

REACTIONS OF ENAMINES II: A NOVEL CONVERSION  
OF AN ENAMINOKETONE TO A CHLOROIMINIUM CHLORIDE

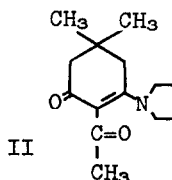
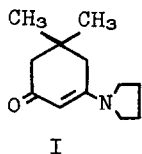
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ENAMINOKETONES have been shown to undergo both O-alkylation<sup>1</sup> and C-alkylation<sup>2</sup>. The only reported acylation of an enaminoketone involves O-acylation<sup>3</sup> as shown by hydrolysis of the intermediate iminium salt to the enol ester of a 1,3-diketone. We have found that reaction of 5,5-dimethyl-3N-pyrrolidylcyclohex-2-en-1-one (I) with acetyl chloride gave exclusively C-acylation to 2-acetyl-5,5-dimethyl-3N-pyrrolidylcyclohex-2-en-1-one (II), m.p. 158-159°,  $\lambda_{\max}^{\text{EtOH}}$  274 m $\mu$  ( $\epsilon$ , 13,300)



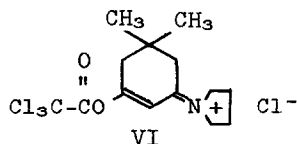
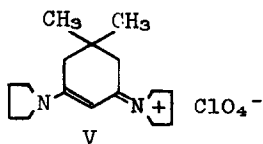
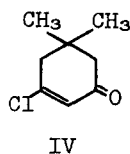
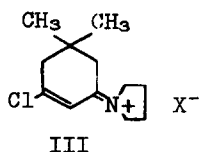
<sup>1</sup> N. J. Leonard and J. A. Adamcik, J. Amer. Chem. Soc. **81**, 595 (1959).

<sup>2</sup> N. K. Kochetkov, Izvest. Akad. Nauk SSSR., Otdel. Khim. Nauk **47** (1954).

<sup>3</sup> S. Hünig, E. Benzing and E. Lücke, Chem. Ber. **90**, 2833 (1957).

310  $\mu$  ( $\epsilon$ , 16,000), n.m.r. spectrum showed no vinyl hydrogen. (Found: C, 71.47; H, 8.73.  $C_{14}H_{21}NO_2$  requires: C, 71.45; H, 9.00%.)

In contrast to the above reactions, we now wish to report another mode of reaction of enaminketones. Treatment of I with trichloroacetyl chloride in benzene or carbon tetrachloride gave N-(3-chloro-5,5-dimethylcyclohex-2-en-1-ylidene) pyrrolidinium chloride (III,  $X = Cl^-$ ) as a hygroscopic solid, m.p. 168-170°,  $\lambda_{max}^{EtOH}$  274  $\mu$  ( $\epsilon$ , 25,000).



(Found: C, 57.99; H, 7.80; N, 5.54; Cl, 28.40.  $C_{12}H_{19}Cl_2N$  requires: C, 58.07; H, 7.72; N, 5.64; Cl, 28.57%.) which was readily converted to the stable perchlorate (III,  $X = ClO_4^-$ ), m.p. 187-188°,  $\lambda_{max}^{CHCl_3}$  272  $\mu$  ( $\epsilon$ , 27,000), n.m.r. spectrum showed presence of a vinyl hydrogen at 3.19  $\tau$ .

(Found: C, 46.13; H, 6.19; N, 4.55; Cl, 22.80.  $C_{12}H_{19}Cl_2NO_4$  requires: C, 46.16; H, 6.08; N, 4.49; Cl, 22.75%) by treatment of its aqueous solution with sodium perchlorate or perchloric acid. The structure of III is based on the U.V.

spectrum<sup>4</sup> and on the conversion of III on mild alkaline hydrolysis to the known 3-chloro-5,5-dimethylcyclohex-2-enone (IV) identical in physical properties with an authentic sample<sup>5</sup> and by comparison of their semicarbazones. Further evidence in support of III is smooth transformation of its perchlorate salt by the action of 1 mole of pyrrolidine in methanol to N-(5,5-dimethyl-3N'-pyrrolidylcyclohex-2-en-1-ylidene) pyrrolidinium perchlorate (V) identical with authentic material.<sup>1</sup>

The formation of III may be rationalized by assuming that the initial step in the reaction is the O-acylation of I by trichloroacetyl chloride to give the intermediate VI, followed by replacement of trichloroacetate by chloride ion. In support of this, treatment of I with tosyl chloride in benzene solution gave a hygroscopic salt from which III (X = ClO<sub>4</sub><sup>-</sup>) was obtained in good yield by treatment of its aqueous solution with perchloric acid or sodium perchlorate.

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<sup>4</sup> J. L. Johnson, M. E. Herr, J. C. Babcock, R. P. Holysz, A. E. Fonken, J. E. Stafford and F. W. Heyl, J. Amer. Chem. Soc. 78, 430 (1956) have reported  $\lambda_{\max}$  274-278 m $\mu$  ( $\epsilon > 20,000$ ) for ternary iminium salts of the type  $>C=C-C=N^+$ . See also G. Opitz and W. Merz, Liebigs Ann. 652, 139 (1962).

<sup>5</sup> A. W. Crossley and H. R. LeSueur, J. Chem. Soc. 83, 110 (1903).