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METALLATION-SILYLATION AND KINETIC STUDIES OF ARYLMETHYLACETYLENES

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Summary

Arylmethylacetylenes, $XC_6H_4C{\equiv}CCH_3$, have been metallated with an excess of n-butyllithium in diethyl ether at 0°C. By quenching the metallation mixtures with trimethylchlorosilane at different times, mono-, di- and tri-silyl derivatives have been isolated. Pseudo-first order rate constants for the monometallation were calculated from the rate of formation of the silylated products. A Hammett plot gave $\rho = 1.3$, indicating moderate delocalization into the aromatic ring, of the negative charge developed at the propargylic carbon during the metallation.

Introduction

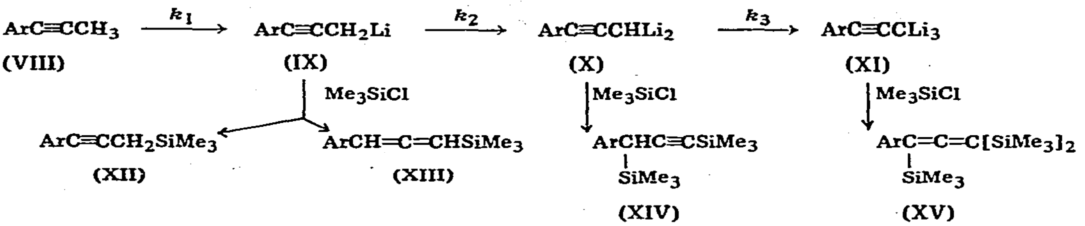
Metallation is one of the most important methods for introducing functional groups into molecules [1,2]. However, little is known about the kinetics of lithiation of hydrocarbons and this may be attributed to some difficulties in handling organolithium compounds and to their structural complexity. They are known to form aggregates [3,4] which are solvent, concentration and temperature dependent. Moreover, in certain cases, the active components are not the parent entities but species formed from them by dissociation, as indicated by fractional order dependence on the alkyllithium compounds [4—6].

Kinetic studies have been reported for the metallation of acidic hydrocarbons, such as fluorene [5,6], triphenylmethane [4,7] and phenylacetylenes [8], but none for hydrocarbons of relatively low acidity.

Results and discussion

Internal acetylenes are known to undergo facile metallation in the propargylic position [9—11]. This paper reports a study of substituent effects on the rate of monometallation by n-butyllithium of the arylmethylacetylenes; 1-phenyl- (I), 1-(*p*-methoxyphenyl)- (II), 1-(*p*-methylphenyl)- (III), 1-(*m*-methylphenyl)- (IV), 1-(*o*-methylphenyl)- (V), 1-(*p*-chlorophenyl)- (VI) and 1-(*m*-chlorophenyl)-1-propyne (VII). As shown in Scheme 1, mono-, di- and tri-metallation took place. The lithiated intermediates yielded mono-, di- and tri-silyl products after quenching with trimethylchlorosilane. Structural assignments for the silylated products are based on elemental analysis and spectroscopic data (NMR and IR).

SCHEME 1



The product distribution varied with the substrate. All substrates gave the monosilyl and disilyl derivatives, XII and XIV. The second type of monosilyl compound, XIII, was obtained only from the metallation-silylation of I and V. Substrates I—III and VI yielded the trisilyl product XV, after about one hour of metallation. No trisilyl product was obtained from IV, V and VII, even after 4 h of metallation.

Compounds I—VII were metallated with an excess of n-butyllithium in diethyl ether at 0°C. The rate of the monometallation was determined by monitoring both the disappearance of the substrate and the formation of the silylated products, the silylation being much faster than the metallation. We found no significant difference between the pseudo-first order rate constants for the first metallation step determined in these two ways. However, monitoring the rate of formation of the products has the advantage, that in most cases we could follow the reaction until just before the onset of dimetallation, whereas by the first method this is impossible. When the only products are from the monometallation the kinetics are simpler and fewer assumptions have to be made (see below). Aliquots were taken from the metallation mixtures at appropriate times and quenched with trimethylchlorosilane, and after work-up the samples were examined by gas chromatography (GLC). The metallation was followed to about 55% completion (10 to 30 min). Under these conditions, compounds IV—VII yielded monosilyl derivatives exclusively (though at longer reaction times the monolithio derivative was metallated further) and so for these substrates the following relation applies: $k_1[\text{VIII}] > k_2[\text{IX}]$. However, compounds I—III underwent dimetallation faster than monometallation, and all the product mixtures contained both mono- and di-silyl derivatives as well as trace amounts of trisilylated products. For these substrates $k_2[\text{IX}] > k_1[\text{VIII}]$. In the metallation of I—III, the total of all silylated products in each aliquot was used to give the rate constant for the monometallation. This may introduce some error which may be minimized if an excess of n-butyllithium is used and if one assumes that the reaction sequence of VIII → IX → X is consecutive and no disproportionation takes place (e.g., 2 $ArC{\equiv}CCH_2Li$ → VIII + X or the reverse reaction; no such disproportionation has been reported for the metallation of acetylenic compounds). Moreover, the fact that the points for I—III in the Hammett correlation (Fig. 1) show

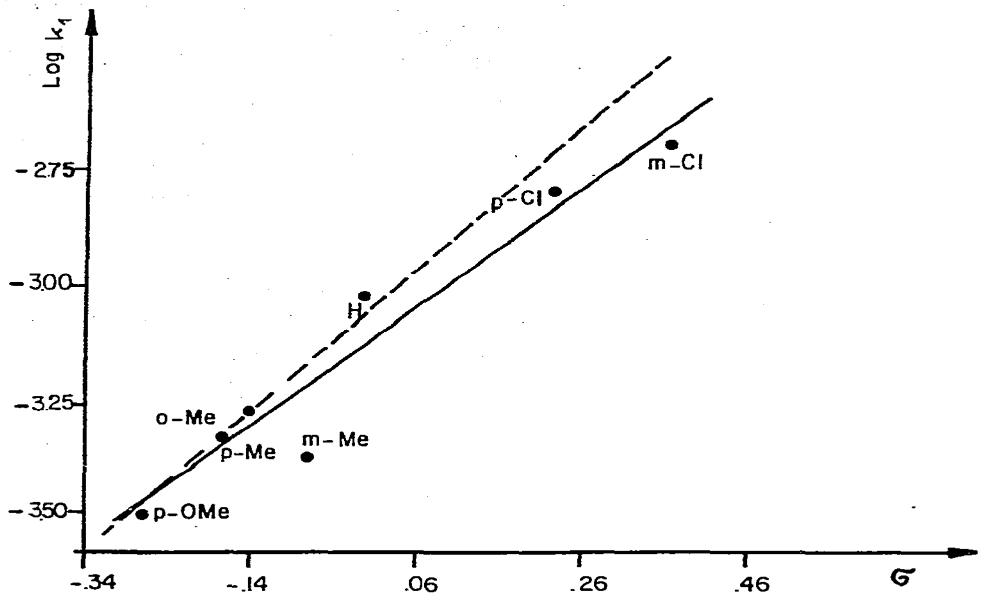


Fig. 1. Hammett σρ correlation for the metallation of I—VII with excess n-butyllithium in diethyl ether at 0°C. The dashed line corresponds to the points without the *meta* substituents.

a "tolerable" deviation, is consistent with our assumptions, and if a disproportionation reaction does exist it must be a minor one.

Pseudo-first order rate constant values (k_1) for the monometallation of I—VII are listed in Table 1. The reaction order with respect to the substrate was found to be unity and 0.5 with respect to the metallating agent [12].

A plot of log k_1 against Hammett σ-constants [13] * for the substituents of

TABLE 1

PSEUDO-FIRST ORDER RATE CONSTANTS (k_1) FOR MONOMETALLATION OF ARYLMETHYLACETYLENES [a]

	$XC_6H_4C{\equiv}CCH_3$ X	k_1 10^{+4} (sec^{-1})
I	H	10.9
II	*p*-OMe	3.1
III	*p*-Me	4.7
IV	*m*-Me	4.4
V	*o*-Me	5.3
VI	*p*-Cl	16.6
VII	*m*-Cl	19.5

[a] All rate-constant values have correlation coefficients higher than 0.98.

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* The *para*-substituents indicated in Fig. 1 have the same σ_p and σ_p values.

compounds I—VII is shown in Fig. 1. It is unlikely that *ortho* substituents can have any serious steric influence because of the geometry of the phenylmethylacetylene system. Eaborn and coworkers [14a] calculated σ_o-constants for several substituents in the phenylalkynyl system, from which a value of −0.14 was obtained for *o*-Me which was used in Fig. 1. However, the use of σ_o- with σ_m- and σ_p-constants in a simple plot was found to be limited [14a].

Fig. 1 illustrates that the substituent dependence on the rate of monometallation of arylmethylacetyles, I—VII, basically conforms to the Hammett equation though the deviation of points for the *meta* substituents suggests that more complex substituent effects may be operating. The observed ρ value of approximately 1.3 (for all substituents) indicates a small amount of carbanionic character in the transition state and suggests that activation is primarily due to the ethynyl group. Excluding the two *meta* substituents yields a ρ value of 1.52 (illustrated by dashed line in the Fig. 1) which does not significantly alter this conclusion. By comparison, the metallation of diphenylarylmethanes [7] gave higher ρ values (2.2—3.0). This result may be ascribed to the fact that such compounds are highly acidic and contain three aromatic rings which can conjugate with the carbon that undergoes metallation. Streitwieser and coworkers [15] measured the exchange rates of ring-substituted α-tritritiotoluenes and obtained a correlation with $\rho = 4.0$, a value which confirmed the relatively high degree of carbanionic character of the transition state. However, our results are in good agreement with Eaborn's studies in which similar ρ values were obtained for base-catalyzed hydrogen-exchange of substituted phenylacetylenes and terminal acetylenes [14].

Experimental

Metallation with n-butyllithium and subsequent silylation

A solution of n-butyllithium in hexane (Foote Mineral Co.) was titrated with sec-butanol in xylene [16]. A measured amount of this solution was introduced in a flask equipped with a T-stopcock and a rubber-capped side arm, in an argon atmosphere. The solvent was evaporated in vacuo and an equivalent amount of

TABLE 2

DATA ON THE PREPARATION OF ARYLMETHYLACETYLENES (II—VII) [a]

XC_6H_4Br X	$ArCH_2C{\equiv}CH$ yield (%)	$ArCH{=}C{=}CH_2$ yield (%)	catalyst/substrate (molar ratio)	Isomerization period (h)	$ArC{\equiv}CCH_3$ yield (%)	B.p. at 25 mmHg (°C)
p-OMe	42	29	1 : 4	20	II 40	85—90
p-Me	54	31	1 : 4.6	17	III 55	80—90
m-Me	24	24	1 : 1	18	IV 30	80—85
o-Me	54	28	1 : 6.4	17	V 17	85—90
p-Cl	25	25	1 : 3	30	VI 30	*b*
m-Cl	12	23	1 : 3	20	VII 30	*b*

[a] 0.1 mol of each aryl bromide was used for the Grignard reaction. The isomers ratio of the coupling products was estimated by NMR integration of the mixture (No attempt was made to optimize the yields in the isomerization reaction). [b] Separated by means of neutral alumina column, using hexane as eluent. They were prepared also by another method [18].

TABLE 3

ANALYTICAL AND SPECTROSCOPIC DATA

Compound	Formula	Found (calc.) (%)		Infrared ν (cm^{-1})
		C	H	
II	$C_{10}H_{10}O$	81.94 (82.19)	6.80 (6.85)	2025
III	$C_{10}H_{10}$	92.08 (92.30)	7.99 (7.70)	2260
IV	$C_{10}H_{10}$	92.76 (92.30)	7.78 (7.70)	2230
V	$C_{10}H_{10}$	92.01 (92.30)	7.82 (7.70)	2220, 2260
VI	C_9H_7Cl	^{a}		2220, 2260
VII	C_9H_7Cl	71.70 (71.76)	4.40 (4.65)	2260

[a] Analyzed by mass-spectroscopy, m/e 150, 152 (M^+).

anhydrous ether was added. The flask was then cooled to 0°C for about 20 min and only then was the substrate added by a syringe. The substrate concentration was 0.31 M and that of the butyllithium, 1.57 M. Aliquots were taken by a cooled syringe every 3—5 min and were quenched with 15 ml of a cold (5°C) solution of trimethylchlorosilane/ether (1 : 2 by volume). This operation resulted in the immediate precipitation of a white salt (LiCl). The reaction mixture was left, for several hours, at room temperature and then poured on ice water. The phases were separated and the organic layer examined by GLC, from which the rate of formation of the monosilyl products was followed. Preparative isolation of the silyl derivatives was accomplished on a 10% SE-30 column, 2 m × $\frac{1}{4}$" on Chromosorb W. Elemental analysis of all silylic derivatives was satisfactory.

Preparation of arylmethylacetylenes.

1-phenyl-1-propyne is a commercial product (Farchan Res. Co.) and used without further purification. Compounds II—VII were synthesized by reacting magnesium propargylbromide (prepared in anhydrous ether) with the corresponding arylbromide. The product mixture which contained two isomers, $ArCH_2C{\equiv}CH$ and $ArCH{=}C{=}CH_2$, was isomerized to $ArC{\equiv}CCH_3$ by using methylsulphinyl carbanion [17] in dimethylsulphoxide as catalyst. Table 2 describes conditions and yields for each step, to form substrates II—VII and Table 3 summarizes their analytical and spectral data.

Acknowledgment

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