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ALKYLATION OF ALLYLIC CARBANIONS. DIRECTIVE EFFECTS

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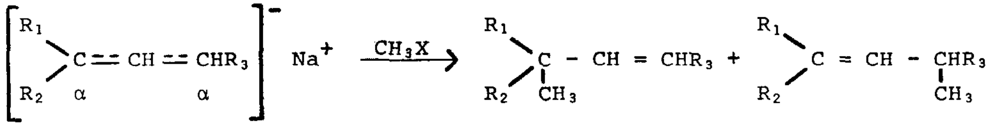
The alkylation of allylic carbanions provides a useful synthetic method.[1] However, a severe limitation is the concomitant formation of both isomers when an unsymmetrical substrate is used[1a,b] (Scheme).



(1) (2) (3)

(a) $R_1 = R_2 = C_6H_5$, $R_3 = H$

(b) $R_1 = C_6H_5$, $R_2 = R_3 = H$

(c) $R_1 = R_2 = C_6H_5$, $R_3 = CH_3$

Scheme

We now wish to report that not only does the nature of the carbanion but also the nature of the leaving group affect the orientation of such reactions. Carbanions (1a)-(1c) formed by the reaction between sodamide and the corresponding hydrocarbon in liquid ammonia were found to undergo smooth alkylation. The results of methylation correlate well with the order of hardness[2] of the leaving group $I < Br < Cl < SO_4 < OTs$. Thus as the hardness of the leaving group is increased a greater proportion of α-attack on the mesomeric anion (1) ensues. The importance of the steric requirements of the carbanion is underlined by the fact that alkylation of (1c) invariably occurred exclusively at the α-position. Trans-3,3-diphenylpent-2-ene only was formed.[3]

These and earlier[4] results emphasise the importance of the leaving group on C- *vs.* O- and mesomeric carbanion alkylations.

TABLE

$(1) + CH_3X \rightarrow (2) + (3)$

Carbanion	Leaving Group X	% Yield[a] (2) + (3)	% (2)[a,b]	% (3)[a,b]
(1a)	I	100	64.5	35.5
"	Br	99	89.6	10.4
"	Cl	98	92.7	7.3
"	SO_4	88	94.3	5.7
"	OTs[c]	78	95.8	4.2
(1b)	I	68[d]	90.5	9.5
"	Br	83[d]	97.2	2.8
"	Cl	82[d]	97.8	2.1
"	SO_4	80[d]	98.4	1.6
"	OTs[c]	84[d]	98.6	1.4

[a] Determined by g.l.c. on a Perkin-Elmer F11 using a 1/8" x 10' column packed with 5% SE 30 on Chromosorb W. [b] Confirmed by n.m.r. [c] OT_s = $OSO_2C_6H_4$-CH_3-p. [d] Mass balance consisted of dimethylated-(1).

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2. R. G. Pearson, J. Amer. Chem. Soc., 85, 3533 (1963).

3. τ 2.8 (10H, m, $2C_6H_5$), 4.1 (1H, dd, J_{AB}15 Hz, H_A), 4.85 (1H, dq overlapping, J_{AB}15 Hz, H_B), 8.38 (3H, s, CH_3), and 8.48 (3H, d, $J_{AX} + J_{BX}$ 5 Hz, CH_3, X_3).

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