Novel Specific Carbon–Carbon Bond Formation; Substituent and Solvent Effects Associated with Hydride Addition to Aromatic Olefins

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Summary 2,2-Diarylpropanes are conveniently prepared from 1,1-diarylethylenes, lithium aluminium hydride, and anisole in tetrahydrofuran while 1,1-diarylethanes are obtained at 140 °C in bis(methoxyethyl) ether; hydride addition to 1,1-diarylethylenes is decelerated by 2-methyl substituents, and *o*- and *p*-methoxy, but not *m*-methoxy, and a novel and selective carbon–carbon bond forming reaction have been discovered.

IT has long been recorded[1–3] that alternant aromatic olefins such as 1,1-diphenylethylene (**1**) do not react with $LiAlH_4$, excluding dibenzofulvenes.[3] Recently, it has been observed[4,5] that (**1**) or 9-methylenexanthene (**2**) react readily with $LiAlH_4$ in boiling tetrahydrofuran (THF) giving, after hydrolysis, mainly 1,1-diphenylethane and 9,9′-dimethyl-9,9′-bixanthyl (**3**), respectively. The different end-products, as well as the theoretical and preparative interest led us to study the scope of these reactions.

TABLE

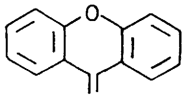
Half-lives of 1,1-diarylethylenes in the presence of $LiAlH_4$ in boiling THF

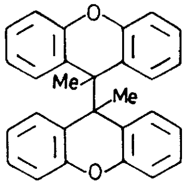
Compound	Half-life/h
(1)	0·33 ± 0·03
(7)	0·50 ± 0·05
(8)	0·30 ± 0·03
(9)	2·0 ± 0·1
(10)	1·5 ± 0·1
(11)	0·33 ± 0·03
(12)	30 ± 2
(13)	2·0 ± 0·1

We have investigated the reaction of $LiAlH_4$ with the olefins (**4**)—(**13**) in several solvents and temperatures, monitoring the reductions by n.m.r. spectroscopy. Final products were isolated, purified, and characterized by standard techniques.† Prominent solvent and substituent effects on the hydride addition to aromatic olefins,

$PhRC{=}CR^1R^2$

(1) R = Ph; $R^1 = R^2 = H$
(4) R = Ph; R^1 = Me; R^2 = H
(5) R = Ph; $R^1 = R^2$ = Me
(6) R = $R^1 = R^2 = H$


(2)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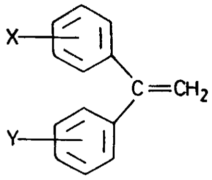
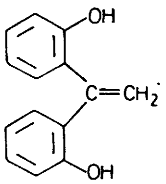

(7) X = H, Y = *o*-MeO
(8) X = H, Y = *m*-MeO
(9) X = H, Y = *p*-MeO
(10) X = Y = *o*-MeO
(11) X = Y = *m*-MeO
(12) X = Y = *p*-MeO
(13) X = Y = *o*-EtO

Ar^1Ar^2CHMe
(14)

$Ar^1Ar^2CMe_2$
(15)


(16)

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† All new compounds gave satisfactory combustion analyses, and n.m.r. and mass spectra.

$LiAlH_4$ reacted smoothly in Et_2O with (**2**), but not with (**1**) or (**4**)—(**13**). The reaction of (**1**) and $LiAlH_4$ in THF proceeded even at ambient temperature.[5] This implies that THF lowered the activation energy of the hydride addition, probably by better solvation of the transition-state complex and/or the intermediate benzylic carbanion. However, (**4**) and (**5**) and (practically; see Table) also (**12**)[5] did not react with $LiAlH_4$ in boiling THF, possibly because of steric and electronic effects. Compound (**5**) was not affected by $LiAlH_4$ in refluxing diglyme [bis(methoxyethyl) ether]. Heating (**4**) or (**12**) for 5—10 min with $LiAlH_4$ at 130—140 °C in diglyme followed by hydrolysis yielded the corresponding 1,1-diarylethanes (**14**). The blood-red carbanions, initially formed, were decolourized rapidly in diglyme by proton abstraction by the carbanions from the solvent, confirmed by the absence of deuterium in the products after deuteriolysis of the reaction mixtures. Proton abstraction from the solvent by the benzylic carbanions occurred also in refluxing dioxan and THF, though it was *ca.* 10^2 times slower in dioxan than in diglyme and even slower in THF.

The aromatic substituent effects on the hydride addition rate were determined as follows. The half-lives of the olefins (**1**) and (**7**)—(**13**) in the presence of a large excess of $LiAlH_4$ in boiling THF under N_2, were measured through monitoring the reactions by n.m.r. spectroscopy (Table). It is evident (Table) that the rate-retarding effect of the *o*- and *p*-MeO groups resulted from increase of the electron density on C-2 by mesomerism. Accordingly, the *m*-MeO compounds added the hydride at essentially the same rate as (**1**). A prominent *ortho*-effect was observed. The higher rate found for the *o*-MeO compounds, compared with their *para*-isomers, suggests a possible solvation interaction of the *o*-MeO with $LiAlH_4$. This 'inner solvation' phenomenon might be rate-enhancing, and this and other possible substituent effects are now being studied.

The carbanions initially formed from compounds (**7**)—(**12**) in boiling THF yielded eventually the 2,2-diarylpropanes (**15**), along with the appropriate phenols, such as (**16**).‡ This novel carbon–carbon bond forming reaction§ seems to be quite specific. Thus, it was not observed when (**13**) was refluxed with $LiAlH_4$ in THF for 24 h. The appropriate diarylethane (**14**) was the sole product of the latter reaction, after hydrolysis. Pure (**15**) was prepared in good yield *via* reaction of the 1,1-diarylethylenes with $LiAlH_4$ in refluxing THF–anisole (1:1). However, no hydride addition to the 1,1-diarylethylenes took place in pure anisole.

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‡ The yields of (**15**; $Ar^1 = Ar^2 = o\text{-}MeOC_6H_4$) and (**16**) were 50 and 10% respectively, based on starting material (**10**). This is in accord with, *e.g.*, production of (**15**) from 2 moles of (**10**).

§ This reaction is remarkable, bearing in mind that Bu^nLi is widely used for the *ortho*-metallation of anisole (I. Granoth, J. B. Levy, and C. Symmes, Jr., *J.C.S. Perkin II*, 1972, 697) or phenetole. In fact, the latter two reactions were used in this study as the first step toward the syntheses of (**10**) and (**13**), respectively, followed by reactions with EtOAc and subsequent dehydrations.

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