Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

NOTE

ADDITION AND OLIGOMERIZATION PRODUCTS FROM THE REACTION OF DIPHENYLACETYLENE WITH TRIPHENYLALUMINUM

JOHN J. EISCH AND ROBERT L. HARRELL, JR.
Maloney Chemical Laboratory, The Catholic University of America, Washington, D.C. 20017 (U.S.A.)

(Received July 22nd, 1969)

INTRODUCTION

The addition of triphenylaluminum to disubstituted acetylenes proceeds readily in hydrocarbon solution in a temperature range of 80–120° to yield the *cis*-adduct in a stereospecific and, often, a regiospecific fashion[1,2]. At temperatures near 200° an unusual metalative cyclization sets in, leading to the evolution of benzene and the formation of the benzaluminole ring system[1]. The present study was undertaken to identify some of the secondary reaction products resulting from heating triphenylaluminum with an excess of diphenylacetylene in a diphenyl ether medium. The results given below provide evidence pertinent to the existence of benzaluminepin and π-complex[3] intermediates in the reactions of arylaluminum compounds with alkynes.

EXPERIMENTAL

The preparation, manipulation and reactions of triphenylaluminum were conducted under an atmosphere of dry, oxygen-free nitrogen according to published procedures[1]. Diphenylacetylene obtained from commercial sources often contains *trans*-stilbene as an impurity; hence all starting material was checked for purity by GLC analysis and chromatographed over alumina where necessary. Reaction solvents were heated over and distilled from metallic sodium before use.

Interaction of diphenylacetylene with triphenylaluminum in diphenyl ether

A homogeneous mixture of 7.12 g (0.040 mole) of diphenylacetylene and 5.16 g (0.020 mole) of triphenylaluminum in 15 ml of diphenyl ether was heated at the oil bath temperature of 190–200° for 9 h. After acidic hydrolysis and the addition of benzene, the insoluble hexaphenylbenzene was collected and the organic extract separated. This extract was shaken with dilute, aqueous sodium hydroxide and the resulting aqueous extracts acidified. From the aqueous layer both phenol and *o*-phenylphenol were isolated and identified (GLC, IR and, for the latter, mixture melting point).

The organic extract, free of phenols, was dried over anhydrous calcium sulfate and then both the benzene and the diphenyl ether removed by distillation under reduced pressure. The residue was chromatographed on activated alumina and eluted successively with petroleum ether (b.p. 30–60°) and with petroleum ether/benzene (9/1, v/v). The residual diphenyl ether was eluted first, followed by triphenylethylene. The 1,2,3-triphenylindene accompanied the 1,2,4-triphenylnaphthalene off the column and these components had to be separated by fractional crystallization from aqueous ethanol. Finally came the 1,2,3,4-tetraphenylnaphthalene. Any hexaphenylbenzene not previously isolated remained at the top of the column. Yield of products: (1) triphenylethylene, 5.10 g; (2) hexaphenylbenzene, 0.19 g; (3) 1,2,3,4-tetraphenylnaphthalene, 0.14 g; (4) 1,2,4-triphenylnaphthalene, 0.10 g; (5) 1,2,3-triphenylindene, 0.05 g; (6) *o*-phenylphenol, 0.18 g; and (7) phenol. No tolane could be detected by GLC analysis. Because of recrystallization losses and difficulties in separation only 65–70% of the material could be accounted for as pure products.

The foregoing products 1, 2, 3, 6 and 7 were identified by melting point and spectral comparisons with authentic samples. The 1,2,4-triphenylnaphthalene was identified by chromic acid oxidation to *o*-dibenzoylbenzene, by mass spectral, NMR and IR data, and by melting point[4]. The 1,2,3-triphenylindene was identified by its NMR and mass spectral data, by chromic acid oxidation to *o*-dibenzoylbenzene and, finally, by synthesizing an authentic sample[5] for comparison.

From one run conducted for 70 h at 220–225° 0.10 g of tetraphenylethylene and 0.01 g of 9,10-diphenylphenanthrene were detected, but it is uncertain whether these may stem from small amounts of *trans*-stilbene possibly present in the starting material for this run.

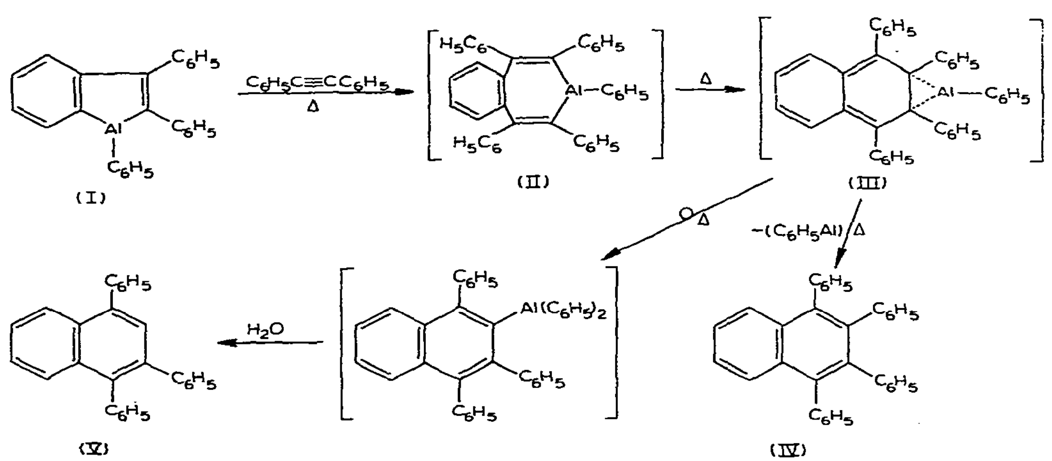
In one run a 1/1 molar mixture of the reactants was heated for 9 h at 200°, a second equivalent of diphenylacetylene thereupon added, and the mixture heated for an additional 35 h at 200°. However, there was no significant change in the proportion of products.

Finally, one run conducted at 210–240° without solvent in a 3.5/1 ratio of alkyne/$(C_6H_5)_3Al$ gave a 10% yield of hexaphenylbenzene.

RESULTS AND DISCUSSION

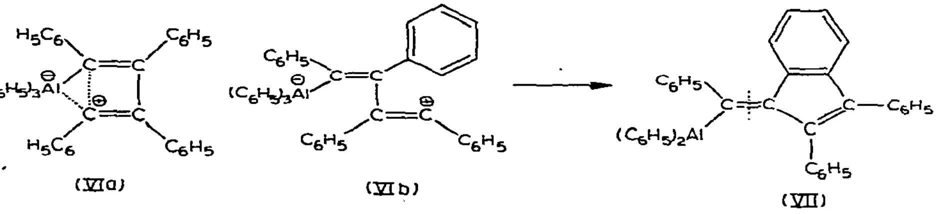
In addition to the expected principal product, triphenylethylene, the smaller but significant amounts of naphthalene and indene derivatives isolated suggest the occurrence of interesting cyclic oligomerizations. At the same time, the presence of hexaphenylbenzene indicates the operation of a cyclic trimerization of the diphenylacetylene. Finally, the diphenyl ether medium is not completely inert under the reaction conditions but does undergo both cleavage of its C–O linkage and rearrangement.

The nature of the reaction products is independent of whether a 2/1 molar ratio of reactants is heated directly at 200° or whether a 1/1 molar ratio is preheated before the second equivalent of the acetylene is added. Because the monoadduct intermediate, diphenyl(triphenylvinyl)aluminum, is known to cyclize to 1,2,3-triphenylbenzaluminole (I) at 200° [1], it is reasonable to entertain (II) as a possible precursor for the naphthalene derivatives:



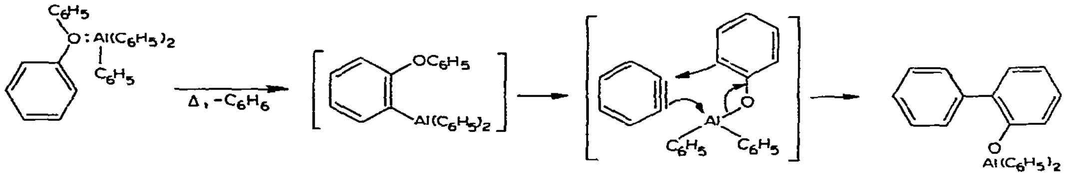
Preferential insertion of the acetylene into the sterically more accessible C–Al bond of (I) would lead to benzaluminepin (II). As with several known heterocyclic systems of type (II)*, aromatization with extrusion of the heteroatomic group would be expected to occur thermally [(II)→(IV)]. Alternatively, phenyl group migration could account for the 1,2,4-triphenylnaphthalene [(II)→(V)].

The formation of the hexaphenylbenzene and the 1,2,3-triphenylindene seems to be explicable in terms of a π-complex between the alkyne and $(C_6H_5)_3Al$[3]:



Interaction of such a π-complex with the alkyne could lead, via a cyclobutadienoid complex (VIa), to hexaphenylbenzene[3]; considered in form (VIb), such a complex could cyclize to yield (VII). Presumably addition of C_6H_5–al to the exocyclic bond of (VII) would lead to an adduct able to rupture at the exocyclic bond, giving the precursor of 1,2,3-triphenylindene.

The cleavage of diphenyl ether to yield phenol upon hydrolysis is analogous to the known cleavage of ethers by various aluminum halides[8]. More interesting is the formation of *o*-phenylphenol, whose origin may involve a benzyne intermediate similar to that suggested in the reaction of phenylsodium with diphenyl ether[9]:



---

* The 3-benzothiepin system, either as the sulfide[6a] or as the 3-dioxide[6b] undergoes thermal extrusion of sulfur or sulfur dioxide, respectively, to yield the naphthalene nucleus. Furthermore, the recently synthesized 3,3-diphenyl-3-benzosilepin[7] undergoes pyrolysis with the formation of naphthalene.

The metalation of the *ortho* position of the ether by $(C_6H_5)_3Al$ finds sounds precedent in the metalative formation of aluminoles themselves[1].

ACKNOWLEDGEMENTS

The authors express their gratitude to the National Science Foundation for support of this research under Grant GP-6679. They are grateful to Professors Henry Gilman and Thomas Kinstle of Iowa State University, the former for an authentic sample of 1,2,3,4-tetraphenylnaphthalene and the latter for assistance with mass spectral analysis. Dr. Rudolf Amtmann verified the formation of hexaphenylbenzene in the solvent-free reaction.

REFERENCES

1 J. J. Eisch and W. C. Kaska, *J. Amer. Chem. Soc.*, 88 (1966) 2976.
2 J. J. Eisch and C. K. Hordis, *152nd Nat. Meeting, Amer. Chem. Soc.*, New York, Sept. 12–16, 1966, *Abstr.* 67S.
3 J. J. Eisch, R. Amtmann and M. W. Foxton, *J. Organometal. Chem.*, 16 (1969) P55.
4 C. F. H. Allen, A. Bell and J. W. Gates, Jr., *J. Org. Chem.*, 8 (1943) 373.
5 D. Y. Curtin, H. W. Johnson, Jr., and E. G. Steiner, *J. Amer. Chem. Soc.*, 77 (1955) 4566.
6 (a) G. P. Scott, *J. Amer. Chem. Soc.*, 75 (1953) 6332;
(b) W. E. Truce and F. J. Lotspeich, *J. Amer. Chem. Soc.*, 78 (1956) 848.
7 L. Birkofer and H. Haddad, *Chem. Ber.*, 102 (1969) 432.
8 *Cf., inter alia*, G. R. Pettit and D. M. Piatek, *J. Org. Chem.*, 25 (1960) 721.
9 R. Huisgen and J. Sauer, *Angew. Chem.*, 72 (1960) 96.