lization from alcohol gave 7.9 g. (63%) of product as colorless matting needles, m.p. 299–300°. The infrared spectrum contained bands for amide groups.

Anal. Calcd. for $C_6H_4F_6N_2O_2$: C, 28.81; H, 1.61; F, 45.58; N, 11.21. Found: C, 28.69; H, 1.66; F, 45.03; N, 11.09.

1,1-Dicyano-2,2-bis(trifluoromethyl)ethylene–*t*-Butyl Isocyanide Adduct.—A solution of 10.7 g. (0.05 mole) of 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene in 10 ml. of ether was added dropwise to a stirred solution of 4.5 g. of *t*-butyl isocyanide in 50 ml. of ether cooled in an ice–methanol bath. The reaction mixture was then cooled to −78°, and the crystalline solid (9.2 g.) that precipitated was collected on a filter. Recrystallization from ether gave 5.7 g. of a white, crystalline 1:2 adduct, m.p. 68–71°. The adduct was not stable when stored at room temperature. The proton n.m.r. spectrum in nitromethane showed two singlets of equal area at 1.42 and 1.60 p.p.m. The F^{19} n.m.r. spectrum showed a singlet in a fresh sample but upon standing other peaks developed.

Anal. Calcd. for $C_{16}H_{18}N_4F_6$: F, 29.97; N, 14.74. Found: F, 29.82; N, 14.67.

Reactions of Enamines. VI. The Protonation of Enamino Ketones[1]

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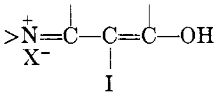
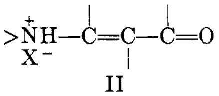
Ultraviolet spectra are shown to be a convenient tool for distinguishing the sites of protonation in enamino ketones. The enamino ketones examined [4-N-pyrrolidyl-3-penten-2-one (IV), 5,5-dimethyl-3-N-pyrrolidylcyclohex-2-en-1-one (VI), 5,5-dimethyl-3-N-morpholinylcyclohex-2-en-1-one (VII), and 5,5-dimethyl-3-cyclohexylaminocyclohex-2-en-1-one (VIII)] were all shown to protonate on oxygen.

Enamino ketones, which may be regarded as vinylogous amides, form stable salts with strong acids. Protonation of these salts can take place on O, N, or C to give I, II, and III, respectively. Leonard and Adamcik[2] on the basis of infrared spectral evidence[3] concluded that these salts were O-protonated. Recently, Kramer and Gompper[4] arrived at the same conclusion by nuclear magnetic resonance (n.m.r.) studies[5] of the perchlorate of 4-dimethylamino-3-penten-2-one. Although ultraviolet spectra have been reported for enamino ketones, their potential as a tool for distinguishing the sites of protonation in enamino ketones has not been fully recognized.[6] Our work is now presented to illustrate the use of ultraviolet spectra for determining the site of protonation in enamino ketones.



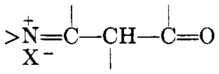
$$\underset{X^-}{>\overset{+}{N}}=\overset{|}{C}-\underset{|}{C}=\overset{|}{C}-OH$$

I



$$\underset{X^-}{>\overset{+}{N}H}-\overset{|}{C}=\underset{|}{C}-\overset{|}{C}=O$$

II



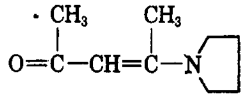
$$\underset{X^-}{>\overset{+}{N}}=\overset{|}{C}-CH-\underset{|}{\overset{|}{C}}=O$$

III

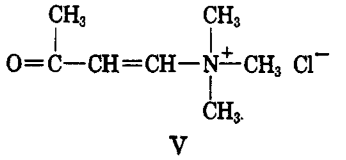
Examination of structures I and II indicates that I should show "diene"-, while II should show "enone"-type absorption. Since the chromophores are no longer in conjugation, III should show only low intensity carbonyl and end absorption. In addition, it would be expected that the O-protonated salts, I, would exhibit absorption maxima in the same range as the unprotonated enamino ketones and their O-alkylated salts. Both have essentially the same chromophoric system and would thus be good models for O-protonation.

The N-protonated salts, II, would be expected to absorb at much lower wave lengths and with lower intensities, as the electrons on nitrogen are not available for participation in the chromophoric system. The absorption of II would therefore be expected to be close to that of simple α,β-unsaturated ketones or of the N-alkylated salts, which should serve as good models for N-protonation.

Table I shows the ultraviolet spectra of some enamino ketones and their salts, together with those of model compounds for O- and N-protonation. 4-N-Pyrrolidyl-3-penten-2-one (IV) did not form a crystalline hydrochloride but the perchlorate had λ_{max}^{EtOH} 302 mμ (ε 24,000). The models for O-protonation, *i.e.*, the free enamino ketone and the O-alkylated salt, have λ_{max}^{EtOH} 312 mμ (ε 32,000) and 302 mμ (ε 24,600), respectively, while the models for N-protonation, β-acetylvinyltrimethylammonium chloride (V) and mesityl oxide, have λ_{max}^{EtOH} 206.5 mμ (ε 7300) and 239 mμ (ε 10,000), respectively. As C-protonation is excluded *a priori*, the perchlorate of IV is clearly O-protonated.

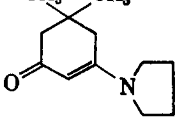


IV

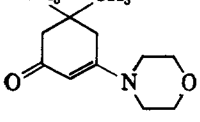


$$O=\overset{\overset{CH_3}{|}}{C}-CH=CH-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{\overset{+}{N}}}-CH_3\ Cl^-$$

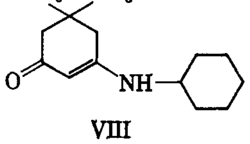
V



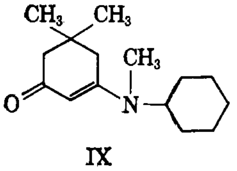
VI



VII



VIII



IX

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(1) Part V: G. H. Alt and A. J. Speziale, *J. Org. Chem.*, **29**, 798 (1964).

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

(3) D. Cook [*Can. J. Chem.*, **40**, 2362 (1962)] has recently used infrared spectra to show that amides protonate on the oxygen of the carbonyl group. C. L. Bell, J. Shoffner, and L. Bauer [*Chem. Ind.* (London), 1435 (1963)] have used a similar technique to show that the salts of 2- and 4-pyridones are protonated on oxygen [see also S. F. Mason, *J. Chem. Soc.*, 4874 (1957)].

(4) H. E. A. Kramer and R. Gompper, *Tetrahedron Letters*, 969 (1963).

(5) Nuclear magnetic resonance studies on the site of protonation in amides and 2- and 4-pyridones have been previously reported by A. R. Katritzky and R. A. Jones [*Chem. Ind.* (London), 722 (1961); *Proc. Chem. Soc.*, 313 (1960)] and A. R. Katritzky and R. E. Reavill [*J. Chem. Soc.*, 753 (1963)] who showed that protonation occurs on oxygen.

(6) S. F. Mason in his studies of the tautomerism of N-heteroaromatic hydroxy compounds adumbrated the use of ultraviolet spectra for this purpose [*J. Chem. Soc.*, 5010 (1957)]. See also H. Specker and H. Gawrosch, *Ber.*, **75**, 1338 (1942).

TABLE I

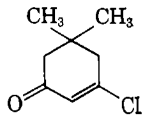
ULTRAVIOLET SPECTRA OF ENAMINO KETONES, THEIR SALTS, AND MODEL COMPOUNDS

Compound	M.p., °C.	$\lambda_{\max}^{\mathrm{EtOH}}$, m$\mu$[a]	ϵ	Ref.
IV	114–116	312	32,000	*b*
IV perchlorate	110–111	302	24,000	
IV O-ethiodide	113–114	302	24,600	*b*
V	154–158 dec.	206.5	7,300	*c*
Mesityl oxide	...	239	10,000	
VI	129–132	303	35,000	*b, d*
VI hydrochloride	229–230	298	27,000	*d*
VI perchlorate	179–181	298	28,600	*b*
VI O-methoperchlorate	132–133	286	24,300	*b*
VII	127–129	303	32,000	*d*
VII hydrochloride	234–236	301	28,000	*d*
VII perchlorate	193.5–194.5	302	30,000	
VII O-methiodide	174–175	294	24,000	*d*
VIII	170–172	292.5	32,000	
VIII hydrochloride	211–214	291	26,800	
VIII perchlorate	210–212	290	28,500	
VIII O-methoperchlorate	174–176	282	23,200	
XI	75–80	224	7,500	
Isophorone	...	234	15,000	

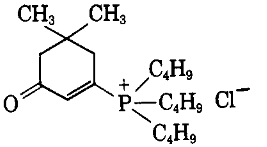
[a] Beckman DK2A recording spectrophotometer. [b] See ref. 2. [c] See ref. 8. [d] See ref. 10.

Similar relationships may be used to show that the salts of the enamino ketones VI and VII (derived from dimedone and pyrrolidine and morpholine, respectively) as well as those of the mono Schiff base VIII[7] (derived from dimedone and cyclohexylamine) are also protonated on oxygen. The known O-alkylated salts of VI and VII serve as models for O-protonation. O-Alkylated salts of the mono Schiff base VIII are not known but were obtained readily by alkylation of VIII with methyl iodide or with methanol and perchloric acid. The constitution of this compound was established by comparison with the perchlorate of the authentic N-methylated derivative (IX) prepared from dimedone and N-methylcyclohexylamine. C-Methylation of VIII could be excluded as the compound showed a vinyl proton in the n.m.r. spectrum.

No quaternary ammonium salts are known in this series to serve as models for N-protonation, and attempts to prepare them by reaction of the chloro ketone X with tertiary amines failed.[8] The chloro ketone X reacted smoothly with tributylphosphine in methylcyclohexane solution to give the hygroscopic 5,5-dimethyl-3-oxocyclohex-2-en-1-yltributylphosphonium chloride (XI) which is isoelectronic with the corresponding quaternary ammonium salt. The phosphonium salt XI and isophorone serve as models for N-protonation.



X



XI

Inspection of the data in Table I clearly shows all the enamino ketone salts to be O-protonated. These salts have absorption maxima and intensities much closer to the O-protonated than to the N-protonated model compounds.

Experimental[9]

4-N-Pyrrolidyl-3-penten-2-one Perchlorate (IV Perchlorate).—To a solution of 4-N-pyrrolidyl-3-penten-2-one[2] (1.0 g., 0.007 mole) in ether (20 ml.) and ethanol (2 ml.) was added 70% perchloric acid (2 ml.). The precipitated salt was isolated by filtration and recrystallized from acetone–ethyl acetate to give 1.3 g. (78%) of IV perchlorate as colorless plates, m.p. 110–111°.

Anal. Calcd. for $C_9H_{16}ClNO_5$: C, 42.61; H, 6.36; Cl, 13.98; N, 5.52. Found: C, 42.82; H, 6.47; Cl, 14.13; N, 5.79.

5,5-Dimethyl-3-N-morpholinylcyclohex-2-en-1-one Perchlorate (VII Perchlorate).—To a solution of 5,5-dimethyl-3-N-morpholinylcyclohex-2-en-1-one[10] (1.0 g., 0.005 mole) in ether (20 ml.) and ethanol (2 ml.) was added 70% perchloric acid (2 ml.). The precipitated salt was isolated by filtration and recrystallized from acetone–ethyl acetate to give 1.3 g. (84%) of VII perchlorate as prisms, m.p. 193.5–194.5°.

Anal. Calcd. for $C_{12}H_{20}ClNO_6$: C, 46.53; H, 6.51; Cl, 11.45; N, 4.52. Found: C, 46.77; H, 6.65; Cl, 11.77; N, 4.26.

5,5-Dimethyl-3-cyclohexylaminocyclohex-2-en-1-one (VIII).—A solution of 14.0 g. (0.1 mole) of 5,5-dimethylcyclohexane-1,3-dione and 11 g. (0.11 mole) of cyclohexylamine in 100 ml. of benzene was refluxed and the water was removed azeotropically during 6 hr. The benzene was evaporated *in vacuo* and the residue was recrystallized from benzene–methylcyclohexane to give 22 g. (99%) of VIII, m.p. 168–170°. Two crystallizations from benzene gave analytically pure material, m.p. 170–172°. The n.m.r. spectrum showed a vinyl proton at τ 4.90. The infrared spectrum showed no hydroxyl absorption spectrum and no carbonyl bands below 6 μ.

Anal. Calcd. for $C_{14}H_{23}NO$: C, 75.97; H, 10.47; N, 6.33. Found: C, 76.26; H, 10.49; N, 6.18.

5,5-Dimethyl-3-cyclohexylaminocyclohex-2-en-1-one Hydrochloride (VIII Hydrochloride).—A solution of the enamino ketone VIII (1 g.) in benzene (20 ml.) was saturated with dry hydrogen chloride. The precipitated solid was filtered and dried *in vacuo* to give the hydrochloride, m.p. 211–214°. The n.m.r. spectrum showed a vinyl proton at τ 3.75.

Anal. Calcd. for $C_{14}H_{24}ClNO$: C, 65.22; H, 9.38; N, 5.43; Cl, 13.75. Found: C, 65.09; H, 9.34; N, 5.58; Cl, 13.99.

5,5-Dimethyl-3-cyclohexylaminocyclohex-2-en-1-one Perchlorate (VIII Perchlorate).[11]—5,5-Dimethyl-3-cyclohexylaminocyclohex-2-ene-1-one hydrochloride (see above) (0.0031 mole, 0.8 g.) in ethanol (10 ml.) was added to a solution of sodium perchlorate monohydrate (0.0035 mole, 0.5 g.) in ethanol (20 ml.). Sodium chloride precipitated immediately and was filtered; the ethanol was removed *in vacuo*, leaving a pale yellow solid. Recrystallization from ethylene chloride–benzene gave 0.6 g. (60%) of VIII perchlorate, m.p. 210–212.°

Anal. Calcd. for $C_{14}H_{24}ClNO_5$: C, 52.25; H, 7.52; N, 4.35; Cl, 11.02. Found: C, 52.18; H, 7.39; N, 4.48; Cl, 11.18.

N-(5,5-Dimethyl-3-methoxycyclohex-2-en-1-ylidene)cyclohexyliminium Perchlorate (VIII O-Methoperchlorate). A. By Alkylation with Methyl Iodide.—The enamino ketone VIII (2.2 g., 0.01 mole) and methyl iodide (10 ml.) were heated under reflux in benzene (15 ml.) for 4 hr. Evaporation of the solvents gave 3.5 g. of intractable gum, which was taken up in aqueous ethanol and treated with 3 ml. of 70% perchloric acid. The crystalline precipitate (3 g., 90%) was filtered Two recrystallizations from aqueous ethanol gave material, m.p. 174–176°. The n.m.r. spectrum showed a vinyl proton at τ 4.12.

Anal. Calcd. for $C_{15}H_{26}ClNO_5$: C, 53.64; H, 7.80; N, 4.17; Cl, 10.56. Found: C, 53.66; H, 7.74; N, 4.28; Cl, 10.48.

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(7) Mono Schiff bases of 1,3-diketones have been shown to exist in the enamino ketone form: see G. O. Dudek and R. H. Holm, *J. Am. Chem. Soc.*, **84**, 2691 (1962).

(8) W. R. Benson and A. E. Pohland, *J. Org. Chem.*, **29**, 385 (1964).

(9) Melting points were taken with a Mel-Temp capillary melting point apparatus and are uncorrected. Ultraviolet spectra were taken on a Beckman DK2A spectrophotometer in ethanol solution. Infrared spectra were taken on a Perkin-Elmer Infracord Model 137 in chloroform solution. N.m.r. spectra were taken with a Varian A60 instrument in deuteriochloroform solution using tetramethylsilane as internal standard.

(10) G. H. Alt and A. J. Speziale, *J. Org. Chem.*, **29**, 794 (1964).

(11) It is interesting to note that VIII perchlorate could not be obtained by treatment of VIII with 70% perchloric acid in methanol solution. Under these conditions O-methylation of VIII to give VIII O-methoperchlorate was always observed.

B. By Alkylation with Methanol and Perchloric Acid.—5,5-Dimethyl-3-cyclohexylaminocyclohex-2-en-1-one (VIII, 0.00453 mole, 1.0 g.) in ether (30 ml.) and methanol (5 ml.) was treated with perchloric acid (1.5 ml.). The clear solution was evaporated and the residual oil crystallized from acetone–ether in Dry Ice–acetone to give a white solid, m.p. 111–120°. Three recrystallizations from aqueous ethanol gave 0.4 g. of colorless needles (38%), m.p. 174–176°, not depressed in admixture with authentic material above.

5,5-Dimethyl-3-(N-methylcyclohexylamino)cyclohex-2-en-1-one (IX).—A solution of 7.0 g. (0.05 mole) of 5,5-dimethylcyclohexane-1,3-dione and 5.7 g. (0.05 mole) of N-methylcyclohexylamine in 150 ml. of benzene was refluxed and water was removed azeotropically during 36 hr. Evaporation of the benzene gave 12 g. of red gum which on chromatography over alumina gave 5.3 g. (45%) of the enamino ketone IX. Recrystallization from methylcyclohexane gave yellow needles, m.p. 92–94°, $\lambda_{\max}^{\mathrm{EtOH}}$ 303 mμ (ε 32,500).

Anal. Calcd. for $C_{15}H_{25}NO$: C, 76.54; H, 10.71; N, 5.95. Found: C, 76.32; H, 10.61; N, 6.16.

5,5-Dimethyl-3-(N-methylcyclohexylamino)cyclohex-2-en-1-one Perchlorate (IX Perchlorate).—The enamino ketone IX above (1.2 g., 0.005 mole) in ethanol (10 ml.) was treated with 70% perchloric acid (2 ml.). Addition of water gave a crystalline perchlorate, m.p. 185–194°. Three crystallizations from aqueous ethanol gave pure material, m.p. 204–207°, $\lambda_{\max}^{\mathrm{EtOH}}$ 302 mμ (ε 28,000).

Anal. Calcd. for $C_{15}H_{26}ClNO_5$: C, 53.64; H, 7.80; N, 4.17; Cl, 10.56. Found: C, 53.65; H, 7.54; N, 3.99; Cl, 10.81.

Tributyl(5,5-dimethyl-3-oxocyclohex-2-en-1-yl)phosphonium Chloride (XI).—The chloro ketone X[12] (1.6 g., 0.01 mole) in methylcyclohexane (15 ml.) was treated with tributylphosphine (2.0 g., 0.01 mole) at the reflux temperature under nitrogen for 5 hr., during which time an oil came out of solution. After this was allowed to cool, the methylcyclohexane was decanted and the residual oil was washed with methylcyclohexane and benzene. Last traces of solvent were then removed by evaporation *in vacuo* to give 3.2 g. (89%) of the hygroscopic phosphonium chloride as an oil which solidified on standing. Two recrystallizations from ethyl acetate gave analytically pure material, m.p. 75–80°.

Anal. Calcd. for $C_{20}H_{38}ClOP$: C, 66.55; H, 10.61; Cl, 9.82; P, 8.58. Found: C, 66.45; H, 10.81; Cl, 9.64; P, 8.77.

The phosphonium chloride (1.5 g., 0.0042 mole) in ethanol (10 ml.) was poured into a solution of sodium tetraphenylboron (1.6 g., 0.0047 mole) in aqueous ethanol (15 ml.). There was an immediate precipitate of fine needles which was isolated by filtration to give 2.7 g. (100%) of the phosphonium tetraphenylborate, m.p. 185–189°. Two recrystallizations from ethyl acetate afforded analytically pure material, m.p. 190–192°.

Anal. Calcd. for $C_{44}H_{58}BOP$: C, 81.97; H, 9.07; P, 4.81. Found: C, 82.17; H, 9.27; P, 4.78.

The mesityl oxide and isophorone were obtained from Aldrich Chemical Co. and were redistilled before use.

Acknowledgment.—Thanks are due to Mr. F. B. Clarke for technical assistance.

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

Spirans. V.[1] Synthesis of Spiro Ketones Employing Enamines[2]

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Received December 15, 1964

The Stork addition of the pyrrolidine enamines of cyclopentanone and cyclohexanone to dibenzalacetone gave after hydrolysis the monoaddition products IVa and IVb. These could easily be cyclized *via* a Michael reaction to the diphenyl spiro ketones Va and Vb. Both spiro ketones were reduced to the spiro monoketones VIIa and VIIb, while VIIb was reduced to the diphenylspirohydrocarbon IX. The addition of cyclopentanone pyrrolidine enamine to dibenzalacetone, when carried out under vigorous conditions, gave the bridged product X, which contains the rare bicyclo[5.2.1]decane ring system.

In earlier publications the double Michael reaction between dibenzalacetone (II) and cyclohexane-1,3-diones, giving 7,11-diphenylspiro[5.5]undecane-1,5,9-triones in one step has been described.[1a,c] This paper deals with an extension of this reaction to the *mono* ketones, cyclopentanone and cyclohexanone, as donors.

The double Michael reaction between cyclohexanone itself and dibenzalacetone (II) was carried out under the same conditions as described earlier,[1a] *viz.*, with sodium ethoxide in ethanol. The spiro diketone Vb was indeed obtained in one step, but the highest yield amounted only to 5.3% and the reaction was attended by considerable tar formation, which made isolation of Vb tedious (see Experimental part). When the same reaction was carried out with cyclopentanone, only intractable tars were obtained. Great improvement was realized by using the pyrrolidine enamines of cyclopentanone and cyclohexanone as starting materials. The reaction between these enamines and dibenzalacetone was carried out as described by Stork, *et al.*,[3] for the reaction between cyclohexanone pyrrolidine enamine and ethyl vinyl ketone, *viz.*, in dioxane at room temperature. After hydrolysis with dilute acetic acid, the monoaddition products IVa and IVb were obtained in good yields. The physical constants, spectral data, and yields are recorded in Table I. The ultraviolet and infrared spectra correspond well with those of monobenzalacetone[4] [$\lambda_{\max}^{\mathrm{EtOH}}$ 287 mμ (ε 20,900), $\nu_{C=O}$ 1673 and 1697 cm.$^{-1}$].

The "open-chain" products IVa and IVb could easily be cyclized *via* an intramolecular Michael reaction under the influence of sodium ethoxide in absolute ethanol. The spiro diketone Va was obtained after benzene extraction in 64% yield, while Vb crystallized immediately from the solution in 67% yield. Theoretically the cyclization of IVa and IVb could also take place on the other side of the carbonyl group, which would lead to bridged compounds. However, the spiro structure of Va is established unambiguously, because the alternative structure, namely the bridged compound X, could be prepared from IIIa (see below). The spiro structure of Vb is in accord with its reactions.

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[1] (a) Part I: H. A. P. de Jongh and H. Wynberg, *Rec. trav. chim.*, **82**, 202 (1963). (b) Part II: H. A. P. de Jongh and H. Wynberg, *ibid.*, **82**, 602 (1963). (c) Part III: H. A. P. de Jongh and H. Wynberg, *Tetrahedron*, **20**, 2553 (1964). (d) Part IV: H. A. P. de Jongh and H. Wynberg, *ibid.*, **21**, 515 (1965).

[2] Partly taken from H. A. P. de Jongh, Ph.D. Thesis, Groningen, 1964.

[3] G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Am. Chem. Soc.*, **85**, 207 (1963).

[4] R. L. Erskine and E. S. Waight, *J. Chem. Soc.*, 3425 (1960).