The Reaction of Enamines with Carbon Tetrachloride: a Synthesis of α-Dichloromethylene Ketones

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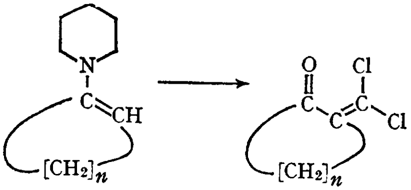
WE report a novel and general procedure for the preparation of α-dichloromethylene ketones which involves the alkylation of enamines with carbon tetrachloride.

Treatment of one equivalent of an enamine with a large excess of carbon tetrachloride at 60—75° for 20—28 hr. in diffuse light or total darkness under a nitrogen atmosphere, in the presence of 2 equivalents of triethylamine as a scavenger for hydrogen chloride,[1] affords 1·5—2·0 equivalents of triethylamine hydrochloride. The triethylamine hydrochloride is removed and the dark solution is stirred with water for 1—10 hr. The organic phase is separated, diluted with ether and extracted with dilute hydrochloric acid. Steam distillation of the combined aqueous phases affords the α-dichloromethylene ketone (Tables 1 and 2). The reaction appears to be general for enamines from alicyclic and cyclic ketones. For example, cyclopentanone morpholine enamine is converted into 2-dichloromethylenecyclopentanone in 70% yield. The structure of the ketone[2] was demonstrated by spectral analysis and by catalytic hydrogenation, over a 5% palladium on carbon catalyst, to 2-methylcyclopentanone in 61% yield.

TABLE 1

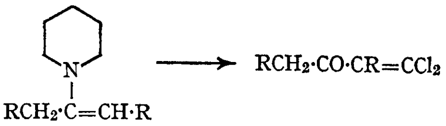


Cylic α-dichloromethylene ketones

n	% Yield		λ_{max} (ϵ) [in EtOH]
3	70	m.p. 49—50°	256 (13,820)
4	23[a]	b.p. 70—72° (0·8 mm.)	248 (5,260)
6	8	b.p. 84—86° (0·75 mm.)	248 (2,050)
10	22	m.p. 25—26°	248 (3,630)

[a] 2-Chloromethylenecyclohexanone (J. Wolinsky, D. Chan, and R. Novak, *Chem. and Ind.*, **1965**, 720) is an important by-product in this reaction.

TABLE 2

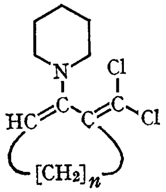


Alicyclic α-dichloromethylene ketones

R	% Yield		λ_{max} (ϵ) [in EtOH]
Me	31	b.p. 40—44° (1·4 mm.)	244 (3,490)
Et	31	b.p. 47—50° (1·2 mm.)	244 (3,340)

Although the yield of the α-dichloromethylene ketone is generally low the procedure is still of great synthetic utility because the starting materials are readily available and other synthetic routes[3] do not lend themselves to the production of these compounds.

Finally, it is of interest to note that enamines of type (I) can be isolated from the enamine–carbon tetrachloride reaction mixture prior to the hydrolytic work-up. Direct alumina chromatography of the solution from the reaction of cyclohexanone piperidine enamine and carbon tetrachloride gave, with pentane, an unstable oil whose spectral properties, λ_{max} (iso-octane) 236 mμ (ϵ 6,200), broad multiple δ 1·42—2·0 (8H, CH_2), triplet δ 2·18 (2H, $-CH_2-C{=}C-$), multiplet δ 2·28—2·85 (6H, $-CH_2-C{=}C-$ and $-CH_2-N-CH_2-$) and triplet δ 4·94 (1H, $-CH{=}C-$); and conversion into the 2,4-dinitrophenylhydrazone derivative of 2-dichloromethylenecyclohexanone, m.p. 176—178°, established its constitution as 3-dichloromethylene-2-piperidinocyclohex-1-ene. In similar fashion, 3-dichloromethylene-2-piperidinocyclododec-1-ene was obtained from 1-piperidinocyclododec-1-ene and carbon tetrachloride. The twelve-membered-ring enamine derivative is stable and very resistant to hydrolysis. Prolonged heating with 5% hydrochloric acid partly converted it into 2-dichloromethylenecyclododecanone, the remainder being accounted for as the hydrogen chloride salt of the enamine.



(I)

A discussion of the mechanistic details of the enamine-carbon tetrachloride reaction is reserved for a later publication.

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[1] A solution of 1-piperidinocyclohex-1-ene in carbon tetrachloride begins to deposit a white solid, identified as 1-piperidinocyclohex-1-ene hydrochloride, in a matter of seconds. The precipitation of the hydrochloride is complete in 4 days at room temperature and in *ca.* 20 hr. at 70°. Triethylamine does not react with carbon tetrachloride to an appreciable extent under these conditions. For light- and copper-catalyzed reactions of carbon tetrachloride with amines see: R. W. Foster, *Chem. and Ind.*, 1957, 704; D. P. Stevenson and G. M. Copinger, *J. Amer. Chem. Soc.*, 1962, **84**, 149; G. Drefahl and G. Heublein, *J. prakt. Chem.*, 1963, **20**, 323, and references cited therein.

[2] Satisfactory elemental analyses and spectral data were obtained for the α-dichloromethylene ketones listed in Tables 1 and 2.

[3] J. Boeseken and P. Dujarden, *Rec. Trav. chim.*, 1913, **32**, 97; I. Heilbron, E. R. H. Jones, and M. Julia, *J. Chem. Soc.*, 1949, 1430; M. S. Kharasch, E. Simons, and W. Nudenberg, *J. Org. Chem.*, 1953, **18**, 328; A. Roedig and H. J. Becker, *Chem. Ber.*, 1956, **89**, 1726.