

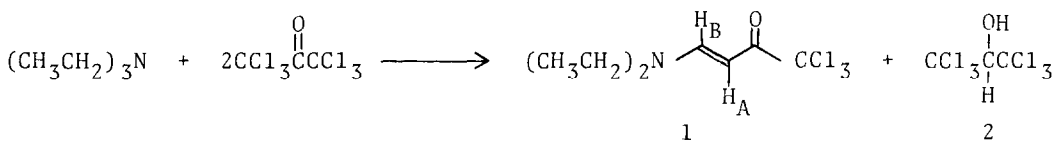
OXIDATION OF TERTIARY AMINES BY HEXACHLOROACETONE

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**Abstract:** Triethylamine and ethyldiisopropylamine are oxidized by hexachloroacetone. The vinyl dialkylamines are acylated by hexachloroacetone, a discussion of the mechanism is presented.

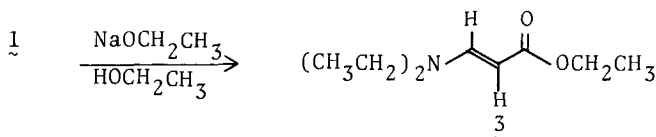
Hexachloroacetone has been reduced to hexachloroisopropylalcohol by dihydro-nicotinamide models in good yield.<sup>1</sup> Tertiary amines have been oxidized photo-chemically in the presence of suitable electron acceptors,<sup>2</sup> electrochemically, by trifluoroacetic anhydride,<sup>3</sup> and by one electron oxidants.<sup>4,5</sup> We now wish to report that simple tertiary amines are efficiently oxidized by hexachloroacetone and that the incipient enamines are acylated by excess hexachloroacetone.

In connection with another study we attempted to trichloroacetylate an amine using hexachloroacetone in the presence of triethylamine.<sup>6</sup> We found, however, that hexachloroacetone had reacted with triethylamine to form 1,1,1-trichloro(E)-4-(N,N-diethylamino)buten-2-one **1**, 80%, mp 55-56°C, and an equivalent amount of hexachloroisopropyl alcohol **2**. The structure was based on spectral and chemical

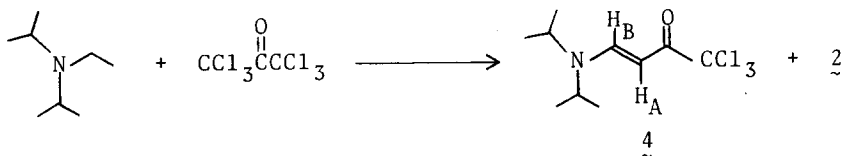


data. The <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of **1** showed δ 1.14 (3H, t), 1.23 (3H, t), 3.33 (2H, q), 3.43 (2H, q), 5.67 (H<sub>A</sub>, d, J<sub>AB</sub> = 12.5 Hz), 7.83 (H<sub>B</sub>, d, J<sub>AB</sub> = 12.5 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 11.6 (q), 14.6 (q), 43.3 (t), 51.1 (t), 84.8 (d), 98.3 (s), 155.5 (d), 180.8 (s); IR (CHCl<sub>3</sub>) 1660, 1570 cm<sup>-1</sup>; U.V. (CH<sub>3</sub>OH) λ<sub>max</sub> 330 nm, log ε<sub>max</sub> = 4.41; the mass spectrum was consistent with the assigned structure.<sup>7</sup>

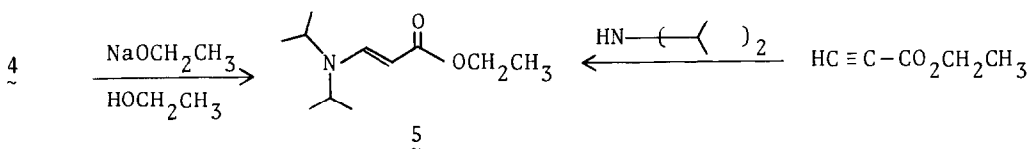
Further structural proof was obtained by conversions of **1** to the known<sup>7</sup> ethyl (E)-3-(N,N-diethylamino)-propenoate, **3**, 95%, on treatment of **1** with sodium ethoxide in ethanol. Hexachloroisopropyl alcohol was identified by comparison with an authentic sample prepared by lithium aluminum hydride reduction of hexachloroacetone.<sup>8</sup>



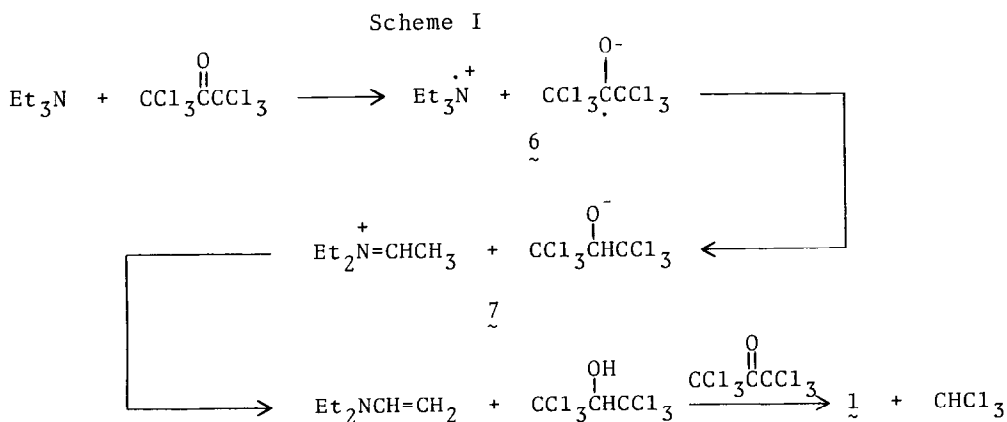
Similarly, ethyldiisopropylamine reacted with hexachloroacetone to produce 1,1,1-trichloro-(E)-4-(N,N-d-isopropyl)buten-2-one 4 65%, mp 131-132°C and hexachloroisopropyl alcohol. The spectral properties were consistent with the assigned structure.<sup>9</sup> Treatment of 4 with sodium ethoxide in ethanol provided ester 5 which was identical to an authentic sample prepared from ethyl propiolate and diiso-



propylamine.<sup>10</sup> No oxidation towards the isopropyl groups was observed.<sup>11</sup>

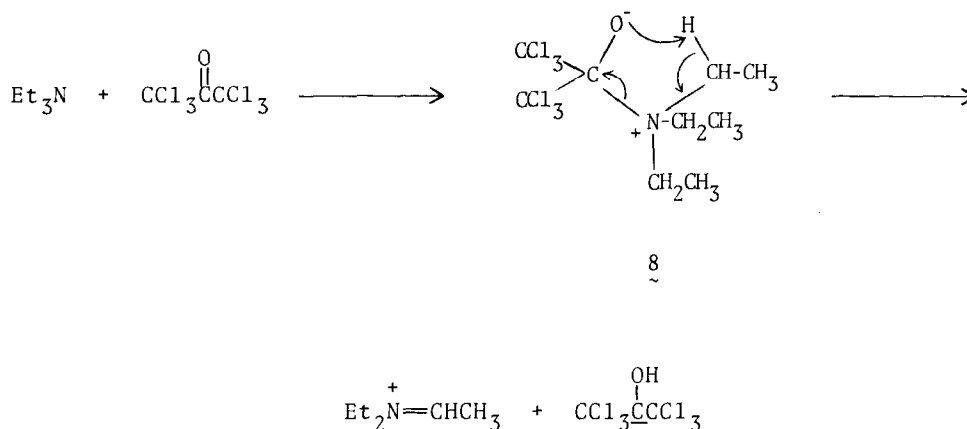


A plausible mechanism for the formation of 1 is presented in Scheme I. Electron transfer from triethylamine to hexachloroacetone would produce hexachloroacetone ketyl and the triethylamine radical ion pair, 6. Subsequent hydrogen



atom and proton transfer from triethylamine radical cation to the ketyl completes the redox step. Isomerization of the immonium salt, 7, to produce vinyl-diethylamine, followed by acylation with hexachloroacetone would result in trichloro-ketone 1. Dittmer has shown that tetramethyl-p-phenylenediamine gives the deep blue color of Würster's radical cation in the presence of hexachloroacetone.<sup>1c</sup> An alternate explanation (Scheme II) involves attack of triethylamine on hexachloroacetone to produce zwitterionic intermediate<sup>12</sup> 8 followed by collapse to produce iminium ion 7 and reduced hexachloroacetone. A direct hydride transfer from triethylamine to hexachloroacetone cannot be ruled out as a possibility.

Scheme II



The vinyl-diethylamine produced in this reaction was acylated by hexachloroacetone whereas cyclic enamines are chlorinated by hexachloroacetone.<sup>13</sup> Apparently the reaction between hexachloroacetone and enamines is sensitive to steric and electronic effects. We have observed that tertiary amines bearing  $\beta$ -alkyl substituents (eg. tri-n-propylamine) react with hexachloroacetone to give complex mixtures of products including hexachloroisopropylalcohol and penta-chloroacetone. The amine oxidation products were not identified.

In summary, we have shown that dialkylethylamines are oxidized by hexachloroacetone to produce  $\beta$ -trichloroacetyl-vinyl-dialkylamines. The trichloromethyl group was easily cleaved under haloform-type conditions. Further studies in this area are in progress.

#### References and Notes

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  9.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.30 (12H, d), 3.70 (1H, s) 4.00 (1H, s), 5.77 ( $\text{H}_A$ , d,  $J_{AB} = 12.0$  Hz), 7.93 ( $\text{H}_B$ , d,  $J_{AB} = 12.0$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ .  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  19.7 (q), 23.6 (q), 49.3 (d), 50.2 (d), 85.0 (d), 98.4 (s), 152.4 (d), 180.8 (s); IR ( $\text{CHCl}_3$ ) 1660, 1560  $\text{cm}^{-1}$ ; U.V. ( $\text{CH}_3\text{OH}$ )  $\lambda_{\text{max}}$  326 nm,  $\log \epsilon_{\text{max}} = 3.83$ ; mass spectrum was consistent.
  10. Equivalent amounts of diisopropylamine and ethyl propiolate were mixed at room temperature for 2 hours. Distillation of the contents at reduced pressure afforded ethyl (E)-3-diisopropylamino]propenoate, 90%, bp 108-109°C 0.35 mm.
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