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_3 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 sp^2-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]

Nortricyclanone (**2c**) was prepared by the method of Meinwald.[3] 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*-CH_2– (1.65 ppm) protons remained constant (±1 Hz) on going from a neat sample to a 2.5% CCl_4 solution. The C_4 H^9 and the *endo*-CH_2– (1.97 ppm) protons were shifted *ca.* 8 and 4 Hz, respectively, upon dilution.

3-Methylenetricyclo[2.2.1.0^{2,6}]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 (CCl_4) 1684 cm^{-1}; nmr (CCl_4), 4.48, 1 H (singlet), 4.60 ppm, 1 H (d, $J \sim 1$ Hz) (see Table I).

Tricyclo[3.3.0.0^{2,8}]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 (CCl_4), 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.

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

(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

M. J. STRAUSS,[1] T. C. JENSEN, H. SCHRAN, AND K. O'CONNER

Department of Chemistry, University of Vermont, Burlington, Vermont 05401

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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.

(1) To whom all inquiries should be addressed.

(2) R. Foster and C. A. Fyfe, *Rev. Pure Appl. Chem.*, **16**, 61 (1966).

(3) E. Buncel, A. R. Norris, and K. E. Russell, *Quart. Rev.* (London), 123 (1968).

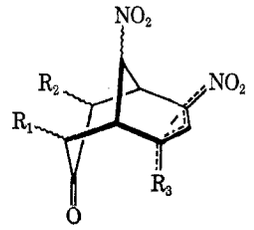
(4) M. J. Strauss and H. Schran, *J. Amer. Chem. Soc.*, **91**, 3974 (1969).

(5) R. Foster, M. I. Foreman, and M. J. Strauss, *Tetrahedron Lett.*, 4949 (1968).

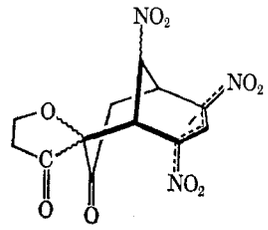
(6) M. I. Foreman, R. Foster, and M. J. Strauss, *J. Chem. Soc.*, in press.

TABLE I

TRINITRO, CYANODINITRO, AND CARBOMETHOXYDINITRO ANIONS



1–7 and 9–13



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Compd	Aromatic compd	Amine	Ketone or keto ester	Product
1	*sym*-Trinitrobenzene	$HN(CH_2CH_3)_2$	Acetone	$R_1 = R_2 = H$; $R_3 = NO_2$
2	*sym*-Trinitrobenzene	$N(CH_2CH_3)_3$	Dibenzyl ketone	$R_1 = R_2 = C_6H_5$; $R_3 = NO_2$
3	*sym*-Trinitrobenzene	$HN(CH_2CH_3)_2$	Acetylacetone	$R_1 = COCH_3$; $R_2 = H$; $R_3 = NO_2$
4	*sym*-Trinitrobenzene	$N(CH_2CH_3)_3$	Acetylacetone	$R_1 = COCH_3$; $R_2 = H$; $R_3 = NO_2$
5	*sym*-Trinitrobenzene	*t*-$BuNH_2$	Acetylacetone	$R_1 = COCH_3$; $R_2 = H$; $R_3 = NO_2$
6	*sym*-Trinitrobenzene	Piperidine	Acetylacetone	$R_1 = COCH_3$; $R_2 = H$; $R_3 = NO_2$
7	*sym*-Trinitrobenzene	$N(CH_2CH_3)_3$	Ethyl acetoacetate	$R_1 = CO_2CH_2CH_3$; $R_2 = H$; $R_3 = NO_2$
8	*sym*-Trinitrobenzene	$N(CH_2CH_3)_3$	α-Acetylbutyrolactone	
9	*sym*-Trinitrobenzene	$N(CH_2CH_3)_3$	1,3-Dicarbomethoxyacetone	$R_1 = R_2 = CO_2CH_3$; $R_3 = NO_2$
10	3,5-Dinitrobenzonitrile	$N(CH_2CH_3)_3$	Ethyl acetoacetate	R_1 or $R_2 = CO_2CH_2CH_3$; R_2 or $R_1 = H$; $R_3 = CN$
11	3,5-Dinitrobenzonitrile	$N(CH_2CH_3)_3$	1,3-Dicarbomethoxyacetone	$R_1 = R_2 = CO_2CH_3$; $R_3 = CN$
12	Methyl 3,5-dinitrobenzoate	$N(CH_2CH_3)_3$	1,3-Dicarbomethoxyacetone	$R_1 = R_2 = CO_2CH_3$; $R_3 = CO_2CH_3$
13	Methyl 3,5-dinitrobenzoate	$HN(CH_2CH_3)_2$	Acetone	$R_1 = R_2 = H$; $R_3 = CO_2CH_3$

The various complexes investigated are summarized in Table I.

Nmr Spectra.—The adducts **1–13** are moderately soluble in polar organic solvents such as acetone and methanol. They are also slightly soluble in water and in some cases chloroform. Nmr spectra were obtained from solutions prepared by dissolving recrystallized adduct in acetone-d_6, DMSO-d_6, chloroform-d_1, or a mixture of the latter two. In many cases the resulting products are a mixture of stereoisomers. Unsuccessful attempts at separation were made by fractional crystallization and column chromatography. The resulting nmr spectra of the crude adducts are consequently difficult to interpret in certain instances. The spectra were run on a Varian A-60 instrument with TMS as an internal reference. Some pertinent spectral data are summarized in Table II.

Visible Spectra.—The trinitro complexes **1–9** are brilliant red-orange crystals. Substitution of a cyano or carbomethoxy group on the delocalized anionic portion of the structure results in bright yellow crystals of **10–13**. These qualitative color characteristics result from changes in the delocalized propenide portion of the molecule and are illustrated in a more quantitative fashion by the visible absorption maxima in acetone and methanol solution. For the complexes **1–9**, λ_{max} is 505 ± 10 mμ and ϵ_{max} is 30,000–50,000, and for **10–13**, λ_{max} is 377 ± 5 mμ and ϵ_{max} is 18,000–22,000. The absorption maxima are summarized in the Experimental Section. The visible spectra were run on a Perkin-Elmer 202 UV-Visible spectrophotometer.

Discussion

The Acetone and Acetylacetone Adducts.—The nmr spectrum of the bicyclic anion **1** formed from *sym*-trinitrobenzene, acetone, and diethylamine has previously been described.[4] The dinitropropenide proton appears as a singlet at δ 8.52. The bridging $HCNO_2$ proton appears as a triplet centered at δ 5.72 and probably lies over the bridging carbonyl function. This stereochemistry has been assigned on the basis of chemical-shift comparisons with other aliphatic nitro compounds in acetone solution.[4] The two bridgehead protons appear as a poorly resolved doublet at δ 4.53. When methyl 3,5-dinitrobenzoate is used as the electron-difficient aromatic compound, the nmr spectrum of the adduct **13** is consistent with a structure in which the CO_2CH_3 group is part of the delocalized anionic function. Although a small quantity of DMSO-d_6 was added to aid dissolution of **13**, the major chemical-shift differences between this adduct and **1** are most likely due to structural changes and not solvent effects. The bridging $HCNO_2$ proton appears at essentially the same frequency as in **1**. The propenide proton in **13** appears 0.55 ppm upfield from that in **1**. This would be expected if the CO_2CH_3 function is attached to the delocalized propenide portion of the molecule. Since this group is much less electronegative than NO_2, electron density should then be higher on the carbon framework in **13** and result in greater shielding of the propenide proton. The bridgehead positions in **13** are not equivalent and appear as two broad absorptions at δ 4.45 and 3.98. This

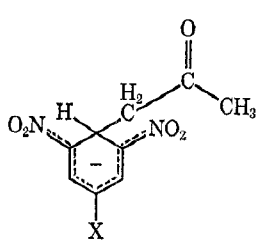
TABLE II

CHEMICAL SHIFTS (δ VALUES) AND SPLITTING[a] OF PROTONS IN THE BICYCLIC ANIONS **1–3, 8, 10,** AND **13** (MEASURED AT 60 MHz)

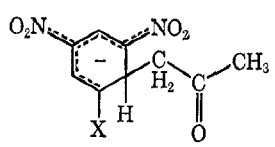
	Protons					
Adduct	Propenide	Bridgehead	Bridging $HCNO_2$	α to keto bridge	Other	Solvent
1[b]	8.52 (s, 1 H)	4.53 (m, 2 H)	5.72 (t, 1 H, J = 3 cps)	2.3–3.0 (m, 4 H)		Acetone-d_6
2[c]	8.59 (s, 1 H)	4.62 (m, 2 H)	5.97 (t, 1 H, J = 3 cps)	4.42 (m, 2 H)	7.13 (m, 10 H, aromatic H)	DMSO-d_6
3	8.40 (s, 1 H)	5.18 (m, 1 H) 4.20 (m, 1 H)	5.31 (m, 1 H)	Under acetyl group and cation absorptions	2.50 (s, 3 H, CH_3CO)	DMSO-d_6
8	8.50 (s, 1 H)	4.88 (t, 1 H, J = 3 cps) 4.4 (m, 1 H), under lactone OCH_2	6.18 (t, 1 H, J = 3 cps)	2.58 (m, 2 H), overlaps cation and CH_2C of lactone	4.4 (m, 2 H, OCH_2 of lactone) 2.58 (m, 2 H, CCH_2 of lactone)	$CDCl_3$–DMSO-d_6 (1:1)
10	7.43 (s, 1 H)	4.05 (br, 2 H), overlaps CH_2 of CO_2Et	5.11 (t, 1 H, J = 3 cps)	2.67 (m, 2 H), overlaps cation absorptions; $CHCO_2Et$ not observed (rapid exchange)[d]	4.27 (q, 2 H) 1.32 (t, 3 H) (both CO_2Et)	DMSO-d_6
13	7.97 (s, 1 H)	4.45 (br, 1 H) 3.98 (br, 1 H)	5.68 (t, 1 H, J = 3 cps)	Obscured by cation absorption	3.59 (s, 3 H, CO_2CH_3)	DMSO-d_6

[a] s = singlet; t = triplet; q = quartet; m = multiplet; br = broad. [b] Reference 4. [c] Reference 5. [d] Exchange with DMSO-d_6 solvent catalyzed by free amine should diminish the intensity of this absorption considerably.

difference cannot be explained on the basis of electronegativity effects, as other interactions might be quite important in this rigid structure. The CO_2CH_3 singlet in **13** appears at δ 3.59, 0.6 ppm upfield from that in the starting methyl 3,5-dinitrobenzoate, supporting the conclusion that the CO_2CH_3 function is part of the delocalized propenide system. The protons α to the carbonyl in **13** are obscured by partially protonated DMSO-d_6 solvent and the diethylammonium cation quartet. We have previously proposed[4] that **1** arises from an enamine σ complex as shown in Scheme I. A more direct path to **1**, through internal cyclization of a σ complex formed by attack of acetonate anion on *sym*-trinitrobenzene, is less likely, for reasons to be discussed shortly. A route involving an enamine σ-complex intermediate might also lead to **13**. Foreman and Foster have shown[7] that formation of σ complexes from 1-substituted 3,5-dinitrobenzenes, acetone, and triethylamine (which cannot form an enamine intermediate) occurs to give a mixture of both possible isomers, **14** and **15**, where X = CN or CF_3. If both



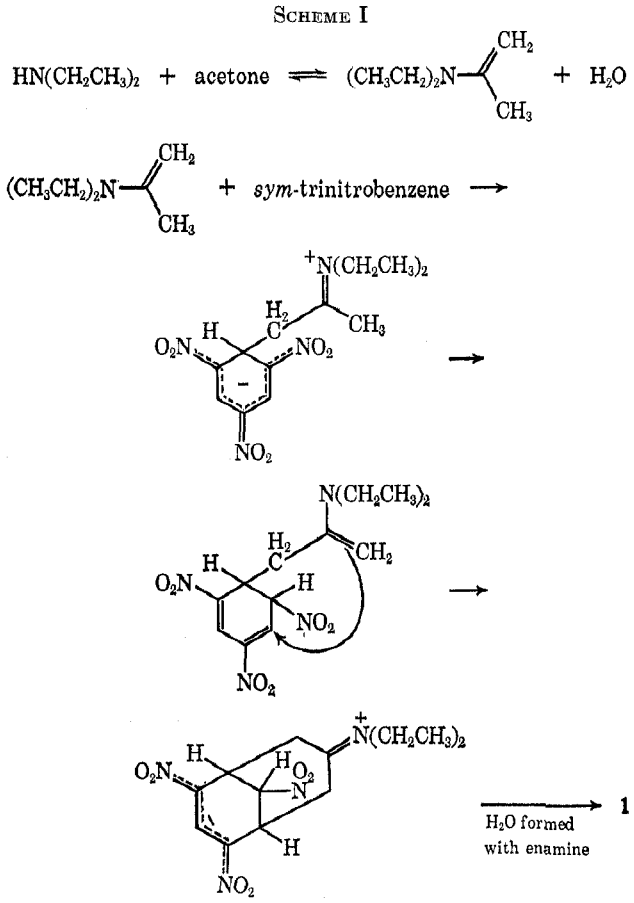
14



15

isomeric enamine σ complexes **16** and **17** are formed from methyl 3,5-dinitrobenzoate, acetone, and diethylamine, either one could lead directly to **13** (Scheme II). Although both **16** and **17** are probably in rapid equilibrium, since only **13** and not **18** is obtained as the final product, either **17** proceeds solely to **13** or

SCHEME I



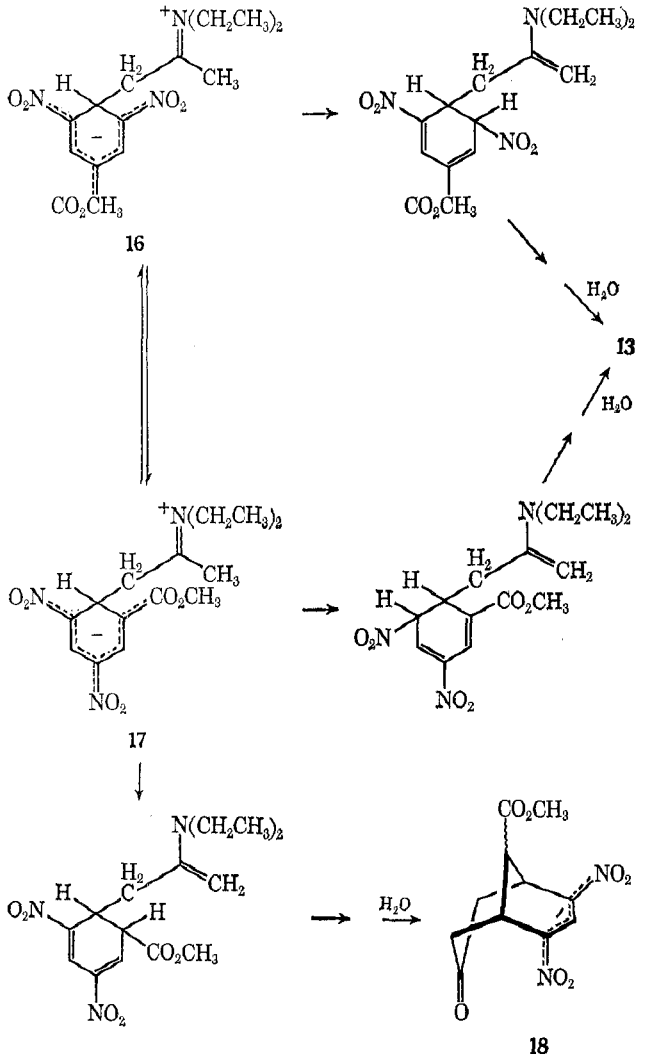
the conversion of **16** into **13** is kinetically or thermodynamically favored.

An alternative mechanistic pathway can be formulated which does not involve enamine intermediates (Scheme III). If triethylamine is used instead of diethylamine, the reaction with *sym*-trinitrobenzene and acetone stops at the σ-complex state and **19** can be isolated as the crystalline triethylammonium salt.[8]

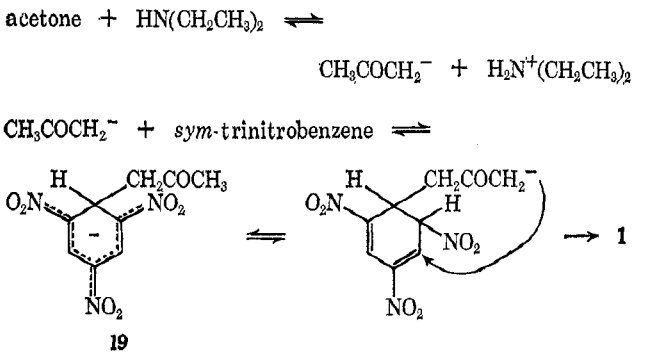
(7) M. I. Foreman and R. Foster, *Can. J. Chem.*, **47**, 729 (1969).

(8) R. Foster and C. A. Fyfe, *J. Chem. Soc., B*, 53 (1966).

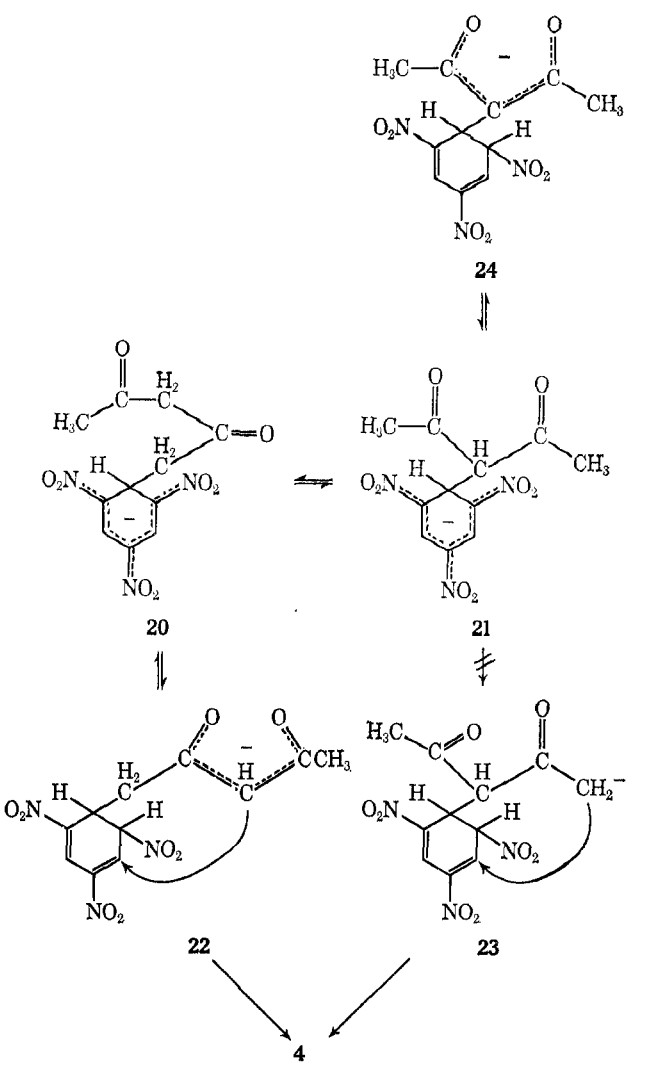
SCHEME II



SCHEME III



from the most acidic hydrogen available on the acetylacetonate moiety. In the case of **20** this would yield **22**, which is conformationally able to undergo intramolecular cyclization to **4**. With **21**, the result might be **24**, in which intramolecular cyclization cannot occur (except for unobserved intramolecular oxygen attack). Proton abstraction from the terminal methyl group in **21** is not favored even though the resultant **23** could



proceed directly to the bicyclic anion **4**. This is confirmed by the observation that with acetone itself the reaction stops at the σ-complex stage. These observations are consistent with the fact that diethylamine and triethylamine are effective in producing bicyclic structures like **2–12** with acidic ketones and

We have observed similar behavior with methyl 3,5-dinitrobenzoate, acetone, and triethylamine. If these reagents are mixed and left standing for 4 days, a purple solution results with a visible spectrum characteristic of anionic σ complexes.[2] In this case the complex cannot be isolated, presumably because the equilibrium lies far on the side of the reactants. With more acidic ketones and keto esters (*i.e.*, acetylacetone, ethyl acetoacetate), bicyclic structures like **2–12** are formed with both triethylamine and diethylamine, presumably by a route analogous to Scheme III. The enamines formed from such acidic species should be much less reactive than the enamine of acetone and diethylamine. In addition, σ complexes resulting from reaction of acetylacetone, triethylamine, and *sym*-trinitrobenzene, while they are detectable in the visible spectrum of the reaction solution, cannot be isolated. The bicyclic product **4** precipitates soon after the reagents are mixed. This is in marked contrast to the behavior of acetone itself, where the only isolable product is the σ complex **19**.

There are two possible initial complexes, **20** and **21**, which may form from acetylacetone, *sym*-trinitrobenzene, and triethylamine. Probably **20** and **21** would be in equilibrium and further intramolecular cyclization would favor that route which involves proton abstraction (intramolecularly or by solvent)

keto esters, but only diethylamine is effective with acetone, yielding **1** and **13**, where an enamine intermediate is probably involved.

The adducts formed from diethylamine and triethylamine with acetylacetone, **3** and **4**, are much less soluble in acetone than **1**. To obtain sufficiently resolved nmr spectra of the acetylacetone adducts, solutions were prepared with DMSO-d_6. These adducts are a mixture of stereoisomers, due to asymmetric centers at the $HCNO_2$ bridge and adjacent to the keto bridge, and exhibit complex nmr spectra. Similar isomerism has previously been observed in **2** where the phenyl groups can be *cis* or *trans*, and in that case the isomers were separated.[6] All the adducts **3–7** and **9–12** probably exist as a keto–enol equilibrium mixture containing a greater amount of the enolic structure. This point is further supported by the infrared spectra (*vide infra*). Since exchange with DMSO-d_6 catalyzed by traces of free amine is also a complicating factor, it is not surprising that the enolic and ammonium cation absorptions are difficult to detect in the nmr spectra determined in this solvent. Similar exchange resulting in a diminished $^+$NH absorption and increasing protonated solvent absorption has previously been observed in related systems.[4] The quadrupole moment of nitrogen also contributes to broadening of the $^+$NH signal.

The Ethyl Acetoacetate Adducts.—Ethyl acetoacetate condenses with *sym*-trinitrobenzene and with 3,5-dinitrobenzonitrile in the presence of triethylamine to yield the anions **7** and **10**, respectively. A number of isomers are possible in each case, resulting in complex nmr spectra. The propenide proton in **7** appears as a broad singlet at δ 8.33 (1 H), almost the same value observed for the propenide proton(s) in **4**. Evidently, the chemical shift of this kind of proton is very similar in the various isomers of **7**, a conclusion supported by the slight variation in shift of the propenide protons in all the trinitro adducts (Table III). Using

TABLE III

CHEMICAL SHIFT OF PROPENIDE PROTON(S) (δ VALUES) IN THE BICYCLIC ANIONS 1–9

Anion	Shift
1	8.52
2	8.59
3	8.40
4	8.36
5	8.40
6	8.40
7	8.33
8	8.50
9	8.52

3,5-dinitrobenzonitrile as the aromatic substrate, the resulting adduct **10** shows a propenide absorption at δ 7.43 (1 H), 0.9 ppm upfield from that in the trinitro adduct **7**. This is definitive evidence for the conclusion that the less electronegative cyano group is part of the delocalized anionic portion of the molecule. Further corroborating evidence for this point results from the visible spectrum of **10** which, like **11**, has an absorption at *ca.* 380 mμ characteristic of the cyanonitropropenide function, and not at *ca.* 500 mμ, which characterizes **1–9**.

The infrared spectra of **7** and **10** are also of interest. The CN stretch in **10** appears at 2180 cm^{-1}, about 45 cm^{-1} lower in frequency than conjugated nitriles and 70 cm^{-1} lower than unconjugated nitriles. This in indicative of charge delocalization onto this function. The carbonyl region is broad at 1620–1670 cm^{-1} in both **7** and **10**. In considering the carbonyl region of the infrared for all the acetylacetone, ethyl acetoacetate, and α-acetylbutyrolactone adducts, it should be noted that in the former two cases there is no appreciable absorption above 1690 cm^{-1}, presumably because the β-diketo function in each exists to a considerable extent in the enol form (a very small absorption above 1700 cm^{-1} probably does result from the diketo structure). In the spiro cyclic adduct **8**, where the carbon atom joining the two carbonylic functions has no hydrogen (*i.e.*, the spiro carbon atom), both the lactone and bridging carbonyls are clearly observed at 1760 and 1755 cm^{-1}.

The 1,3-Dicarbomethoxyacetone Adducts.—1,3-Dicarbomethoxyacetone condenses with *sym*-trinitrobenzene, 3,5-dinitrobenzonitrile, and methyl 3,5-dinitrobenzoate in the presence of triethylamine to yield the corresponding bicyclic anions **9**, **11**, and **12**. The nmr spectra of these adducts are quite complex owing to the isomeric mixtures. 1,3-Dicarbomethoxyacetone appears to be the most reactive of all the keto esters used, as the characteristic orange and yellow colors of the adducts developed very soon after mixing the reagents. Some difficulty was encountered in recrystallizing these products. A 9:1 mixture of ether–methanol was found to be a reasonably effective solvent for recrystallization. The 1600–1800-cm^{-1} region of the infrared spectra of **9**, **11**, and **12** is quite interesting. In **9** and **11** this region is characterized by three peaks at 1610, 1645, and 1730 cm^{-1}. In **12** an added peak appears at 1685 cm^{-1}. This must be due to the CO_2CH_3 on the delocalized propenide function of **12**. In the starting ester, the CO_2CH_3 carbonyl absorbs at 1725 cm^{-1}. The shift to lower frequency in **12** is consistent with attachment to the delocalized anionic system.

The α-Acetylbutyrolactone Adduct.—A spiro bicyclic structure should form when the starting keto ester is part of a ring. Thus, reaction of *sym*-trinitrobenzene with α-acetylbutyrolactone yields orange crystals of what might be the spiro adduct **8**. A definite structural assignment must wait the difficult task of isomer separation.

Experimental Section

All the adducts **1–13** were prepared by dissolving a maximum amount of electron-deficient aromatic compound in about 2 ml of the ketonic substrate. The solution was gently warmed to about 30–35° to aid dissolution, and a two- to threefold excess of amine was then added (based on a limiting amount of aromatic). The intensely colored solution was kept at 30–40° and agitated occasionally. After 4–12 hr, *ca.* 100 ml of cold anhydrous ether was added. In most cases, an orange-yellow solid precipitated immediately from solution. This solid was filtered, washed with cold anhydrous ether, redissolved in 150–250 ml of boiling ether with just enough methanol added to effect dissolution, and kept at 0–10° for 3 days. The resulting crystals were filtered and dried under vacuum at 30–40°. In some instances, the initial product did not precipitate from solution on addition of ether but deposited as a highly colored oil on the bottom of the flask. In these cases, the oil was washed with copious amounts of anhydrous ether and redissolved in an ether–methanol solution, which after standing for 3 days at 0–10° deposited crystals of the adduct.

TABLE IV
CHARACTERIZATION OF THE BICYCLIC ANIONS

Adduct	Mp, °C	λ_{max}, mμ	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
1[a]	171–172	510[b]	45.35	5.85	16.27	45.40	5.78	16.25
2[c]	190–191	500[b]	61.82	6.15	10.68	61.72	6.18	10.80
3	157–158	515[b]	46.63	5.74	14.50	46.89	6.00	14.80
4	152–153	506[d]	49.27	6.57	13.52	49.46	6.33	13.38
5	144–160[e]	507[b]	46.63	5.74	14.50	46.76	5.62	14.22
6	180–181	504[d]	48.24	5.57	14.06	48.44	5.86	13.86
7	147–148	504[d]	48.64	6.35	12.60	48.60	6.43	12.50
8	157–164	504[d]	48.86	5.92	12.66	48.58	6.00	12.90
9	119–122	500[b]	46.71	5.78	11.47	46.84	5.83	11.36
10	146–151[e]	374[d]	53.76	6.65	13.20	53.91	6.80	13.24
11	126–127	382[d]	51.27	6.03	11.96	50.93	5.92	12.09
12	118–119	375[d]	50.30	6.23	8.38	50.55	6.35	8.33
13	140–150[e]	372[d]	50.39	6.49	11.76	50.40	6.59	11.54

[a] Reference 3. [b] In acetone. [c] Reference 4. [d] In methanol. [e] Melts with decomposition.

A typical example is outlined below. The elemental analyses, melting points, and visible maxima of **1–13** are summarized in Table IV.

1,3-Dicarbomethoxyacetone-1,3,5-trinitrobenzene (9).—A mixture of 1.3 ml of 1,3-dicarbomethoxyacetone and 2.13 g (0.01 mol) of trinitrobenzene was warmed until the aromatic compound dissolved, and *ca.* 3 ml of triethylamine was then added. The greenish, tarlike mixture was kept at room temperature for 4 hr and 5 ml of methanol was added. The resultant slurry was added to 75 ml of anhydrous ether and the mixture was cooled. The crude product which precipitated was filtered and recrystallized from a 1:1 ether–methanol mixture to give a 30% yield of brilliant red crystals, mp 119–122°.

Registry No.—**1**, 12379-55-4; **2**,12 379-64-5; **3–6**, mixture, 12379-56-5; **7**, 12379-59-8; **8**, 12379-58-7; **9**, 12379-61-2; **10**, 12379-60-1; **11**, 12379-62-3; **12**, 12379-63-4; **13**, 12379-57-6.

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Conformational Equilibria for 2- and 3-Bicyclo[3.3.1]nonanols[1]

ELLIOT N. MARVELL AND R. STEPHEN KNUTSON

Department of Chemistry, Oregon State University, Corvallis, Oregon 97331

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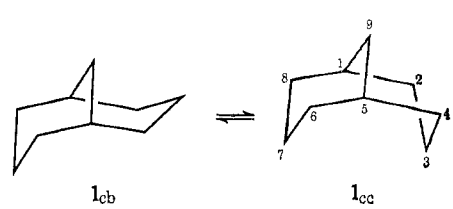
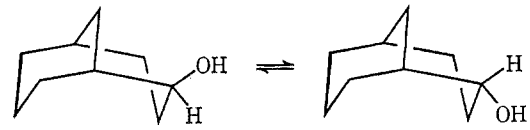
Equilibration of either the *exo*- or *endo*-3-bicyclo[3.3.1]nonanols with aluminum isoproxide in isopropyl alcohol at 94° gave 96.9% *exo* isomer. The ΔG^0 of −2.5 kcal/mol obtained is a reasonable approximation of the energy difference between the chair-boat and double-chair conformers of bicyclo[3.3.1]nonane. Equilibration of either of the two isomers of 2-bicyclo[3.3.1]nonanol under the same conditions gave 68.7% *endo* isomer (equatorial hydroxyl). In this protic solvent, $\Delta G^0_{OH} = -0.56$ kcal/mol. Equilibration over Raney nickel in cyclohexane gives a ΔG^0_{OH} of −0.25 kcal/mol for an aprotic solvent.

Bicyclo[3.3.1]nonane provides an interesting vehicle for the study of conformational effects. Thus it has been established,[2] contrary to most expectations,[3] that the molecule adopts preferentially the double-chair rather than the chair–boat conformation. No estimate of the energy difference between these two conformations was available when the study reported here was made.[4] X-Ray studies[2] showed that the ring distorts readily parallel to the plane of symmetry through C_3, C_7, and C_9, but is resistant to distortions which destroy this as a symmetry element. Little has been done to ascertain the influence of these ring distortions on the conformational preferences of ring substituents.



1_{cb} 1_{cc}

Equilibration of 2-Bicyclo[3.3.1]nonanols.—The two epimeric 2-bicyclo[3.3.1]nonanols, *exo*-**2** and *endo*-**2**,



exo-**2** *endo*-**2**

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(2) M. Dobler and J. Dunitz, *Helv. Chim. Acta*, **47**, 695 (1964); W. A. C. Brown, J. Martin, and G. A. Sim *J. Chem. Soc.* 1844 (1965).

(3) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 295–296.

(4) See, however, R. A. Appleton, C. Egan, J. M. Evans, S. H. Graham, and J. Dixon, *J. Chem. Soc., C*, 1110 (1968).