

progestational in rats or rabbits, even at high dose levels.

The unusual activity observed with the above compounds has led to the preparation of steroidal pyrazoles related to the progestational and cortical hormones, as well as to the fusion of steroids with other heterocyclic rings.

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**TITANIUM TETRACHLORIDE-TRIALKYLALUMINUM  
COMPLEX—A CYCLIZING CATALYST FOR  
ACETYLENIC COMPOUNDS**

Sir:

Heretofore reactions of acetylene and terminal acetylenic compounds with catalyst such as obtained from the reaction of triisobutylaluminum with titanium tetrachloride resulted only in the polymerization of these compounds to high polymers.<sup>1</sup> Using the same type of catalyst we have found that by regulating the ratio of  $(i\text{-Bu})_3\text{Al}$  to  $\text{TiCl}_4$  we can trimerize symmetrical acetylenic compounds to hexasubstituted benzenes. Thus (as shown in Fig. 1) diphenylacetylene can be

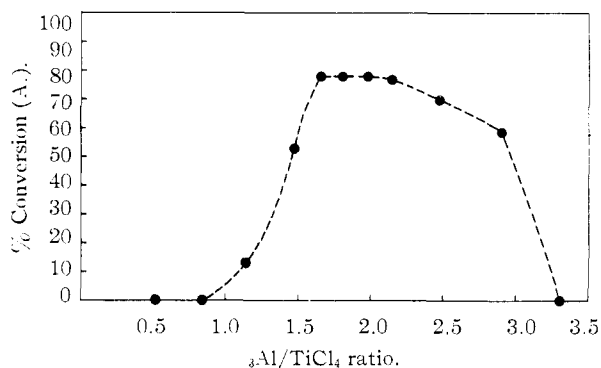


Fig. 1.—Conversion to hexaphenylbenzene versus mole ratio  $(i\text{-Bu})_3\text{Al}/\text{TiCl}_4$ : (A) conversions taken after 10 minutes at room temperature except those cases where there was 0% conversion, in which case more rigorous conditions were used after the 10 minutes had elapsed.

trimerized to hexaphenylbenzene only between  $(i\text{-Bu})_3\text{Al}/\text{TiCl}_4$  ratios of 1/1 to 3/1, although polymerization of olefins readily occurs outside these limits. Control experiments demonstrated that neither triisobutylaluminum, titanium tetrachloride, nor titanium trichloride alone could effect cyclic trimerization. In fact the  $(i\text{-Bu})_3\text{Al}/\text{TiCl}_4$  polymerization catalyst does not catalyze cyclic trimerization of any acetylenes reported in this paper.

This type of cyclic trimerization is not limited to diphenylacetylene. Any symmetrical dialkyl or diarylacetylene will trimerize at the proper catalyst ratio. Dimethylacetylene trimerizes to hexamethylbenzene in 100% yield at  $(i\text{-Bu})_3\text{Al}/\text{TiCl}_4$  ratios of 1.8/1. The "crude" product melted at

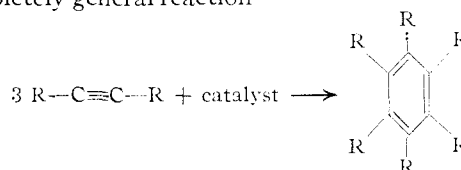
(1) (a) G. Natta, P. Pino and G. Mazzanti, Belgian Patents 546,151, Mar. 16, 1956; (b) 548,927, June 22, 1956.

161–162° compared to 162° obtained by Smith and Lux<sup>2</sup> after recrystallization. One hundred per cent. yields of hexaethylbenzene (m.p. "crude" product 127–128° compared to 126–128° obtained by Smith and Guss<sup>3</sup> after recrystallization) were obtained from diethylacetylene using the  $(i\text{-Bu})_3\text{Al}/\text{TiCl}_4$  catalyst. Seventeen moles of cyclic trimer per mole of catalyst were obtained, indicating the "catalytic" nature of this reaction.

Identities of the hexasubstituted benzenes were established by comparison of infrared spectra with those of authentic samples. Hexamethylbenzene and hexaethylbenzene were available but hexaphenylbenzene was synthesized<sup>4</sup> by condensation of diphenylacetylene<sup>5</sup> with tetraphenylcyclopentadienone. The infrared and X-ray spectra of the authentic and unknown samples were identical.

Recently, using organometal compounds, Zeiss<sup>6</sup> has obtained cyclic trimers of two acetylenic compounds. The organometal compound was used in stoichiometric amounts, rather than in the small quantities normally considered as catalytic amounts, and the reaction has required specific organometal compounds for specific symmetrical acetylenes. Nevertheless, the similarity of products obtained from Zeiss' systems and the  $(i\text{-Bu})_3\text{Al}/\text{TiCl}_4$  system might reflect a relationship between the two which will provide a valuable clue to the  $(i\text{-Bu})_3\text{Al}/\text{TiCl}_4$  catalyst structure.

In summary, the catalytic system  $(i\text{-Bu})_3\text{Al}/\text{TiCl}_4$  previously believed applicable only to the polymerization of olefins (or acetylenes) to form high polymers can now be used for cyclic trimerization of disubstituted acetylenes in the completely general reaction



- (2) L. I. Smith and A. R. Lux, *THIS JOURNAL*, **51**, 2997 (1929).  
 (3) L. I. Smith and C. O. Guss, *ibid.*, **62**, 2625 (1946).  
 (4) W. Dilthey and G. Hurtig, *Ber.*, **67B**, 495, 2005 (1934).  
 (5) L. I. Smith and M. M. Falkof, *Org. Syn.*, **22**, 50 (1942).  
 (6) (a) H. H. Zeiss and W. Herwig, *THIS JOURNAL*, **80**, 2913 (1958);  
 (b) M. Tsutsui and H. Zeiss, p. 59-P, Abstracts of Papers, 134th Meeting American Chemical Society, September 7–12, Chicago, Illinois.

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**PARTIAL ASYMMETRIC SYNTHESIS IN THE  
ADDITION OF DIPHENYLDIAZOMETHANE TO  
OLEFINS<sup>1</sup>**

Sir:

Cram and Abd Elhafez<sup>2</sup> and Prelog and co-workers<sup>3,4</sup> have studied the course of asymmetric syntheses in a number of systems and have found

- (1) This work was supported by a grant from the National Science Foundation.  
 (2) D. J. Cram and F. A. Abd Elhafez, *THIS JOURNAL*, **74**, 5828 (1952).  
 (3) V. Prelog, *et al.*, *Helv. Chim. Acta*, **36**, 308 (1953).  
 (4) For a review of this work, see J. A. Mills and W. Klyne, Ch. 5 in "Progress in Stereochemistry," Vol. I, Academic Press Inc., New York, N. Y., pp. 198–201.