl benzoate. *Anal.* Calcd. for $C_{13}H_{14}O_2$: C, 77.40; H, 6.96. Found: C, 77.35; H, 6.71. Similarly, 1-octene gives oct-1-en-3-yl benzoate. *Anal.* Calcd. for $C_{15}H_{20}O_2$: C, 78.00; H, 8.63. Found: C, 78.25; H, 8.99. No isomeric oct-2-en-1-yl benzoate can be detected by examination of the infrared spectra of all fractions from repeated distillations of this material. Under the same conditions, 1-hexene gives only hex-1-en-3-yl benzoate. *Anal.* Calcd. for $C_{13}H_{16}O_2$: C, 76.60; H, 7.85. Found: C, 76.87; H, 8.17.

On the other hand, the reaction of cyclohexene and benzoyl peroxide under comparable experimental conditions gives a mixture of the saturated cyclohexyl and the unsaturated cyclohexenyl benzoates in a ratio of about 35 to 65. *Anal.* Calcd. for $C_{13}H_{14}O_2/C_{13}H_{16}O_2 = 65/35$: C, 76.84; H, 7.50. Found: C, 77.13; H, 7.70; ozonolysis, 66% unsaturation. The reaction of benzoyl peroxide and 1-octene under these conditions gives, among other products, a mixture of allylic benzoates which was analyzed by determining its infrared spectrum.[6]

The mechanism and applications of this reaction are now being investigated; results will be reported at a later date.

(6) M. S. Kharasch and A. Fono, J. Org. Chem., in press.

(7) Deceased, manuscript prepared by G. S.

INSTITUTE OF ORGANIC CHEMISTRY
THE UNIVERSITY OF CHICAGO   M. S. KHARASCH[7]
CHICAGO 37, ILLINOIS   GEORGE SOSNOVSKY
            RECEIVED NOVEMBER 14, 1957

BRANCHED-CHAIN HIGHER SUGARS[1,2]

Sir:

Formation of normal ketohexoses by aldol condensation of glycerose has been known since 1890.[3] The production of a branched-chain hexose by condensation of 2,3-*O*-isopropylidene-glycerose was reported in 1930.[4] Treatment of higher sugars with alkali yields a variety of rearrangement and degradation products,[5] but except for a normal-chain dodecitol, described as a product of "reductive coupling" and isolated from an electrolyzed sugar–alkali mixture,[6] no products of self-condensation with more than 6 carbons have been reported. It has now been found that aldoses, substituted to preclude ketose and 2,3-enediol formation, undergo aldol condensation to form (in reasonably good yield) branched-chain aldoses having twice the number of carbon atoms. By selec-

(1) This work was sponsored by the Division of Research, Atomic Energy Commission.

(2) Presented before the Division of Carbohydrate Chemistry at the 132nd Meeting of the American Chemical Society at New York, N. Y., September 11, 1957.

(3) E. Fischer, Ber., 23, 2114 (1890).

(4) H. O. L. Fischer and E. Baer, ibid., 63, 1749 (1930).

(5) J. U. Nef, Ann., 357, 294 (1907); 376, 1 (1910); 403, 204 (1913).

(6) M. L. Wolfrom, W. W. Binkley, C. C. Spencer and B. W. Lew. THIS JOURNAL, 73, 3357 (1951).