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# THE RATES OF MONOMETALLATION OF ALKYLPHENYLACETYLENES

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## Summary

Alkylphenylacetylenes, $C_6H_5C{\equiv}CCH_2R$, have been metallated at the propargylic positions with an excess of n-butyllithium in diethyl ether at 0°C. Mono- and di-silyl derivatives have been isolated by quenching the metallation mixtures with $Me_3SiCl$ at different times. Pseudo-first order rate constants have been calculated for the monometallation from the rate of formation of the silylated products. A Taft correlation gives $\rho^* = 1.8$.

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## Introduction

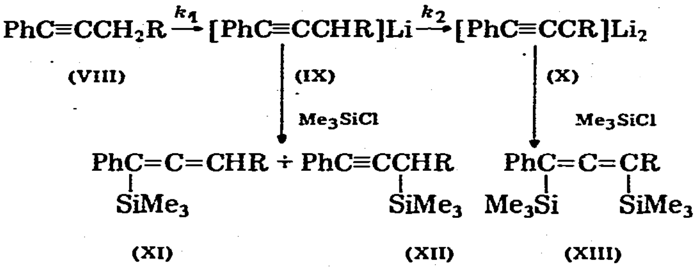
Metallation of acetylenic compounds have been studied extensively in the past decade. Kinetic studies on metallation of acidic hydrocarbons (e.g., terminal acetylenes [1,2], fluorene [3], triarylmethane [4]) have been reported, but little is known about hydrocarbons of relatively low acidity. Recently [5], we investigated the substituent effects on the rate of monometallation of arylmethylacetylenes and now we wish to report on the influence on the course of this reaction of alkyl groups attached to propargylic carbons.

## Results and discussion

Alkylphenylacetylenes namely 1-phenyl-1-propyne (I), -1-butyne (II), -1-pentyne (III), -1-hexyne (IV), -4-methyl-1-pentyne (V), -5-methyl-1-hexyne (VI) and -3-methyl-1-butyne (VII) were metallated with an excess of n-butyllithium in diethyl ether at 0°C. Mono- and di-metallo derivatives were formed, and yielded mono- and di-silyl products after quenching with $Me_3SiCl$ (Scheme 1). Structural assignments for the silylated products are based on elemental analysis, NMR and IR.

The rate of monometallation was determined by quenching with $Me_3SiCl$ and determination of the amount of the silylated products, the silylation being much

SCHEME 1



faster than the metallation. Aliquots were taken from the metallation mixtures at appropriate times, and after work-up the samples were examined by gas chromatography. The metallation was followed to about 45% completion (2—5 h). Under these conditions, compounds II—VII yielded monosilyl derivatives almost exclusively, though in some cases trace amounts of disilyl derivatives were detected. At longer reaction times the monolithio derivative was metallated further, and so for these substrates the rate of monometallation is faster than that of the dimetallation. However, compound I underwent dimetallation faster than monometallation, and in this case the total of all silylated products in each aliquot was used to calculate the rate constant for the monometallation. (this feature has been discussed [5]).

The product distribution varied with the substrate. All substrates gave the corresponding monosilyl derivative XI, but XII was obtained only from I—IV and VI. Substrates II—VI yielded the disilyl derivative of type XIII. However, only compound I yielded a different type of disilyl product, $PhCH(SiMe_3)C{\equiv}CSiMe_3$, instead of XIII.

Pseudo-first order rate constants values ($k_1$) for the monometallation of I—VII are listed in Table 1 *. A plot of $\log_{10}k_1$ against Taft $\sigma^*$ (polar) constants [6] of the alkyl groups is shown in the Fig. 1. In order to include the point for compound VII in the plot, the combined effect of R1 and R2, attached to the propargylic carbon, has been represented by the sum of their individual sigmas (Table 1). From a theoretical point of view, simple additivity is to be expected

TABLE 1

PSEUDO-FIRST ORDER RATE CONSTANTS ($k_1$) FOR MONOMETALLATION OF ALKYLPHENYLACETYLENES AND $\sigma^*$ (polar) VALUES OF THE ALKYL GROUPS

| | $C_6H_5C{\equiv}CCHR^1R^2$ | | $k_1 \times 10^{+2}$ (min$^{-1}$) | $\sigma^*$ $\sigma^*(R^1) + \sigma^*(R^2)$ |
|---|---|---|---|---|
| | $R^1$ | $R^2$ | | |
| I | H | H | 5.70 | 0.98 |
| II | H | Me | 0.47 | 0.49 |
| III | H | Et | 0.55 | 0.39 |
| IV | H | n-Pr | 0.40 | 0.375 |
| V | H | i-Pr | 0.11 | 0.30 |
| VI | H | i-Bu | 0.34 | 0.365 |
| VII | Me | Me | 0.10 | 0.0 |

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* The reaction order with respect to substrate was found to be unity.

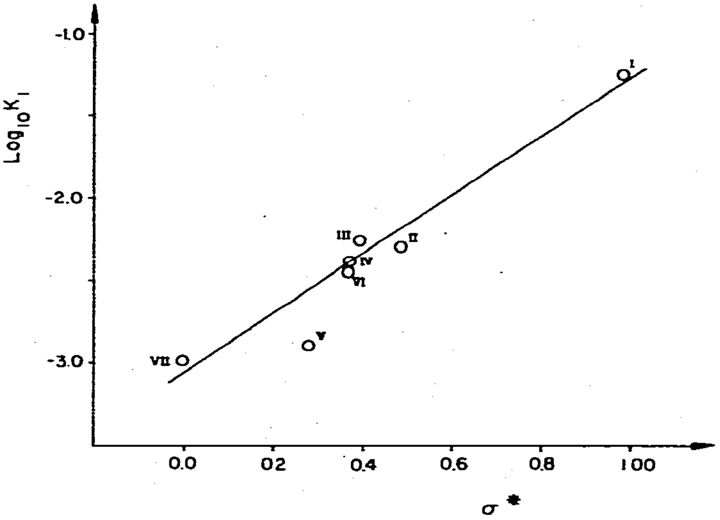
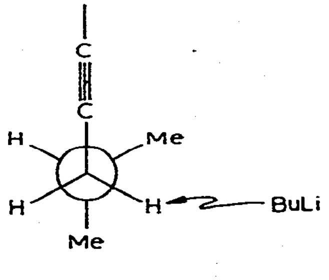


Fig. 1. $\sigma^*\rho^*$ correlation for the monometallation of alkylphenylacetylenes (I—VII).

for those reactions for which the $\sigma\rho$ correlation is linear and the interaction of the two substituents with each other is not changed by the reaction [7]. As shown in Fig. 1, the point for VII fits well the line, in spite of the "expected" steric interference between the methyl groups (see below). Figure 1 illustrates that the substituent dependence on the rate of monometallation of the studied alkylphenylacetylenes basically conforms to the "polar" Taft equation. It is generally accepted that the mechanism of the metallation involves an attack of the base at hydrogen rather than carbon and this provides a possible explanation to the "fitting" of compound VII in the general plot on one hand, and the deviation of the point corresponding to V on the other hand. The latter can be ascribed to steric hindrance between the attacking butyllithium and the methyls on the carbon adjacent to that from which the proton is abstracted (see XIV). This type of deviation is not unusual [8].



(XIV)

The observed $\rho^*$ value of 1.89 ± 0.28 indicates a moderate carbanionic character in the transition state, but greater than that found (1.3—1.5) for the monometallation of arylphenylacetylenes [5]. This difference can be attributed to the direct influence of the substituent at the reaction site, in the alkylphenylacetylenes. The results suggest that activation is primarily due to the ethynyl group. Excluding the point for V yields a better straight line with $\rho^* = 1.79 \pm 0.15$ (c.c. 0.987). It is noteworthy that Eaborn and coworkers obtained $\rho^* = 1.67$ for the base-catalysed hydrogen-exchange in substituted acetylenes [1b].

Recently, Charton reported [9] that the basic assumption of Taft in his separation of polar and steric effects is unwarranted. He has demonstrated that the electrical effects of alkyl groups are essentially constant, at least in the acid-catalysed esterification and base-catalysed hydrolysis. He claims that the rates of these reactions are solely a function of steric effects, and thus defines new steric-effect substituent constants ($\nu$), which are purely based on van der Waals radii and with no corrections concerning resonance and hyperconjugation effects. Therefore, it is of interest to examine application Charton's steric parameters on the monometallation of the alkylphenylacetylene system. A plot of $\log_{10}k_1$ against $\nu = \nu(R^1) + \nu(R^2)$ gives a worse straight line (c.c. 0.900) and a slope of $\psi = -1.51 \pm 0.33$. These results indicate that electrical effects cannot be ignored in our case, as in some others (e.g. [1b]).

## Experimental

*Metallation with n-butyllithium and subsequent silylation.* The general procedure was described previously [5]. The concentrations of 1.24 *M* of n-butyllithium and 0.3 *M* of substrate were used in all runs. Preparative separation of the silyl derivatives was on a 10% SE-30 column, 2 m × 1/4", on Chromosorb W. Elemental analysis of all silyl derivatives was satisfactory. The allenic absorptions of the monosilyl compounds in the infrared were in the region of 1930—1940 cm$^{-1}$, those of the allenic disilyl at 1895—1900 cm$^{-1}$, and those of the acetylenic derivatives at 2200—2300 cm$^{-1}$.

TABLE 2

BOILING POINTS, YIELDS AND ANALYTICAL DETAILS OF COMPOUNDS III—VII

| Compound | B.p. (°C/mmHg) | Yield (%) | Molecular formula | Analysis (%) | |
|---|---|---|---|---|---|
| | | | | C | H |
| III | 100—105/25 | 50 | $C_{11}H_{12}$ | 91.50<br>(91.66) | 8.49<br>(8.34) |
| IV | 110—120/25 | 60 | $C_{12}H_{14}$ | 90.90<br>(91.13) | 8.85<br>(8.87) |
| V | 120—130/15 | 25 | $C_{12}H_{14}$ | 91.48<br>(91.13) | 8.82<br>(8.87) |
| VI | 110—120/4.5 | 52 | $C_{13}H_{16}$ | 90.60<br>(90.70) | 9.15<br>(9.30) |
| VII | 95/25 | 31 | $C_{11}H_{12}$ | 91.82<br>(91.66) | 8.49<br>(8.34) |

*Preparation of alkylphenylacetylenes.* 1-Phenyl-1-propyne and 1-phenyl-1-butyne are commercially available (Farchan Res. Co.). Compounds III—VI were synthesized on a 0.1 mole scale by reacting the corresponding alkyl bromide with sodium phenylacetylide [10]. Compound VII was prepared by a different procedure [11], with tetrahydrofuran as solvent instead of dioxane. Analytical details of compounds III—VII are summarized in Table 2, together with their yields and boiling points.

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