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Preliminary communication

A CONVENIENT DEHALOGENATION OF ORGANIC HALIDES VIA ORGANOZINC COMPOUNDS

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Summary

A simple, nonreductive procedure for the dehalogenation of organic halides to hydrocarbons is described, involving treatment with zinc in dimethylformamide followed by hydrolysis.

The replacement of halogen by hydrogen in an organic substrate is important in synthesis [1,2]. Generally the dehalogenation is brought about by reductive cleavage of the carbon—halogen bond with complex hydrides [3] or metal-amine [4] reagents. An alternative [5] involves hydrolysis of the derived organometallic reagents as exemplified in eqn. 1.

$$RX + M^0 \longrightarrow RMX \xrightarrow{H_2O} R{-}H + M(OH)X \quad (1)$$

Due to the predominance of organomagnesium reagents in synthesis and difficulty of preparing organozinc compounds, zinc has not been much used for dehalogenation; for instance, the preparations of organozinc compounds of the type RZnX or R_2Zn involve treatment of either activated zinc or the Zn—Cu couple with organolithium and organomagnesium compounds [6]. We now find that ordinary zinc powder reacts with a wide variety of alkyl halides in dipolar aprotic medium of dimethylformamide (DMF) [7] to furnish solutions of corresponding organozinc compounds. Aqueous decomposition of these solutions furnish the corresponding hydrocarbons in good yield, and provide a convenient method for dehalogenation of organic halides.

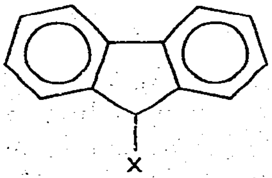
The procedure is illustrated by the conversion of the assorted halides (I) to (VI) into the corresponding hydrocarbons, with the results summarized in Table 1. The following procedure is representative. In a 100 ml round bottomed flask was placed 2.5 g of 1-bromocyclododecane (I) and 0.7 g of zinc dust and 30 ml of DMF. The mixture was stirred for 4 h at 130-140° (preferably under N_2) then was poured into 150 ml of water. The precipitate was filtered off by use of a sintered glass disc and washed with 50 ml of pentane. The filtrate was extracted with 50 ml

TABLE 1

ZINC-DMF DEHALOGENATION OF VARIOUS HALIDES

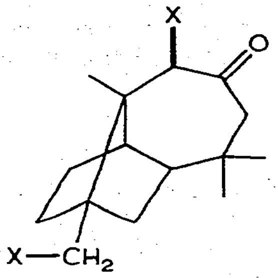
Starting halide	Time (h)/ Temp.(°)	Product(s)[a]	Yield (%)
1-Bromocyclododecane (I)[b]	4/130-140	Cyclododecane (VII)	65
2-Bromododecane (II)[b]	4/130-140	Dodecane (VIII)	50
Benzyl chloride (III)	4/120-130	Toluene (IX) and 1,2-Diphenylethane (X) (85/15)	45
Diphenylmethyl chloride (IV) (Benzhydryl chloride)	3/120-130	Diphenylmethane (XI) and 1,1,2,2-tetraphenylethane (XII) (70/30)	42
9-Bromofluorene (V)	4/130-140	Fluorene (XIII)	85
8,15-Dibromolongibornan-9-one (VI)[c]	10/95-100	Longibornan-9-one (XIV)	82

[a] All the products were characterized by spectroscopic comparison with authentic specimens. [b] The bromides (I) and (II) were prepared by addition of HBr—AcOH to 1-cyclododecene and 1-dodecene respectively. [c] This preparation will be reported elsewhere.



(V) X = Br

(XIII) X = H



(VI) X = Br

(XIV) X = H

pentane, the combined pentane solutions were washed with brine. Removal of solvent and crystallization from pentane gave 1.1 g (65%) of cyclododecane (VII), m.p. 59—60° (lit. [8] m.p. 60—61°).

The hydrocarbons (VII) to (XIV) in zinc dehalogenation are probably formed via the corresponding organozinc compound, as indicated by deuterium incorporation on quenching with deuterium oxide. The formation of dimeric products (X) and (XII) is reminiscent of the analogous behaviour of magnesium compounds [9-11].

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