Short Communications

Facile metalation of terminal alkynes by triphenylaluminum

Under mild conditions, unsolvated aluminum alkyls and dialkylaluminum hydrides add to many acetylenic linkages in a *cis* fashion[1]. Recent evidence suggests that *trans* addition in such reactions proceeds via a diaddition–elimination pathway[2]. In contrast, with tertiary amine adducts of dialkylaluminum hydrides or of aluminum alkyls, terminal alkynes undergo smooth metalation, rather than addition[3] (eqn. 1):

$$R_2Al{-}R'{\cdot}NR_3'' + R'''{-}C{\equiv}C{-}H \xrightarrow{20-40^\circ} R'''{-}C{\equiv}C{-}AlR_2{\cdot}NR_3'' + R'{-}H \quad (R' = H, \text{alkyl}) \qquad (1)$$

A similar substitution reaction between terminal alkynes and aluminum alkyls also has been achieved under more stringent conditions[4] (110°), but the extent of any concurrent addition reaction was not mentioned.

Our interest in unsaturated organoaluminum compounds has prompted us to study the behavior of triphenylaluminum toward alkynes[5,6]. Both alkylarylacetylenes and symmetrical acetylenes were found to undergo addition in the temperature range of 50–150° and the resulting adducts to cyclize at higher temperatures with the formation of aluminoles[5,7]. In an extension of this research we have observed that terminal alkynes, such as 1-hexyne and phenylacetylene, are metalated quite readily by triphenylaluminum in benzene solution[6] (eqn. 2):

$$(C_6H_5)_2Al{-}C_6H_5 + R{-}C{\equiv}C{-}H \xrightarrow{20-50^\circ} \underset{\text{(I)}}{(C_6H_5)_2Al{-}C{\equiv}C{-}R} + C_6H_6 \quad (R = n\text{-}C_4H_9, C_6H_5) \qquad (2)$$

The alkynyldiphenylaluminum products (I), formed in excellent yield, were obtained as crystalline solids and were characterized by hydrolysis, aluminum analysis and spectral data. Since only benzene and the original alkyne were detected upon the hydrolysis of (I), metalation, rather than addition, is the principal reaction between terminal alkynes and triphenylaluminum*[,8]. Thus, the reaction described in eqn. 2 constitutes an excellent synthetic method for these alkynylaluminum types.

The infrared spectra of (I) displayed prominent, sharp bands in the 2110–2120 cm^{-1} region, characteristic of the –C≡C– stretching frequency. Since the corresponding terminal alkynes themselves absorb in the 2120 cm^{-1} region, the adjacent $(C_6H_5)_2Al$ group has little effect, if any, on the –C≡C– stretching frequency. The NMR spectrum

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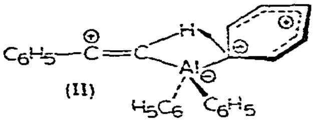
* On the other hand, in unpublished studies we have found that a 1:1 mixture of phenylacetylene and diisobutylaluminum hydride interacts at 40–50° to evolve hydrogen gas. Infrared examination and hydrolytic work-up indicate that metalation (34%) *and* both mono- (55%) and diaddition (11%) occur. (*Cf.* ref. 1).

of (phenylethynyl)diphenylaluminum showed a low-field quartet and a triplet (as does the spectrum of triphenylaluminum itself), in addition to higher-field multiplets associated with the phenylethynyl group. Spectral studies with tri(phenyl-*m*-*d*)-aluminum have permitted the assignment of the low-field quartet to the *ortho* protons and of the triplet to the unresolved *meta* and *para* protons in such phenylaluminum systems (C_6H_5–Al).

Finally, it is noteworthy that indene, a hydrocarbon having a acidity comparable to phenylacetylene (pK_a of 21)[9], reacted with triphenylaluminum in benzene solution only to a small extent after a prolonged reaction time. Hence, the terminal alkynes studied underwent metalation far more rapidly than indene. This conclusion assumes, of course, that the observed extent of metalation of these hydrocarbons is not due to a markedly altered thermodynamic acidity toward triphenylaluminum. Such a pronounced difference in hydrocarbon reactivity can be interpreted in terms of the four-center transition state previously proposed for alkyne–Group III alkyl interactions[10] (*cf.* II). The absence of donor π-electrons at the benzylic carbon of indene (bearing the "normally" acidic hydrogens) suggests that a donor–acceptor transition state, as shown in (II) for phenylacetylene, could not be attained as readily with indene. Indeed, with pseudoacidic hydrocarbons of the benzylic type (*e.g.* indene and fluorene[5]), the aromatic protons actually may be attacked.



(II)

Experimental

Procedures and starting materials. All operations involved in the preparation, reactions and transfer of organoaluminum compounds were conducted under an atmosphere of dry, oxygen-free nitrogen. An inert atmosphere chamber was employed for the transfer of analytical and spectral samples. All glassware was dried scrupulously and the reagent-grade solvents were distilled directly from lithium aluminum hydride into the prepared reaction vessel.

The aluminum analyses were performed according to the procedure of Watts[11]. Organic hydrolysis products were analysed with a Barber-Coleman gas chromatograph, Model 10, employing a 30 % silicone oil-on-firebrick column. Infrared spectra of the aluminum compounds in dry mineral oil mulls were obtained with a Perkin-Elmer Model 21 infrared spectrophotometer. The NMR spectra were obtained with solutions of the aluminum compound in tetrahydrofuran and in benzene-d_6- containing ordinary benzene as an internal standard. The spectra were recorded on a Varian A-60 spectrometer.

The 1-hexyne (Farchan) and phenylacetylene (Eastman) were fractionally distilled from a carefully dried apparatus before use. The indene (minimum purity of 97.5 %), kindly furnished by the Neville Chemical Co., was distilled just before use, in order to remove the *p*-toluhydroquinone inhibitor.

The triphenylaluminum was prepared from diphenylmercury and aluminum chips (99.992 %, min.) in boiling xylene[12]. The melting point of this product, determined on samples in a sealed capillary, ranged up to 238°; some preliminary decomposition seemed to occur[*]. However, the satisfactory aluminum analyses and the preparation of the sharp-melting etherate, m.p. 129–129.5°, attest to the purity of the triphenylaluminum. A sample of triphenylaluminum in tetrahydrofuran solution containing a small amount of benzene was examined by NMR spectroscopy. The spectrum was recorded with a 150 cps audio frequency sideband. The bulk susceptibility of the solvent was neglected in obtaining the chemical shift data. The spectrum consisted of a quartet and a triplet with relative areas of 2:3 in the direction of increasing magnetic field. (By preparing a sample of triphenylaluminum containing some deuterium in the *meta* positions, it was shown that the *ortho* protons rather than the *meta* protons, were responsible for the quartet). The benzene internal standard showed its resonance superposed upon the *meta–para* triplet and the chemical shift of the *ortho* protons with respect to benzene was —0.49 ± 0.1 ppm. Another sample measured in benzene-d_6 yielded a somewhat broadened quartet and a triplet, with the *ortho* protons shifted —0.74 ± 0.1 ppm from benzene[**].

Triphenylaluminum and 1-hexyne. A suspension of 3.14 g (0.0122 mole) of triphenylaluminum in 1.50 g (0.0183 mole) of 1-hexyne and 20 ml of benzene was stirred at room temperature for 12 h. During this period all the triphenylaluminum dissolved and the solution became yellow. After a 3 h heating period at 50° the reaction solution was set under a vacuum of 0.02 mm, in order to remove the volatile material. The viscous, dark yellow oil, formed in essentially quantitative yield, was dissolved in dry pentane and the resulting solution filtered through a sintered glass disc of fine porosity. Cooling caused the deposition of fine, almost colorless needles. After several recrystallizations, needles of 1-hexynyldiphenylaluminum melting at 86–87° (sealed capillary) were obtained. (Found: Al, 10.19. $C_{18}H_{19}Al$ calcd.: Al, 10.28 %.)

Vapor phase chromatographic analysis of a hydrolyzed sample of the organoaluminum product showed the presence of only 1-hexyne and benzene. Moreover, the infrared spectrum of the aluminum compound displayed an intense absorption at 2120 cm^{-1} (C≡C), but no acetylenic C–H absorption.

Triphenylaluminum and phenylacetylene. A suspension of 5.0 g (0.0193 mole) of triphenylaluminum in 100 ml of benzene turned yellow when 2.1 g (0.020 mole) of phenylacetylene was introduced. The system became almost completely clear (except for a small amount of orange solid) upon stirring for 12 h without heating. After a 1 h heating period at 50° the solution was filtered from the small amount of suspended solid. From the concentrated benzene filtrate yellow rectangular plates were obtained. Further recrystallization from benzene and washing with pentane produced light yellow rhombic crystals of (phenylethynyl)diphenylaluminum, m.p. 142–144° (turning deep red at 141°). (Found: Al, 9.37. $C_{20}H_{15}Al$ calcd.: Al, 9.55 %.)

Hydrolysis of a sample yielded phenylacetylene and benzene, as shown by vapor phase chromatography. The infrared spectrum of the ethynylaluminum compound exhibited a strong absorption at 2110 cm^{-1}, but again no acetylenic C–H band. The NMR spectrum of the aluminum product in benzene-d_6 with benzene as an internal standard consisted of a quartet at —0.996 ppm from benzene, a triplet at —0.184

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[*] Unpublished work in these Laboratories has shown that triphenylaluminum undergoes decomposition at 200–250° with the evolution of benzene. Others (A. W. Laubengayer of Cornell University and T. Mole of C.S.I.R.O. Chemical Research Laboratories, Melbourne, Australia) have also observed this metalative decomposition.

[**] A more extensive study of the NMR spectra of unsaturated organoaluminum compounds is planned.

ppm and a series of peaks at +0.117 and +0.446 ppm. The area ratio of the low-field quartet to the triplet was 2:3. This accords with the relation of the *ortho* protons to the *meta–para* protons in the spectrum of triphenylaluminum and hence identifies the low field multiplets with the phenyl groups attached to the aluminum atom. The higher peaks at +0.117 and +0.446 ppm would then be assigned to the phenylethynyl group.

Triphenylaluminum and indene. A suspension of 2.0 g (0.0077 mole) of triphenylaluminum and 0.90 g (0.0086 mole) of indene in 100 ml of benzene was heated in a bath at 125–130° for 100 h. Thereupon the pale yellow solution was set under vacuum to remove the benzene and unreacted indene. The solid residue was dissolved in warm benzene, and the solution filtered. The filtrate slowly deposited a colorless solid, melting from 207 to 230°. Its infrared spectrum strongly resembled that of triphenylaluminum, except for a distinct band at 800 cm^{-1}. Hydrolysis of a sample and analysis by vapor phase chromatography showed the presence of benzene and indene (*ca.* 99:1).

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