Condensation–Cyclization Reactions of Electron-Deficient Aromatics. V. Formation of Enolic Bicyclononanone and Benzobicyclononanone Nitronates by Intramolecular Cyclization in Benzenoid and Naphthalenoid σ Complexes[1]

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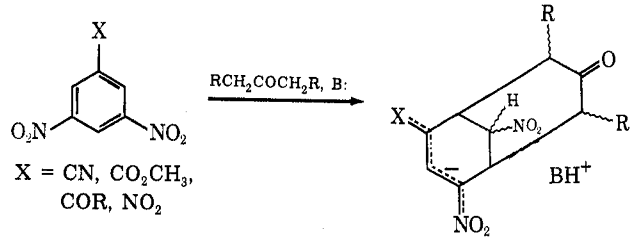
Intramolecular cyclizations in naphthalenoid σ complexes have been observed to occur, analogous to those previously observed in benzenoid systems. The condensation–cyclization reactions of 1,3-dicarbomethoxyacetone with *sym*-trinitrobenzene, 1,3,6,8-tetranitronaphthalene, and 1,3-dinitronaphthalene are compared, and the products isolated in each case are characterized. The reaction in the latter two instances yields interesting benzobicyclic nitronates.

The recent and rapidly growing interest in the chemistry of anionic σ complexes has been enhanced during the past few years by a number of interesting reports of structures prepared from several different types of aromatic compounds. Included in these studies have been characterizations of σ complexes prepared from electron-deficient benzenes,[2] naphthalenes,[2,3–11] anthracenes,[8] thiophenes,[12] purines,[13] pyridines, and diazines.[9,14–19] Two years ago we reported that simple anionic σ complexes formed from electron-deficient benzenes and carbanions readily undergo internal cyclization to yield novel new bicyclic nitronates which are remarkably stable.[1] Our initial studies were extended using a variety of different electron-deficient benzenes and ketonic carbanion sources, and we have found the reaction to be quite general.[1] It occurs readily with 1-X-3,5-dinitrobenzenes when X is electron withdrawing[1] and with 1-X-2,4,6-trinitrobenzenes when X is electron withdrawing or donating.[20] In the latter case isomeric products containing the X substituent on the bridgehead and on the nitronate function can be isolated when X is electron withdrawing, but only on the nitronate function when X is electron donating. Almost any active ketone or keto ester will bridge sufficiently electron-deficient benzenes. The mechanistic details of this stepwise process have been discussed previously.[1,21]



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As a logical extension of the study of benzenoid σ complexes, characterization of naphthalenoid complexes was reported by Fendler and others in the latter part of the 1960's.[2,6–9] This interesting work is continuing, as evidenced by very recent reports.[3–5,10,11] Since we supposed that our originally reported internal cyclization reactions would not be unique to benzenoid systems, we thought it of interest to investigate the possibility of preparing benzobicyclic nitronates from naphthalenoid σ complexes. Such systems would be of considerable value in comparative studies of simple bicyclic nitronates, much as the studies of benzenoid and naphthalenoid σ complexes have complemented each other. In addition, the observation of internal cyclization in naphthaleonoid systems would provide substantial evidence that such cyclizations may well occur in other systems, *i.e.*, pyridine, purine, thiophene σ complexes, etc. Since nitronates can easily be hydrolyzed to ketones in certain instances, the synthetic value of such a reaction for the preparation of bicyclic systems cannot be overlooked. We report here the first example of internal cyclizations in naphthalene σ complexes, and characterization of the isolated crystalline products.

We have found that 1,3-dicarbomethoxyacetone (DCA) is one of the most reactive ketonic substrates in condensation–cyclization reactions with benzenoid aromatics. We therefore decided to study the reactions of naphthalenoid systems using DCA. Since the detailed structure of bicyclic nitronate DCA adducts with electron-deficient benzenes had not been established previously, we found it necessary to first

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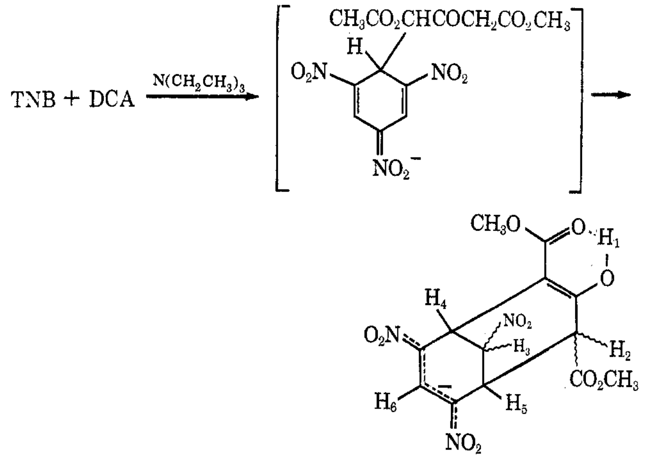
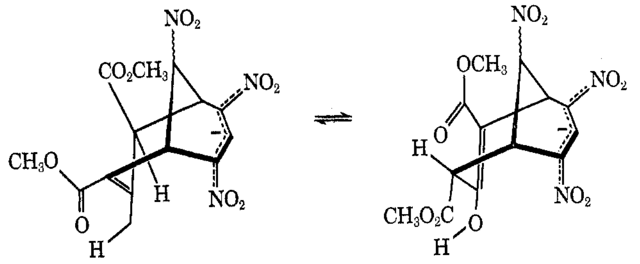
characterize the detailed structure of the *sym*-trinitrobenzene (TNB) adduct with DCA. This nitronate was found to be completely enolic, in contrast to the previously reported nitronates analogous to 1, which are ketonic.

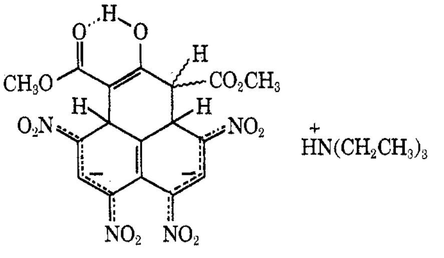
In dimethyl sulfoxide (DMSO) a 1:1 equivalent mixture of DCA, TNB, and triethylamine shows visible and pmr spectral absorptions characterizing the rapid formation of a benzenoid σ complex and subsequent cyclization to bicyclic nitronate.[2,22] Bright red crystals of this latter product can be isolated (see Experimental Section). The pmr ($CDCl_3$) and ir (KBr) spectra, as well as the elemental analysis, are consistent with structure 2. The strong maximum at 500 nm in the visible spectrum is characteristic of the nitropropene nitronate function of 2.[1,2,23] Two intense bands in the ir spectrum at 1730 and 1648 cm^{-1} provide strong evidence for the ester–enol structure of 2. The 1730-cm^{-1} absorption results from the unconjugated CO_2CH_3 carbonyl, whereas the 1648-cm^{-1} absorption results from the other CO_2CH_3 carbonyl bonded to the enolic hydroxyl group. These bands are almost of equal intensity, whereas in neat DCA the 1730-cm^{-1} band is broader and much more intense. The pmr spectrum ($CDCl_3$) provides confirming evidence for the total structure of 2. The triplet and quartet of the $(CH_3CH_2)_3NH^+$ cation are centered at δ 1.36 and 3.18 ppm. The H-2 proton appears as a sharp doublet (1 H, $J < 3$ cps) at δ 3.78 ppm. The significance of the small J value will be discussed later. Two very sharp and closely spaced singlets for the CO_2CH_3 methyls appear at δ 3.84 and 3.86 ppm (3 H each). The H-3 proton α to NO_2 appears as a double doublet centered at δ 4.10 ppm (1 H). It is coupled to the bridgehead protons H-4 and H-5, with $J_{3,4}$ and $J_{3,5}$ both less than 2.5 cps. Both bridgehead protons appear centered at δ 5.31 ppm as an unsymmetrical broadened doublet (2 H). The nitropropene nitronate proton H-6 appears as a sharp singlet at δ 8.52 as expected.[1] The enolic proton H-1 and the cationic NH absorptions appear as a very broad symmetrical absorption at δ 12.25 (2 H). The configuration at the carbons bonded to H-2 and H-3 cannot be determined from this pmr data. It is known that the bridging $CHNO_2$ carbon remains configurationally stable in DMSO, however,[1] and the profound changes in the pmr spectrum of 2 in this solvent provide additional evidence for the enolic structure and the possibility for epimerization at the $CHCO_2CH_3$ carbon. In DMSO-d_6, the nitropropene nitronate proton H-6 no longer appears as a singlet as in $CDCl_3$, but as two singlets of unequal intensity. The rest of the spectrum becomes quite complex, except for the cation absorptions, which remain a sharp triplet and quartet. The two CO_2CH_3 singlets in $CDCl_3$ are transformed into three broader absorptions of unequal intensity in DMSO-d_6. A complex multiplet occurs centered at δ 3.8 ppm for H-2 instead of the sharp doublet observed in $CDCl_3$. Four separate absorptions appear in the region from δ 4.1 to 6.0 ppm. These are complex multiplets of nonintegral intensity individually, and result from H-3, H-4, and H-5. Because absorptions from one isomer (2a or 2b) overlap with those of the other in this region, it is impossible to assign all these peaks. Such a solvent effect on the spectrum may simply be related to the increased basicity of nitronate anions in DMSO relative to $CHCl_3$, resulting in intermolecularly catalyzed epimerization.





2a 2b

We have carried out a similar reaction of DCA with 1,3,6,8-tetranitronaphthalene (TNN) in order to characterize the kind of product which might be iso-



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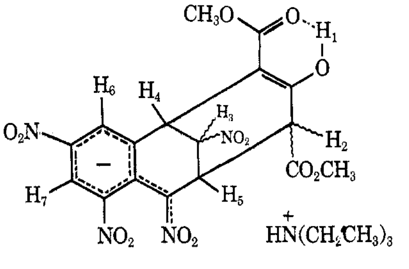
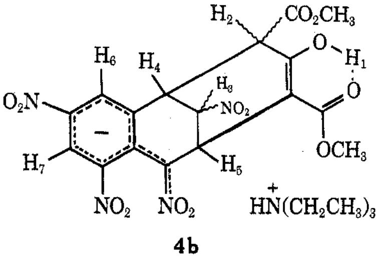


4a



4b

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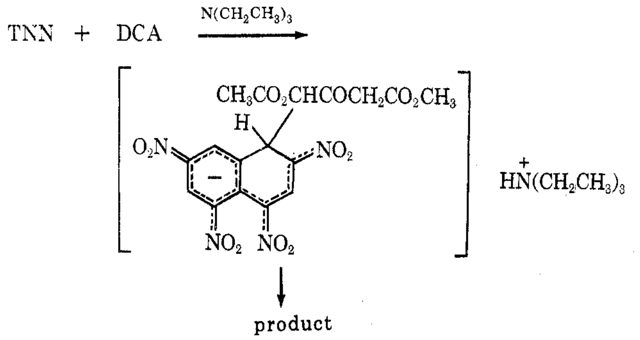
[22] M. I. Foreman, R. Foster, and M. J. Strauss, *J. Chem. Soc. C*, 2112 (1969).

[23] M. J. Strauss and E. Weltin, *Tetrahedron Lett.*, 629 (1971).

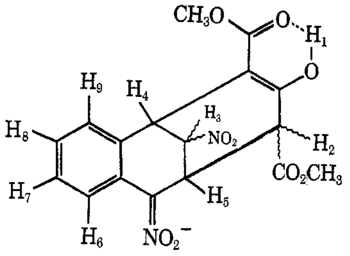
lated in this instance. Since twofold addition to tetranitroacenaphthalene has previously been reported to give a double σ complex,[11] and since the peri positions in TNN were both expected to be quite reactive, a 4, 5 condensation product, **3**, in addition to the two isomeric 2, 4 bridged products, **4a** and **4b**, seemed possible. When the reaction was carried out in neat DCA in the presence of excess triethylamine, two distinct visible spectral changes occurred in rapid succession. The instantaneous change occurring upon addition of triethylamine to a colorless saturated solution of TNN in DCA is the appearance of a strong maximum at 490 nm. This spectral development is similar to that described by Fendler for the formation of hydroxide and methoxide σ complexes of TNN.[3] In the present system, however, the 490-nm maximum rapidly diminishes and is replaced by another strong maximum at 526 nm. The changes are much too rapid to follow conveniently by pmr, but are undoubtedly due to formation of the intermediate σ complex, followed by cyclization to product. Washing the reaction mixture with anhydrous ether to remove the excess DCA and triethylamine leaves a red-orange oil, which when worked up (see Experimental Section) yielded bright red crystals, mp 140.5–141°, which analyzed correctly for a 1:1:1 adduct of DCA, TNN, and amine. The infrared spectrum of this product (KBr) in the 1650–1740-cm^{-1} range is identical with that of **2**, again providing substantial evidence for an enol–ester structure. The pmr spectrum ($CDCl_3$) confirms the structure as **4**. There are significant differences between this pmr spectrum and that of **2**, caused by the benzo fusion in **4**. Nevertheless, the overall similarity of the two spectra provides additional evidence for analogous structures. The cation triplet and quartet again appear centered at δ 1.32 and 3.10 ppm. The next high field peaks are the two CO_2CH_3 absorptions at δ 3.74 and 3.83 ppm. The H-2 doublet in **4** is shifted downfield about 1 ppm from the corresponding resonance in **2**, and appears at δ 4.55 ($J_{2(4\text{or}5)} \cong$ 2.5 cps). The H-3, H-4, and H-5 protons absorb in the region from δ 4.3 to 5.4 ppm and appear as two poorly resolved four-peak multiplets and one sharp double doublet. These peaks, centered at δ 4.4, 4.7, and 5.3 ppm, respectively, integrate for one proton each. The complexity of the absorptions results from the fact that in such bicyclic compounds containing nonequivalent bridgehead protons, long-range coupling can commonly occur.[1] Several sets of $J_{4,5}$, $J_{3,4}$, and $J_{2(4\text{or}5)}$ coupling constants within the range of 2 to 3 cps can account qualitatively for the observed splitting patterns, but decoupling experiments proved difficult owing to the close proximity of irradiated and observed peaks. Downfield at δ 8.2 ppm the AB system of the benzo fusion shows the expected double doublet. The $^{+}HNEt_3$ and enolic hydroxyl protons appear as a very broad band centered at δ 11.0 ppm. Using DMSO-d_6 as the pmr solvent does not change the pmr spectrum substantially, in contrast to the observations made with **2**. This must result from considerable stability associated with the isomer isolated.



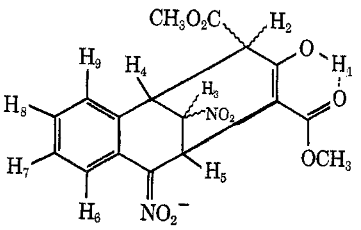
It is impossible to unambiguously assign the structure of **4** to either **4a** or **4b** from the pmr spectral data. There is one feature of the spectrum of particular interest, however. The $J_{2(4\text{or}5)}$ coupling constant of 2.5 cps suggests that the CO_2CH_3 group is trans to the $CHNO_2$ bridge. If it were cis, a value of 5–7 cps would be expected since the dihedral angle (based on Dreiding models) in this latter case is ~30°. In the case of a trans system, the dihedral angle is ~50°, resulting in the expected J value of ~2.5 cps. These angles apply to models of both **4a** and **4b**. The configuration of H_2 in **2** is likely the same as in **4** for similar reasons (*vide supra*).

The condensation–cyclization reaction of 1,3-dinitronaphthalene (DNN) parallels that of TNN. Although development of visible absorption characterizing a DNN σ complex intermediate occurs quite rapidly on mixing the reagents, transformation to product occurs more slowly than with TNN. These qualitative reactivity changes are related to the stability of σ complexes formed from TNN and DNN, which are determined for the most part by the number of nitro groups on each system.[5] An initially colorless saturated solution of DNN in DCA turns violet on addition of triethylamine. The color corresponds to a maximum at 548 nm, similar to that previously reported for carbanionic σ complexes of DNN.[2,9] This maximum eventually disappears and the solution turns pale yellow, with a maximum at 322 nm. Washing the solution with copious quantities of ether to remove the excess amine and ketone results in a viscous, yellow-brown oil. When this oil is dissolved in a minimum amount of a hot 4:1 mixture of ether–ethanol, colorless crystals are formed when the solution is cooled to 0°. These contain solvent of crystallization. After filtration and drying at 0.5 mm for several hours, the crystals turn opaque, and melt sharply at 84–84.5°. The ir spectrum of this product is essentially identical with that of **4** in the 1600–1750-cm^{-1} range. The visible spectrum (MeOH) shows a maximum at 322 nm. The pmr spectrum ($CDCl_3$) provides definitive evidence for structure **5**. The triplet and quartet cation absorptions appear at δ 1.3 and 3.1 ppm, and the two CO_2CH_3 absorptions at δ 3.85 and 3.9 ppm. The H-2 proton doublet absorbs at δ 4.48, and the two bridgehead protons (H-4, H-5) are centered at δ 4.59 and 4.68 ppm. The latter two absorptions are complex multiplets with a total of over ten transitions. The H-3 proton α to NO_2 is again a clearly resolved double doublet at δ 5.40 ppm. The H-7, H-8, and H-9 protons of the fused benzene ring occur as a complex multiplet centered at δ 7.2 ppm. Interestingly, the H-6 proton absorbs far downfield at δ 9.20 ppm as a double doublet ($J_{6,7}$ = 8, $J_{6,8}$ = 1.5 cps). The unusually low field resonance for this proton is likely due to deshielding by the closely positioned peri nitrogen atom of the nitronate function. In this regard, it should be pointed out that the charge density on nitronates is greatest on oxygen, and that nitrogen carries a formal positive charge. The chemical shifts for a series of previously prepared nitropropene nitronates support this supposition.[1,2] The ^{+}NH and OH absorption appears as a broad symmetrical band at δ 10.48 ppm.

The very small coupling constant for H-2 in **5** again suggests that the CO_2CH_3 group is trans to the $CHNO_2$ bridge (*vide supra*). A distinction between **5a** and **5b** cannot be unambiguously made. As with **4**, DMSO does not induce epimerization, again suggesting that the isomer obtained (**5a** or **5b**) is much more stable than its epimer. We have no explanation for such a stability difference.



5a



5b

The characterization of bridged naphthalenes provides support for the possibility that a large number of other types of electron-deficient aromatics may also be bridged by ketones, keto esters, and other potential biscarbanions. The types of new and interesting bicyclic nitronate structures which may be prepared might well approach the number of carbanionic σ complexes studied thus far, since any aromatic substrate reactive enough to form a carbanionic addition complex could theoretically be bridged. The synthetic possibilities for such reactions could well be of substantial importance in carbobicyclic and heterobicyclic synthesis. These possibilities will be considered in future work.

Experimental Section

Pmr spectra were obtained on JEOL MH-100 and C-60 HL nmr spectrometers. Chemical shifts are relative to internal TMS. Visible and infrared spectra were measured on Perkin-Elmer 402 and 21 spectrophotometers, respectively. Elemental analyses were performed by G. I. Robertson, Jr., Florham Park, N. J. 07932, and Galbraith Laboratories, Knoxville, Tenn. 37921. All melting points are uncorrected.

Preparation of 2.—A mixture of 1.3 ml of DCA and 2.13 g (0.01 mol) of TNB 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°.

Anal. Calcd for $C_{19}H_{28}N_4O_{11}$: C, 46.71; H, 5.78; N, 11.47. Found: C, 46.84; H, 5.83; N, 11.36.

Preparation of 4.—Triethylamine (1 ml) was added to a saturated solution of 1 g (0.005 mol) of TNN in DCA at 40°. After 10 min, the oily red-orange reaction mixture was washed with copious amounts of dry ether to remove the excess amine and ketone. The resulting oil was dissolved in hot ether containing just enough ethanol to effect dissolution. Upon cooling at 0°, large red crystals of **4**, mp 140-141°, were obtained in 60% yield. These were quite stable and showed no evidence for decomposition after several weeks at room temperature.

Anal. Calcd for $C_{23}H_{29}N_5O_{13}$: C, 47.34; H, 5.01; N, 12.00. Found: C, 47.44; H, 5.26; N, 12.00.

Preparation of 5.—A solution of DNN, DCA, and triethylamine was prepared in a fashion similar to that described for **4**. The initially dark violet solution turned yellow after 15 min at room temperature. Washing this yellow solution with three 25-ml portions of dry ether yielded a yellow-brown oil, which was dissolved in hot ether by adding just enough ethanol to effect dissolution. After standing at 10° for 12 hr, large colorless crystals were deposited. When these were filtered and dried over $CaCl_2$ at 0.1 mm and 40° for 2 hr they turned pale yellow and opaque. This change is likely due to a loss of solvent of recrystallization. The yield of dry recrystallized product was *ca.* 50%. The crystals of **5** are quite sensitive to moisture, and after standing for 12 hr decompose to a brown tar.

Anal. Calcd for $C_{23}H_{31}N_3O_9$: C, 55.98; H, 6.33; N, 8.51. Found: C, 55.80; H, 6.15; N, 8.43.

Registry No.—**2**, 37703-25-6; **4a**, 37767-75-2; **4b**, 37703-26-7; **5a**, 37767-79-6; **5b**, 37767-80-9; DCA, 1830-54-2; TNB, 99-35-4; TNN, 28995-89-3; DNN, 606-37-1; triethylamine, 121-44-8.

Acknowledgments.—This research was supported by the Army Research Office at Durham, Grant No. 69C 0064, and by the Petroleum Research Fund administered by the American Chemical Society.