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RELATIVE REACTIVITY OF DOUBLE AND TRIPLE BONDS TOWARD A CARBONIUM ION[1]

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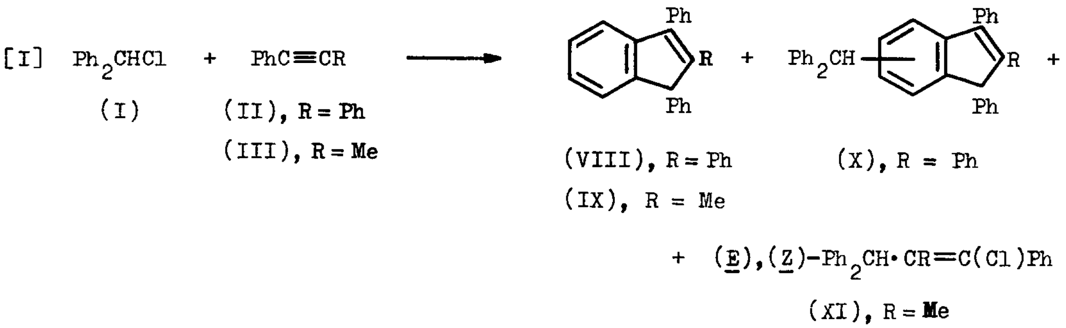
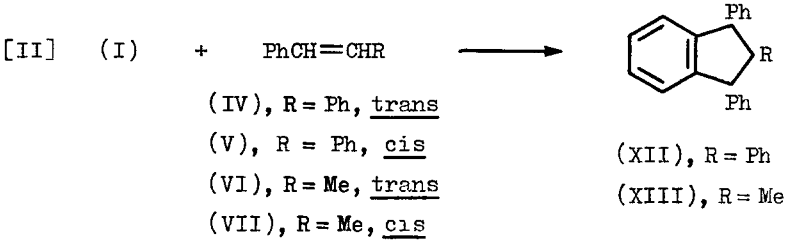
The debated problem of the relative reactivity of olefins and acetylenes toward electrophilic reagents[2,3a] has prompted both experimental[3] and theoretical[4] studies in order to compare the ease of formation or the relative stabilities of saturated and unsaturated cationic intermediates. The electrophiles exploited so far for this purpose have been halogens, sulphenyl derivatives, and protons. To our knowledge, no similar study has been carried out with a common electrophile such as a carbonium ion. As an extension of our research on the Lewis acid catalysed addition of alkyl halides to acetylenes[5] we wish to report the preliminary results of a study of the reactivities of phenyl-substituted olefins and acetylenes toward diphenylmethyl chloride, i.e., toward a fairly stable carbonium ion.

A competition method was chosen since a conventional kinetic approach was made difficult by the heterogeneous nature of our reactions. In a typical experiment 25 mmol of each unsaturated compound were allowed to react with 5 mmol of diphenylmethyl chloride (I) in the presence of 0.5 mmol of powdered anhydrous zinc chloride in 90 ml of boiling dichloromethane until most of (I) was consumed. Chromatography of the reaction residue on silica gel permitted separation of the excess of the reagents from the reaction products, whose relative amounts were determined by integration of the NMR spectrum of their mixture. The results obtained in the competition reactions of diphenylacetylene (II) with trans- and cis-stilbene (IV) and (V) and of 1-phenylprop-1-yne (III) with trans- and cis-1-phenylprop-1-ene (VI) and (VII) are reported in the Table.

The products isolated from the competition reactions were carefully compared with those obtained in addition reactions carried out independently in the same conditions, following equations [I] and [II]. This excluded formation of significant amounts of products of oligomerisation and/or co-oligomerisation of the unsaturated substrates and also of products of addition of the hydrogen chloride





formed in the cyclisation reactions. The structure of all the reaction products was consistent with a mechanism of electrophilic addition.[5]

With the exception of the reactivity ratio diphenylacetylene : *cis*-stilbene, which will be discussed later on, the data reported in the Table clearly show a comparable reactivity of phenyl-substituted olefins and acetylenes in our reaction conditions. The analogy with the relative reactivity values reported by Yates *et al.*[3a] for the hydration of similarly substituted unsaturated compounds, where ratios $\underline{k}_{\text{olefin}}/\underline{k}_{\text{acetylene}}$ in the range of 0.65–1.5 were found, would suggest a similar behaviour of the proton and of carbonium ions. However, the coincidence between the two series of results might be fortuitous, since they were obtained in media of very different polarity. In fact, the proton addition was carried out in aqueous sulphuric acid;[3a] in this case, the similar reactivity of double and triple bonds was mainly imputed to differential solvation of the intermediates. This interpretation cannot be applied to our carbonium ion additions, which indicate that acetylenes may be as reactive as olefins also in a weakly polar medium. In our system, therefore, other factors are implicated in the equalisation of reactivity. As a matter of fact, recent work from this laboratory[6] has shown that also in the proton addition solvation effects are unlikely responsible for the equalisation of reactivity of double and triple bonds.

A steric factor, related to the size of the carbonium ion used as an electrophile, is probably responsible for the unusually low[7] reactivity of *cis*-stil-

TABLE

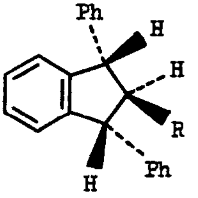
Results of the competition reactions

Substrates	Reagent ratio [a]	Acetylene adducts [%]	Olefin adducts [%]	Reactivity ratio [b]
$\frac{PhC\equiv CPh}{\textit{trans}\text{-}PhCH=CHPh}$	1:5:5	(VIII)[74.7] + (X)[1.4]	(XII)[23.9]	3.2
	1:5:10	(VIII)[60.0] + (X)[0.3]	(XII)[39.7]	3.0
$\frac{PhC\equiv CPh}{\textit{cis}\text{-}PhCH=CHPh}$	1:5:5	(VIII)[94.7] + (X)[5.3]	not detectable	==
	1:1.2:11.3	(VIII)[*ca*.92]+(X)[*ca*.5]	(XII) [*ca*.3] [c]	> 300
$\frac{PhC\equiv CMe}{\textit{trans}\text{-}PhCH=CHMe}$	1:5:5	(IX)[20.6] + (XI)[14.4]	(XIII) [65.0]	0.5
	1:9:4.5	(IX)[25.1] + (XI)[21.6]	(XIII) [53.3]	0.4
$\frac{PhC\equiv CMe}{\textit{cis}\text{-}PhCH=CHMe}$	1:2:2	(IX)[44.0] + (XI)[33.8]	(XIII) [22.2]	3.5
	1:3.7:5.5	(IX)[33.2] + (XI)[36.5]	(XIII) [30.3]	3.4

[a] Ratio diphenylmethyl chloride : acetylene : olefin (approximate figures). [b] Calculated on the actual amounts of reagents used. [c] Formed at the estimated limit of detection of the NMR spectrum of the mixture of adducts.

bene (V). In our conditions (V) was found at least 100 times less reactive than *trans*-stilbene (IV). An analoguous reactivity ratio was reported in the literature by Brackman and Plesch[8] in a study on the cationic oligomerisation of stilbenes in hydrocarbon solvents; *cis*-stilbene was found more reactive than *trans*-stilbene in the initiation step (corresponding, in the conditions used, to the addition of a proton) and *ca*. 100 times less reactive in the propagation step (corresponding to the addition of a protonated stilbene, *i.e*,, of a 1,2-diphenylethyl carbonium ion). This was mainly imputed to steric inhibition of resonance in the carbonium-ion addition transition state of *cis*-stilbene. An explanation of this kind may account also for our addition reactions, where repulsive interactions between the bulky diphenylmethyl group and the phenyl groups of the stilbene moiety may as well be presumed. This is indirectly confirmed by the results obtained in the addition to 1-phenylprop-1-enes (VI) and (VII), where a diminished steric crowding decreases the difference in reactivity between the two isomers.

Besides the reactivity data, we wish to point out another interesting feature of our addition reactions, which indicates that both *cis* and *trans* olefins react via an identical intermediate. We have noticed the stereospecific formation, both in the addition to stilbenes and to 1-phenylpropenes, of the same geometrical isomer of 1,2,3-triphenylindane (XII) and 1,3-diphenyl-2-methylindane (XIII) respectively. On the basis of their NMR spectra and by comparison with the other isomeric indanes, synthesised independently,[9] to indanes (XII) and (XIII) the *trans*-*trans* configuration (XIV) was assigned.



(XIV)

R = Ph, m.p. 125-126°

R = Me, m.p. 91-92°

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9. A full account of the synthesis and of the determination of configuration of all the isomeric indanes corresponding to structures (XII) and (XIII) will be given in a forthcoming publication.