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KINETICS OF NUCLEOPHILIC SUBSTITUTION AT AN ACETYLENIC CARBON

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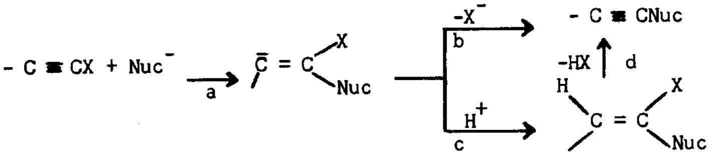
PREVIOUS attempts to effect nucleophilic substitution at an acetylenic carbon have usually failed.[1] On the Conant scale of reactivity of various organic chlorides towards potassium iodide in acetone at 60°, with chlorobutane taken as unity, phenylchloroacetylene was rated at zero.[2] Only recently has the possibility of the wide synthetic application of a-b of equation (1) been noted.[1]



(1)

We report here the first kinetic data on such a reaction

$$\underline{p} - C_7H_7S^- \, Na^+ + C_6H_5C \equiv CCl \xrightarrow{DMF} \underline{p} - C_7H_7SC \equiv CC_6H_5 + Na^+ \, Cl^- \quad (2)$$

Since the solvent was dimethylformamide (DMF), one must rule out the familiar addition-elimination sequence a-c of equation (1) which often renders equivocal the path of such substitutions.[1]

For a supposedly inert system, reaction 2 was extremely fast with a half-life of the order of several minutes at -25°. Rate measurements were made in thermostated batch reactors in which all operations up to the point

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[1] S.I. Miller, C.E. Orzech, C.A. Welch, G.R. Ziegler and J.I. Dickstein, J. Amer. Chem. Soc. 84, 2020 (1962); H.G. Viehe and E. Franchimont, Chem. Ber. 95, 319 (1962).

[2] M.J. Murray, J. Amer. Chem. Soc. 60, 2662 (1938).

of aliquot quenching could be done rapidly under nitrogen. The stoichiometry was established by product isolation and by the equivalence of the total chloride produced to the thiolate consumed. The reaction was clearly first order in phenylchloroacetylene and first order in sodium p-toluenethiolate. The rate data are summarized in Table 1.

TABLE 1

Rate Data for Equation (2)

Temperature ($\pm 0.1^\circ$)	$C_6H_5C \equiv CCl$ (mole l^{-1})	$\underline{p}$ - $C_7H_7S^- Na^+$ (mole l^{-1})	k ($l.mole^{-1} min^{-1}$)
-25.0	0.1218	0.0110	3.60
-25.0	0.2706	0.0078	3.65
-25.0	0.0598	0.0133	3.77
-35.0	0.1177	0.0129	1.28
-35.0	0.2354	0.0112	1.32
-45.0	0.2374	0.0121	0.436
-45.0	0.3561	0.0105	0.401

In order to have some standard of comparison, we also obtained kinetic data for the reaction

$$\underline{p} - C_7H_7S^- Na^+ + \underline{n} - C_4H_9Cl \xrightarrow{DMF} \underline{p} - C_7H_7SC_4H_9 - \underline{n} + Na^+ Cl^- \quad (3)$$

These data are given in Table 2.

Arrhenius activation energies for the phenylchloroacetylene and n-butyl chloride are 12.3 ± 1.0 and 14.5 ± 1.0 kcal/mole^{-1} respectively. The enhanced reactivity of an alkyl halide with a thiolate in DMF is now well established.[3] Previous reports on the reactions of a nucleophile with haloaromatics and haloalkenes have suggested the order of reactivity haloalkane$\gg$ halounsaturate.[4] That the phenylchloroacetylene should have a

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[3] A.J. Parker, J. Chem. Soc. 1328, 4398 (1961).

[4] S.I. Miller and P.K. Yonan, J. Amer. Chem. Soc. 79, 5931 (1957).

TABLE 2

Rate Data for Equation (3)

Temperature ($\pm 0.1^\circ$)	$\underline{n}$ - C_4H_9Cl (mole l^{-1})	$\underline{p}$ - $C_7H_7S^- Na^+$ (mole l^{-1})	k ($l.mole^{-1} min^{-1}$)
9.2	0.1345	0.00963	1.62
9.2	0.2690	0.00904	1.65
-1.0	0.1220	0.01175	0.72
-1.0	0.2710	0.00974	0.75
-12.2	0.2735	0.00995	0.248
-12.2	0.5470	0.00967	0.249

reactivity comparable to butyl chloride under any conditions is unusual;[1] that it has a greater reactivity appears to be unprecedented for any halo-unsaturate.

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