(19) It should be pointed out that the stoichiometry of the reaction requires 2 mol of diphenylazirine for every mole of bisamide **4** produced. Benzaldehyde was also detected in small quantities in the reaction mixture. When the solvent was rigorously dried, the yield of bisamide **4** (or trisamine **6**) was significantly diminished.
(20) The reaction of benzamide with benzoylimine, **7** to form bisamide **4** has been reported[21] to require an acid catalyst (BF_3). Our reaction conditions, however, are much more vigorous than that previously reported.[21] This would account for the reaction proceeding in the absence of a catalyst.
(21) S. Breuer, T. Bernath, and D. Ben-Ishai, *Tetrahedron Lett.*, 4569 (1966).

Condensation–Cyclization Reactions of Electron-Deficient Aromatics with Organic Bases. VIII.[1] Ortho Substituent Attack *vs.* Meta Ring Attack in 3,5-Dinitrobenzophenone

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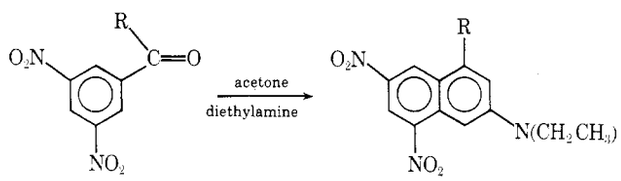
A recent report of the formation of naphthalene derivatives, **2**, from reaction of 3,5-dinitroacetophenone and related aromatics with acetone and diethylamine was of considerable interest to us.[2] The conclusions that only naphthalenoid products result from such reactions conflicted with expectations based on our earlier work[1a] and prompted us to attempt the reaction on related substrates.



1 **2**

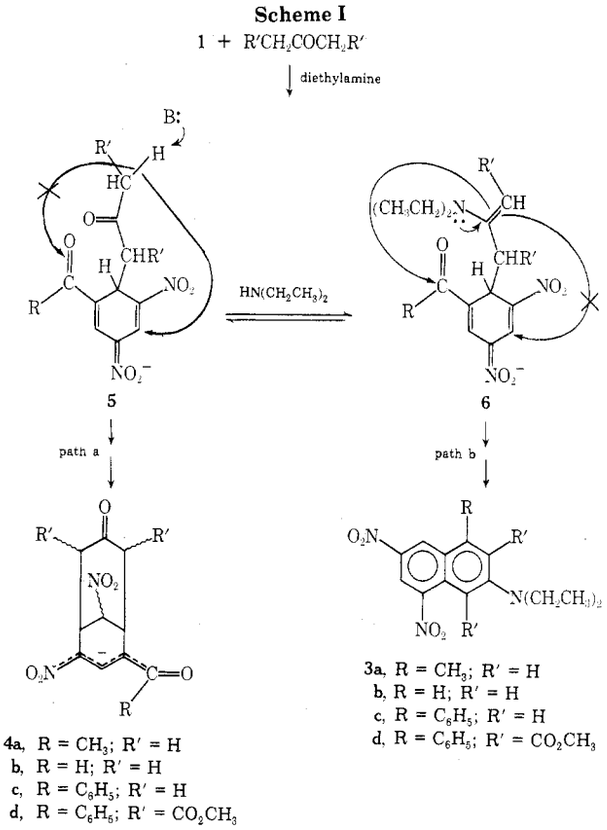
Previous observations of meta-bridged products isolated from other 3,5-dinitro-X-substituted aromatics under similar conditions lead us to believe that internal meta bridging in ketonic σ complexes of **1** could lead to compounds like **4** with appropriate ketones and secondary amines (Scheme I, path a). Although all our previous work with 3,5-dinitro-X-substituted aromatics had been done with substrates in which X = NO_2, CN, and CO_2CH_3,[1a] we suspected that the particular mode of cyclization would depend on the nature of the ketone, not the X substituent, and that either **3** or **4** could be obtained from the same aromatic precursor.

The previously published report[2] considers reaction of acetone with 3,5-dinitroacetophenone or 3,5-dinitrobenzaldehyde. With these reactants only **3a** and **3b** are formed by a postulated mechanism involving enamine intermediates. There was no evidence for products like **4a** or **4b**, analogous to those we have previously isolated with more acidic ketones and 3,5-dinitro-X-substituted aromatics.[1a]

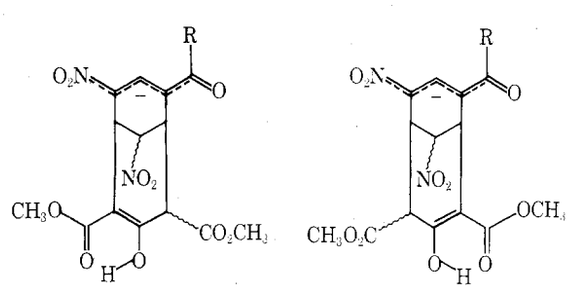
We have found that under conditions reported for the formation of **3a** and **3b** 3,5-dinitrobenzophenone, **1** (R = C_6H_5), reacts rapidly with acetone and diethylamine to yield black needles of the analogous 1-phenyl-3-diethylamino-5,7-dinitronaphthalene (**3c**). The pmr and visible spectra as well as the elemental analysis are completely in accord with this structure[2] (see Experimental Section). There was no evidence for the bicyclic structure **4c**. Such results are in agreement with those reported for the reactions of **1** (R = CH_3 or H) with diethylamine in acetone.[2]

Most interestingly, substituting 1,3-dicarbomethoxyacetone for acetone in this reaction yields bright yellow crystals of the bicyclic anion **4d** as the diethylammonium salt.

Scheme I



The pmr and visible spectra as well as the elemental analysis strongly support this structure. There was no evidence for even trace amounts of the naphthalene **3d**. Formation of **4d** is the first example of a 3-substituted propene nitronate in which the stabilizing group is a carbonyl function. This product likely forms through σ-complex intermediates, analogous to formation of meta-bridged products resulting from the reaction of 1-cyano- and 1-carbomethoxy-3,5-dinitrobenzene studied earlier.[1a,g] The double maxima in the visible spectrum of the reaction solution is characteristic of anionic σ-complex intermediates.[1h] As with other bicyclic adducts prepared from dicarbomethoxyacetone, the anion of **4d** exists in one enolic form in solution. A distinction between the two possible isomers cannot be made on the basis of the spectral data at hand.



The mechanism for ortho substituent attack and the factors favoring this mode of reaction over meta bridging in the case of acetone but not dicarbomethoxyacetone deserve some comment. There has been considerable evidence presented in earlier reports that condensations of ketones with electron-deficient aromatics involve enamine or carbanion intermediates.[1b,g] The latter are important for acidic ketones in the presence of secondary amines. Assuming that initial attack occurs para to NO_2 in **1**[1f] the possibilities for cyclization to **3** and **4** are shown in Scheme I.

It has been shown earlier that internal cyclizations involving dicarbomethoxyacetone, R′ = CO_2CH_3 in Scheme I, do not involve enamine intermediates like **6**.[1a,g] Complex **5** (R′ = CO_2CH_3; R = C_6H_5) is thus most likely the precursor to **4d**. Detailed kinetics of similar cyclizations have been reported earlier.[1g] It appears that **5** (R′ = CO_2CH_3; R = C_6H_5) cyclizes by path a and not b in Scheme I.

It is well known that σ complexes prepared from acetone and *sym*-trinitrobenzene are quite stable in the presence of *tertiary* amines.[3,4] Addition of *secondary* amines causes rapid reaction to a variety of products through enamine intermediates.[4,5] In the case of the σ complex of acetone with *sym*-trinitrobenzene a bridged product analogous to **4** is rapidly formed with the negative charge delocalized on a nitropropene nitronate function.[1b,4,5] Since 3,5-dinitroacetophenone does not react with acetone in the presence of tertiary amines to give isolable products, it is thus quite likely that **6** (R = C_6H_5; R′ = H) is the precursor to **3c** and that attack on the ortho substituent occurs *via* path a as previously proposed[2] (Scheme I). An attempt was made to directly observe **6** in the pmr spectrum of the reaction solution. In the region without reactant or product absorption two overlapping triplets develop at δ ~5 (about 1% of the total absorption) and rapidly disappear as those for **3c** increase. These could result from protons on the tetrahedral ring carbons of **5** and **6** (R′ = H; R = C_6H_5).[6]

The reactivity differences causing **5** (R′ = CO_2CH_3; R = C_6H_5) to cyclize *via* path a and **6** (R′ = H; R = C_6H_5) *via* path b could result from increased flexibility in the side chain of the former relative to the latter. Such flexibility would allow the nucleophilic site in **5** (R′ = CO_2CH_3; R = C_6H_5) to more closely approach the meta ring position. Such ideas are supported by Drieding models of **5** and **6**. Alternately it may be that the initial product of intramolecular ortho substituent attack in **5** does not have a suitable route for aromatization to **3**.

Experimental Section

Melting points are uncorrected. Pmr spectra were obtained on a Jeol MH-100 spectrometer in $CDCl_3$ or DMSO-d_6 using tetramethylsilane as an internal standard. Uv spectra were obtained on a Perkin-Elmer 402 spectrometer in anhydrous methanol. Elemental analyses were performed by George I. Robertson Laboratories, Florham Park, N. J.

1-Phenyl-3-diethylamino-5,7-dinitronaphthalene (3c). To a solution of 0.5 g (0.0018 mol) of 3,5-dinitrobenzophenone[7] in the minimum of distilled dry acetone to effect dissolution was added 0.5 ml of diethylamine. The dark greenish-black solution which developed was kept at 25° for 12 hr and then cooled to about 8° for 2 days. Black needles deposited from the solution. These were filtered, washed with a small portion of cold ether, and dried at 0.5 mm and 50° for 8 hr. The resulting product (~0.25 g) melted at 167–168° and had uv-visible maxima in MeOH at 245, 320, 355, 420, and 468 nm. The pmr spectrum in DMSO-d_6 (saturated) had absorptions at δ 8.95 (d, 1 H, $J \simeq 2$ Hz), 8.75 (d, 1 H, $J \simeq 2$ Hz), 7.75 (d, 1 H, $J \simeq 2$ Hz), and 7.2 (d, 1 H, $J \simeq 2$ Hz) for the aromatic ring protons of **3c**. The phenyl group appeared as a complex multiplet centered at δ 7.5 (5 H) and the $N(CH_2CH_3)_2$ absorptions appeared as a coupled triplet (6 H) and doublet (4 H) at δ 1.25 and 3.6, respectively, J = 7.0 Hz. *Anal.* Calcd for $C_{20}H_{19}N_3O_4$: C, 65.74; H, 5.24; N, 11.50.Found: C, 65.71; H, 5.49; N, 11.28.

Preparation of 4d. The procedure for the preparation of **3c** was followed exactly except that dicarbomethoxyacetone (Aldrich) was used instead of acetone. The reaction solution turned brilliant yellow and did not deposit crystals on cooling, however. It was extracted with five 100-ml portions of anhydrous ether, yielding a yellow oil. The oil was covered with 20 ml of ether and enough ethanol was added to effect dissolution with warming. After standing at 8° for 3 days bright yellow crystals were formed. These were filtered and dried at 0.5 mm and 50° for 8 hr. The resulting product (~0.5 g) melted at 110–113° and had uv-visible maxima in MeOH at 245, 252, and 411 nm. The pmr spectrum of a saturated solution in acetone-d_6 had absorptions at δ 7.5 (m, 6 H) for the C_6H_5 and $-CCHC{=}NO_2^-$ protons, δ 5.25 (br, 1 H) and 5.15 (br, 1 H) for the bridgehead protons, and δ 4.30 (br, 1 H) for the $CHNO_2$ bridge in **4d**. The $CHCO_2CH_3$ proton appears at δ 3.9 (s, br, 1 H). The two CO_2CH_3 methyls appear as sharp singlets at δ 3.8 and 3.7 (3 H each). The triplet and quartet of the $H_2N(CH_2CH_3)_2^+$ cation appear at δ 1.2 and 2.8 (6 H and 4 H, respectively). Although this spectrum is not particularly well resolved, comparison with similar spectra of other bicyclic adducts of 3,5-dinitro-X-substituted benzenes and dicarbomethoxyacetone[1a,f] supports the proposed structure. The visible maximum and elemental analysis further substantiate the compound as **4d**. *Anal.* Calcd for $C_{24}H_{29}N_3O_{10}$: C, 55.49; H, 5.63; N, 8.09. Found: C, 55.47; H, 5.87; N, 7.79.

Acknowledgment. The author thanks the U. S. Army Research Office at Durham for support of this work.

Registry No.—**1** (R = Ph), 51911-74-1; **3c**, 51911-76-3; **4d**, 51911-79-6; diethylamine, 109-89-7.

References and Notes

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(2) S. R. Alpha, *J. Org. Chem.*, **38**, 3136 (1973).
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(4) M. J. Strauss and H. Schran, *J. Amer. Chem. Soc.*, **91**, 3974 (1969).
(5) R. Foster and C. A. Fyfe, *Tetrahedron*, **22**, 1831 (1966).
(6) The possibility that these result from two isomeric complexes formed by nucleophilic attack para to NO_2 and para to COC_6H_5 cannot be ruled out, however.
(7) W. Waters, *J. Chem. Soc.*, 2110 (1929).

A Convenient Stereospecific Synthesis of (+)-α-Cyperone[1]

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The eudesmane derivative (+)-α-cyperone (**1**)[2] has been rather widely used as a starting material for the synthesis of various other fused-ring sesquiterpenes.[3] However, convenient syntheses of **1** itself are rather limited. The original Howe and McQuillin synthesis of **1** which involves the Robinson annelation of (+)-dihydrocarvone with the methiodide of 1-diethylaminopentan-3-one allows the isolation of **1** in less than 5% yield.[2] This is because **1** is formed only as a minor product of the reaction and its separation from (−)-10-*epi*-α-cyperone (**2**) and the corresponding ketol which are the major reaction products is difficult. Piers and Cheng have found that (−)-α-santonin can be converted into **1** *via* an eight-step sequence.[4] Although lengthy, this synthesis represents a significant improvement over the method of Howe and McQuillin, since **1** was obtained in about 20% yield overall. Fringuelli, Taticchi, and Traverso have recently reported an apparently useful synthesis of α-cyperone.[5] These workers found that the tricyclic enone **3**, prepared by annelation of *cis*-4-caranone with 1-penten-3-one, undergoes preferential cleavage of the 8,11 bond of the cyclopropane ring with hydrogen bromide to form the 2-bromopropane derivative **4a** which could be converted into a mixture of α- and β-cyperone on dehydrohalogenation. An important feature of this synthesis is that annelation of the bicyclic ketone allows the establishment of the cis relationship of the angular methyl group and the dimethyl-substituted cyclopropane ring which ultimately becomes the three-carbon side chain in **1**. We wish to report a