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UNUSUAL REARRANGEMENT MECHANISM OF SUBSTITUTED β-CHLOROETHOXIDES

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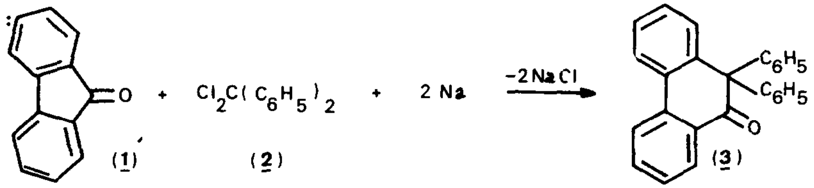
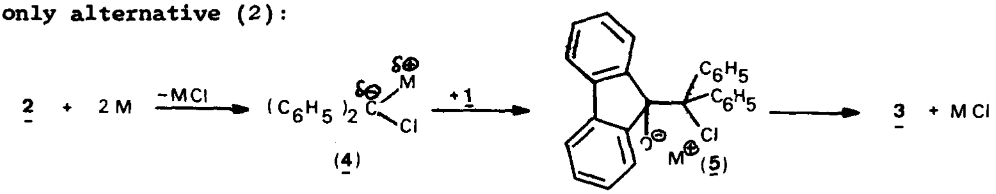
When equimolar amounts of fluorenone (1) and dichlorodiphenylmethane (2) in diethyl ether solution are allowed to react with two equivalents of sodium under an inert atmosphere, 10,10-diphenyl-9-phenanthrone (3) can be isolated in about 20% yield (1,2):

(A)



The earlier assumption (1) of a fluorenone anion as an intermediate has been ruled out by adding (2) to a solution of fluorenone anions in ether. No (3) was ever obtained. The intermediacy of a carbenoid, chlorodiphenylmethyl-sodium (4b, M= Na), is the only alternative (2):

(B)



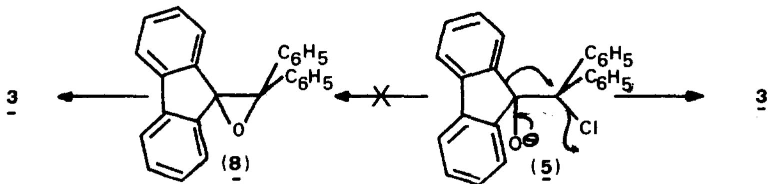
Careful work-up of the products of reaction (A) (M = Li, Na, K) showed that the yield of (3) was always within the range of 17-23% and that 10% of tetraphenylethylene (6) was invariably found as by-product. By using a 0.5 M concentration of (1) and (2) in the reaction mixture instead of 0.2 M, 4-5% of 1,1-diphenyl-2,2-diphenylenethylene (7) were found in addition to (3) and (6).

In order to gather more evidence in favour of (4) as an intermediate, diphenyl chloromethyl-lithium (4a, M = Li) was prepared at -100°C (3) in tetrahydrofuran (THF) and an equimolar ammount of fluorenone added. It was possible to isolate about 25% of (3) and 4-10% of (6). In a solvent mixture, similar to " Trapp's mixture " (4) of THF, diethyl ether and petroleum ether in a 4:2:1 volume ratio, about 5% of (7) was obtained in addition to 19% of (3) and 10% of (6):

The low temperature nucleophilic reactions of stable α-halogenoorgano-lithium solutions have been thoroughly investigated, mainly by Köbrich et al. (for reviews see ref. 5).

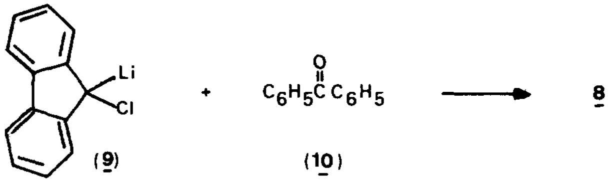
We were able to prove the mechanism of the rearrangement of the β-chloroethoxide (5) to the ketone (3) to be a one step concerted process, and that (8) is not an intermediate, as oxiranes usually appear to be (5) in similar reactions:

(C)



For this purpose, we prepared 9-chloro-9-fluorenyl-lithium (9) at low temperature, and added benzophenone (10). We obtained a 35% yield of (8) and no (3) at all This result rules out effectively (8) as an intermediate, and with it the two step mechanism for this case:

(D)



The formation of alkene (7) is explained by a further chlorine-metal interchange reaction undergone by (5) whenever its lifetime is increased by decreasing lithium solvation (hence oxygen nucleophilicity). This is the predictable effect of the above reported concentration and solvent changes (6).

The base catalyzed single-step rearrangement (C) seems to be a very rare occurence. The electrophilically (Ag^+) catalyzed rearrangement of iodohydrines occurs on the contrary very easily (7) and is thermally allowed according to the theory of sigmatropic rearrangements, if it has a carbenium-ion as intermediate.

Mechanism (C) in an electron-rich system should be the more difficult, the more the transition state differs from a carbenium-ion (the more the negative charge on oxygen pushes electrons and the less the chlorine anion is pulled away by the metal cation).

This may be the explanation, why the addition of chlorodiphenylmethyl-lithium 4a,M = Li) to cyclohexanone and tribenzotropone* yields the corresponding oxiranes instead of ketones and why its addition to α-tetralone yielded only 2-3% of α, α-diphenylbenzosuberone.

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