Free-radical Chloroalkylation of Olefins

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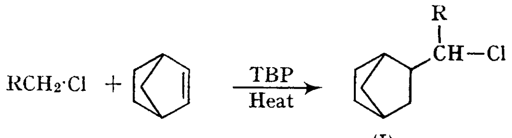
WE report a direct, one-step procedure for the chloroalkylation of olefins. Under free-radical conditions essentially analogous to earlier polyhalogenoalkane additions,[1,2] monochloroalkanes bearing at least one α-hydrogen are brought into reaction with olefinic substrates. In order to minimize higher telomerization, a substantial excess of the chloroalkane addend is necessarily maintained.

Thus, chloromethane (23·4 moles), norbornene (0·30 mole) and di-t-butyl peroxide (0·07 mole) were heated at 130°C for sixteen hours in an autoclave (850 p.s.i.). *exo*-2-(Chloromethyl)norbornane (Ia) was obtained in 48% yield as the only isolable adduct. A mixture of higher telomers constituted the remainder of the reaction product. Compound (Ia) was identified by n.m.r. spectroscopy (doublet with $J = 8$ c./sec. centred at τ 6·73, assigned to the chlorine-adjacent methylene protons; no methyl proton signal) and dehydrochlorination to the known 2-methylenenorbornane.



(I)

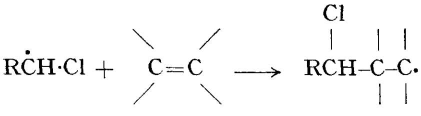
(a) R=H; (b) R=Me

(TBP=di-t-butyl peroxide)

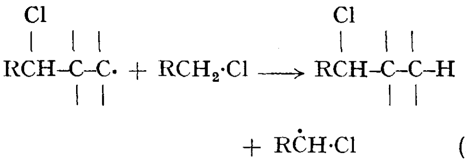
In similar fashion, chloroethane was added to norbornene to afford *exo*-2-(1-chloroethyl)norbornane (Ib) in 40% yield, and chloromethane was condensed with oct-1-ene to give 1-chlorononane in 23% yield.[3] Reactions of chloromethane with other olefins gave analogous adducts, each ultimately a product of chloromethylation.

These results are consistent with a free-radical chain reaction of short kinetic chain length, in which the initiation step and the principal propagating steps are (i—iii). That the α-hydrogen atom and not the chlorine was abstracted in the chain-transfer step reflects the ability of the chloro-substituent to provide resonance stabilization of the incipient radical,[4] apparently *via* interaction of the odd electron with the non-bonding *p*-electrons on chlorine.[5] A similar explanation may be advanced

$$RCH_2\cdot Cl + in\cdot \longrightarrow inH + R\underset{\bullet}{C}H\cdot Cl \qquad \text{(i)}$$



$$R\dot{C}H\cdot Cl + \;\rangle C{=}C\langle\; \longrightarrow RC\overset{\overset{Cl}{|}}{H}\text{–}\underset{|}{\overset{|}{C}}\text{–}\underset{|}{\overset{|}{C}}\cdot \qquad \text{(ii)}$$



$$RC\overset{\overset{Cl}{|}}{H}\text{–}\underset{|}{\overset{|}{C}}\text{–}\underset{|}{\overset{|}{C}}\cdot + RCH_2\cdot Cl \longrightarrow RC\overset{\overset{Cl}{|}}{H}\text{–}\underset{|}{\overset{|}{C}}\text{–}\underset{|}{\overset{|}{C}}\text{–}H + R\dot{C}H\cdot Cl \qquad \text{(iii)}$$

$$R\underset{\bullet}{C}H\text{–}Cl \longleftrightarrow \underset{-}{RCH}\text{–}\underset{+}{\overset{\bullet}{Cl}}$$

for the preference for attack at the α- rather than the β-hydrogen of chloroethane, although strictly inductive and electrostatic considerations would tend to favour attack at the primary C–H bond.[4]

Finally, it should be noted that these results, obtained at moderate temperatures and under forced liquid-phase conditions, are in contrast to recent vapour-phase studies (200—250°C), in which *both* chlorine and hydrogen atoms were abstracted from chloroalkanes by methyl radicals.[6]

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[1] M. S. Kharasch, E. V. Jensen, and W. H. Urry, *J. Amer. Chem. Soc.* 1947, **69**, 1100.

[2] For reviews, see J. I. G. Cadogan and D. H. Hey, *Quart. Rev.*, 1954, **8**, 308, and G. Sosnovsky, "Free Radical Reactions in Preparative Organic Chemistry," MacMillan, New York, 1964, p. 19 ff.

[3] In each instance, yields were based on the amount of olefin.

[4] J. M. Tedder, *Quart. Rev.*, 1960, **14**, 336.

[5] $D(ClCH_2\text{–}H)$ may be taken as 98 ± 1 Kcal./mole. *Cf.* L. A. Errede, *J. Phys. Chem.*, 1960, **64**, 1031; and G. Glockler, *ibid.*, 1959, **63**, 828.

[6] K. D. King and E. S. Swinbourne, *Austral. J. Chem.*, 1965, **17**, 121.