$C_{21}H_{22}$: C, 91.97; H, 8.03. Found: C, 91.93; H, 8.04.

1-Phenyl-9-methylbicyclo[3.3.1]nonan-9-ol (8). Ketone 11 (3 g) in Et_2O was added to a stirred ethereal solution of methylmagnesium iodide prepared from Mg (0.35 g) and CH_3I (1.2 mL). After 0.5 h under stirring, the usual workup afforded a residue (2.9 g) which was adsorbed on SiO_2 (150 g). Elution with hexane–ethyl acetate (8:2) gave 8: 2.5 g; bp 160 °C (3 mm; short path); ^1H NMR (CCl_4) 7.15 (s, 5 H), 2.55 (br s, 1 H, exchanged with D_2O), 2.25 (s, 3 H), 2.40–1.00 (m, 13 H); IR (CCl_4) 3600 cm^{-1}; mass spectrum, m/e (relative intensity) 230 (M^+, 0.6), 214 (100), 196 (34), 186 (36), 157 (42), 143 (44). Anal. Calcd for $C_{16}H_{22}O$: C, 83.48; H, 9.56. Found: C, 83.40; H, 9.45.

Dehydration of 1-Phenyl-9-methylbicyclo[3.3.1]nonan-9-ol (8): *cis*-3a-Methyl-4-phenyl-2,3,3a,6,7,7a-hexahydroindene (8a) and 1-Phenyl-9-methylenebicyclo[3.3.1]nonane (8d). Alcohol 8 (1 g) was dehydrated us usual. After 4 h the substrate was consumed, and the GC analysis showed two peaks in 2:1 ratio. The amount of the more abundant compound increased as the reaction time was prolonged. After 24 h, **8a** was isolated as the only product: bp 108 °C (0.1 mm; short path); ^1H NMR (CCl_4) 7.10 (s, 5 H), 5.75 (t, J = 5 Hz, 1 H), 2.75 (br s, 2 H), 1.06 (s, 3 H, 2.40–1.00 (m, 9 H); mass spectrum, m/e (relative intensity) 212 (M^+, 74), 197 (28), 169 (52), 155 (22), 141 (18), 130 (100), 91 (26). Anal. Calcd for $C_{16}H_{20}$: C, 90.57; H, 9.43. Found: C, 90.50; H, 9.40.

In a second run 0.5 g of 8 was used, the reaction was stopped after 4 h, and the less abundant compound was identified as **8d**: ^1H NMR (CCl_4; in 1:2 mixture with **8a**; the integration values are referred to the methyl signal at δ 1.06) 7.10 (m, 7.5 H), 5.75 (t, J = 5 Hz, 1 H), 4.67 (d, J = 2 Hz, 0.5 H), 4.00 (d, J = 2 Hz, 0.5 H), 2.70–1.00 (m, 17.5 H), 1.06 (s, 3 H); mass spectrum (via GC/MS coupling), m/e (relative intensity) 212 (M^+, 100), 183 (29), 169 (43), 155 (21), 141 (31), 131 (61).

1-Methyl-9-phenylbicyclo[3.3.1]nonan-9-ol (9). Pyridinium dichromate (25 g) was added to a solution of **2** (3 g) in dry CH_2Cl_2 (250 mL), and the mixture was stirred overnight. After filtration through Celite, solvent removal gave **13** (2.95 g).[9] This latter compound (2.5 g), dissolved in Et_2O (10 mL), was treated with an ethereal solution of phenylmagnesium bromide prepared from Mg (0.45 g) and bromobenzene (2.9 g). After 0.5 h under reflux, the usual workup afforded 2.65 g of **9**: bp (short path) 135 °C (0.1 mm); ^1H NMR (CCl_4) 7.67 (m, 2 H), 7.15 (m, 3 H), 1.68 (s, 1 H, exchanged with D_2O), 2.50–1.20 (m, 13 H), 0.92 (s, 3 H); IR (CCl_4) 3620 cm^{-1}; mass spectrum, m/e (relative intensity) 230 (M^+, 100) 212 (27), 159 (31), 120 (36), 105 (68), 91 (27). Anal. Calcd for $C_{16}H_{22}O$: C, 83.48; H, 9.56. Found: C, 83.42; H, 9.52.

Dehydration of 1-Methyl-9-phenylbicyclo[3.3.1]nonan-9-ol (9): *cis*-3a-Phenyl-4-methyl-2,3,3a,6,7,7a-hexahydroindene (9a). Alcohol **9** (2 g) was dehydrated in the usual conditions. After 0.5 h, the work-up gave 1.8 g of liquid **9a**: bp 150 °C (3 mm; short path); ^1H NMR (CCl_4) 7.16 (m, 5 H), 5.73 (br t, 1 H), 1.43 (q, J = 1.5 Hz, 3 H), 2.50–1.20 (m, 11 H); mass spectrum, m/e (relative intensity) 212 (M^+, 98) 197 (37), 183 (23), 169 (100), 129 (45), 91 (73). Anal. Calcd for $C_{16}H_{20}$: C, 90.57; H, 9.43. Found: C, 90.52; H, 9.45.

Quantitative GC Analyses. All described dehydrations were repeated with 50 mg of substrate and addition of an equimolecular amount of the appropriate GC standard. Standards, reaction conditions, and product yields are reported in Tables I and II.

Registry No. 1, 36399-43-6; **1a**, 83846-13-3; **1b**, 83846-14-4; **1c**, 83846-15-5; **2**, 21328-58-5; **2a**, 83846-16-6; **2b**, 60223-07-6; **2c**, 83846-17-7; **3**, 15598-80-8; **3a**, 6731-22-2; **3b**, 695-90-9; **4**, 83846-18-8; **4a**, 83846-19-9; **4b**, 29494-35-7; **5**, 33832-17-6; **6**, 33832-25-6; **6d**, 61097-71-0; **7**, 83846-20-2; **7a**, 83846-21-3; **8**, 83846-22-4; **8a**, 83846-23-5; **8d**, 51953-76-5; **9**, 83846-24-6; **9a**, 83846-25-7; **13**, 22516-97-8; **14**, 83846-26-8; **15**, 824-22-6; **18**, 83846-27-9; **19**, 83846-28-0.

Condensation–Cyclization of Acetoacetanilides with 1,3,5-Trinitrobenzene. Formation and Structure of Some Stable Delocalized Anions Containing the Bicyclo[3.3.1]nonane Skeleton

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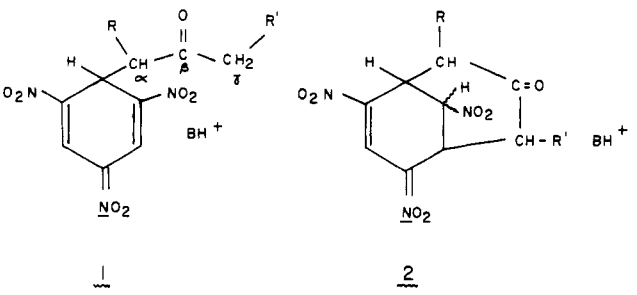
Received June 1, 1982

A series of new bicyclic anions containing the bicyclo[3.3.1]nonane skeleton have been prepared from 1,3,5-trinitrobenzene and carbanions derived from substituted acetoacetanilides. The condensation–cyclizations are initiated by triethylamine. A mechanistic picture for the cyclization is shown as proceeding through a delocalized carbanion intermediate.

The study of σ complexes arising from the interaction of electron-deficient aromatics with bases has developed widely in the last 2 decades.[1-6] It has been known that Meisenheimer complexes like 1 are formed from 1,3,5-trinitrobenzene, ketones, and aliphatic amines.[2-6] The σ complexes such as 1 can be readily converted to 2 provided the following conditions are fulfilled. (1) There should be a potential nucleophilic site γ to the tetrahedral ring carbon in 1. (2) No bulky substituents should be present at the C-γ position. (3) The ketone used should be acidic



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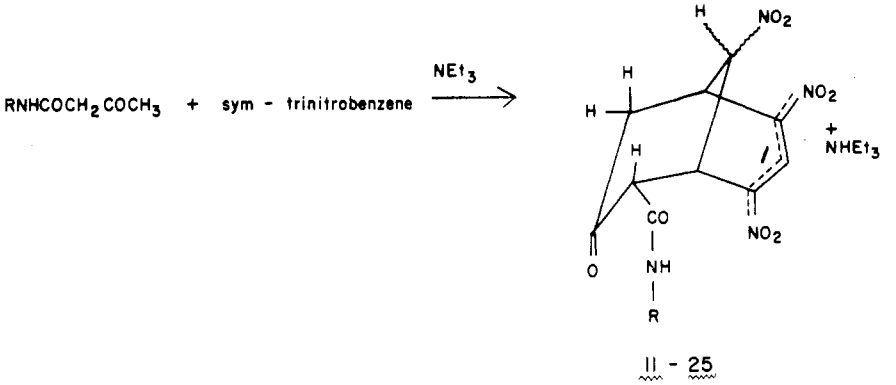
0022-3263/83/1948-0570$01.50/0

Table I[a]



II - 25

adduct	X for R = C_6H_4X	mp, °C	λ_{max}, nm	adduct	X for R = C_6H_4X	mp, °C	λ_{max}, nm
11	H	177	480	19	*m*-NO_2	187	470
12	*p*-NO_2	186	475	20	*m*-Cl	180	480
13	*p*-$COOC_2H_5$	151	475	21	*m*-CH_3	169	480
14	*p*-$COCH_3$	159	475	22	*o*-Cl	165	485
15	*p*-Br	198	480	23	*o*-CH_3	177	485
16	*p*-Cl	193	480	24	*o*-OCH_3	146	495
17	*p*-CH_3	190	481	25	*b*	148	485
18	*p*-OCH_3	186	480				

[a] All the complexes gave satisfactory elemental analyses for C, H, and N. [b] R = $C_6H_5CH_2$.

enough; otherwise, a strong base should be used.

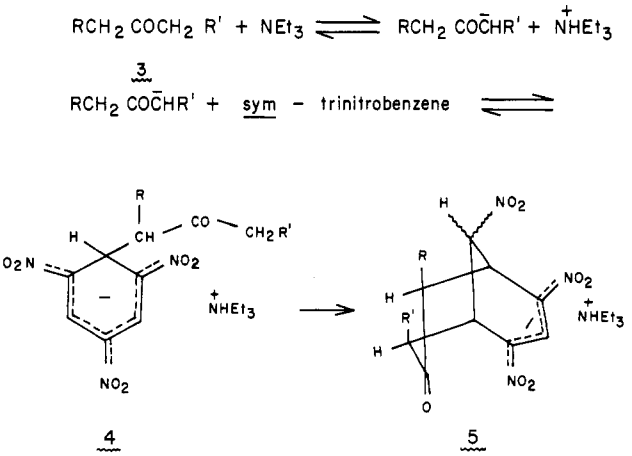
Several reports[2-15] have so far appeared on such condensation–cyclization reactions of electron-deficient aromatics with primary, secondary, and tertiary aliphatic amines and ketones, keto esters, urethanes, and amidines, the conjugate bases of which are the effective nucleophiles.

A survey of the literature has indicated that such studies have not been carried out with the conjugate base obtained from acetoacetanilide. In order to expand the scope of the reactions of electron-deficient aromatics with compounds of the type $RNHCOCH_2R'$ to yield compounds containing the nitropropene nitronate moiety, we have investigated the reactions of different substituted acetoacetanilides with 1,3,5-trinitrobenzene and triethylamine. The present work gives a detailed report of the isolation, characterization, and mechanism of formation of such bicyclic adducts.

When a ketone (3; R = alkyl, R′ = H) and triethylamine are added to a solution of 1,3,5-trinitrobenzene, an immediate coloration occurs, and the visible spectrum exhibits a double maxima characteristic of the trinitrocyclohexadienate function in 4.[2-6] This spectrum slowly changes to one with a maximum at ~500 nm, characteristic of the dinitropropenide function in 5. The reactions can be represented as in Scheme I.

Depending on the acidity of the ketone and basicity of the amine used, either 4 or 5 can be isolated. In the presence of acetone and triethylamine the only isolable product is 4,[16] whereas 5 can be isolated by using a strong base such as sodium hydroxide or diethylamine.[17,18] With

Scheme I



more acidic ketones such as acetylacetone or ethyl acetoacetate, 4 could not be isolated in the presence of triethylamine, but the product 5 precipitates soon after the reagents are mixed.[7]

Addition of excess triethylamine to a solution of acetoacetanilide and 1,3,5-trinitrobenzene in dimethyl sulfoxide–water (75% v/v) resulted initially in a solution with absorption maxima at 467 and 552 nm which rapidly changed to give a peak at 510 nm, characteristic of 5. Thus the visible spectral data indicate that 4 is a precursor to 5. In ethanol the cyclization to 5 is so fast that only a single peak is obtained at 480 nm right from the time of mixing. Similarly, α-[bromo-($C_6H_5NHCOCH(Br)COCH_3$) and ω-bromo- ($C_6H_5NHCOCH_2COCH_2Br$) acetoacetanilides exhibit a single peak at ~490 nm. When diphenylurea, ω-phenylacetanilide, acetanilide, and glutarimide are separately mixed with 1,3,5-trinitrobenzene and triethylamine in ethanol, the visible absorption spectra exhibit a double maxima with peaks at ~465 and ~540 nm, respectively.

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Table II. Chemical Shifts (δ Values) and Splitting[a] of Protons in Bicyclic Anions 11-25

adduct	proton type				
	propenide	bridgehead	bridging $HCNO_2$	aromatic	NH
11	8.28 (s, 1 H)	4.13 (m, 1 H), 4.93 (m, 1 H)	5.3 (m, 1 H)	7.05-7.7 (m, 5 H)	11.05 (s, 1 H)
12	8.23 (s, 1 H, overlaps aromatic absorptions)	4.13 (m, 1 H), 5.05 (m, 1 H)	5.3 (m, 1 H)	7.875, 8.275 (dd, J = 9 Hz each, 4 H, overlaps propenide absorption)	11.65 (s, 1 H)
13	8.28 (s, 1 H)	4.32 (m, 1 H, overlaps CH_2 of $COOC_2H_5$), 5.04 (m, 1 H)	5.28 (m, 1 H)	7.79, 7.99 (dd, J = 8.5, 9 Hz, 4 H)	11.36 (s, 1 H)
14	8.25 (s, 1 H)	4.15 (m, 1 H), 5.01 (m, 1 H)	5.3 (m, 1 H)	7.66, 8.01 (dd, J = 9 Hz, each, 4 H)	11.35 (s, 1 H)
15	8.29 (s, 1 H)	4.15 (m, 1 H), 5.02 (m, 1 H)	5.29 (m, 1 H)	7.52, 7.655 (dd, J = 9, 9.5 Hz, 4 H)	11.23 (s, 1 H)
16	8.35 (s, 1 H)	4.2 (m, 1 H) 5.06 (m, 1 H)	5.21 (m, 1 H)	7.33, 7.70 (dd, J = 9 Hz each, 4 H)	11.19 (s, 1 H)
17	8.36 (s, 1 H)	4.19 (m, 1 H), 5.04 (m, 1 H)	5.26 (m, 1 H)	7.19, 7.56 (dd, J = 8.5 Hz each, 4 H)	10.94 (s, 1 H)
18	8.30 (s, 1 H)	4.15 (m, 1 H), 5.01 (m, 1 H)	5.30 (m, 1 H)	6.93, 7.57 (dd, J = 9, 9.5 Hz, 4 H)	10.92 (s, 1 H)
19	8.65 (s, 1 H)	4.16 (m, 1 H), 5.07 (m, 1 H)	5.27 (m, 1 H)	7.54-8.36 (m, 4 H)	11.61 (s, 1 H)
20	8.32 (s, 1 H)	4.16 (m, 1 H), 5.04 (m, 1 H)	5.31 (m, 1 H)	7.12-7.82 (m, 4 H)	11.3 (s, 1 H)
21	8.32 (s, 1 H)	4.16 (m, 1 H), 5.02 (m, 1 H)	5.29 (m, 1 H)	6.90-7.57 (m, 4 H)	11.0 (s, 1 H)
22	8.32 (s, 1 H)	4.19 (m, 1 H), 5.07 (m, 1 H)	5.37 (m, 1 H)	7.3-7.76 (m, 4 H)	10.82 (s, 1 H)
23	8.33 (s, 1 H)	4.17 (m, 1 H), 5.06 (m, 1 H)	5.28 (m, 1 H)	7.12-7.4 (m, 4 H)	10.56 (s, 1 H)
24	8.32 (s, 1 H)	4.18 (m, 1 H), 5.03 (m, 1 H)	5.36 (m, 1 H)	6.87-7.82 (m, 4 H)	10.42 (s, 1 H)
25	8.31 (s, 1 H)	4.16 (m, 1 H), 4.9 (m, 1 H)	5.25 (m, 1 H)	7.34 (s, 5 H)	9.44 (t, 1 H, J = 6-7 Hz)

[a] s = singlet, dd = double doublet, t = triplet, and m = multiplet.

In these cases the single maximum at ~480 nm could not be observed even when the reaction mixture was allowed to stand for 1 week. When a similar experiment was carried out with benzoylacetanilide, the characteristic double maxima of the 1:1 adduct changed slowly over a period of 7 days to that of the diadduct.

The visible absorption maxima and melting points of the isolated complexes are summarized in Table I and some important NMR data are listed in Table II.

Discussion

When acetoacetanilide and excess of triethylamine interact, proton abstraction can take place from three different positions, i.e., from the methylene group flanked on either side by >C=O groups, from the hydrogen on nitrogen, and from the methyl group at the ω position. The anionic entities thus formed can condense with 1,3,5-trinitrobenzene, resulting in three different σ complexes, **6**–**8**. In our opinion, the σ complex **8** is not formed for the following reasons. 1,3,5-Trinitrobenzene is classified as a soft acid, and the carbanionic centers constitute soft bases. Hard acids prefer to bind to hard bases, and soft acids prefer to bind to soft bases. Hence, σ-complex formation with 1,3,5-trinitrobenzene is likely to take place through the carbanionic center rather than through the anion created by proton abstraction from the anilido nitrogen. The bicyclic adduct reported[7] to be formed from acetylacetone, triethylamine, and 1,3,5-trinitrobenzene has been assigned a structure involving condensation through a carbanion and not through an enolate anion even though acetylacetone itself is known to exist largely in the enolic form. All bicyclic adduct preparations involving 1,3,5-trinitrobenzene, triethylamine, and the compounds diphenylurea, ω-phenylacetanilide, acetanilide, glutarimide, and benzoylacetanilide under the same experimental conditions as for the formation of **11** resulted in failure. While dibenzyl ketone gives rise to a bicyclic adduct readily,[7-19] diphenylurea, in which the two methylenes are replaced by NH and by ω-phenylacetanilide in which one methylene is replaced by an NH, does not form bicyclic adducts. In the case of α-bromo- and ω-bromoacetoacetanilides, though the visible absorption maxima correspond to a diadduct, a stable bicyclic adduct could not be isolated under identical conditions. This is probably due to the operation of a steric effect due to the presence of a bulky bromine at the site of condensation. The only detailed report that has so far appeared on formation of a bicyclic adduct in which condensation has occurred at nitrogen is that of Strauss and Bard,[20] who have isolated a number of bicyclic adducts through condensation of 1,3,5-trinitrobenzene with different substituted acetamidines (Scheme II). Even in this case the hydrogen on nitrogen is not removed, and the electrons present in the double bond are involved in the formation of a new bond with the electron-deficient aromatic. The most conclusive evidence for the fact that the NH proton is not abstracted during the cyclization process is the presence of an NH peak in NMR spectra (Table II) in all the bicylic adducts from 1,3,5-trinitrobenzene and acetoacetanilides. The above-mentioned facts thus rule out the possibility of **8**, leaving only **6** and **7** as structues for the σ complex. As illustrated in Scheme III, **7** is the initial product which is likely to rearrange to **6** in view of the facile cyclization of **6** to **11** through proton abstraction from the most acidic methylene

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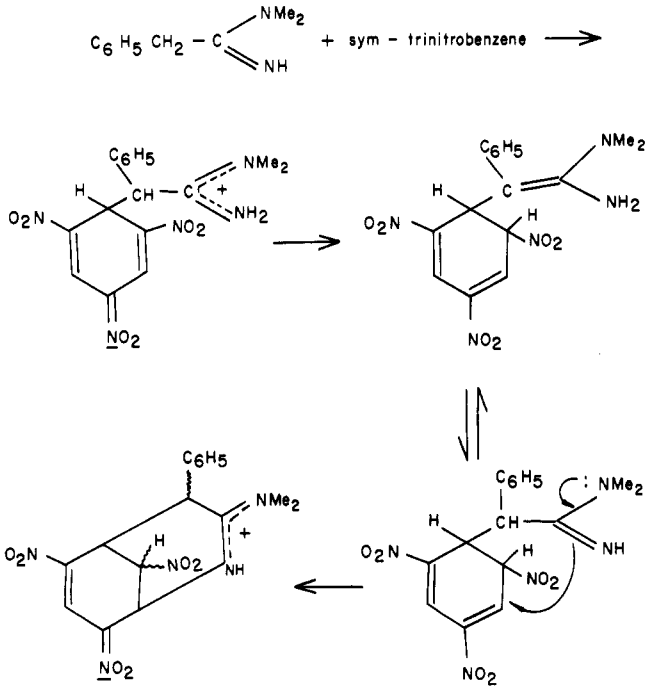
Scheme II

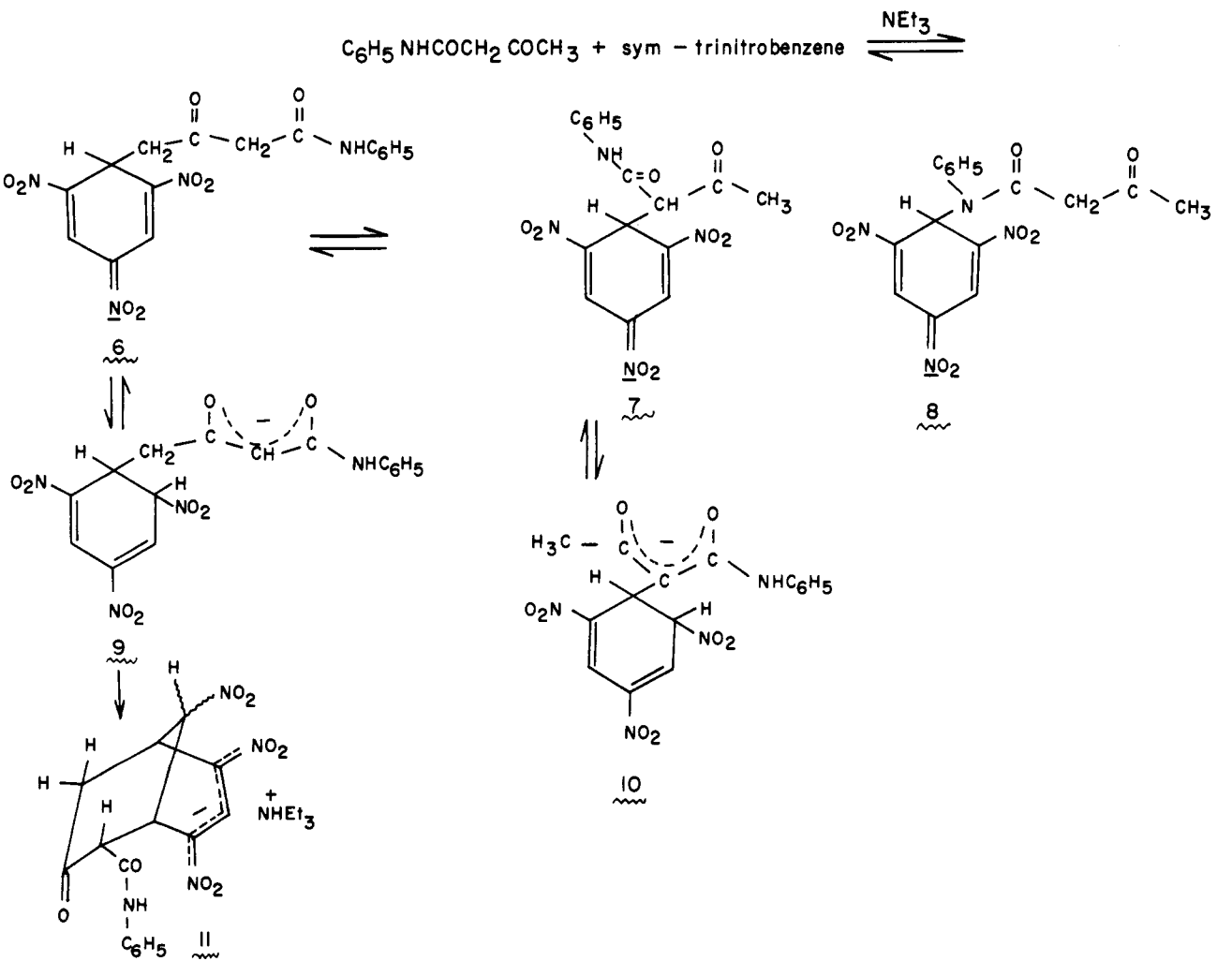


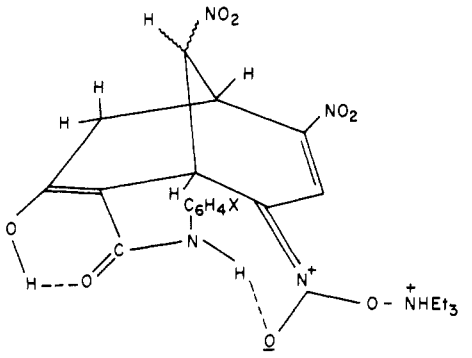
carbon in **6**. Direct conversion of **7** to **11** is not possible as it would require proton abstraction from a less acidic center.[8] Abstraction of a proton from the most acidic hydrogen in **7** would lead to **10**, which obviously cannot cyclize.

The isolated adducts are a mixture of stereoisomers due to the asymmetric center at the $HCNO_2$ bridge. Since exchange with Me_2SO-d_6 is a complicating factor, the ammonium cation absorptions are difficult to detect in the NMR spectra determined in this solvent. Similar exchange resulting in diminished NH^+ absorption and increased protonated solvent absorption has been previously reported in related systems.[7,18]

The propenide protons in all the adducts appear as a singlet at ~8.3 ppm, which is almost the same value observed for the propenide protons by earlier workers.[7,14,18] The bridging $HCNO_2$ appears as a mulitplet at ~5.24 ppm, and the two bridgehead protons appear as a poorly resolved multiplet at ~4 and ~4.9 ppm. The absorptions of hydrogens α to keto bridge are masked by cation absorptions. The aromatic protons in the para-substituted compounds **12–18** exhibit the characteristic double doublets (Table II), and those in meta- (**19–21**) and ortho-substituted (**22–24**) compounds show multiple absorptions from ~6.8 to 8.36 ppm. The aromatic protons in **25** appear as a singlet at 7.34 ppm. The NH protons in **11–24** appear as a singlet around 11 ppm. The position of this peak is about 1–2 ppm downfield compared to that of acetoacetanilides, indicating that in the complex this hydrogen is involved in hydrogen bonding with the oxygen of the nitro group as shown in **26**. In **25** the NH proton appears as a triplet due to coupling with the adjacent CH_2 protons. The appearance of a peak around 14 ppm in all the com-

Scheme III





26

plexes **11–25** indicates that there is an enolic hydrogen which is hydrogen bonded to the carbonyl adjacent to the NH group.

On consideration of the carbonyl region of the infrared spectra, all the adducts **11–25** have no appreciable absorptions above 1630 cm^{-1} although in acetoacetanilides a peak is observed at 1720 cm^{-1}. This can be explained by considering again the enolization[7] of the diketo structure leading to **26**. The absorpotions at 1500–1445 and 1320 cm^{-1} are due to the anionic NO_2 asymmetric and symmetric stretching modes.

The visible absorption maxima for all the adducts **11–25** in methanol are observed at 480 ± 10 nm and have molar extinction coefficients from 12 000 to 30 000. The ortho-substituted complexes exhibit a slight bathochromic shift of 5–10 nm (Table I). This is probably due to the phenyl group being twisted out of plane with the NH group which in turn will be only weakly involved in hydrogen bonding. As a result, the internal energy of the molecule is raised, and the energy gap between the ground state and excited state is reduced. This is consistent with a structure such as **26**.

Experimental Section

General Methods. All melting points are uncorrected. The visible data were obtained on a Carl-Zeiss VSU2-P spectrophotometer. The NMR data were recorded on a Varian XL-100 (100MHz) spectrometer with Me_2SO-d_6 as solvent and Me_4Si as an internal reference. The IR spectra were recorded on a Perkin-Elmer 597 infrared spectrophotometer as KBr pellets.

The acetoacetanilides and benzoylacetanilide were prepared from the corresponding anilines and ethyl acetoacetate or benzoyl acetoacetate, respectively, in a continuous reactor.[21] The α-bromo[22] and ω-bromo[23] acetoacetanilides were prepared by known procedures.

All the adducts **11–25** were prepared by dissolving 1,3,5-trinitrobenzene (0.01 mol) and acetoacetanilide (0.01 mol) in ethanol to give a hot saturated solution. A two- to threefold excess of triethylamine was added, and the intensly colored solution was kept at 30–40 °C for 12 h, when bright orange crystals separated out. The crystals were filtered off, the mother liquor was concentrated, and an oily mass was obtained. Upon addition of ether and stirring, a fresh crop of orange crystals was obtained. These were recrystallized twice from absolute ethanol. The yield of the complex is more than 80% in all the cases. All the complexes gave satisfactory elemental analyses for C, H, and N.

Reaction of Diphenylurea, ω-Phenylacetanilide, Glutarimide, Benzoylacetanilide, and α-Bromo- and ω-Bromoacetoacetanilides with 1,3,5-Trinitrobenzene and Triethylamine. 1,3,5-Trinitrobenzene (0.01 mol) and each one of the above compounds (0.01 mol) were dissolved in ethanol to give a hot saturated solution. A two- to threefold excess of triethylamine was added and the mixture allowed to stand for 24 h. The solution was concentrated, and the resulting oily mass was washed with copious amounts of ether. No crystallizable solid mass was obtained in any one of these experiments.

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