A Nuclear Magnetic Resonance Evaluation of Cyclopropyl Participation in Rigid, Tricyclic Cyclopropyl Ketones

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The geometric requirements for ground-state cyclopropyl ketone delocalization were probed by comparing the chemical-shift behavior of the H_β cyclopropyl protons in conformationally defined, rigid ketones and the corresponding hydrocarbons. The tricyclo[2.2.1.0^{2,6}]heptan-7-yl (2) and the tetracyclo[2.2.1.0.^{2,6}0^{3,5}]heptan-7-yl (3) skeletons were used as models for the bisected conformation (A). Tricyclo[3.3.0.0^{2,8}]octan-3-yl (8) derivatives served as models for the unsymmetrical, "bicyclobutonium ion" conformation (B). Nonconjugative carbonyl group contributions to the cyclopropyl proton shifts were estimated using appropriate bicyclic models. These effects as well as ring strain effects were found to be minimal. The downfield shifts observed for the bisected systems follow: 2, 1.1 ppm; 3, 0.8 ppm. For the unsymmetrical model 8, the shift was 0.1–0.5 ppm. These data provide direct support for the hypothesis of maximum delocalization in the bisected conformation. Delocalization in B did not involve preferential conjugation of the cyclopropane carbon–carbon bond "geometrically disposed for overlap."
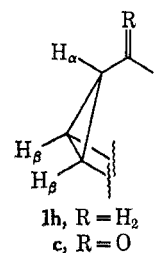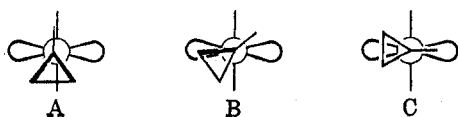
The presence or absence of specific geometric requirements for conjugative interaction of a cyclopropane ring with an adjacent chromophore constitutes an area of active interest.[2] Three distinct conformations have been considered: the bisected species A, the unsymmetrical or bicyclobutonium ion geometry B, and the symmetrical arrangement C. Recent structural studies on freely rotating systems containing a cyclopropyl moiety adjacent to an electron-deficient center (carbonyl group[3] or carbonium ion[4,5]) have established that the bisected conformer A represents a conformational energy minimum.[6] These data, in turn, have been interpreted as evidence supporting the hypothesis of maximum overlap in conformation A.[4-7] With respect to conformer C, this conclusion seems justified. Studies in hindered systems[5] have shown that interaction between a cyclopropane ring and an adjacent cationic center is reduced considerably[5a] (or becomes negligible[5b]) when the system is constrained to geometry C.[6b] The analogous comparison between conformers A and B, however, is less firmly established. While the cumulative evidence suggests clearly that A provides the optimum geometry for interaction, an

independent, direct determination of the ground-state delocalization *possible* in B would provide a more rigorous test of this hypothesis.

Since conformationally mobile systems are not suited for such an investigation, an examination of cyclopropyl ketone participation in geometrically defined, rigid systems was undertaken. In this way the conjugative participation possible in each conformation, A and B, could be evaluated individually using proton nmr. The results described provide support for the hypothesis of maximum delocalization in conformation A (compared with B), and they qualitatively define the nature of delocalization in conformation B.

Methods and Results

The ground-state participation in each tricyclic cyclopropyl ketone was probed by comparing the chemical shift behavior of the more remote H_β proton (see part structure 1 for notation) in the ketone (1c) with that in the reference hydrocarbon (1h). In order

1h, R = H$_2$
c, R = O

to interpret these data in terms of cyclopropyl ketone resonance, however, the contribution of several nonconjugative effects to the chemical-shift behavior of the H_β protons required evaluation. These include carbonyl group anisotropy and inductive effects, ring strain effects within a given system, and the effect of strain differences in the series of systems examined. The transoid relationship of the carbonyl group and the H_β protons (see 1c) tentatively suggested that the carbonyl group effects should be relatively unimportant. Verification of this assumption was obtained in the following way. The steric and spacial relationships of the H_β protons and the carbonyl group were approximated by means of bicyclic systems. Since these systems do not contain a cyclopropyl group and consequently conjugation is not possible, a comparison of

(1) Partial financial support from the University of Texas Research Institute is gratefully acknowledged.

(2) Reviews: (a) R. Breslow in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y. 1963, Chapter 3; (b) J. P. Pete, *Bull. Soc. Chim. Fr.*, 357 (1967); (c) M. Hanack and H. J. Schneider, *Angew. Chem., Intern. Ed. Engl.*, **6**, 666 (1967).

(3) L. S. Bartell and J. P. Guillory, *J. Chem. Phys.*, **43**, 647, 654 (1965); L. S. Bartell, J. P. Guillory, and A. P. Parks, *J. Phys. Chem.*, **69**, 3043 (1965).

(4) N. C. Deno, H. G. Richey, Jr., J. S. Liu, D. N. Lincoln, and J. O. Turner, *J. Amer. Chem. Soc.*, **87**, 4533 (1965); C. U. Pittman, Jr., and G. A. Olah, *ibid.*, **87**, 5123 (1965); P. von R. Schleyer and G. W. VanDine, *ibid.*, **88**, 2321 (1966); H. G. Richey, Jr., and J. M. Richey, *ibid.*, **88**, 4971 (1966).

(5) (a) T. Sharpe and J. C. Martin, *ibid.*, **88**, 1815 (1966); (b) H. C. Brown and J. D. Cleveland, *ibid.*, **88**, 2051 (1966).

(6) For similar studies, also see (a) G. L. Closs and H. B. Klinger, *ibid.*, **87**, 3265 (1965); W. G. Dauben and G. H. Berezin, *ibid.*, **89**, 3449 (1967); C. H. Heathcock and S. R. Poulter, *ibid.*, **90**, 3766 (1968); M. J. Jorgenson and T. Leung, *ibid.*, **90**, 3769 (1968); G. R. De Mare and J. S. Martin, *ibid.*, **88**, 5033 (1966); G. A. Russell and J. Malkus, *ibid.*, **89**, 160 (1967); A. H. Cowley and T. A. Furtsch, *ibid.*, **91**, 39 (1969). (b) Conformation C is preferred, however, for cyclopropyl interaction with an adjacent electron-rich center; *cf.* N. L. Bauld, R. Gordon, and J. Zoeller, *ibid.*, **89**, 3948 (1967).

(7) R. Hoffmann, *Tetrahedron Lett.*, 3819 (1965); K. Shimizu, H. Kato and T. Yonezawa, *Nippon Kagaku Zasshi*, **88**, 1050 (1967); *Chem. Abstr.*, **68**, 77601 (1968).

the chemical-shift parameters for the appropriate H_β proton models in the ketone and the hydrocarbon provided an estimate of the nonconjugative carbonyl group effects. These bicyclic systems also provide a crude estimate of the strain effects due to the introduction of a sp^2-hybridized carbon atom in a given system. As discussed below in detail for each specific system, the introduction of a carbonyl group has a negligible influence on the relative H_β proton chemical shifts. The internal ring strain contributions to the H_β proton shifts were minimized by restricting chemical shift comparisons to a given system.

In addition to differences in the relative geometries of the cyclopropane ring and the carbonyl group, the series examined differ in ring strain. The possibility that these changes in strain make a significant, non-conjugative contribution to the comparative results obtained seems unlikely, however, since both un-strained, acyclic cyclopropyl ketones[3-5] and the more strained of the systems examined in the present work (*i.e.*, 2 and 3; *vide infra*) show qualitatively the same interaction.

As models for cyclopropyl ketone delocalization in the rigid, bisected conformation A, tricyclo[2.2.1.0^{2,6}]-heptan-7-one (2c)[8,9] (nortricyclanone) and tetracyclo-[2.2.1.0^{2,6}0^{3,5}]heptan-7-one (3c)[10] (quadricyclanone) were used. These nmr data, together with those for related systems and for the nonrigid 1-acetylnortri-cyclanone (4),[11] are given in Table I. A preliminary

2h, R = H$_2$
c, R = O
m, R = CH$_2$

3h, R = H$_2$
c, R = O

4

5, R = O; R' = H$_2$
6, R = H$_2$; R' = O

7
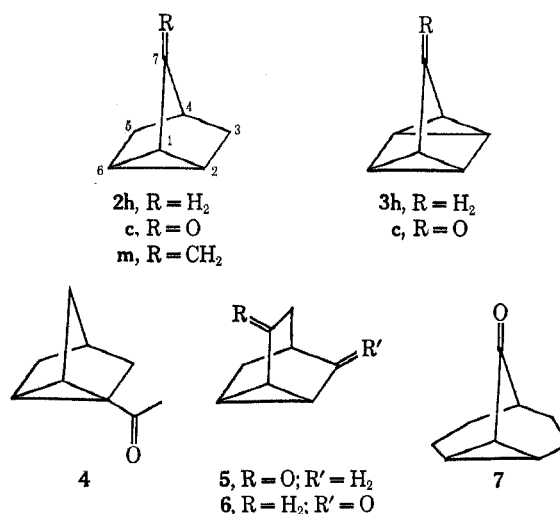
Tricyclo[3.3.0.0^{2,8}]octan-3-one (8c)[14] was used as a model for cyclopropyl ketone participation fixed in the unsymmetrical geometry B. An inspection of stereo-models shows that the system is quite rigid and that the C_2–C_8 σ-cyclopropane carbon–carbon bond forms a dihedral angle of *ca.* 25° with the π bond of the carbonyl group. Thus this cyclopropane bond is preferentially oriented for overlap with the adjacent carbonyl group. The chemical-shift data for this ketone and the related hydrocarbon (8h) are given in Table II. In addition, tentative assignments for the published nmr spectrum[15] of the vinylcyclopropane 9 are included in Table II.

TABLE I
100-MHz NMR DATA FOR
SOME BISECTED CYCLOPROPYL KETONES[a]

	Hα	Hβ	H$_4$	–CH$_2$–
2h	0.95	0.95	1.90	1.18
2c	1.10	2.07	1.80	1.65, 1.97
2m	1.4	1.4	2.10	1.4
3h[b]	1.4	1.4		2.0
3c[c]	1.02	2.21		
4		1.83	2.08	1.38 (4H), 1.47 (2H)

[a] Chemical shifts determined in this work are reported for 10–20% carbon tetrachloride solutions, in parts per million downfield from internal tetramethylsilane. Using 2c as a model, the cyclopropyl proton chemical shifts were shown to be independent of concentration (see Experimental Section for details). [b] Values from W. G. Dauben and R. L. Cargill, *Tetrahedron*, **15**, 197 (1961), carbon tetrachloride solution, concentration not specified. [c] Values from P. R. Story and S. R. Fahrenholtz, ref 10, carbon tetrachloride solution, concentration not specified.

examination of two less strained models for A, namely tricyclo[3.2.1.0^{2,7}]octan-3-one (5)[12] and tricyclo-[3.3.1.0^{2,8}]nonan-9-one (7),[13] as well as the slightly skewed tricyclo[3.2.1.0^{2,7}]octan-8-one (6),[13] was made. Unfortunately, a coalescence of all protons in the nmr spectra of these ketones precluded precise assignments for the H_β protons.

TABLE II
100-MHz NMR DATA FOR
THE TRICYCLO[3.3.0.0^{2,8}]OCTAN-3-YL SKELETON[a]

	Hα	——Hβ——		——H$_4$——		H$_5$	–CH$_2$–
		C$_1$	C$_8$	*exo*	*endo*		
8h	1.4[b]	1.8[c]	1.4[b]			2.55	1.4, 1.8
8c[d]	1.80	2.65	1.96	2.38	1.56	2.90	1.56, 2.05
9[e]	1.92	2.42	1.7[f]			3.04	1.7[f]

[a] See Table I. [b] Range of 1.17–1.65 ppm. [c] Range of 1.65–2.05 ppm. [d] Data from ref 14, 20% carbon tetrachloride solution. [e] See text and ref 15, degassed deuteriochloroform solution, concentration not specified. [f] Range of 1.45–1.90 ppm.

These assignments are based on the analysis presented by Chapman and coworkers[15] and on analogy with the presence of a low-field, one-proton quartet in both 8c and 9.

The nonconjugative effects of introducing a carbonyl group into a bisected framework, (*i.e.*, skeleton 2 or 3) were estimated with the bicyclo[2.2.1]heptan-2-yl system (10). Stereomodels show that the C$_4$-bridge-head proton in ketone 10c reasonably approximates the spacial arrangement of the H_β proton in ketones 2c and 3c with respect to the carbonyl group. The increase in strain accompanying the introduction of an sp^2 carbon, however, is only qualitatively the same for 2, 3, and 10. Since conjugation is not possible in 10c, a comparison of the chemical-shift behavior of the C$_4$ H in hydrocarbon 10h with that in the ketone 10c will give an estimate of the composite nonconjugative carbonyl group effects.

(8) J. Meinwald and J. K. Crandall, *J. Amer. Chem. Soc.*, **88**, 1292 (1966); *Org. Syn.*, **45**, 74 (1965).

(9) R. R. Sauers and P. E. Sonnet, *Chem. Ind.* (London), 786 (1963).

(10) P. R. Story and S. R. Fahrenholtz, *J. Amer. Chem. Soc.*, **86**, 1270 (1964).

(11) Kindly provided by Professor H. Hart: H. Hart and R. A. Martin, *J. Org. Chem.*, **24**, 1267 (1959).

(12) W. R. Moore, W. R. Moser, and J. E. LaPrade, *ibid.*, **28**, 2200 (1963).

(13) W. von E. Doering, E. T. Fossel and R. L. Kaye, *Tetrahedron*, **21**, 25 (1965).

(14) S. A. Monti, D. J. Bucheck, and J. C. Shepard, *J. Org. Chem.*, **34**, 3080 (1969).

(15) O. L. Chapman, G. W. Borden, R. W. King, and B. Winkler, *J. Amer. Chem. Soc.*, **86**, 2660 (1964).

In norbornane (10h) this proton appears at 2.2 ppm.[16] The chemical shift of this proton in camphor (10c, 1,7,7-trimethyl) is *ca.* 2.2 ppm.[17] Thus the nonconjugative effects in these ring systems appear negligible.

8h, R = H₂
c, R = O

9

10h, R = H₂
c, R = O

11h, R = H₂
c, R = O

12h, R = H₂
c, R = O
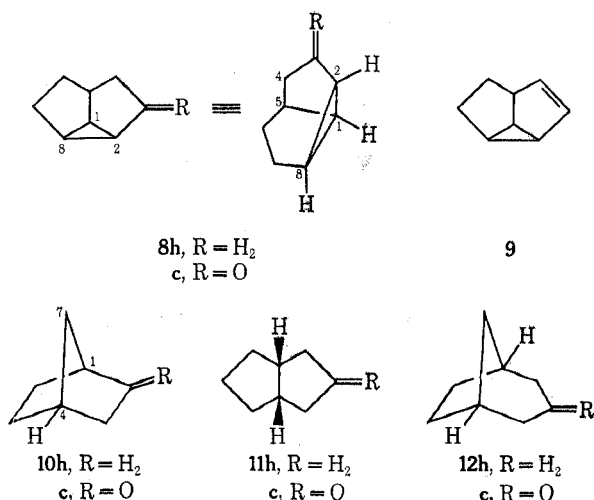
In the unsymmetric ketone 8c, the H_β protons are nonequivalent. As a model for the H_1 proton in 8c, the tertiary protons in the *cis*-tricyclo[3.3.0]octan-3-yl skeleton (11) were used. Once again, stereomodels confirm the appropriateness of this model. In hydrocarbon 11h, this proton resonates at 2.4 ppm[18] and in the ketone 11c at 2.6 ppm.[14] Thus a *ca.* 0.2-ppm *downfield* shift results from nonconjugative carbonyl effects at H_1. In a similar way, the bridgehead protons in the bicyclo[3.2.1]octan-3-yl system (12) were used as a model for the H_8 proton in 8c. Although two conformations are possible for 12c, stereomodels show that this system constitutes a reasonable model. In ketone 12c, the bridgehead proton appears at 2.5 ppm.[14] Literature data for the hydrocarbon 12h are unavailable, but an estimate of 2.2–2.4 ppm for this tertiary proton seems reasonable on comparison with 10h and 11h. Thus, a *downfield* shift of *ca.* 0.1–0.3 ppm would also be expected for H_8 in 8c. This is in the same direction and of approximately the same magnitude as that estimated for H_1. Consequently these nonconjugative carbonyl effects essentially cancel one another when a relative comparison of the H_1 and H_8 chemical shifts is made.

Discussion

In the bisected conformation A, charge delocalization in the cyclopropyl ketone system is postulated to involve equal participation of two cyclopropane σ bonds (bonds darkened in A). Since nonconjugative effects associated with the introduction of a carbonyl group into the bisected skeleton were shown to be minimal, any resonance effects would be reflected in a downfield shift for the H_β protons. An inspection of the data in Table I clearly verifies the presence of such charge delocalization in this conformation. In the nortricyclene skeleton 2, a paramagnetic shift of 1.12 ppm for the magnetically identical H_β protons results on going from nortricyclene (2h) to nortricyclanone

(16) MIT Seminars in Organic Chemistry, Fall semester, 1961, Spectrum No. 52.
(17) Sadtler NMR Spectra Catalogue, Spectrum No. 30.
(18) W. B. Moniz and J. A. Dixon, *J. Amer. Chem. Soc.*, **83**, 1671 (1961).

(2c). A further indication of the charge delocalization to the C_2 and C_6 carbon atoms of 2c is provided by a comparison of the methylene proton chemical shifts in 2h and 2c. Both the *exo* and *endo* methylene protons of 2c are shifted downfield by *ca.* 0.5–0.8 ppm. Since the *exo* protons are located in the *shielding* cone of the carbonyl group, they are assigned to the 1.65-ppm resonance and the *endo* protons to the 1.97-ppm signal. The paramagnetic shift of both sets of methylene protons strongly supports the presence of two electron-deficient cyclopropyl carbon atoms in 2c.

A similar examination of the data for the cross-conjugated quadricyclene system (3) shows that the H_β protons of 3c are shifted downfield by 0.8 ppm. Both the cross-conjugated nature of 3c and the electrostatic consequences of the vicinal relationship of the two sets of H_β carbon atoms could account for the diminished participation qualitatively suggested by the relative magnitudes of the H_β proton shifts for 3c (0.8 ppm) *vs.* 2c (1.12 ppm). A more quantitative interpretation of this difference seems unwarranted, however, since the effect of subtle nonconjugative environmental differences between the two system cannot be evaluated accurately.

If one assumes that the nonconjugative anisotropy and strain effects of a methylene group are similar to those of a carbonyl group, the data in Table I for the exocyclic methylene derivative 2m support vinylcyclopropane conjugation in the bisected conformation A. The magnitude of the H_β proton shift (*ca.* 0.45 ppm) suggests less charge delocalization than observed for the carbonyl group, as expected. Once again these data support only general trends and should not be interpreted quantitatively.

By way of comparison, the magnetically equivalent H_β protons of the nonrigid 1-acetylnortricyclene (4)[11] appear *ca.* 0.9 ppm lower field than in the reference hydrocarbon 2h. Since this molecule can adopt both a cisoid and a transoid bisected conformation, the observed shift most probably reflects charge delocalization as well as carbonyl group anisotropy effects.

In the unsymmetrical geometry B, participation is postulated to involve preferential overlap of only *one* cyclopropane σ bond with the adjacent carbonyl group (bond darkened in B). As a consequence of this selective overlap, delocalization in a conformationally rigid system would result in nonequivalent chemical-shift behavior for the two H_β protons. In terms of the tricyclo[3.3.0.0²,⁸]octan-3-yl skeleton 8, this hypothesis requires that the C_8 H_β proton experience a greater downfield shift than the C_1 H_β proton upon introduction of a carbonyl group. As seen in Table II, the data for this system are at variance with this postulate. The C_1 H_β proton is shifted downfield *ca.* 0.7 ppm in ketone 8c and the C_8 H_β proton *ca.* 0.4 ppm. If one corrects for the nonconjugative carbonyl group effects, *ca.* 0.2 ppm for the C_1 H position and *ca.* 0.1–0.3p pm for the C_8 H position, the C_1 H_β proton experiences a greater paramagnetic shift (*ca.* 0.5 ppm) than the C_8 H_β proton (*ca.* 0.1–0.3 ppm).

These results suggest that for rigid tricyclic systems, cyclopropyl ketone delocalization in the unsymmetrical geometry B does not involve preferential conjugation of the cyclopropane carbon–carbon bond "geometrically disposed for overlap" (bond darkened in B). Com-

parison of the downfield shifts observed in the bisected geometry A (2, 1.1, and 3, 0.8 ppm) and in the unsymmetrical geometry B (8, 0.1–0.5 ppm) provides direct support for the proposition that ground-state cyclopropyl ketone delocalization is maximized in the bisected conformation.

An examination of the relevant data for the unsymmetrical vinylcyclopropane 9 (see Table II) leads to conclusions analogous to those obtained for carbonyl group conjugation. There is no evidence to support selective overlap of the C_2–C_8 σ bond. Since an accurate estimate of the carbon–carbon double-bond anisotropy and other nonconjugative effects on the H_β proton resonances due to the presence of two sp²-hydridized carbons in 9 is more tenuous, these tentative conclusions concerning the geometric parameters for vinylcyclopropane participation require further support.

Experimental Section

Nmr spectra were obtained on a Varian Associates Model HA-100 spectrometer; infrared spectra were measured on a Perkin-Elmer Model 237 or 257 grating infrared spectrometer.

Nortricyclene (2h) was prepared by the method of Schleyer.[19] The cyclopropyl hydrogen–carbon-13 coupling constant of $^1J_{^{13}CH} = 175$ Hz was measured.[20]

(19) P. von R. Schleyer, *J. Amer. Chem. Soc.*, **80**, 1700 (1958).

Nortricyclanone (2c) was prepared by the method of Meinwald.[8] The $^1J_{^{13}CH}$ for the H_α position was 184 Hz and for the H_β position 185 Hz.[20] The chemical shifts of the H_α, H_β, and *exo*-CH₂- (1.65 ppm) protons remained constant (±1 Hz) on going from a neat sample to a 2.5% CCl₄ solution. The C_4 H⁹ and the *endo*-CH₂- (1.97 ppm) protons were shifted *ca.* 8 and 4 Hz, respectively, upon dilution.

3-Methylenetricyclo[2.2.1.0²,⁶]heptane (2m) was prepared from nortricyclanone (2c) using the Corey[21] modification of the Wittig reaction. The crude product was purified by chromatography on silica gel using pentane. Distillation furnished pure 2m: bp 113–114°; average yield of three runs *ca.* 16%; ir (CCl₄) 1684 cm⁻¹; nmr (CCl₄), 4.48, 1 H (singlet), 4.60 ppm, 1 H (d, J ~ 1 Hz) (see Table I).

Tricyclo[3.3.0.0²,⁸]octane (8h) was prepared from ketone 8c[14] using the Huang-Minlon adaptation of the Wolff–Kishner reduction.[22] The crude product was purified by preparative vpc to give hydrocarbon 8h:[23] mol wt (mass spectrum) 108; nmr (CCl₄), 1.17–1.65 (6 H, complex), 1.65–2.05 ppm (5 H, complex) (see Table II).

Registry No.—2c, 279-19-6; 2h, 695-05-6; 2m, 1974-87-4; 4, 22482-71-9; 8h, 2401-89-0.

(20) The generous assistance of Dr. M. Gordon in obtaining these data is gratefully acknowledged.

(21) R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, **28**, 1128 (1963).

(22) *Cf.* N. A. LeBel and R. M. Liesemer, *J. Amer. Chem. Soc.*, **87**, 4301 (1965).

(23) Alternate preparations: J. Zirner and S. Winstein, *Proc. Chem. Soc.* (London), 235 (1964); M. Schwarz, A. Besold, and E. R. Nelson, *J. Org. Chem.*, **30**, 2425 (1965).

Condensation–Cyclization of Diketones and Keto Esters with Electron-Deficient Aromatics. I. Formation and Structure of Some Stable Delocalized Anions Containing the Bicyclo[3.3.1]nonane Skeleton

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A series of new bicyclic anions containing the bicyclo[3.3.1]nonane skeleton have been prepared from *sym*-trinitrobenzene, 3,5-dinitrobenzonitrile, and methyl 3,5-dinitrobenzoate. The electron-deficient aromatics are bridged across the *ortho* and *para* positions with various ketones and keto esters such as acetone, dicarbomethoxyacetone, ethyl acetoacetate, α-acetylbutyrolactone, and acetylacetone. The condensation–cyclizations are initiated with primary, secondary, and tertiary amines. Two distinct mechanistic routes are indicated. With acetone and secondary amines, an enamine intermediate is proposed as a precursor to the bicyclic anion. With more acidic ketones and keto esters (*i.e.*, acetylacetone and ethyl acetoacetate) a delocalized carbanion intermediate is involved.

The chemistry of σ complexes arising from the interaction of electron-deficient aromatics and bases has received considerable attention during the past five years and has recently been reviewed.[2,3] We have reported preliminary investigations of a new type of extremely stable bicyclic anion which results from internal cyclization in certain σ complexes.[4,5] The bicyclic structure 1 was observed to form upon addition of diethylamine to a solution of *sym*-trinitrobenzene in acetone,[4] whereas 2 was formed upon addition of triethylamine to a mull of *sym*-trinitrobenzene and dibenzyl ketone.[5] The total stereochemistry of 2 has not yet been determined, but isomers with the phenyl groups *cis* and *trans* have been isolated.[6] It was

originally supposed that formation of such bicyclic anions occurred only with *sym*-trinitrobenzene and specific ketones. We have since discovered that the reaction is quite general and occurs with a variety of structurally different diketones and keto esters with various electron-deficient benzenes in the presence of primary, secondary, and tertiary amines. We report here results of investigations carried out with *sym*-trinitrobenzene, 3,5-dinitrobenzonitrile, and methyl 3,5-dinitrobenzoate. Acetone, ethyl acetoacetate, acetylacetone, α-acetylbutyrolactone, and 1,3-dicarbomethoxyacetone all were utilized as ketonic addends. Piperidine, *t*-butylamine, diethylamine, and triethylamine all were effective in promoting reaction, but the triethylammonium salts crystallized particularly well (see Experimental Section). The mechanistic routes leading to the bicyclic anions are discussed and two different reaction paths are proposed.

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(4) M. J. Strauss and H. Schran, *J. Amer. Chem. Soc.*, **91**, 3974 (1969).

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(6) M. I. Foreman, R. Foster, and M. J. Strauss, *J. Chem. Soc.*, in press.