tion of the mixture was filtered under reduced pressure in a prepurified nitrogen atmosphere, and the adduct (**3a**) was washed with dry hexane and dried *in vacuo;* its nmr spectrum ($CDCl_3$) showed peaks at δ 6.57–8.15 (m, 20 H, aromatic) and 13.55 (broad s, 1 H, NH).

The remainder of the mixture was filtered and washed with dry hexane and the adduct (**3a**) was added to 30–40 ml of water, cooled with an ice bath, and stirred for 1 hr. While cold, the mixture was neutralized with concentrated sodium hydroxide and extracted three times with $CHCl_3$. The combined organic layers were dried over sodium sulfate and evaporated to give a crude solid which after crystallization from CH_2Cl_2–hexane gave 6.20 g of **4a** (75% based on phenylazostilbene used in preparing **3a**). The nmr spectrum ($CDCl_3$) of the crude product showed two isomers in a 3:2 ratio (cis:trans) (estimated by relative integration of methine peaks). Separation of small amounts of the pure isomers was accomplished by chromatography on a silica gel column and elution was performed by benzene–ether (8:2) mixture. The cis isomer **4a** had mp 202–204°; its nmr spectrum ($CDCl_3$) showed absorption at δ 4.55 (d, 1 H, J_{PCH} = 7.5 Hz) and 6.7–7.8 (m, 20 H, aromatic).

The trans isomer had mp 174–177°; its nmr spectrum ($CDCl_3$) showed peaks at δ 5.0 (d, 1 H, J_{PCH} = 22.5) and 6.6–7.8 (m, 20 H, aromatic). Ir spectra were consistent with the assigned structures. Larger quantities of isomer were obtained by fractional crystallization. The first fractions were richer in cis, the final fractions in trans.

Anal. Calcd for $C_{26}H_{21}N_2OP$: C, 76.45; H, 5.10; N, 6.80; P, 7.59. Found: C, 76.51; H, 5.20; N, 6.75; P, 7.70.

Synthesis of 3b and 4b. The same procedure as above was followed, using 5.86 g (0.02 mol) of **1b** in 400 ml of hexane and 3.74 g (0.02 mol) of phenyldichlorophosphine. The reaction was completed in a 27–30-hr period. A small amount of the mixture was filtered under reduced pressure under a nitrogen atmosphere; the adduct **3b** was dissolved in $CDCl_3$ and its nmr spectrum showed peaks at δ 6.25–8.1 (m, 21 H, aromatic and –NH) and 4.2 (broad s, 2 H, CH_2Ph). The remainder of the mixture was treated as above, yielding 6.30 g (74%) of the isomeric oxides **4b**. The nmr spectrum ($CDCl_3$) of the crude product showed an isomer ratio of about 5:2 (cis:trans).

The isomer mixture was separated by silica gel column chromatography as well as by fractional crystallization.

Nmr spectra revealed the isomer's purity to be about 98%. The cis isomer **4b** had mp 171–173°; its nmr spectrum ($CDCl_3$) showed absorption at δ 3.20–3.98 (AB multiplet of ABX system, 2 H, $-CH_2Ph$), 3.89 (d, 1 H, J_{PCH} = 6 Hz), and 6.7–7.9 (m, 20 H, aromatic).

The trans isomer **4b** had mp 163–165°; its nmr spectrum ($CDCl_3$) showed peaks at δ 3.32–4.0 (AB multiplet of ABX system, 2 H, CH_2Ph), 4.29 (d, 1 H, J_{PCH} = 22.8 Hz), and 6.4–7.5 (m, 20 H, aromatic).

Anal. Calcd for $C_{27}H_{23}N_2OP$: C, 76.74; H, 5.97; N, 6.65; P, 7.34. Found: C, 76.92; H, 5.90; N, 6.50; P, 7.28.

Acknowledgment. We thank Professor G. Rosini for his personal communications and the Italian C. N. R. for financial support.

Registry No.—**1a,** 25769-36-2; **1b,** 51849-76-4; **3a,** 51849-77-5; **3b,** 51898-95-4; *cis*-**4a,** 51849-78-6; *trans*-**4a,** 51849-79-7; *cis*-**4b,** 51849-80-0; *trans*-**4b,** 51849-81-1; phenyldichlorophosphine, 644-97-3.

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Reaction of 2*H*-Azirines with Nitrones

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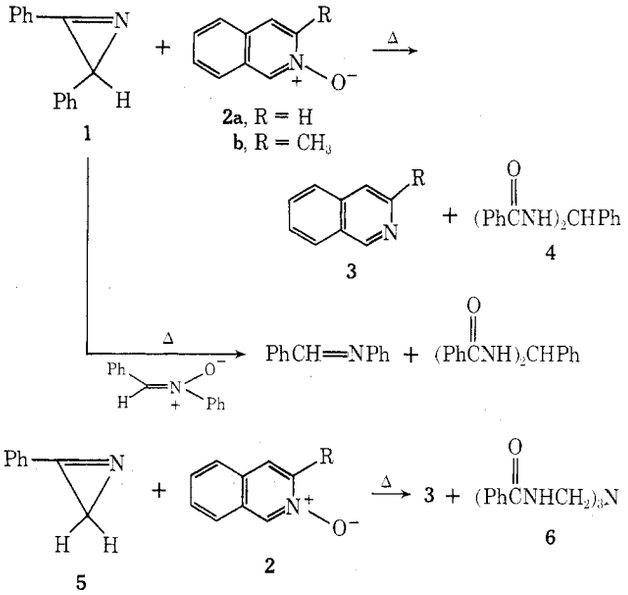
2*H*-Azirines represent versatile substrates which can serve as useful precursors for the synthesis of other heterocyclic rings.[1-6] An unusual feature of this three-membered heterocyclic ring is that it is susceptible to attack by both electrophilic and nucleophilic reagents.[7] In addition, the 2-π electrons present in the ring can participate in thermally allowed [$_\pi4_s$ + $_\pi2_s$] cycloadditions as dienophiles[8,9] or as dipolarophiles.[10] Azirines are also known to act as 1,3-dipoles in photochemical reactions.[11,12] Another intriguing aspect of this ring system is that it can participate as a dipolarophile in 1,3-dipolar cycloaddition reactions.[10,13,14] Reaction with diazoalkanes[10,13,14] and nitrile oxides[10] transforms the 2*H*-azirine system into allylic azides and carbodiimides, respectively. The photodimerization of 2*H*-azirines has been recently shown to produce 1,3-diazabicyclo[3.1.0]hex-3-enes as primary photoproducts.[15] The formation of these dimers was explained in terms of 1,3-dipolar addition of an initially generated nitrile ylide onto the azirine ring.[16] As part of our continued interest in the 1,3-dipolar cycloaddition reactions of arylazirines, we have investigated the reaction of the 2*H*-azirine system with several nitrones.

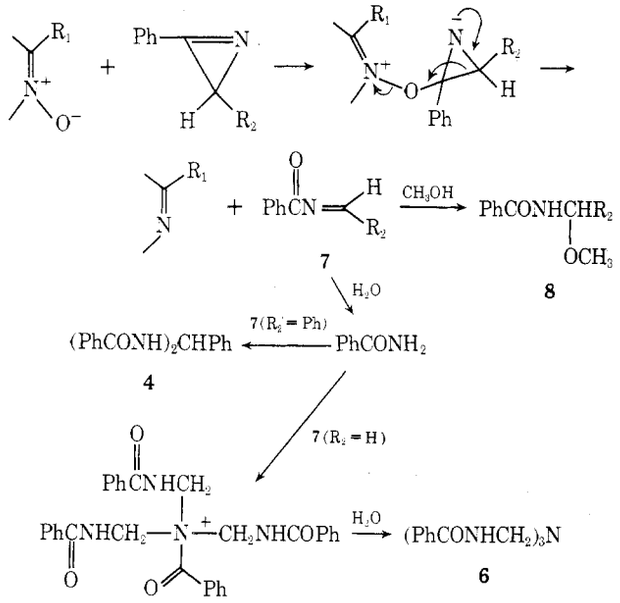
When diphenylazirine (**1**) was heated with isoquinoline *N*-oxide (**2a**) in benzene at reflux temperature for 18 hr, two new compounds were formed in high yield and were identified as isoquinoline (**3a**) and bis(benzamino)phenylmethane (**4**) by comparison with authentic samples.[17] Similar results were observed with **1** and 3-methylisoquinoline *N*-oxide (**2b**). *N*-Benzylideneaniline and bis(benzamino)phenylmethane were the major products obtained upon treatment of **1** with *N*,*C*-diphenylnitrone. Reaction of phenylazirine (**5**) with isoquinoline *N*-oxide (**2a** or **2b**) gave the corresponding isoquinoline and tris(benzaminomethyl)amine (**6**). The structure of **6** was verified by comparison with an authentic sample.[18]



We suggest that the reaction responsible for the deoxygenation of the isoquinoline *N*-oxide involves initial attack

* Alfred P. Sloan Foundation Fellow, 1968–1972.

of the nitrone oxygen on the reactive C=N double bond of the azirine ring. This step bears close resemblance to the formation of alkoxyaziridines from the reaction of 2*H*-azirines with alkoxide anions.[7] The reaction is completed by bond reorganization, which gives the deoxygenated nitrone and *N*-benzoylimine (**7**) as a transient intermediate. Partial hydrolysis of **7** will produce benzamide, which reacts further with the reactive imine to give **4** or **6**.[19,20]



In agreement with this interpretation, we have found that when the above reactions involving diphenylazirine were carried out in the presence of methanol, a new product was formed and identified as the methanol adduct of *N*-benzoylbenzaldimine (**8b**, R_2 = Ph), mp 102–104°.[21] Similar results were obtained with the corresponding phenylazirine system (*i.e.*, **8a**, R_2 = H): nmr ($CDCl_3$) τ 6.63 (3 H, s), 5.11 (2 H, d, J = 7.0 Hz), 2.4–2.8 (5 H, m), and 2.1–2.4 (1 H, broad s); mass spectrum *m/e* 150, 133, 121, 105 (base), and 77. Careful examination of the residue revealed no detectable amounts of **4** or **6**. The isolation of the methoxyamides (**8**) strongly supports the presence of a transient benzoylimine which reacts with the added methanol to give a product different from that previously observed (*i.e.*, **4** or **6**), but which is totally compatible with the mechanism outlined above.

Experimental Section

Reaction of 2,3-Diphenylazirine with 3-Methylisoquinoline *N*-Oxide. A solution containing 1.26 g (0.065 mol) of diphenylazirine and 0.98 g (0.062 mol) of 3-methyisoquinoline *N*-oxide in 100 ml of benzene was heated at reflux for 5 days. Upon cooling, a white solid (0.6 g, 0.018 mol, 58%) precipitated from the reaction mixture. Recrystallization of this material from ethanol gave white needles: mp 229–230°; ir (KBr) 3.08, 6.05, 6.46, 6.65, 6.75, 7.41, 7.86, 8.76, 9.52, 12.40, 13.90, and 14.36 μ; nmr (DMSO) τ 2.83 (1 H, t, J = 9.0 Hz), 1.9–2.6 (15 H, m), 0.91 (2 H, d, J = 9.0 Hz); mass spectrum *m/e* 209, 180, 121, 105 (base), and 77.

Anal. Calcd for $C_{21}H_{18}N_2O_2$: C, 76.34; H, 5.49; N, 8.48. Found: C, 76.24; H, 5.55; N, 8.42.

This material was identified as bis(benzamino)phenylmethane (**4**) by comparison with an authentic sample.[17] The only other product which could be identified from the filtrate was 3-methylisoquinoline.

When the above reaction was carried out in the presence of methanol (2-mol excess) a reddish-brown residue was obtained. This material was chromatographed on a thick layer plate using an acetone–cyclohexane (1:4) mixture as the eluent. The major product obtained was identified as the methanol adduct of *N*-benzoylbenzaldimine (**8b**),[21] mp 102–104°, ir (KBr) 2.95, 3.42, 5.98, 6.23, 6.32, 6.70, 7.44, 8.00, 8.82, 9.12, 9.28, 9.70, 10.22, and 11.05 μ, nmr ($CDCl_3$) τ 6.46 (3 H, s), 3.60 (1 H, d, J = 9.0 Hz), 2.3–2.8 (10 H, m), and 2.0–2.2 (1 H, br s), mass spectrum *m/e* 209, 197, 180, 121, 105 (base), and 77, by comparison with an authentic sample.

A similar set of results was obtained when diphenylazirine was heated in the presence of isoquinoline *N*-oxide (**2a**).

Reaction of 2,3-Diphenylazirine with *N,C*-Diphenylnitrone. A solution containing 0.96 g (0.048 mol) of *N,C*-diphenylnitrone and 0.94 g (0.018 mol) of diphenylazirine in benzene was heated at reflux for 4 days. Upon cooling, 0.5 g of a white, crystalline solid (64%) precipitated from the reaction mixture. Recrystallization of this material from ethanol gave a white solid, mp 229–230°, whose structure was identified as bis(benzamino)phenylmethane by comparison with an authentic sample. The residue obtained on removal of the solvent was chromatographed on a thick layer plate using chloroform as the eluent. The two solids obtained were identified as benzanilide (15%) and *N*-benzylideneaniline (60%) by comparison with authentic samples.

Reaction of Phenylazirine with 3-Methylisoquinoline *N*-Oxide. A solution containing 1.58 g (0.01 mol) of 3-methylisoquinoline *N*-oxide and 1.18 g (0.01 mol) of 2-phenylazirine in 175 ml of benzene was heated at reflux for 24 hr. Removal of the solvent left a yellow oil which was recrystallized from methanol to afford 0.42 g (42%) of a white solid: mp 193–194°; ir (KBr) 3.00, 6.07, 6.50, 6.70, 7.22, 7.48, 7.64, 7.70, 8.48, 9.27, 9.60, 7.72, 12.32, and 14.35 μ; nmr ($CDCl_3$) τ 5.32 (2 H, d, J = 7.0 Hz), 2.3–2.9 (5 H, m), and 1.8–2.0 (1 H, br s); mass spectrum *m/e* 148, 134, 121, 105 (base) and 77; uv (methanol 230 nm (ϵ 21,500).

Anal. Calcd for $C_{24}H_{24}N_4O_3$: C, 69.21; H, 5.81; N, 13.45. Found: C, 68.86; H, 5.87; N, 13.45.

This material was identified as tris(benzaminomethyl)amine(**6**) by comparison with an authentic sample.[18] The only other product which could be identified from the filtrate was 3-methylisoquinoline. A similar set of results was obtained when phenylazirine was heated in the presence of isoquinoline *N*-oxide.

When the above reaction was carried out in the presence of methanol (2 *M* excess) a reddish brown residue was obtained. This residue was chromatographed on a thick layer plate and the major product obtained was identified as methoxy amide **8a**: ir ($CHCl_3$) 2.95, 3.42, 5.98, 6.23, 6.42, 6.62, 6.73, 7.20, 7.65, 7.78, 8.92, 9.30, and 10.96 μ; nmr ($CDCl_3$) τ 6.63 (3 H, s) 5.11 (2 H, d, J = 7.0 Hz), 2.42–2.80 (5 H, m), and 2.1–2.3 (1 H, br s); mass spectrum *m/e* 150, 133, 121, 105 (base), and 77.

Acknowledgment. We gratefully acknowledge support of this work by the National Institutes of Health (Grant CA-12195-07). The National Science Foundation provided financial assistance in the purchase of the nmr spectrometer used in this research.

Registry No.—**1**, 16483-98-0; **2a**, 1532-72-5; **2b**, 14548-00-6; **4**, 14328-15-5; **5**, 7654-06-0; **6**, 51912-07-3; **8a**, 13156-28-0; **8b**, 10387-93-6.

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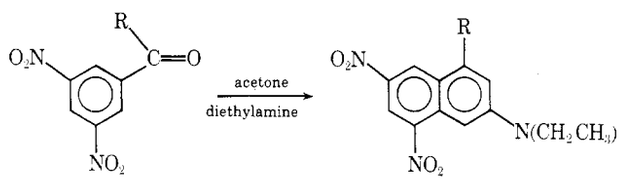
A recent report of the formation of naphthalene derivatives, **2**, from reaction of 3,5-dinitroacetophenone and related aromatics with acetone and diethylamine was of considerable interest to us.[2] The conclusions that only naphthalenoid products result from such reactions conflicted with expectations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



1 **2**

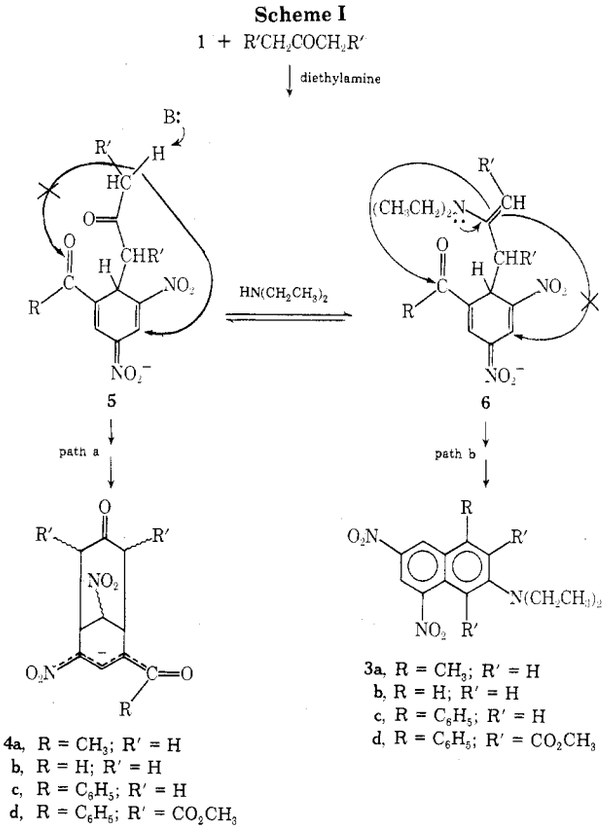
Previous observations of meta-bridged products isolated from other 3,5-dinitro-X-substituted aromatics under similar conditions lead us to believe that internal meta bridging in ketonic σ complexes of **1** could lead to compounds like **4** with appropriate ketones and secondary amines (Scheme I, path 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]

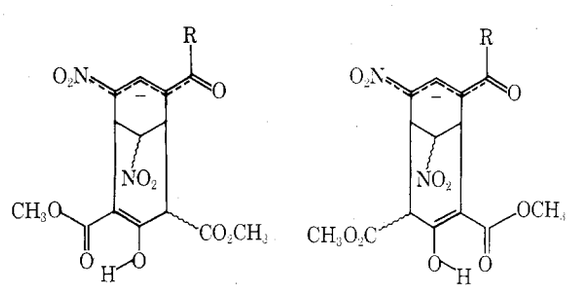
We have found that under conditions reported for the formation of **3a** and **3b** 3,5-dinitrobenzophenone, **1** (R = C_6H_5), reacts rapidly with acetone and diethylamine to yield black needles of the analogous 1-phenyl-3-diethylamino-5,7-dinitronaphthalene (**3c**). The pmr and visible spectra as 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.