Bicyclic Enamines. V. Cumulated Cyclopropylenamines[1,2]

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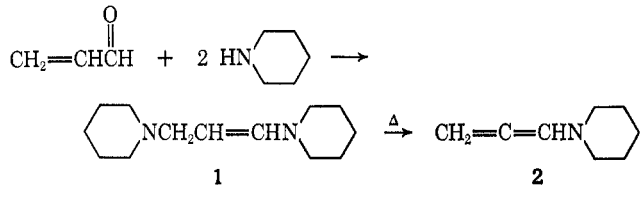
Received September 16, 1969

Cyclopropylcarbinylaminals were studied. Certain of these aminals possess double bonds in such a steric position that they aid in the formation of cumulated cyclopropylenamines. These cumulated cyclopropylenamines show uv maxima of high intensity in the 300-nm region. The origins of these observed phenomena are discussed. The basicities of various cyclopropyl methyl ketones are reported and compared with those of other methyl ketones. The basicity of the tricyclic 2-acetyltricyclene is much stronger than that of other reported cyclopropyl ketones, with a pK_{BH^+} of −4.06.

One of the earliest reports of the formation of enamines[3] describes the formation of what is probably a cumulated dienamine.[4] This synthesis is carried out by treating an α,β-unsaturated aldehyde such as acrolein with 2 mol of a secondary amine such as piperidine

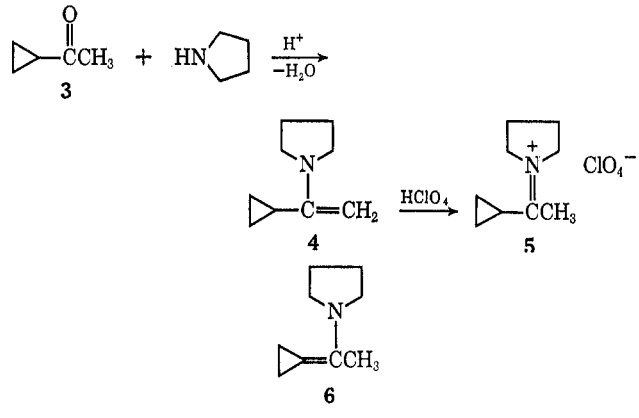


to form amino enamine **1** (a vinylogous aminal). Vacuum distillation of **1** produced cumulated dienamine **2**. This type of compound has been virtually ignored since this early report.[5]

The cyclopropyl group has many chemical and physical properties which are analogous to those observed in alkene groups.[6] This would lead one to suspect that tertiary cyclopropylamines behave like enamines in such typical reactions as alkylation and acylation. However, this similarity in chemical behavior between cyclopropylamines and enamines has not been observed.[7]

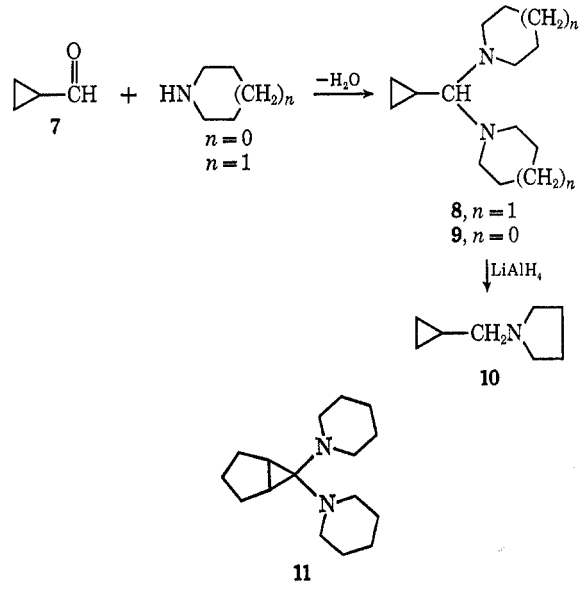
Although cyclopropylamines themselves do not show any of the typical enamine properties, the properties of cumulated cyclopropylenamines is a significant area for investigation. The problem of constructing such a system for investigation then arises. The reaction of secondary amines with ketones or aldehydes is the most widely used method of synthesizing enamines,[3] so the reaction of secondary amines with cyclopropyl ketones or aldehydes should be a fruitful approach.

The treatment of methyl cyclopropyl ketone (**3**) with pyrrolidine in the presence of an acid catalyst produced, beside ring-fission products,[8] a small amount of enamine **4**. Identification of **4** was made through its ir spectrum and spectral and elemental analysis of its perchlorate salt **5**.[9] The ir spectrum of the enamine



product indicated that a trace of cumulated cyclopropyl enamine **6** might also be present, but it was very unstable and was not positively identified.

The reaction of cyclopropanecarboxaldehyde (**7**) with piperidine results in the formation of aminal **8**.[10] In a similar manner aminal **9** is produced when **7** is



treated with pyrrolidine. These aminals are thermally stable, and hence they are distillable and not readily converted into "cumulated" enamines, as was vinylogous aminal **1**, which was studied by Mannich and coworkers.[4] Aminals are commonly produced by the reaction of a secondary amine with an aldehyde,[3,11-13]

(1) For the previous article in the series, see A. G. Cook and W. M. Kosman, *Tetrahedron Lett.*, 5847 [1966].

(2) Support of this work by a grant from the Petroleum Research Fund of the American Chemical Society and by a Valparaiso University Grant is gratefully acknowledged.

(3) For a comprehensive review of enamines, see "Enamines: Synthesis, Structure, and Reactions," A. G. Cook, Ed., Marcel Dekker, Inc., New York, N. Y., 1969.

(4) C. Mannich, K. Handke, and K. Roth, *Chem. Ber.*, **69**, 2112 (1936).

(5) L. A. Paquette and M. Rosen, *J. Amer. Chem. Soc.*, **89**, 4102 (1967).

(6) M. Yu Lukina, *Usp. Khim*, **31**, 419 (1962).

(7) R. A. Fouty, Ph.D. Dissertation, University of Pennsylvania, 1962.

(8) A. G. Cook and K. E. Ungrodt, unpublished data.

(9) J. V. Paukstelis, Ph.D. Dissertation, University of Illinois, 1964. He made this ternary iminium salt by the direct reaction of ketone **3** with pyrrolidium perchlorate.

(10) K. C. Brannock, A. Bell, R. D. Burpitt, and C. A. Kelly, *J. Org. Chem.*, **29**, 801 (1964).

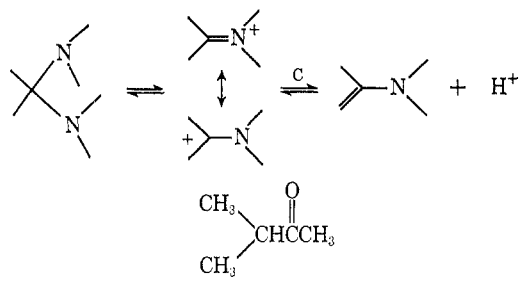
(11) C. Mannich and H. Davidsen, *Chem. Ber.*, **69**, 2106 (1936).

(12) R. Dulou, E. Elkik, and A. Veillard, *Bull. Soc. Chim. Fr.*, 967 (1960).

(13) A. Dornow and W. Schacht, *Chem. Ber.*, **82**, 464 (1949).

but upon distillation 1 mol of the amine is usually eliminated and an enamine is formed. It has been shown that aminals and enamines are in equilibrium in some cases.[14] Aminal **9** is reduced to amine **10** by treatment with lithium aluminum hydride, a reaction parallel to the borohydride reduction of aminal **11** to the monoamine reported by Szmuszkovicz.[15]

Stable aminals are formed from aldehydes with no α hydrogens such as benzaldehyde,[16] from cyclopropanones,[15,17,18] and from cyclopropylcarboxaldehydes such as **7**. Apparently, cyclopropanones form stable aminals rather than enamines because of the excessive ring strain that would be introduced by the formation of an enamine, but the question remains as to the reluctance of aminals formed from cyclopropylcarboxaldehydes to yield enamines under the normal conditions. There are three steps which together determine the overall rate of enamine formation,[3,19] and the last of



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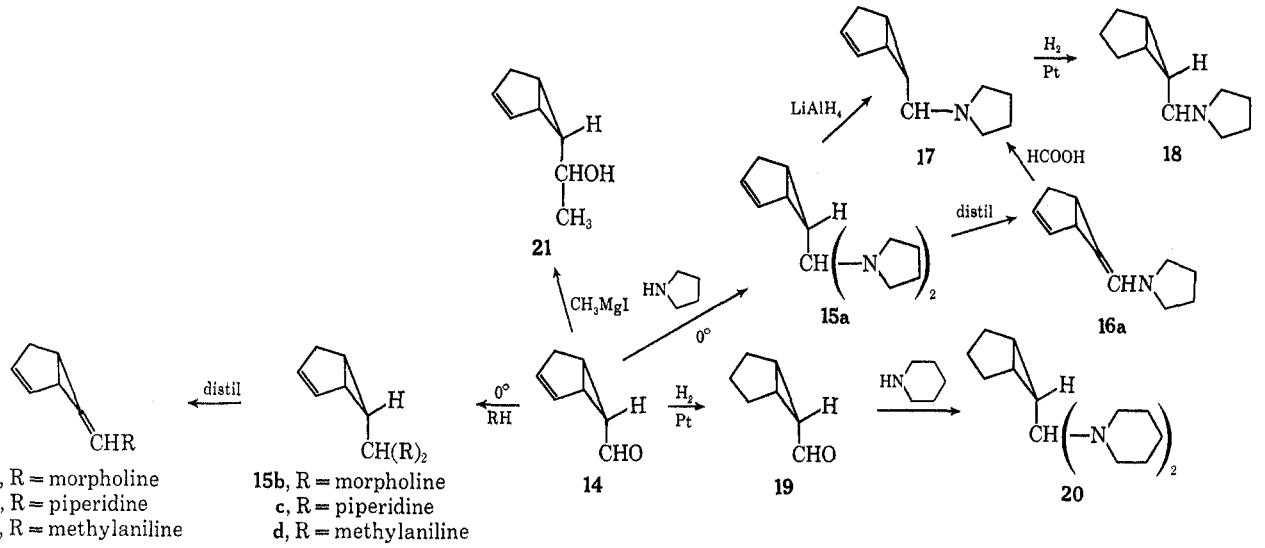
these steps (step C) has direct bearing on the question at hand. Step C depends upon the ease of losing a proton from the β-carbon atom of the ternary iminium ion.

The base-catalyzed exchange of deuterium for the methine hydrogen in isopropyl methyl ketone (**13**) is much more rapid than that for the methine hydrogen in cyclopropyl methyl ketone (**3**).[20,21] In fact, the base-catalyzed exchange of deuterium for cyclopropyl methine hydrogens is essentially nonexistent[22] in spite of the s character of the exocyclic bonding orbitals.[23] The endocyclic carbon–carbon bonds in cyclopropane are $sp^{4.12}$ hybridized[24–27] and can have pseudoconjugation with an adjacent π-electron system when the plane of the cyclopropane ring is parallel to the axis of the p orbital.[28–35] The exocyclic carbon–carbon bonds are $sp^{2.28}$ hybridized. Any change in the endocyclic carbon–carbon bonds toward sp^3 hybridization causes increased strain in the ring. Thus the orbital geometry of the carbanionlike transition states in this base-catalyzed hydrogen exchange makes meaningful delocalization of charge impossible; *i.e.*, because of the cyclopropane ring the unshared electron pair is in an orbital with a smaller amount of p character than would be desirable for maximum overlap with the carbonyl p orbital. The formation of an enamine from an hemiaminal or an aminal is an analogous situation, since the transition state in step C in going from the ternary iminium ion to the enamine would be very similar to the carbanion-like transition states in the base-catalyzed hydrogen exchange, and for similar reasons the enamine does not readily form. It has been shown from heats of hydrogenation studies that a double bond exocyclic to a cyclopropane ring is very highly strained,[36] as would be expected from the theoretical model, since this would mean the use of a p orbital in the cyclopropyl carbon and sp^x would have $x < 4.12$. Thus it would take some special type of stabilization to cause aminals such as **8** or **9** to form their respective enamines.

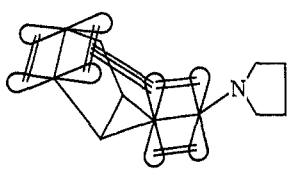
Bicyclo[3.1.0]hex-2-ene-6-*endo*-carboxaldehyde[37] (**14**) possesses within its structure the potential for such stabilization. Treatment of **14** with pyrrolidine and anhydrous potassium carbonate at 0° causes a very exothermic reaction to take place with the production of aminal **15a**, which, upon slow distillation, gives enamine **16a** in an overall 70% yield. This cumulated cyclopropylenamine can be reduced with 98% formic acid[38] to produce amine **17**. The exact stereochemistry of the reduction product was not determined, but it is probably a mixture of *endo* and *exo* isomers. The pure *endo* isomer of amine **17** was synthesized by the reduction of aminal **15a** with lithium aluminum hydride. This in turn was catalytically hydrogenated to saturated amine **18**. Similar sequences of aminal formation followed by enamine production upon distillation were carried out using morpholine, piperidine, and N-methylaniline as the secondary amines. These enamines are typically very unstable in the presence of air. Treatment of these cumulated cyclopropylenamines with strong acid such as perchloric acid resulted in immediate decomposition of the enamine and formation of dark, gummy tar. Allowing enamine **16a** to stand with a large excess of pyrrolidine for an extended period of time both at room temperature and elevated temperatures did not cause the formation of any noticeable amount of aminal **15a**. Aldehyde **14** underwent normal addition with methylmagnesium iodide to form alcohol **21**.

The source of the stabilization for this system which allows it to form cumulated cyclopropylenamines,

(14) P. Ferruti, D. Pocar, and G. Bianchetti, *Gazz. Chim. Ital.*, **97**, 109 (1967).
(15) J. Szmuszkovicz, E. Cerda, M. F. Grostic, and J. F. Zieserl, Jr., *Tetrahedron Lett.*, 3969 (1967).
(16) R. A. Henry and W. M. Dehn, *J. Amer. Chem. Soc.*, **71**, 227 (1949).
(17) W. J. M. Van Tilborg, S. E. Schaafsma, H. Steinberg, and T. J. DeBoer, *Rec. Trav. Chim. Pays-Bas*, **86**, 417 (1967).
(18) N. J. Turro, *Accounts Chem. Res.*, **2**, 25 (1969).
(19) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Amer. Chem. Soc.*, **85**, 207 (1963).
(20) C. Rappe and W. H. Sachs, *Tetrahedron*, **24**, 6287 (1968).
(21) W. T. Van Wijnen, H. Steinberg, and T. J. DeBoer, *Rec. Trav. Chim. Pays-Bas*, **87**, 844 (1968).
(22) H. W. Amburn, K. C. Kauffman, and H. Shechter, *J. Amer. Chem. Soc.*, **91**, 530 (1969).
(23) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, pp 23 and 49–52.
(24) C. A. Coulson and W. E. Moffitt, *Phil. Mag.*, **40**, 1 (1949).
(25) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).
(26) L. L. Ingrahm, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, p 479.
(27) W. A. Bernett, *J. Chem. Educ.*, **44**, 17 (1967).
(28) N. C. Deno, H. G. Richey, Jr., J. S. Lui, D. N. Lincoln, and J. O. Turner, *J. Amer. Chem. Soc.*, **87**, 4533 (1965).
(29) H. C. Brown and J. D. Cleveland, *ibid.*, **88**, 2051 (1966).
(30) (a) P. von Schleyer and G. W. Van Dine, *ibid.*, **88**, 2321 (1966); (b) P. von R. Schleyer and V. Buss, *ibid.*, **91**, 5880 (1969).
(31) L. S. Bartell and J. P. Guillory, *J. Chem. Phys.*, **43**, 647 (1965).
(32) A. P. Krapcho and R. C. H. Peters, *Tetrahedron Lett.*, 4827 (1968).
(33) (a) C. U. Pittman, Jr., and G. A. Olah, *J. Amer. Chem. Soc.*, **87**, 5123 (1965); (b) G. A. Olah and J. M. Bollinger, *ibid.*, **90**, 6082 (1968).
(34) J. E. Baldwin and W. D. Foglesong, *ibid.*, **90**, 4303, 4311 (1968).
(35) J. C. Martin and B. R. Ree, *ibid.*, **91**, 5882 (1969).
(36) R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *ibid.*, **90**, 4315 (1968).
(37) J. Meinwald, S. S. Labana, and M. S. Chadha, *ibid.*, **85**, 582 (1963).
(38) (a) P. L. deBenneville and J. H. Macartney, *ibid.*, **72**, 3073 (1950); (b) P. L. de Benneville, U. S. Patent 2,578,787 (1951); (c) N. J. Leonard and R. R. Sauers, *J. Amer. Chem. Soc.*, **79**, 6210 (1957).



whereas other cyclopropyl systems such as cyclopropanecarboxaldehyde (**7**) will not, lies with the orientation of the carbon–carbon double bond in the fused five-membered ring relative to the cyclopropane ring and relative to the developing enamine double bond. The reaction of bicyclo[3.1.0]hexane-6-*endo*-carboxaldehyde (**19**) with piperidine yields only distillable aminal **20**, which demonstrates that the source of stabilization must be the cyclopentene double bond, since it is the only element missing in aldehyde **19**.



16a

Direct conjugation between the enamine double bond and the cyclopropane ring in **16a** is not possible because of their orthogonal geometry. However, the cyclopropane ring is pivital in the conjugation of this system in two ways. First, it is situated in such a manner that the axis of the π bond in the five-membered ring and the plane of the cyclopropane ring are nearly parallel, a situation allowing almost maximum overlap and pseudoconjugation. The conjugation of an olefin with cyclopropane has minimal conformational requirements[39] compared with those systems which have a greater electron demand and hence require a "bisected" geometry.[40-42] Second, the cyclopropane ring rigidly holds the enamine double bond in a position such that one of its p orbitals overlaps the π-electron cloud of the cyclopentene double bond in a homoconjugative manner.

The conjugative interaction of the cyclopentene double bond with both the enamine double bond and the cyclopropane ring (even though the enamine double bond and cyclopropane ring cannot be directly conjugated with each other) is shown by the ultraviolet maximum of 302 nm (ϵ 39,000) for enamine **16a**.

(39) C. H. Heathcock and S. R. Poulter, *J. Amer. Chem. Soc.*, **90**, 3766 (1968).
(40) W. G. Dauben and G. H. Berezin, *ibid.*, **89**, 3449 (1967).
(41) M. J. Jorgenson and T. Leung, *ibid.*, **90**, 3769 (1968).
(42) R. C. Hahn, P. H. Howard, S. M. Kong, G. A. Lorenzo, and N. L. Miller, *ibid.*, **91**, 3558 (1969).

Similar maxima are exhibited by the other enamines, **16c** and **16d** (see Table I). This maximum cannot be

TABLE I
ULTRAVIOLET MAXIMA

Compd	λ_{max}^{EtOH}, nm (ϵ)
14	205 (4,350)[a]
16a	302 (39,000)
	237 (23,000)
	220 (28,000)
16c	293 (21,000)
16d	329 (32,000)
17	205 (2500)
22	Below 200[b]
23	273 (34,200)[c]
	193.5 (11,200)[d]

[a] Reference 37. [b] T. C. Shields, personal communication. [c] G. Opitz and W. Merz, *Justus Liebigs Ann. Chem.*, **652**, 139 1962). [d] Reference 39.

due to the cumulated enamine double bond–cyclopropane ring alone, because similar compounds have shown no ultraviolet maxima above 200 nm,[43] nor can it be due to conjugation between the cyclopentene double bond and the cyclopropane ring alone, because vinyl cyclopropanes show maxima only below 200 nm[39] (see Table I). The rigid bicyclic configuration of systems such as enamine **16a** is necessary for the interaction of the three groups (*i.e.*, cyclopropane ring, cyclopentene, and enamine double bond). This is demonstrated by another compound which possesses these three groups in the same relative positions, but without the rigidity of the bicyclic system, namely vinylmethylenecyclopropane (**22**).[44] This compound possesses only a shoulder just past 200 nm in its ultraviolet spectrum.[45]

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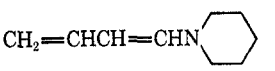

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The ultraviolet spectrum of enamine **16a** can be best accounted for by considering it as a dienamine whose

(43) E. F. Ullman and W. J. Fanshawe, *ibid.*, **83**, 2379 (1961).
(44) T. C. Shields, W. E. Billups, and A. R. Lepley, *ibid.*, **90**, 4749 (1968).
(45) See Table I, footnote *b*.

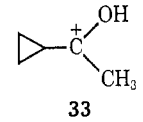
conjugation is *extended* by a cyclopropyl group.[39-42,46,47] For example, dienamine **23** (possessing a piperidine moiety) shows a uv maximum at 273 nm (ϵ 34,200).[48] A cyclopropyl group imparts a bathochromic shift of from 8 to more than 15 nm to the transition of an olefin.[39] Therefore, a cyclopropyl extended dienamine would show a uv maximum of *ca.* 288 nm, which corresponds well with the uv maximum of enamine **16c** (also possessing a piperidine moiety) of 293 nm.

Since cyclopropyl ketones and aldehydes were of great interest to us in this study, a study of the basicity of several methyl ketones was carried out, comparing the influence of a cyclopropyl ring with that of other groups. The method used to determine the basicity of these ketones is that described by Haake.[49] This method involves the measurements of the chemical shift of acetyl methyl groups as a function of sulfuric acid concentration, using the equation

$$\log \frac{\delta_B - \delta_{obsd}}{\delta_{obsd} - \delta_{BH^+}} = \log \frac{[BH^+]}{[B]} = m(pK_{BH^+} - H_0)$$

Since the H_0[50,51] scale is used to determine effective sulfuric acid concentration, the m value is a measure of the protonation behavior of the base relative to Hammett bases; *i.e.*, if $m = 1$, the base is a Hammett base. The chemical shifts were found using the methyl protons in trimethylammonium chloride as reference, and the slope (m) and intercept ($c = mpK_{BH^+}$) were determined by least squares. A summary of the results is found in Table II. The cyclopropane rings were not ruptured in the cold sulfuric acid solutions,[33a,52] as shown by comparison of the nmr spectra of the compounds both in concentrated sulfuric acid and in pure water.

A cyclopropyl ketone or aldehyde possesses greater s character in its exocyclic carbon–carbonyl carbon bond ($sp^{2.28}$–sp^2) than the isomeric acyclic ketone or aldehyde (sp^3–sp^2).[6,24-27] Therefore the cyclopropyl group is electron attracting in its inductive effect (s-character effect)[23] in a manner analogous to unsaturated groups.[53] On the other hand its mesomeric effect is similar to that of an aromatic system or an unsaturated group because of its ability to delocalize the positive charge of a cyclopropylcarbinyl cation.[54] Cyclopropylamines are weaker bases than their acyclic counterparts because of the inductive effect of the cyclopropyl group.[55,56] Cyclopropyl methyl ketone (**3**) is a stronger base than the corresponding acyclic isopropyl methyl ketone (**13**) owing to the greater importance of delocalization of positive charge in planar carbonium ion **33** than the cyclopropyl inductive effect. The base strength of **3**



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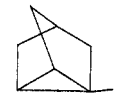
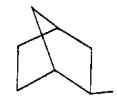
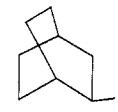
corresponds well with that of acetophenone (**25**), and substitution of an α methyl group into **3** to give **29** increases the basicity by *ca.* one pK unit just as a *para* methyl group does to acetophenone (**26**). Whether this is due strictly to an inductive effect, a mesomeric effect, a steric effect, or some combination of these in the cyclopropyl case is not known, although it is interesting to note that in the acyclic series of ketone **13**, introduction of a methyl group does not have this pronounced effect, as illustrated by the pK of *t*-butyl methyl ketone (**24**). Both the *endo* and *exo* isomers of the bicyclo[2.2.1]heptyl ketone **31** had identical basicities of about the same order of magnitude as the bicyclo[2.2.2] acetyl ketone **32** and the cyclohexyl ketone **27**. When the cyclopropane ring was placed in the rigid and strained tricyclic system of nortricyclyl ketone **30**, the basicity was greatly enhanced. This correlates well with the observation that a cyclopropane ring in bicyclic compounds is more basic toward hydrogen bonding and charge-transfer agents than when it is in a monocyclic compound.[57] This is attributed to an increase in the π character of the bicyclic compounds.

TABLE II

BASICITIES OF SOME METHYL KETONES[a]

Compd	R	pK_{BH^+}[b]	c[b]	m[b]	No. of points[c]
3		−6.52	−3.30 ± 0.10	0.505	10
13	$(CH_3)_2CH$	−7.42	−3.84 ± 0.05	0.518	9
24[d]	$(CH_3)_3C$	−7.1[d]			
25[e]	Phenyl	−6.51[e]		0.52	
26[f]	*p*-Tolyl	−5.47[f]			
27	Cyclohexyl	−7.03	−2.93 ± 0.013	0.416	11
28	Cyclobutyl	−6.86	−2.24 ± 0.010	0.326	9
29		−5.47	−2.55 ± 0.007	0.466	9
30		−4.06	−1.49 ± 0.002	0.367	11
31	 [g]	−7.04	−3.06 ± 0.014	0.435	11
32		−7.03	−2.85 ± 0.015	0.406	8

[a] Used nmr chemical-shift method described in ref 49 with $(CH_3)_3NH^+Cl^-$ as reference compound and H_0 values from ref 50 and 51. [b] By least squares using $\log [BH^+]/[B] = m(pK - H_0)$ with c = intercept = mpK and m = slope. Standard deviations are also given. [c] Number of points between 5 and 95% protonation used in the least-squares determination. [d] Reference 49. [e] Reference 50. [f] H. J. Campbell and J. T. Edward, *Can. J. Chem.*, **38**, 2109 (1960). [g] *exo* and *endo*.

(46) J. P. Pete, *Bull. Soc. Chim. Fr.*, 357 (1967).
(47) S. Nishida, I. Moritani, E. Tsuda, and T. Teraji, *Chem. Commun.*, 781 (1969).
(48) See Table I, footnote *c*.
(49) P. Haake, R. D. Cook, and G. H. Hurst, *J. Amer. Chem. Soc.*, **89**, 2650 (1967).
(50) F. A. Long and M. A. Paul, *Chem. Rev.*, **57**, 1 (1957).
(51) M. J. Jorgenson and D. R. Hartter, *J. Amer. Chem. Soc.*, **85**, 878 (1963).
(52) C. U. Pittman, Jr., and S. P. McManus, *ibid.*, **91**, 5915 (1969).
(53) M. J. S. Dewar and J. M. Harris, *ibid.*, **90**, 4468 (1968).
(54) (a) R. Breslow, "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, Chapter 4; (b) N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 129 (1964); (c) M. Hanack and H. J. Schneider, *Angew. Chem. Int. Ed. Engl.*, **6**, 666 (1967); (d) D. Bethell and V. Gold, "Carbonium Ions," Academic Press, London, 1967, Chapter 7.
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(56) J. D. Roberts and V. C. Chambers, *J. Amer. Chem. Soc.*, **73**, 5030 (1951).
(57) Z. Yoshida, N. Ishibe, and H. Kusumoto, *ibid.*, **91**, 2279 (1969).

Experimental Section

The instruments used in this work were the Beckman DK-2A recording spectrophotometer, the JEOL C-60HL high-resolution nuclear magnetic resonance spectrometer, and a Perkin-Elmer Model 137 infrared spectrometer. The analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Methyl Ketones.—Cyclopropyl methyl ketone and methylcyclopropyl methyl ketone were obtained from Aldrich Chemical Co., Milwaukee, Wis. 3-Methyl-2-butanone was obtained from Distillation Products Inc., Rochester, N. Y. Cyclohexyl and cyclobutyl methyl ketones were prepared by the method of Walker and Hauser.[58] Bicyclo[2.2.2]octyl methyl ketone was prepared by the method of Ouellette and Booth.[59] A mixture of *exo*- and *endo*-bicyclo[2.2.1]heptyl methyl ketone was prepared by catalytic hyrogenation of *exo*- and *endo*-bicyclo[2.2.1]hept-2-enyl methyl ketone,[60] and pure *exo*-bicyclo[2.2.1]heptyl methyl ketone was synthesized by the method of Stockmann.[61] 2-Acetylnortricyclene was prepared by the acetylation of nortricyclene.[62]

General Procedure for Aminal and Enamine Formation from Aldehydes.—To a mixture of 1 mol of aldehyde and some anhydrous potassium carbonate was added 2 mol of secondary amine. The mixture was allowed to stand overnight under nitrogen at 0°. The reaction mixture was filtered and excess reactants were removed at room temperature *in vacuo*. The resultant aminal was purified by recrystallization or distillation. Distillation also produces enamine in some cases.

A. Cyclopropanecarboxaldehyde[63] (7) and Pyrrolidine.—1,1-Di(N-pyrrolidino)cyclopropylmethane (9) was obtained as a colorless liquid: yield 27%; bp 126–127° (15 mm); n^{20}D 1.4952; ν_{max}^{film} 3060 cm^{-1} (cyclopropyl hydrogen).

Anal. Calcd for $C_{12}H_{22}N_2$: C, 74.17; H, 11.41; N, 14.42. Found: C, 74.21; H, 11.53; N, 14.25.

B. Bicyclo[3.1.0]hex-2-ene-*endo*-carboxaldehyde (14)[37] and Pyrrolidine.—6-*endo*-[1,1-Di(N-pyrrolidino)methylbicyclo[3.1.0]hex-2-ene (15a) was produced with no enamines present (by ir analysis) at room temperature prior to distillation. Upon distillation this aminal partially decomposed to an enamine, but some of the aminal was obtained as a colorless liquid: bp 122° (1.2 mm); n^{19}D 1.5290; nmr (neat) τ 4.57 ppm (=CH).

Anal. Calcd for $C_{15}H_{24}N_2$: C, 77.53; H, 10.41; N, 12.06. Found: C, 77.55; H, 10.41; N, 11.94.

The corresponding enamine, 6-N-pyrrolidinomethylenebicyclo-[3.1.0]hex-2-ene (16a), was produced in a 70% overall yield upon slow distillation of the product: bp 81.5–83° (0.4 mm); n^{31}D 1.5804; ν_{max}^{film} 1650 cm^{-1} (C=CN); nmr (neat τ 4.50 (cyclopentene =CH) and 4.10 ppm [=C(N)H]; λ_{max}^{EtOH} 302 nm (ϵ 39,000), 237 (23,000), and 220 (28,000).

C. Aldehyde 14 and Morpholine.—6-*endo*-1,1-Di(N-morpholino)methylbicyclo[3.1.0]hex-2-ene (15b) was obtained in the form of colorless plates in quantitative yield: mp 71–73°; ν_{max}^{Nujol} 3050 cm^{-1} (cyclopropyl hydrogen); nmr (neat) τ 4.68 ppm (cyclopentene=CH).

Anal. Calcd for $C_{15}H_{24}N_2O_2$: C, 68.15; H, 9.15; N, 10.60. Found: C, 68.11; H, 8.90; N, 10.43.

Slow distillation of aminal **15b** gave 6-N-morpholinomethylenebicyclo[3.1.0]hex-2-ene (16b) as a colorless liquid: yield 56%; bp 81° (0.12 mm); n^{24}D 1.5783; ν_{max}^{film} 1650 cm^{-1} (C=CN); nmr (neat) τ 4.40 (cyclopentene=CH) and 4.00 ppm [=C(N)H].

Anal. Calcd for $C_{11}H_{15}NO$: C, 74.54; H, 8.53. Found: C, 74.38; H, 9.77.

D. Aldehyde 14 and Piperidine.—Distillation of the product resulted in the formation of 6-N-piperidinomethylenebicyclo-[3.1.0]hex-2-ene (16c) as a colorless liquid: yield 45%; bp 89° (0.4 mm); ν_{max}^{film} 1650 cm^{-1} (C=CN); λ_{max}^{EtOH} 293 mn (ϵ 21,000).

E. Aldehyde 14 and N-Methylaniline.—6-*endo*-1,1-Di(N-methylanilino)methylbicyclo[3.1.0]hex-2-ene (15d), bp 193–194° (0.6 mm), and 6-N-methylanilinomethylenebicyclo[3.1.0]hex-2-ene (16d), bp 99° (0.15 mm), n^{20}D 1.6355, λ_{max}^{EtOH} 329 nm (ϵ 32,000), ν_{max}^{film} 1650 cm^{-1}, were obtained as light yellow liquids upon distillation of the reaction mixture in yields of 11 and 13%, respectively.

F. Bicyclo[3.1.0]hexane-6-*endo*-carboxaldehyde (19)[64] and Piperidine.—6-*endo*-1,1-Di(N-piperidino)methylbicyclo[3.1.0]-hexane (20) was obtained as a stable, distillable product: yield 23%; bp 125° (0.53 mm); n^{26}D 1.5078.

Anal. Calcd for $C_{17}H_{30}N_2$: C, 77.80; H, 11.52. Found: C, 77.76; H, 11.39.

Reaction with Lithium Aluminum Hydride. A. 1,1-Di(N-pyrrolidino)cyclopropylmethane (9).—A stirred slurry of 1.03 g (0.027 mol) of lithium aluminum hydride, 6.98 g (0.027 mol) of aminal 9, and 150 ml of ether was refluxed for 68 hr. The reaction mixture was hydrolyzed with saturated aqueous sodium sulfate, filtered, and distilled to give 2.36 g (47%) of N-cyclopropylmethylpyrrolidine (10): bp 51° (15 mm); n^{24}D 1.4593; ν_{max}^{film} 3050 cm^{-1} (cyclopropyl hydrogen); nmr (neat) τ 2.31 ppm (d, J = 6.0 Hz, $\triangleright$CH$_2$).

Anal. Calcd for $C_8H_{15}N$: C, 76.74; H, 12.08. Found: C, 76.63; H, 11.93.

B. 6-*endo*-1,1-Di(N-pyrrolidino)methylbicyclo[3.1.0]hex-2-ene (15a).—A slurry of 3.7 g of lithium aluminum hydride, 8.15 g (0.03 mol) of aminal 15a, and 200 ml of ether was refluxed overnight, and the product, 6-*endo*-N-pyrrolidinomethylbicyclo-[3.1.0]hex-2-ene (17), was isolated in the usual manner: yield 90%; bp 50° (0.26 mm); n^{25}D 1.5014.

Reduction of 6-N-Pyrrolidinomethylenebicyclo[3.1.0]hex-2-ene (16a) with Formic Acid.—Reduction of 4.08 g (0.025 mol) of enamine 16a with 98–100% formic acid in the usual manner[38] resulted in the formation of 1.3 g (32%) of 6-N-pyrrolidinomethylbicyclo[3.1.0]hex-2-ene (17) (probably a mixture of *endo* and *exo* isomers): bp 53° (0.2 mm); n^{35}D 1.4990, λ_{max}^{EtOH} 205 nm (ϵ 2500).

Anal. Calcd for $C_{11}H_{17}N$: C, 80.92; H, 10.50. Found: C, 81.10; H, 10.51.

Hydrogenation of 6-*endo*-N-Pyrrolidinomethylbicyclo[3.1.0]hex-2-ene (17).—A solution of 2.86 g (0.018 mol) of amine 17 in 95% ethanol was shaken with 0.1 g of PtO_2 and 40 psi of hydrogen. After the hydrogenation was complete, the catalyst and solvent were removed, and a total of 2.00 g (67%) of 6-*endo*-N-pyrrolidinomethylbicyclo[3.1.0]hexane (18) was obtained: bp 58° (0.45 mm); n^{26}D 1.4920; λ_{max}^{film} 3030 cm^{-1} (cyclopropyl hydrogen).

Anal. Calcd for $C_{11}H_{19}N$: C, 79.94; H, 11.59; N, 8.48. Found: C, 79.89; H, 11.49; N, 8.36.

Reaction of Bicyclo[3.1.0]hex-2-ene-6-*endo*-carboxaldehyde (14) with Methylmagnesium Iodide.—To a stirred solution of 0.14 mol of methylmagnesium iodide in 200 ml of ether was added 13.56 g (0.125 mol) of aldehyde 14 in 50 ml of ether. The stirred solution was refluxed for 1 hr, decomposed with saturated aqueous ammonium chloride, filtered, removed of solvent, and distilled. A total of 8.2 g (53%) of 1-hydroxy-1-bicyclo[3.1.0]hex-2-ene-6-*endo*-ethane (21) was obtained: bp 74° (15 mm); n^{24}D 1.4895; ν_{max}^{film} 3350 cm^{-1} (OH); nmr (DMSO) τ 4.50 (cyclopentene C=CH) and 5.90 ppm (-CH$_3$).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.42; H, 9.92.

Reaction of Cyclopropyl Methyl Ketone (3) with Pyrrolidine.—A stirred solution of 8.41 g (0.1 mol) of **3**, 14.22 g (0.2 mol) of pyrrolidine, 0.1 g of *p*-toluenesulfonate, and 300 ml of benzene was refluxed with continuous removal of water for 72 hr. The solvent was removed and the residual oil was distilled to give 1.69 g (12%) of a mixture of enamines **4** and **6**, bp 55° (1.5 mm). Treatment of an ether solution of this reaction product with ethanolic perchloric acid resulted in the formation of ternary iminium perchlorate salt **5**,[9] colorless plates from isopropyl alcohol, mp 173–174°, ν_{max}^{Nujol} 1649 cm^{-1}.

Anal. Calcd for $C_9H_{16}ClNO_4$: C, 45.48; H, 6.79. Found: C, 45.53; H, 6.93.

Registry No.—**3**, 765-43-5; **4**, 23735-64-0; **5**, 23735-65-1; **6**, 23735-66-2; **7**, 1489-69-6; **9**, 23735-68-4; **10**, 23735-69-5; **13**, 563-80-4; **15a**, 23735-71-9; **15b**, 23735-72-0; **15d**, 23735-73-1; **16a**, 23735-74-2; **16b**, 23735-75-3; **16c**, 23735-76-4; **16d**, 23735-77-5; **17**, 23735-78-6; **18**, 23809-48-5; **19**, 4729-42-4; **20**, 23735-80-0; **21**, 23735-81-1; **22**, 19995-92-7; **26**, 122-00-9; **27**, 823-76-7; **28**, 3019-25-8; **29**, 1567-75-5; **30**, 22482-71-9; *exo*-**31**, 824-59-9; *endo*-**31**, 824-58-8; **32**, 23735-46-8.

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