**Addition of *sym*-Tetramethyldisiloxane to Hexene-1.**—*sym*-Tetramethyldisiloxane (100.5 g., 0.75 mole) was added slowly (1.25 hr.) to refluxing hexene-1 (134 g., 1.6 moles) containing $7.5 \times 10^{-5}$ moles of chloroplatinic acid. The reaction was noticeably exothermic. The mixture was kept at 140° for 4.5 hr. and distilled. The typical mixture of hexenes (17.1 g.) was recovered followed by 1,3-dihexyltetramethyldisiloxane (202 g., 90%), $n^{25}D$ 1.4265, $d^{25}_4$ 0.8154, $R_D$ 0.3142, calcd. 0.3157.

*Anal.* Calcd. for $C_{16}H_{38}OSi_2$: Si, 18.5. Found: Si, 18.6, 18.6.

This product was also converted to hexyltrimethylsilane as described; the properties are $n^{25}D$ 1.4132, $d^{25}_4$ 0.7378, $R_D$ 0.3379, calcd. 0.3382.

*Anal.* Calcd. for $C_9H_{22}Si$: Si, 17.7. Found: Si, 17.5, 17.9.

**Acknowledgment.**—The authors wish to express their appreciation to Robert Winger for assistance with analyses and to Joseph Cekada for making 1- and 2-hexyltrimethylsilanes.

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# Reactions of Enamines. IV. The Formation of Chloroiminium Salts from Certain Enamino Ketones[1]

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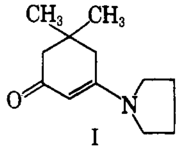
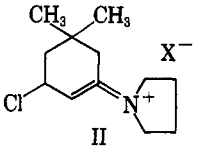
The reaction of enamino ketones with the acid chlorides of acids, the anions of which are also good leaving groups, or with phosphorus pentachloride, lead to chloroiminium salts. The proof of structure and mechanism of formation are discussed. A new synthesis of enamino ketones from β-chloro-α,β-unsaturated ketones is reported.

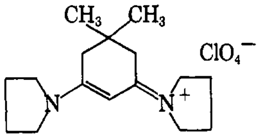
In our preliminary communication[2] it was shown that reaction of 5,5-dimethyl-3-N-pyrrolidylcyclohex-2-en-1-one (I) with trichloroacetyl chloride gave N-(3-chloro-5,-5-dimethylcyclohex-2-en-1-ylidene)pyrrolidinium chloride (II, X = Cl) as a hygroscopic solid readily converted to the stable crystalline perchlorate II (X = $ClO_4$). The structure of II was established by its ultraviolet spectrum[3] (see Table I) and by facile reaction of its perchlorate with 1 mole of pyrrolidine to give the known N-(5,5-dimethyl-3-N′-pyrrolidylcyclohex-2-en-1-ylidene)pyrrolidinium perchlorate (III).[4] Further proof of the structure of II was provided by hydrolysis. The chloroiminium salt II was found to be extremely stable to hydrolysis with aqueous mineral acids (the preferred method for the hydrolysis of iminium salts[5]). Mild alkaline hydrolysis, however, afforded the known 3-chloro-5,5-dimethylcyclohex-2-en-1-one (IV).[6]



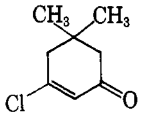
I



II

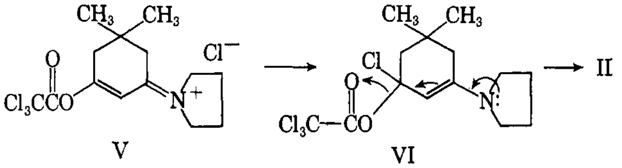


III



IV

It seemed to us, *ab initio*, that the formation of II must proceed by O-acylation of the enamino ketone I to the intermediate V.[7] Addition of chloride ion could then give VI from which the better leaving group (*i.e.*, trichloroacetate ion) would be eliminated.



It follows that the acid chloride of any acid, the anion of which is a good leaving group and a poor nucleophile, should undergo a similar reaction with I. To test this hypothesis, the enamino ketone I was heated with tosyl chloride in benzene solution. The hygroscopic salt, which was not fully characterized, gave II (X = $ClO_4$) in good yield when its aqueous solution was treated with perchloric acid or sodium perchlorate. In further support of our mechanism, picryl chloride underwent a similar reaction. Thus, reaction of I with picryl chloride in benzene solution, followed by treatment of the reaction mixture with water, afforded the picrate of the enamino ketone I and, as the minor product, the perchlorate II (X = $ClO_4$).

Indirect evidence for the reaction sequence is provided by reaction of I with diethylcarbamoyl chloride. It had been reported previously[8] that the enamino ketone I did not react with dimethylcarbamoyl chloride. While this may be true at lower temperatures, we have found that diethylcarbamoyl chloride reacts with I in refluxing chlorobenzene to give the N-(3-diethylamino-5,5-dimethylcyclohex-2-en-1-ylidene)pyrrolidinium salt (VII), isolated as the perchlorate VII (X = $ClO_4$) and characterized by comparison of its physical properties with those of authentic material.[4]

The formation of VII can be rationalized by assuming reaction of the enamino ketone I with diethylcarbamoyl chloride to give the O-acylated intermediate VIII which can add chloride ion. Compound IX can then collapse to the chloroiminium cation, carbon dioxide,

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[1] Part III: A. J. Speziale and L. R. Smith, *J. Org. Chem.*, **28**, 3492 (1963).

[2] G. H. Alt and A. J. Speziale, *Tetrahedron Letters*, 111 (1663).

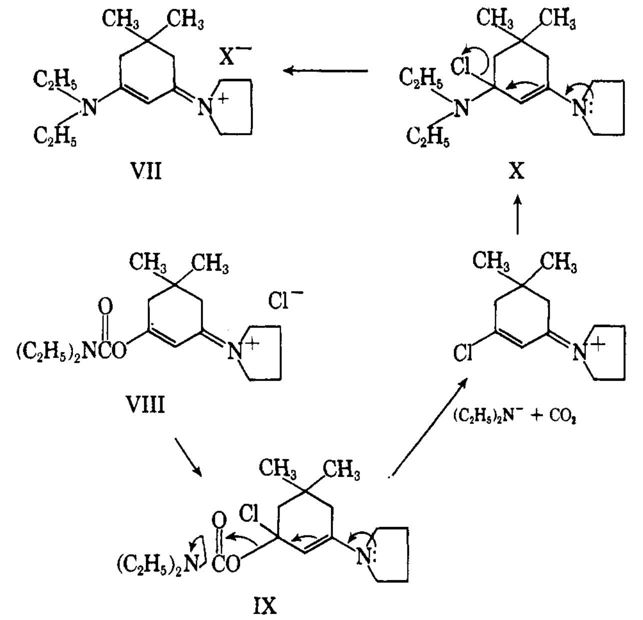
[3] J. L. Johnson, M. E. Herr, J. C. Babcock, R. P. Holysz, A. E. Fonken, J. E. Stafford, and F. W. Heyl [*J. Am. Chem. Soc.*, **78**, 430 (1956)] have reported $\lambda_{max}$ 274–278 mμ (ε >20,000) for ternary iminium salts of the type $>C{=}C{-}\overset{|}{C}{=}\overset{+}{N}<$; see also G. Opitz and W. Merz, *Ann.*, **652**, 139 (1962).

[4] N. J. Leonard and J. A. Adamcik, *J. Am. Chem. Soc.*, **81**, 595 (1959).

[5] *Cf. inter alia:* G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *ibid.*, **85**, 207 (1963).

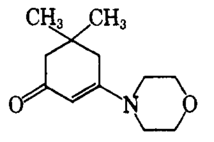
[6] A. W. Crossley and H. R. LeSueur, *J. Chem. Soc.*, **83**, 110 (1903).

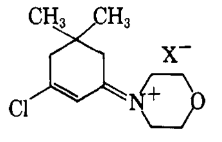
[7] S. Hünig, E. Benzing, and E. Lücke [*Ber.*, **90**, 2833 (1957)] have observed the O-acylation of enamino ketones.

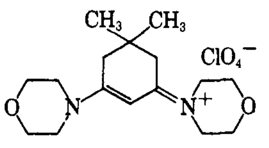


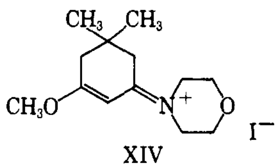
and diethylamine anion. Combination of cation and anion can give X, which is converted to VII by loss of chloride ion.

Since O-acylation is favored by pyrrolidine enamino ketones,[7,8] it seemed desirable to test the generality of our reaction by using the enamino ketone of a weaker base which would decrease the electron availability on oxygen. Treatment of 5,5-dimethyl-3-N-morpholinylcyclohex-2-en-1-one (XI) with trichloroacetyl chloride in carbon tetrachloride gave N-(3-chloro-5,5-dimethylcyclohex-2-en-1-ylidene)morpholinium chloride (XII, X = Cl) as a hygroscopic salt which afforded the stable crystalline perchlorate XII (X = $ClO_4$). The same perchlorate was obtained by reaction of XI with tosyl chloride in benzene solution and treatment of the salt obtained with perchloric acid. The structure of XII was proven by the conversion of its perchlorate with 1 mole of morpholine to N-(5,5-dimethyl-3-N′-morpholinylcyclohex-2-en-1-ylidene)morpholinium perchlorate (XIII), which was identical with an authentic sample prepared from XI *via* the methiodide XIV. As expected by analogy with the chloroiminium salt II, mild alkaline hydrolysis of XII (X = Cl) gave the chloro ketone (IV).


XI

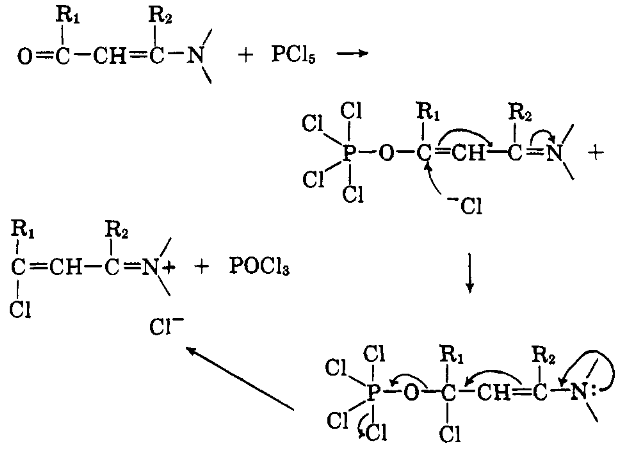

XII


XIII


XIV

An attempt was made to synthesize II and XII from the chloro ketone (IV) by treatment with the corresponding amines in benzenes olution. Instead of the chloroiminium salts there were obtained the hydrochloride salts of the enamino ketones I and XI, respectively, from which the enamino ketones could be obtained by treatment with base. This constitutes an alternative synthesis of enamino ketones which may be useful when they are not obtainable by conventional methods.

Finally it was found that the chloroiminium salts II and XII could be obtained in excellent yield by treatment of the corresponding enamino ketones (I and XI) with 1 mole of phosphorus pentachloride in refluxing benzene. As the enamino ketones may be regarded as vinylogous amides, the formation of the chloroiminium salts in this instance may proceed in a manner similar to the formation of amido chlorides by reaction of phosphorus pentachloride with N,N′-disubstituted amides.[9] At present, this method of preparation constitutes the best synthesis of chloroiminium salts.



All of the ultraviolet spectra (Table I) are entirely consistent with the structures assigned. However, a striking bathochromic shift of 9 ± 2 mμ was observed in the absorption maxima of the ternary iminium salts based on morpholine compared with those based on pyrrolidine. This shift was not observed in comparing the spectra of the enamino ketones I and XI or those of their hydrochlorides.[10]

In the n.m.r. spectra of compounds in Table I in deuteriochloroform solution the vinyl protons appear as sharp singlets. The position of the vinyl hydrogen varies considerably with the basicity of the amine, especially in the ternary iminium salts, in contrast with the position of the vinyl protons in enamines which are reported[5] to be essentially independent of the basicity of the amine.

## Experimental[11]

**5,5-Dimethyl-3-N-pyrrolidylcyclohex-2-en-1-one** (I) was prepared according to the procedure of Leonard and Adamcik[4] and gave yellow prisms, m.p. 129–132°, lit.[4] m.p. 131–133°. The compound formed a yellow picrate, m.p. 185–186° (from chloroform-methanol).

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(8) A. Brizzolara, Ph.D. thesis, Columbia University, 1960.

(9) (a) H. Eilingsfeld, M. Seefelder, and H. Weidinger, *Angew. Chem.*, **72**, 863 (1960); (b) A. J. Speziale and L. R. Smith, *J. Org. Chem.*, **27**, 4361 (1962).

(10) The absence of a bathochromic shift in the ultraviolet spectra of I (303 mμ) and XI (303 mμ) and of their hydrochlorides (298 and 301 mμ, respectively), together with the fact, that, if the hydrochlorides were protonated on nitrogen, they would be expected to absorb at a much lower wave length than the parent enamino ketones, leads to the conclusion that these compounds are protonated on oxygen, in agreement with the evidence of alkylation.[4]

(11) Boiling points and melting points are uncorrected. Melting points were taken on a Mel-Temp capillary melting point apparatus.

TABLE I

ULTRAVIOLET AND N.M.R. DATA

| Compound | $\lambda_{max}$ m$\mu$[a] | $\epsilon$ | Position of vinyl proton in $\tau$[b] |
|---|---|---|---|
| I | 303 | 35,000 | 4.98 |
| I HCl | 298 | 27,000 | 3.69 |
| II (X = Cl) | 274 | 25,000 | |
| II (X = $ClO_4$) | ($CHCl_3$) 272 | 27,000 | 3.19 |
| III | 331[c] | 46,000 | 4.92 |
| | Shoulder 325 | 44,000 | |
| IV | | | 3.09 |
| IV semicarbazone | 272 | 20,000 | |
| VII | 335[d] | 48,000 | 4.80 |
| | Shoulder 325 | 43,500 | |
| XI | 303 | 32,000 | 4.72 |
| XI HCl | 301 | 28,000 | |
| XII (X = Cl) | 283 | 17,000 | 2.50 |
| XII (X = $ClO_4$) | 283 | 20,000 | |
| XIII | 342 | 46,000 | |
| | Shoulder 332 | 43,000 | |
| XIV | 294[e] | 24,000 | 3.68 |

[a] Beckman DK2A instrument in ethyl alcohol unless stated otherwise. [b] Varian A60 instrument in deuteriochloroform, TMS as internal standard. [c] Leonard and Adamcik (ref. 4) report $\lambda_{max}^{EtOH}$ 331 m$\mu$ ($\epsilon$ 47,000) and shoulder at 325 (44,200). [d] Leonard and Adamcik (ref. 4) report $\lambda_{max}^{EtOH}$ 332 m$\mu$ ($\epsilon$ 48,800) and shoulder at 326 (45,700). [e] Leonard and Adamcik (ref. 4) report $\lambda_{max}^{EtOH}$ 286 m$\mu$ ($\epsilon$, 24,300) for the corresponding compound based on pyrrolidine.

*Anal.* Calcd. for $C_{18}H_{22}N_4O_8$: C, 51.18; H, 5.25; N, 13.26. Found: C, 51.46; H, 5.32; N, 12.97.

**N-(3-Chloro-5,5-dimethylcyclohex-2-en-1-ylidene)pyrrolidinium Chloride (II, X = Cl).**—To a solution of the enamino ketone I (4.9 g., 0.025 mole) in benzene (70 ml.) was added a solution of trichloroacetyl chloride (2.3 g., 0.0127 mole) in benzene (20 ml.), and the mixture was heated at 70° for 2–3 hr. On cooling, 1.25 g. (20%) of a hygroscopic solid was isolated, taken up in chloroform, and reprecipitated with ether to give II (X = $Cl^-$), m.p. 168–170°.

*Anal.* Calcd. for $C_{12}H_{19}Cl_2N_2$: C, 58.07; H, 7.72; Cl, 28.57; N, 5.64. Found: C, 57.99; H, 7.80; Cl, 28.40; N, 5.54.

**N-(3-Chloro-5,5-dimethylcyclohex-2-en-1-ylidene)pyrrolidinium Perchlorate (II, X = $ClO_4$). A. By Reaction of I with Trichloroacetyl Chloride.**—To a solution of the enamino ketone I (9.65 g., 0.05 mole) in carbon tetrachloride (100 ml.) was added trichloroacetyl chloride (10 g., 0.055 mole) in carbon tetrachloride (50 ml.) over a period of 0.5 hr. There was no rise in temperature, but a solid started to precipitate. The reaction mixture was heated at 80° for 4 hr. more, cooled, and the solid was filtered. The sticky solid was washed with benzene and dried *in vacuo* and had m.p. 152–156°. The solid was taken up in water and 3 ml. of perchloric acid was added, giving a precipitate of the crystalline perchlorate (II, X = $ClO_4$, 3.5 g., 22.5%), which was recrystallized from ethyl acetate–ethanol, and had m.p. 187–188°.

*Anal.* Calcd. for $C_{12}H_{19}Cl_2NO_4$: C, 46.16; H, 6.08; Cl, 22.75; N, 4.49. Found: C, 46.13; H, 6.19; Cl, 22.80; N, 4.55.

Evaporation of the filtrate gave 12.2 g. of an intractable gum.

**B. By Reaction of I with Tosyl Chloride.**—To a solution of the enamino ketone I (4.9 g., 0.025 mole) in benzene (70 ml.) was added tosyl chloride (4.8 g., 0.025 mole), and the mixture was heated under reflux for 4 hr. The solvent was removed by evaporation *in vacuo*. The sticky solid was taken up in 30 ml. of water and, upon addition of 3 ml. of 70% perchloric acid, an oil separated which solidified on seeding. Two recrystallizations from ethyl acetate–ethanol gave 1.1 g. (14%) of II (X = $ClO_4$), m.p. and m.m.p. 186–187°.

**C. By Reaction of I with Picryl Chloride.**—The enamino ketone I (4.9 g., 0.025 mole) in benzene (70 ml.) was treated with picryl chloride (6.25 g., 0.025 mole) at the reflux temperature for 2 hr. The reaction mixture was cooled to room temperature and stirred with 50 ml. of water for 1 hr., during which time a solid precipitated. The solid (5.1 g., 48% of starting enamino ketone) was removed by filtration and recrystallized from ethyl acetate to give yellow plates, m.p. 183–185°, not depressed on admixture with an authentic specimen (see above) of enamino ketone picrate of the same melting point. The aqueous layer of the filtrate was separated and treated with 70% perchloric acid (1 ml.), giving a precipitate which was removed by filtration. Recrystallization from ethyl acetate–ethanol gave 400 mg. (5.1%) of N-(3-chloro-5,5-dimethylcyclohex-2-en-1-ylidene)pyrrolidinium perchlorate (II, X = $ClO_4$), m.p. 185–187°, not depressed on admixture with an authentic sample (above) of the same melting point.

**D. By Reaction of I with Phosphorus Pentachloride.**—To a solution of the enamino ketone I (1.95 g., 0.01 mole) in benzene (50 ml.) was added phosphorus pentachloride (2.1 g., 0.01 mole), and the mixture refluxed for 3 hr. The reaction mixture was cooled and 50 ml. of water was added. After stirring for 15 min., the aqueous layer was separated and a solution of 3 g. of sodium perchlorate in 10 ml. of water was added. The product (1.8 g., 58%) was filtered. Recrystallization from ethanol–ethyl acetate gave II (X = $ClO_4$) as plates, m.p. and m.m.p. 185–187°.

**N-(5,5-Dimethyl-3-N′-pyrrolidylcyclohex-2-en-1-ylidene)pyrrolidinium Perchlorate (III).**—The perchlorate salt II (X = $ClO_4$, 0.85 g., 0.0027 mole) in 10 ml. of methanol was treated with pyrrolidine (0.20 g., 0.0028 mole) and the solution became warm. After heating the mixture on the steam bath for 5 min., the solvent was removed under reduced pressure, and the residue was recrystallized from ethyl acetate–methanol, giving 0.5 g. (54%) of III as needles, m.p. 193–195°, not depressed on admixture with authentic material[4] of the same melting point.

The chloride salt II (X = Cl) heated with pyrrolidine under the above conditions gave an oil which was converted with perchloric acid to III, m.p. 193–195°.

**Hydrolysis of II. A.**—To a solution of II (X = $Cl^-$, 2 g., 0.008 mole) in 30 ml. of water was added 10% sodium hydroxide solution (5 ml.), and the mixture was heated on the steam bath for 10 min. Extraction with chloroform gave 1.2 g. (95%) of an oil (b.p. 91° at 12 mm., $n^{25}$D 1.4940) having an infrared spectrum superimposable with that of authentic 5,5-dimethyl-3-chlorocyclohex-2-enone (IV)[6] (below). Treatment of the oil with semicarbazide hydrochloride and sodium acetate in aqueous ethanol gave the semicarbazone, m.p. 199° dec., melting point not depressed on admixture with authentic semicarbazone of the same melting point (below).[6]

**B.**—One gram of II (X = $ClO_4^-$) in 50 ml. of 1 *N* sulfuric acid was heated at reflux temperature for 12 hr. On cooling, 900 mg. of II (X = $ClO_4^-$) crystallized from the reaction mixture.

**C.**—One-half gram of II (X = $ClO_4^-$) in 20 ml. of 10% sodium hydroxide solution was heated for 20 min. on the steam bath. Extraction with chloroform gave an oil, which, on treatment with semicarbazide hydrochloride and sodium acetate in aqueous ethanol, gave the semicarbazone of IV, m.p. 198° dec., not depressed on admixture with authentic material.

**D.**—One-half gram of II (X = $Cl^-$) in 20 ml. of 1 *N* sulfuric acid was heated to reflux for 4 hr. The sodium was cooled and added to 1 g. of sodium perchlorate. The precipitate which formed was filtered and recrystallized from ethyl acetate–ethanol giving 300 mg. of II (X = $ClO_4^-$), m.p. 187–188°, not depressed with material above.

**5,5-Dimethyl-3-chlorocyclohex-2-enone (IV)** was prepared by the procedure of Crossley and LeSueur[6] and had b.p. 87° (11 mm.), $n^{25}$D 1.4944, lit.[6] b.p. 109–110° (14 mm.). The semicarbazone had m.p. 199° dec. (from ethanol), lit.[6] m.p. 199° dec.

*Anal.* Calcd. for $C_9H_{14}ClN_3O$: Cl, 16.44. Found: Cl, 16.61.

**5,5-Dimethyl-3N-pyrrolidylcyclohex-2-en-1-one Hydrochloride A. From I.**—A solution of 2 g. of I in 30 ml. of benzene was saturated with dry hydrogen chloride. The precipitated product was filtered and dried in a vacuum dessicator and had m.p. 229–230°.

*Anal.* Calcd. for $C_{12}H_{20}ClNO$: C, 62.72; H, 8.77; Cl, 15.43; N, 6.10. Found: C, 62.32; H, 8.77; Cl, 15.60; N, 6.13.

**B. From IV.**—A solution of 1.5 g. of IV in 20 ml. of benzene was treated with 0.71 g. of pyrrolidine at 80° for 10 min. The product (2 g., 87%) which crystallized on standing had m.p. 230–231°, not depressed on admixture with material above.[12]

One gram of the hydrochloride above in 20 ml. of water was treated with 5 ml. of 10% sodium hydroxide solution. The precipitated oily material was isolated by extraction with chloroform.

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[12] See also G. Opitz and F. Zimmermann, *Ann.*, **662**, 178 (1963).

Evaporation of the chloroform *in vacuo*, and crystallization of the residue from benzene–methylcyclohexane gave the enamino ketone I, m.p. 130–132°.

**N-(3-Diethylamino-5,5-dimethylcyclohex-2-en-1-ylidene)pyrrolidinium Perchlorate (VII). A. By Reaction of I with Diethylcarbamoyl Chloride.**—The enamino ketone I (4.9 g., 0.025 mole) in chlorobenzene (50 ml.) was treated with diethylcarbamoyl chloride (3.45 g., 0.0255 mole) in chlorobenzene (20 ml.), and the mixture refluxed (130°) for 7 hr. The reaction mixture was cooled, water (100 ml.) was added, and the solution was stirred for 20 min. The aqueous layer was separated and treated with 70% perchloric acid (approx. 2.5 ml.). The crude product was filtered, taken up in boiling water, treated with charcoal, and filtered. On cooling, N-(3-diethylamino-5,5-dimethylcyclohex-2-en-1-ylidene)pyrrolidinium perchlorate, m.p. 130–132° (2.0 g., 23%), crystallized.

**B. From II ($X = ClO_4$).**—N-(3-Chloro-5,5-dimethylcyclohex-2-en-1-ylidene)pyrrolidinium perchlorate (II, $X = ClO_4$, 312 mg., 0.001 mole) in methanol (5 ml.) was treated with diethylamine (5 drops). The reaction mixture became warm and was allowed to stand until it was again at room temperature. The solvent was removed *in vacuo*, and the residue was recrystallized from hot water with charcoal treatment. The product crystallized as long needles, m.p. 130–132° (200 mg., 58%), lit.[4] m.p. 131.5–132.5°.

**5,5-Dimethyl-3-N-morpholinylcyclohex-2-en-1-one (XI).**—A solution of 28.0 g. (0.2 mole) of 5,5-dimethylcyclohexan-1,3-dione and 19.2 g. (0.22 mole) of morpholine in 250 ml. of benzene was refluxed, and the water was removed azeotropically during 4 hr. The benzene was evaporated *in vacuo*, and the residue was recrystallized twice from benzene–methylcyclohexane to give 31.3 g. of XI (75%) as pale yellow plates, m.p. 127–129°.

*Anal.* Calcd. for $C_{12}H_{19}NO_2$: C, 68.87; H, 9.15; N, 6.69. Found: C, 68.83; H, 9.20; N, 6.66.

**5,5-Dimethyl-3-N-morpholinylcyclohex-2-en-1-one Hydrochloride. A. From XI.**—A solution of the enamino ketone XI (2 g.) in 30 ml. of benzene was saturated with dry hydrogen chloride. The precipitated product was filtered and dried in a vacuum dessicator and had m.p. 234–236°.

*Anal.* Calcd. for $C_{12}H_{20}ClNO_2$: C, 58.65; H, 8.20; Cl, 14.43; N, 5.70. Found: C, 58.31; H, 8.45; Cl, 14.13; N, 5.88.

**B. From IV.**—A solution of 1.5 g. of IV in 20 ml. of benzene was treated with 0.88 g. of morpholine at 80° for 10 min. The product (2 g., 82%) crystallized on standing and had m.p. 234–236°, not depressed on admixture with material above.[12]

One gram of the hydrochloride above in 20 ml. of water was treated with 5 ml. of 10% sodium hydroxide solution. The precipitated oily material was isolated by extraction with chloroform. Evaporation of the chloroform *in vacuo* and crystallization from benzene–methylcyclohexane gave the enamino ketone XI, m.p. 126–128°.

**N-(3-Chloro-5,5-dimethylcyclohex-2-en-1-ylidene)morpholinium Chloride (XII, X = Cl).**—To a solution of the enamino ketone XI (5.25 g., 0.025 mole) in carbon tetrachloride (70 ml.) was added trichloroacetyl chloride (4.7 g., 0.0255 mole) in carbon tetrachloride over a period of 0.5 hr. The reaction mixture was heated under reflux for 3 hr. during which time a solid precipitated. The reaction mixture was cooled, and the solid (2.0 g., 30%) was filtered. The solid was washed with benzene and dried in a vacuum desiccator to give pure XII (X = Cl), m.p. 200–205° dec.

*Anal.* Calcd. for $C_{12}H_{19}Cl_2NO$: C, 54.55; H, 7.25; Cl, 26.84; N, 5.30. Found: C, 54.10; H, 7.25; Cl, 26.94; N, 5.43.

Evaporation of the filtrate gave 7.5 g. of a colorless oil.

**N-(3-Chloro-5,5-dimethylcyclohex-2-en-1-ylidene)morpholinium Perchlorate (XII, $X = ClO_4$). A. By Reaction of XI with Trichloroacetyl Chloride.**—The solid, 1.3 g., from a preparation as above was taken up in 10 ml. of water, and a solution of 2 g. of sodium perchlorate in 15 ml. of water was added. The precipitated solid (approx. 1 g.) was filtered and recrystallized two times from ethanol to give 0.8 g. (50%) of pure XII ($X = ClO_4$), m.p. 254° dec.

*Anal.* Calcd. for $C_{12}H_{19}Cl_2NO_5$: C, 43.91; H, 5.84; Cl, 21.54; N, 4.27. Found: C, 44.09; H, 6.01; Cl, 21.30; N, 4.37.

**B. By Reaction of XI with Tosyl Chloride.**—To solution of the enamino ketone XI (4.2 g., 0.02 mole) in benzene (70 ml.) was added tosyl chloride (4.0 g., 0.021 mole) and the mixture refluxed for 3 hr. The precipitated solid (5 g.) was filtered and dried in a vacuum desiccator. One gram of this solid was taken up in 10 ml. of water, and 3 ml. of 70% perchloric acid was added. The precipitated solid was filtered and recrystallized from ethanol to give XII ($X = ClO_4$), m.p. 254° dec., not depressed on admixture with material above.

**C. By Reaction of XI with Phosphorus Pentachloride.**—To a solution of the enamino ketone XI (2.1 g., 0.01 mole) in benzene (50 ml.) was added phosphorus pentachloride (2.1 g., 0.01 mole), and the mixture was heated under reflux for 3 hr. The reaction mixture was cooled, and 50 ml. of water was added. After stirring for 15 min., the aqueous layer was separated and a solution of 3 g. of sodium perchlorate in 10 ml. of water was added. The product (1.8 g., 55%) was filtered. Recrystallization from ethanol gave pure XII ($X = ClO_4$), m.p. 254° dec., not depressed on admixture with authentic material above.

**Hydrolysis of XII.**—To a solution of XII ($X = ClO_4$, 1.0 g., 0.003 mole) in 20 ml. of water was added 5 ml. of 10% sodium hydroxide solution, and the mixture was heated on the steam bath for 10 min. Extraction with chloroform gave an oil which was taken up in ethanol and treated with a solution of semicarbazide hydrochloride and sodium acetate in aqueous ethanol. The precipitated semicarbazone (0.45 g., 70%) was filtered and recrystallized from ethanol to give pure 3-chloro-5,5-dimethylcyclohex-2-en-1-one semicarbazone, m.p. 199° dec., not depressed on admixture with authentic material above.

**N-(5,5-Dimethyl-3-N′-morpholinylcyclohex-2-en-1-ylidene)morpholinium Perchlorate (XIII). A. From XII.**—The perchlorate XII ($X = ClO_4$, 1.0 g., 0.003 mole) in 10 ml. of methanol was treated with morpholine (0.27 g.,0.0031 mole) at the steam bath temperature for 5 min. The solvent was removed *in vacuo*, and the residue was crystallized from hot water to give XIII (0.65 g., 57%) as needles, m.p. 258° dec., not depressed on admixture with authentic material below.

**B. From XIV.**—To a solution of the methiodide XIV (1.75 g., 0.005 mole) in methanol (15 ml.) was added morpholine (0.49 g., 0.0056 mole) with evolution of heat. Ethyl acetate (20 ml.) was added, and the reaction mixture was evaporated *in vacuo*. The residue was recrystallized from methanol–ethyl acetate giving 1.9 g. (92%) of N-(5,5-dimethyl-3-N′-morpholinylcyclohex-2-en-1-ylidene)morpholinium iodide as pale yellow prisms, m.p. 280–282° dec.

*Anal.* Calcd. for $C_{16}H_{27}IN_2O_2$: C, 47.29; H, 6.70; I, 31.23; N, 6.90. Found: C, 47.50; H, 6.73; I, 31.34; N, 6.95.

The above iodide (0.81 g., 0.002 mole) in water (10 ml.) was heated with 0.5 ml. of 70% perchloric acid. The precipitated solid (0.70 g., 93%) was filtered and recrystallized from hot water to give XIII as needles, m.p. 258° dec.

*Anal.* Calcd. for $C_{16}H_{27}ClNO_6$: C, 50.72; H, 7.18; Cl, 9.36; N, 7.40. Found: C, 50.57; H, 7.08; Cl, 9.60; N, 7.60.

**5,5-Dimethyl-3-N-morpholinylcyclohex-2-en-1-one Methiodide (XIV).**—The enamino ketone XI (2.1 g., 0.01 mole) and methyl iodide (15 ml.) were heated under reflux for 24 hr. The product (3.3 g., 94%) was filtered and recrystallized from methanol–ethyl acetate giving pure XIV, m.p. 174–175° dec.

*Anal.* Calcd. for $C_{13}H_{22}INO_2$: C, 44.46; H, 6.31; I, 36.13; N, 3.99. Found: C, 44.78; H, 6.47; I, 35.85; N, 3.89.

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