A Base-catalyzed Elimination from 4-Phenylbenzhydryl Thiocyanate to give 4-Phenylthiobenzophenone

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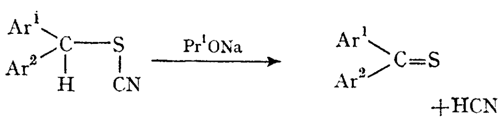
BASE-PROMOTED elimination of HX (where X is an electronegative atom or group) from two adjacent carbon atoms is well known, and the mechanism of such eliminations has been described.[1] However, so far as we are aware, the base-promoted elimination of HX from sulphenic systems, >CH·SX, to give thioaldehydes or thioketones, has not previously been reported. We report such an elimination, brought about by sodium isopropoxide in isopropyl alcohol, from 4-phenylbenzhydryl thiocyanate, a sulphenic cyanide, to give 4-phenylthiobenzophenone.



[Ar^1=Ph; Ar^2=p-C_6H_5–C_6H_4–]

To check the stoicheiometry of the reaction the following experiment was performed. Isopropyl alcohol solutions of 4-phenylbenzhydryl thiocyanate and sodium isopropoxide were mixed under a nitrogen atmosphere. A dark blue colour immediately appeared (absorption maxima at 603 mμ and 345 mμ) while cyanide ion was simultaneously produced. Authentic 4-phenylthiobenzophenone prepared from the oxygen analogue,[2] and purified by chromatography on silica gel,[3] showed the same absorption maxima (in isopropyl alcohol ϵ_{603} = 232; ϵ_{345} = 17,000).[4] Analysis of solutions after reaction showed a quantitative yield of thioketone (100%, by its absorption spectrum) and cyanide ion (94%, by bromine titration[6]).

The kinetics of elimination[7] follow a second-order rate equation as shown by the data in the Table, where the rate constants are reported for a number of concentrations of substrate and base. The data allow two significant observations: (a) the rate of elimination is extremely high; (b) the hydrogen isotope effect, $k_H/k_D = 3{\cdot}1$, although a primary one, is considerably lower than that calculated[8] for an intermediate proton transfer between carbon and oxygen in the transition state, $k_H/k_D = 7{\cdot}09$.

Elimination reactions leading to multiple-bond formation between carbon and a hetero-atom normally occur more readily than the corresponding olefin-forming eliminations and the factors responsible for the higher rate have been discussed by Hine.[9] In our system, high reactivity is particularly favoured by the presence of two α-aryl groups, which stabilize the negative charge on carbon by inductive and resonance effect, as

TABLE

Second-order rate constants for 4-phenylthiobenzophenone formation in isopropyl alcohol at 20°C [a]

$Ar^1Ar^2CH\cdot SCN$, M × 10^3 ..	2·08	1·78	1·39	0·98	1·38	1·33	1·33	2·58[b]	2·58[b]
Pr^iONa, M × 10^3	1·79	3·29	4·50	4·65	5·06	5·59	6·34	3·83	5·14
k_2, M^{-1} sec.$^{-1}$	13·4	13·5	13·5	13·4	13·5	13·8	13·1	4·23	4·32

[a] All runs carried out under a nitrogen atmosphere.
[b] 4-Phenyl-[α-^{2}H]benzhydryl thiocyanate.

well as by the α-sulphur atom which does the same mainly through *d*-orbital resonance effects.

The kinetic isotope effect, although indicating carbanion character of the transition state,[1b] does not provide clear-cut evidence either of the intermediacy of a carbanion or of a concerted elimination process. Carbanion trapping experiments and stereochemical studies are in progress in order to allow a choice between these two possibilities.

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[1] For recent Reviews on this subject, see: (a) D. V. Banthorpe, "Elimination Reactions", Elsevier, London, 1963; (b) J. F. Bunnett, *Angew. Chem.*, 1962, **74**, 731.

[2] H. Standinger and H. Freudenberger, *Ber.*, 1928, **61**, 1576.

[3] R. H. Abeles, R. F. Hutton, and F. H. Westheimer, *J. Amer. Chem. Soc.*, 1957, **79**, 712.

[4] A slightly lower extinction coefficient at 603 mμ has been previously reported (ref. 5).

[5] G. Sartori and C. Furlani, *Ann. Chim.* (*Italy*), 1954, **44**, 95.

[6] G. Charlot and D. Bezier, "Quantitative Inorganic Analysis", Methuen, London, 1957, p. 380.

[7] The appearance of a thioketone was followed by recording the increase in optical density at 603 mμ with a DB Beckmann spectrophotometer.

[8] F. H. Westheimer, *Chem. Rev.*, 1961, **61**, 265.

[9] J. Hine, "Physical Organic Chemistry", 2nd edn., McGraw-Hill, New York, 1962, pp. 206—208.