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Preliminary communication

Specific *ortho*-arylation in the photochemical rearrangements of the tri-*m*- tolyl- and tri-*p*-tolyl-aluminum systems

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Our initial examination of the behavior of triphenylaluminum toward ultraviolet irradiation★ in toluene solution had established that *o*-biphenylylaluminum and hydrogen—aluminum bonds were generated, as well as biphenyl itself and aluminum metal[1]. The generation of an *o*-biphenylylaluminum linkage suggested that a benzyne intermediate might be involved. In our effort to test for the possible intermediacy of benzynes in such photo-rearrangements, we have now investigated the photochemical behavior of the *m*-methyl and *p*-methyl derivatives of triphenylaluminum. This report announces a novel, specific *ortho*-arylation in the photochemical rearrangements of these tolylaluminum compounds and thereby adduces evidence militating against an aryne intermediate.

The irradiation★ of a 0.017 molar solution of tri-*p*-tolylaluminum[2] (I) in toluene for 24 h led to the expected deposition of aluminum metal; as with its phenylaluminum counterpart[1], hydrolytic work-up was accompanied by a vigorous evolution of hydrogen gas. The organic layer was found to contain only bibenzyl (II) (7%) and 3,4'-bitolyl (III) (43%). This sole bitolyl was separated and identified by comparison with an authentic sample; the absence of other bitolyls (3,3' and 4,4') was also demonstrated by recourse to known samples. When a similar photochemical run was worked up with deuterium oxide (99.8%), HD (> 95%) was evolved and the 3,4'-bitolyl isolated was a mixture of (III) (30%) and its 6-deuterio isomer (IV), 70% (Scheme I). The independent synthesis of authentic IV is outlined in Scheme II.

In a similar manner, the irradiation of tri-*m*-tolylaluminum[3] (V) in toluene solution★ and its hydrolytic work-up gave a 1/1 mixture of 3,4'-bitolyl (III) and 2,3'-bitolyl (V) in over-all yield of 45%, in addition to H_2 and small amounts of bibenzyl (< 1%) (Scheme III). Again, the presence of just these two isomeric bitolyls and the absence of other isomers were assured by reference to authentic samples.

If an aryne intermediate of a precedented type[4] had been generated from the *p*-tolylaluminum system, such an intermediate would be expected to react with *p*-tolyl-aluminum bonds without any great preference as to orientation[5] to give a bitolyl mixture

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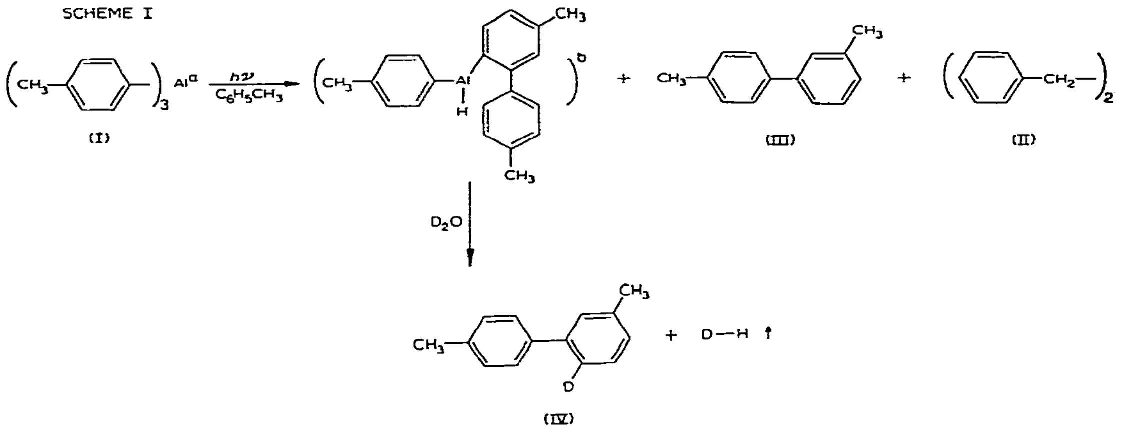
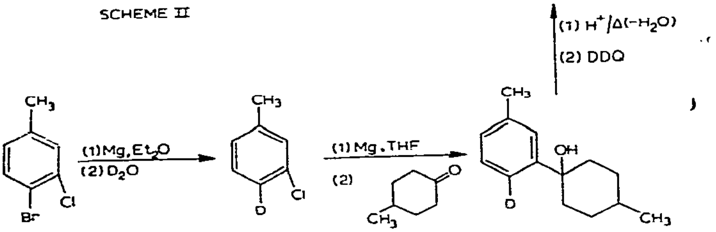
★A Rayonet photochemical reactor, Model 100, equipped with a low-pressure (2537 Å) mercury lamp and operated at an ambient temperature of 45°, was employed.

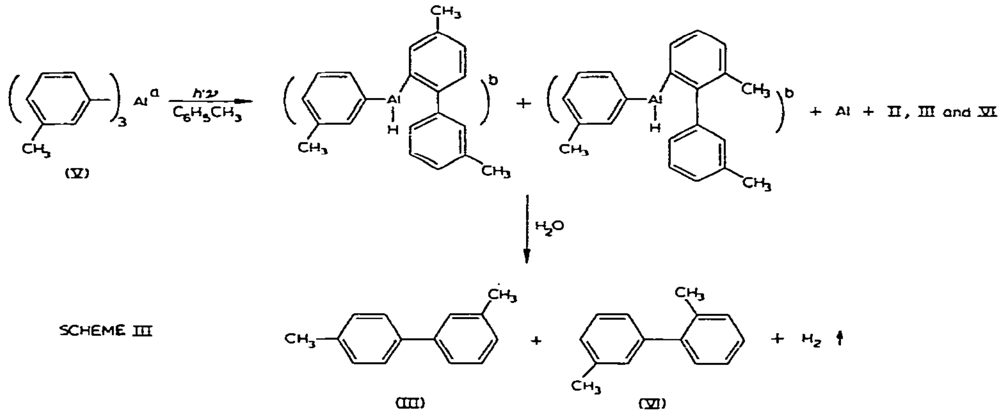
SCHEME I



SCHEME II



[a] These compounds are probably dimeric in aromatic hydrocarbons (ref. 6).
[b] This disposition of groups about a given aluminum is idealized; arylaluminum hydrides tend to disproportionate to symmetrical types (ref. 7).

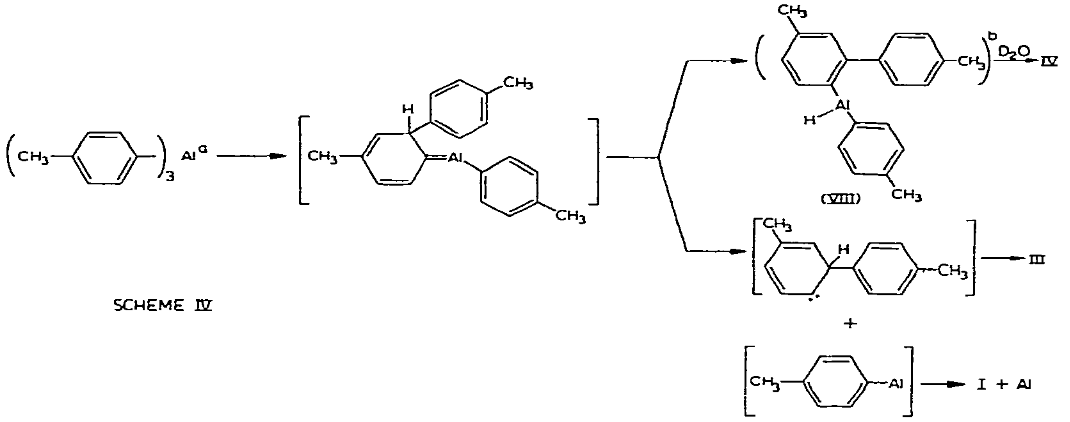


SCHEME III

[a,b] See Scheme I/II

resulting from direct substitution and *ortho*-arylation. Hydrolysis should yield a mixture of 3,4′-bitolyl (III) and 4,4′-bitolyl (VII). Similarly, 3,4-formation of an aryne intermediate from the *m*-tolylaluminum system and reaction with *m*-tolyl—aluminum bonds should produce, upon hydrolysis, 3,3′-bitolyl and 3,4′-bitolyl. Hence, the failure to observe 4,4′-bitolyl in the *p*-tolylaluminum case and 3,3′-bitolyl in the *m*-tolylaluminum case argues strongly against the involvement of an aryne intermediate of the precedented type.

From the formation of only 3,4′-bitolyl from the *p*-tolylaluminum compound, but the formation of two isomers, 3,4′-bitolyl and 2,3′-bitolyl, from the *m*-tolylaluminum compound, it is clear that an arylation specifically *ortho* to the tolyl—aluminum bond has taken place. Competing shifts of hydrogen to aluminum with hydride formation (VIII) or to carbon with loss of arylaluminum(I) (IX) would be consistent with the formation of a mixture of deuterated and undeuterated biaryls, upon work-up with deuterium oxide (Scheme IV).



SCHEME IV

^{a,b} See Scheme I/II

Further specification of the electronic factors leading to this unusual *ortho*-arylation of a substituted arylaluminum is the object of our current studies. In addition, this specific photochemical coupling of aryl groups may find advantageous synthetic applications.

ACKNOWLEDGMENTS

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