Reactions of Lithium Aluminium Hydride with Alternant Aromatic Olefins

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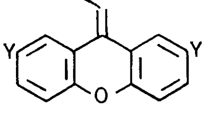
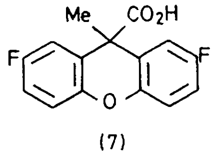
Summary 1,1-Diphenylethylene and some 9-methylenexanthenes react readily with lithium aluminium hydride in refluxing tetrahydrofuran, affording the corresponding benzylic carbanions.

IT has been known for some time that fulvenes[1] react readily with lithium aluminium hydride, whereas heptafulvenes[1] or alternant aromatic olefins such as 1,1-diphenylethylene (**1**)[2] do not, excluding methylenebenzanthrene.[2] Recently, we have observed[3] a hydride addition to the exocyclic double bond of 2,7-difluoro-9-chloromethylenexanthene (**2**).

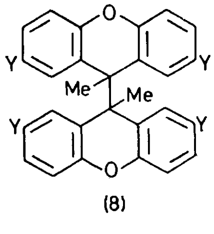
We now report that in fact (**1**), 9-methylenexanthene (**3**) and its derivatives (**4**)—(**6**) react with $LiAlH_4$ in boiling tetrahydrofuran (THF), producing red solutions of the corresponding benzylic carbanions. It appears that in all these cases, hydride attack occurs on the terminal carbon of the double bond. Thus, pure 1,1-diphenyl-2-deuterioethane and 1,1-diphenyl-1-deuterioethane were obtained (80%) in the reactions of (**1**) with $LiAlD_4$ and



(2) X = Cl, Y = F
(3) X = Y = H
(4) X = H, Y = F
(5) X = H, Y = Me
(6) X = H, Y = Br

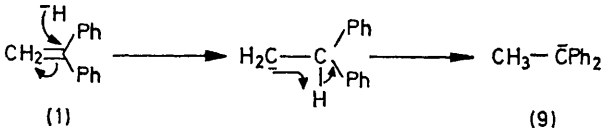


(7)



(8)

LiAlH$_4$, quenched with H_2O and D_2O respectively.† The latter reaction also demonstrated that no proton abstraction from the solvent took place. Monitoring the reduction of (**1**) by n.m.r. spectroscopy, revealed a half-life of *ca.* 20 min and completion of the reaction within 2 h.


(1) (9)

Alternatively, since the terminal carbon of the double bond should be partly negative,[4] the hydride attack might occur on the internal carbon of the double bond (Scheme), followed by rearrangement to form the more stable carbanion (**9**).[5] However, rearrangements with radical and anion intermediates are seldom encountered,[6] and in such a situation, aryl rather than hydrogen migration should have been predominant.[6]

The present observations may also provide a new synthetic route for specifically labelled aromatic compounds.

Quenching the reaction of (**4**) and LiAlH$_4$ after 10 min with solid carbon dioxide, led to the acid (**7**) (50%), m.p. 171°.‡ Similar acids were obtained from the other methylenexanthenes (**3**), (**5**), and (**6**), though in minute amounts. These olefins yielded mainly the dimeric products (**8**).§ This may be an indication to the existence of anion radicals as the intermediates in these reactions. Anion radicals are well known in organic chemistry,[7] especially in aromatic systems. Nevertheless, such anion radicals are usually obtained by metal or electrochemical reductions of carbanions.[7,8]

The reduction of (**6**) was accomplished in ether, since partial hydrogenolysis of the aromatic bromine occurred in THF. Generally, the reductions of the methylenexanthenes (**2**)—(**6**) were much faster than that of (**1**).

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† The only by-products isolated from these reactions were identified spectroscopically as the corresponding dimers 2,2,3,3-tetraphenylbutane (10%) and its 1,4-dideuterio-analogue.

‡ $M^+ = 276$; δ 1·88(3H,s,Me), 7·06 (6H,m,H-Ar), and 8·75 (1H,br.s,HO).

§ The dimers (**8**) were also produced when water was used instead of CO_2. They were identified spectroscopically, *e.g.* (**8**) (Y = H), m.p. 153°; MW = 390 (mass spectrum); δ 1·68(6H,s,Me), and 6·90(16H,m,H-Ar).

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[6] D. J. Cram, 'Fundamentals of Carbanion Chemistry,' Academic Press, New York, 1965, ch. VI.
[7] F. Pietra, *Chem. Rev.*, 1973, **73**, 293.
[8] F. Bickelhaupt, *Angew. Chem. Internat. Edn.*, 1974, **13**, 419, has shown that the formation of Grignard compounds in ethers involves free radicals.