Cycloaddition Reactions of the 2-Azabicyclo[3.1.0]hex-3-ene Ring System[1]

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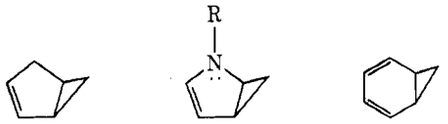
The 2-azabicyclo[3.1.0]hex-3-ene ring system reacts with dimethyl acetylenedicarboxylate and *N*-phenylmaleimide to give derivatives of the 8-azabicyclo[3.2.1]octene ring system. In contrast, tetracyanoethylene reacts with 2-azabicyclo[3.1.0]hex-3-ene ring system to give derivatives of 2-azatricyclo[4.2.0.0^{3,5}] octane. Stereochemical and kinetic results are discussed with respect to mechanistic possibilities for these cycloadditions.

Few reactions rival cycloadditions in the number of bonds that undergo transformation during the reaction, producing products considerably more complex than the reactants. Cycloaddition reactions have had a tremendous impact on both synthetic[2] and theoretical chemistry.[3] The search continues to discover new cycloaddition reactions.

Some reports have appeared recently dealing with cycloadditions to vinylcyclopropanes[4] and these have prompted us to communicate the results of our studies on the 2-azabicyclo[3.1.0]hex-3-ene ring system.

The 2-azabicyclo[3.1.0]hex-3-ene ring system[5] is sterically analogous to bicyclo[3.1.0]hex-2-ene (1). However, the presence of the nitrogen results in a more extensively conjugated π system containing two additional π electrons and electronically it can be considered to be analogous to norcaradiene (3), a species that is unstable with respect to its valence isomer, cycloheptatriene.

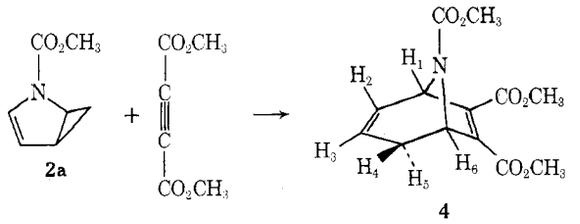


1 2 3

We have observed previously[5] that the presence of the nitrogen can have a profound effect on the thermal rearrangements of the bicyclo[3.1.0]hex-2-ene ring system. Therefore, it was of interest to investigate further the chemical behavior of this heterocycle.

Cycloadditions involving 2-π electron components such as olefins with the carbocycle 1 are, to our knowledge, unknown. In spite of the well-known analogy between a double bond and a cyclopropane,[6] cycloadditions involving a vinylcyclopropane moiety are rare. Cycloadditions of norcaradiene derivatives with olefins or acetylenes usually give Diels–Alder adducts with the diene portion while the cyclopropane function remains intact.[2]

In comparison, we have observed that heating *N*-carbomethoxy-2-azabicyclo[3.1.0]hex-3-ene (**2a**) with dimethyl acetylenedicarboxylate (DMAD) gives a derivative of the 8-azabicyclo[3.2.1]oct-2-ene ring system **4**. The structure of

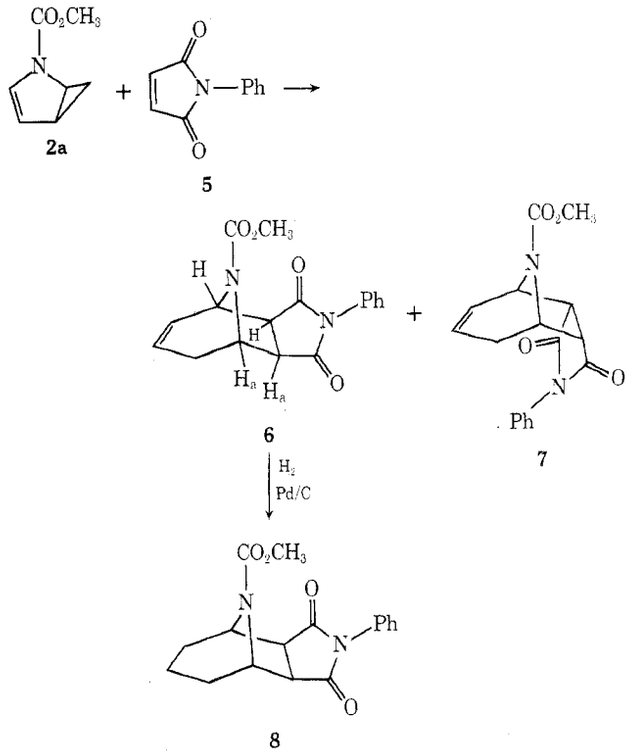


2a **4**

this adduct is based on spectroscopic data, particularly proton magnetic resonance spectroscopy and elemental analyses. The pmr spectrum ($CDCl_3$) showed τ 3.50–3.83 (m, H_3), 4.25–4.61 (m, H_2), 4.90 (d, J = 5.5 Hz, H_6), 5.11 (d, J = 5.0 Hz, H_1), 6.18 (s, 6 H, OCH_3), 6.25 (s, 3 H, OCH_3), and 7.55 (center of a broad AB, H_4 and H_5).

The above assignments were deduced from double-resonance experiments. It is interesting to observe that H_6 occurs as a doublet, suggesting zero coupling between H_6 and either H_4 or H_5. Dreiding molecular models and a comparison with the carbocyclic system[7] indicate that the bond to H_6 forms an angle of approximately 90° with the adjacent bond to the endo hydrogen. This would suggest zero coupling between H_6 and the endo hydrogen H_5.

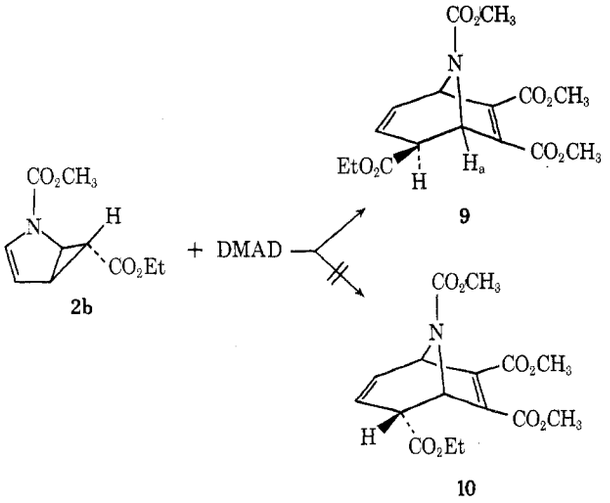
The reaction of **2a** with *N*-phenylmaleimide (**5**) gave adducts **6** and **7** in a ratio of 2:3, respectively, showing only a

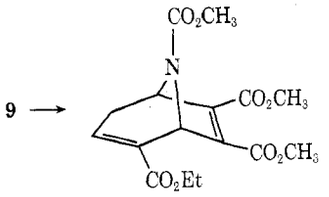


2a **5** **6** **7** **8**

slight preference for the endo isomer. These isomers were readily separated by thin layer chromatography and purified by recrystallization. The product **6** is assigned the exo configuration, since the bridgehead hydrogens H and H′ appear as an AB pattern showing zero coupling to the bridgehead hydrogens H_a, and H_a'. Hydrogenation of **6** gives a symmetrical structure where the hydrogens that were responsible for the AB pattern are now equivalent and appear as a singlet. This result is consistent with the above assignment.

The reaction of *N*-carbomethoxy-6-carbethoxy-2-azabicyclo[3.1.0]hex-3-ene (**2b**) with dimethyl acetylenedicarboxylate can in principle give two isomeric adducts, **9** and **10**. In practice, only the exo isomer **9** was detected. This assignment is based on the nmr spectrum. The bridgehead hydrogen H_a shows zero or nearly zero coupling to the hydrogen α to the carbethoxy function. From the previous





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discussion on the nmr spectrum of adduct **4**, H_a in **9** must occupy the endo position. Attempts to purify the product **9** by thin layer chromatography resulted in double bond isomerization, giving **11**. This indicates that **9** is the primary product and is not formed by epimerization of **10**.

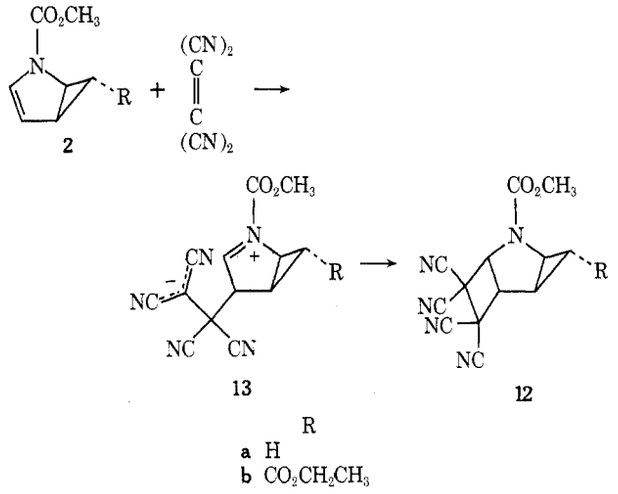
Interestingly, the reaction of tetracyanoethylene (TCNE) with the 2-azabicyclo[3.1.0]hex-3-ene ring system follows a different course. When TCNE in tetrahydrofuran is added to the *N*-carbomethoxy-2-azabicyclo[3.1.0]hex-3-enes (**2a** or **2b**) at room temperature, a colorless solid is produced. The products of these reactions are assigned structures **12a** and **12b.**

This assignment is based partially on the nmr spectrum, which shows high-field absorption indicating the presence of a cyclopropyl substituent and a low-field AB spin system. This low-field AB spin system is assigned to hydrogens that were vinyl in the reactant **2.** The cyclobutyl hydrogen β to the nitrogen atom shows zero or nearly zero coupling with the adjacent cyclopropyl hydrogen. Molecular models indicate that this would be true only in the anti isomer.

Examination of the reactions of vinylcyclopropanes with various dienophiles supports the position that the mechanisms of these reactions appear to be complex. Sarel[4d] and Pasto[4c] have cited dipolar species as reaction intermediates, while Baldwin preferred the concept of a concerted, thermally allowed, $[2_\pi + 2_\sigma + 2_\pi]$ cycloaddition. No specific evidence was obtained for these preferences other than product formation and none of the mechanistic possibilities presented explained the variation of products obtained upon changes in dienophile.

We have made preliminary investigations into the mechanism of the cycloaddition of dienophiles to the 2-azabicyclo[3.1.0]hex-3-ene ring system.

The difference in reactivity of TCNE toward **2a** and **2b** as compared to DMAD is not unprecedented. TCNE is often found to give reaction products arising from a [2 + 2] cycloaddition.[8] Most probably this reaction proceeds through dipole **13,** which can then close to the observed products.



R
a H
b $CO_2CH_2CH_3$

Kinetic results demonstrate that the cycloaddition reaction of **2a** and **2b** with DMAD is second order overall (Table I), while the cycloaddition of **2a** with *N*-phenyl-

Table I
Cycloadditions of the 2-Azabicyclo[3.1.0]hex-3-enes with Dimethyl Acetylenedicarboxylate

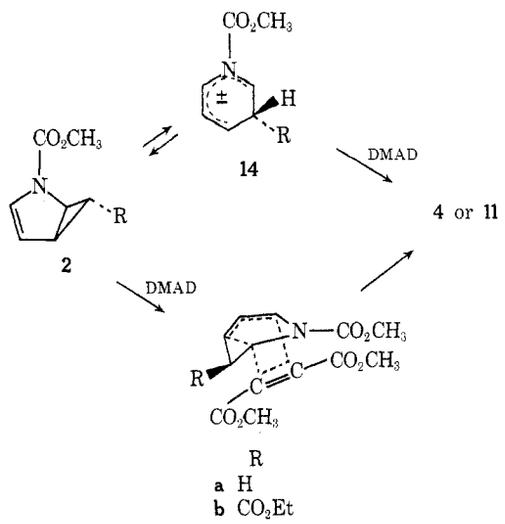
Substrate	Solvent	Mole ratio of DMAD/substrate	Temp, °C	$k \times 10^5$, l. mol^{-1} sec^{-1}
2a	C_6D_6	0.96	91.4	2.98 ± 0.18
2a	C_6D_6	1.92	91.4	2.74 ± 0.07
2b	C_6D_6	0.76	106.3	0.794 ± 0.021

maleimide shows essentially no solvent dependence (Table II). However, two discrete mechanisms are consistent with

Table II
Solvent Dependence of the Cycloaddition of 2a with *N*-Phenylmaleimide

Solvent	Temp, °C	$k \times 10^4$, l. mol^{-1} sec^{-1}
CCl_4	75.8	2.3 ± 0.5
$CH_3C{\equiv}N$	75.8	2.0 ± 0.2

the above results. Compound **2** could be in rapid equilibrium with dipole **14,** which then reacts with DMAD to give the adduct **4** or **9.** Alternatively, DMAD could react with



R
a H
b CO_2Et

the 2-azabicyclo[3.1.0]hex-3-ene ring system in a concerted or nearly concerted fashion.

The stereochemical orientation of the carbethoxy-substituted derivative **9** requires, in the dipole mechanism, that DMAD attack the dipole **14b** from the sterically less hindered side. If a concerted or nearly concerted mechanism is operative in these cycloadditions, then DMAD must attack from the endo direction. Although this would appear to be a sterically unfavorable mode of attack, it is most favorable electronically. Endo attack has been established for electrophilic[9] and radical reactions[10] of fused cyclopropanes. Theoretical calculations[11] and physical measurement[12] are consistent with this phenomenon.

If the dipoles **14a** and **14b** were involved in the cycloaddition reactions, then the second-order kinetics suggest that the dipoles **14a** and **14b** must be involved in a rapid preequilibrium with **2a** and **2b.** Also, the effect of the carbethoxy substituent on the rate of reaction would be expected to be electronic in nature, as the approach of DMAD would have to occur exclusively on the sterically less hindered face of the dipole to account for the product stereochemistry.

Using the steady-state approximation the complete kinetic expression for the 1,3-dipole mechanism is

$$\text{rate} = \frac{k_2[\text{DMAD}]k_1[\mathbf{2}]}{k_2[\text{DMAD}] + k_{-1}}$$

Furthermore, it can be shown that

$$k_{\text{obsd}} = K_{\text{eq}}k_2$$

where

$$K_{\text{eq}} = k_1/k_{-1}$$

and k_{obsd} is the observed rate constant.

The substitution of a carbethoxy group at position 6 in **2** might thus be expected to retard the rate of cycloaddition of **2b** as compared to **2a** in two possible ways. First, the substitution of a carbethoxy group will cause a decrease in k_2 qualitatively, assuming that the reaction of dipole **14** with DMAD is controlled by the properties of the highest occupied molecular orbital.[13] Second, the strengthening effect of the 6-carbethoxy group upon the C_1–C_5 bond[5,14] would shift the preequilibrium between dipole **14** and **2** toward **2b** as compared to **2a** and thus $K_{eq}^{(2b)} < K_{eq}^{(2a)}$.

If the breaking of the C_1–C_5 bond in **2** occurs during the rate-determining step, as it does in the concerted mechanism, the strengthened C_1–C_5 bond in **2b** as compared to **2a** could account for the relative slowness of cycloaddition to **2b.** Table III shows that the difference between ΔH^* values for the cycloaddition of **2a** and **2b** to DMAD is 3.1 kcal/mol.

Table III
Thermodynamic Functions for the Reaction of 2 with Dimethyl Acetylenedicarboxylate

Substrate	E_a, kcal/mol	A, l. mol^{-1} sec^{-1}	ΔH^*, kcal/mol	ΔS^*, eu
2a	17.6	1.00×10^6	16.8	−33.3
2b	20.7	6.5×10^6	19.9	−29.9

It has been shown[15] that the retarding effect of a cyano group on the electrocyclic rearrangement of "folded" 9-cyanobicyclo[6.1.0]nonatriene is 3.5 kcal/mol. In light of this, a bond-strengthening effect of 3.1 kcal/mol attributed to a carbethoxy group is not unreasonable.

Experimental Section[16]

Reaction of *N*-Carbomethoxy-2-azabicyclo[3.1.0]hex-3-ene (2a) with Dimethyl Acetylenedicarboxylate. 2a (130 mg) and 152 mg of DMAD were heated on a steam bath for 15.5 hr. The product **4** proved to be a high-boiling liquid and was purified by preparative thin layer chromatography, giving a 51% yield of **4**: nmr ($CDCl_3$) τ 3.50–3.83 (m, 1 H, C=CH), 4.25–4.61 (m, 1 H, C=CH), 4.90 (d, J = 5.5 Hz, 1 H, NCH), 5.11 (d, J = 5.0 Hz, 1 H, NCH), 6.18 (s, 6 H, OCH_3), 6.27 (s, 3 H, OCH_3), and 7.55 (center of broad AB, J = 19 Hz, $W_{1/2}$ low-field half = 10 Hz, $W_{1/2}$ high-field half = 6.5 Hz, CH_2). Irradiation of the olefinic multiplet at τ 3.50–3.83 caused the doublet at τ 5.11 to collapse into a broad singlet, indicating that these are the H_2 and H_1 protons, respectively. Irradiation of the lower half of the AB centered at 7.55 caused the doublet at τ 4.90 to collapse into a broad singlet. This indicates that the lower half of the AB is H_4 and the doublet at τ 4.90 is the bridgehead proton at H_6. The ir spectrum (neat) showed a broad, strong absorption at 1715 (C=O) and 1640 cm^{-1} (C=C).

Anal. Calcd for $C_{13}H_{15}NO_6$: C, 55.51; H, 5.37. Found: C, 55.76; H, 5.51.

Reaction of *N*-Carbomethoxy-2-azabicyclo[3.1.0]hex-3-ene (2a) with *N*-Phenylmaleimide (5). To 139 mg of **2a** was added 173 mg of *N*-phenylmaleimide. The reaction mixture was heated to 100° under argon for 12 hr. Preparative thin layer chromatography of the product on silica gel (3:1 benzene–ether) separated two products. The major band (116 mg, 38%) proved to be the endo isomer **7**: R_f 0.24; mp 143–145°; nmr ($CDCl_3$) τ 2.42–2.97 (m, 5 H), 3.90–4.25 (m, 2 H), 5.02–5.42 (m, 2 H), 6.13–6.37 (m, 2 H), 6.28 (s, 3 H) and 6.83–h8.00 (m, 2 H); ir (KBr) 1775 and 1710 (C=O) and 1595 cm^{-1} (C=C).

Anal. Calcd for $C_{17}H_{16}N_2O_4$: C, 65.37; H, 5.16; N, 8.97. Found: C, 65.20; H, 5.31; N, 8.90.

The minor band (80 mg) proved to be the exo isomer **6**: R_f 0.34; mp 173–175°; nmr ($CDCl_3$) τ 2.38–2.92 (m, 5 H), 3.67–4.50 (m, 2 H), 5.05–5.35 (m, 2 H), 6.33 (s, 3 H), 6.22 (center of AB, J = 7.5 Hz), and 6.87–8.17 (m, 2 H); ir (KBr) 1778 and 1705 (C=O) and 1593 cm^{-1} (C=C).

Anal. Calcd for $C_{17}H_{16}N_2O_4$: C, 65.37; H, 5.16. Found: C, 65.37; H, 5.02.

Hydrogenation of 6. To 53 mg of **6** was added 20 ml of ethyl acetate and 10% palladium on carbon. Subjecting the solution to 1 atm of hydrogen led to the absorption of 1 equiv of hydrogen within 0.5 hr. Removal of the solvent gave a colorless oil **8**, which could be recrystallized from ethyl acetate–pentane: mp 157–158°; nmr ($CDCl_3$) τ 2.38–2.92 (m, 5 H), 5.28 (s, broad, $W_{1/2}$ = 5 Hz, 2 H), 6.33 (s, 3 H), 6.78 (s, 2 H), and 8.25 (s, broad, $W_{1/2}$ = 4 Hz, 6 H); ir (KBr) 1781 (w) and 1705 cm^{-1} (s, C=O).

Anal. Calcd for $C_{17}H_{18}N_2O_4$: C, 64.95; H, 5.77; N, 8.91. Found: C, 64.88; H, 5.83; N, 9.13.

Reaction of *N*-Carbomethoxy-6-carbethoxy-2-azabicyclo-[3.1.0]hex-3-ene (2b) with Tetracyanoethylene. To a solution of 255 mg of **2b** in 5 ml of anhydrous THF with stirring was added a solution of 155 mg of freshly sublimed TCNE in 5 ml of THF. Immediately upon addition, a yellow-gold color appeared. After a period of 15 min, the solvent was removed *in vacuo*, leaving a red-brown solid which was recrystallized by dissolving in acetone and adding ether until cloudiness developed. **12b** (229 mg, 56% yield) was obtained as small, colorless crystals: mp 135–136°; nmr (acetone-d_6) τ 4.79 (d, 1 H, J = 7.5 Hz), 5.48 (d, 1 H, J = 7.5 Hz), 5.59–5.99 (m, 3 H), 6.14 (s, 3 H, NCO_2CH_3), 7.11 (dd, 1 H, J = 6.0, J' = 4.25 Hz), 7.71 (dd, 1 H, J = 4.25, J' = 1.5 Hz), 8.74 (t, 3 H, J = 7.0 Hz, OCH_2CH_3); ir (KBr) 3010 (CH), 2230 (C≡N), 1720 cm^{-1} (C=O).

Anal. Calcd for $C_{16}H_{13}N_5O_4$: C, 56.63; H, 3.86; N, 20.64; O, 18.86. Found: C, 56.58; H, 3.93.

Reaction of *N*-Carbomethoxy-2-azabicyclo[3.1.0]hex-3-ene (2a) with Tetracyanoethylene. To 129 mg of **2a** in 2 ml of THF was added 128 mg of TCNE in 0.5 ml of THF. The reaction mixture was allowed to stand at room temperature for 1 hr and the solvent was removed at room temperature *in vacuo*. The nmr spectrum of the crude product show only the presence of **12a.** The crude product was dissolved in acetone and ether was slowly added until precipitation of **12a** no longer occurred. This produced 111 mg of yellow crystals, mp 134° dec. The analytical sample was produced by recrystallization from acetone–ether at room temperature: mp 135° dec; nmr (acetone-d_6) τ 4.73 (center AB, 2 H, J = 7.5 Hz), 3.97–3.37 (m, 1 H), 3.84 (s, 3 H, OCH_3), 2.75–2.00 (m, 1 H), and 1.58–0.82 (m, 2 H); ir (KBr) 2259 (C≡N), 1736 (C=O), and strong absorptions at 1451, 1392, and 1339 cm^{-1}.

Anal. Calcd for $C_{13}H_9O_2N_5$: C, 58.42; H, 3.39; N, 26.21. Found: C, 58.40; H, 3.39; N, 26.15.

Reaction of *N*-Carbomethoxy-6-carbethoxy-2-azabicyclo-[3.1.0]hex-3-ene (2b) with Dimethyl Acetylenedicarboxylate. To a Pyrex tube was added 316 mg of **2b** and 228 mg of DMAD. The tube was flushed with argon and sealed. The reaction mixture was heated in an oil bath at 170° for 24 hr. Nmr analysis, by comparing the bridgehead to total methoxyl hydrogens of the crude product, reveals an 87% yield of **9**. The product was purified first by molecular distillation and then by vapor phase chromatography (1 ft × 0.25 in., 212°, 3% SE-30 on Chromosorb Cr 60/70, He 50 cc/min): nmr ($CDCl_3$) τ 3.38–3.73 (m, 1 H), 4.12–4.47 (m, 1 H), 4.42 (s, broad, $W_{1/2}$ = 3 Hz), 5.75 (q, J = 7 Hz, 2 H), 6.18 (s, 6 H), 6.32 (s, 3 H), 6.68–6.83 (m, 1 H), and 8.53 (t, J = 7 Hz, 3 H); ir (neat) 1721 (C=O) and 1645 cm^{-1} (C=C).

Anal. Calcd for $C_{16}H_{19}NO_8$: C, 54.39; H, 5.42. Found: C, 54.12; H, 5.42.

Attempts to purify the above product by preparative thin layer chromatography (20 × 20 × 0.2 cm silica gel, 3:1 ether–benzene) resulted in the production of isomeric compound **11**: nmr ($CDCl_3$) τ 3.17–3.38 (m, 1 H), 4.55 (s, broad, $W_{1/2}$ = 2.5 Hz, 1 H), 4.90 (d, broad, $W_{1/2}$ = 3 Hz, 1 H), 5.77 (q, J = 7 Hz, 2 H), 6.20 (s, 3 H), 6.22 (s, 3 H), 6.30 (s, 3 H), 6.87–7.95 (m, 2 H), and 8.80 (t, J = 7 Hz, 3 H); ir (neat) 1726 cm^{-1} (C=O).

Anal. Calcd for $C_{16}H_{19}NO_8$: C, 54.39; H, 5.42. Found: C, 54.11; H, 5.25.

Kinetics of the Cycloaddition of 2 with Dimethyl Acetylenedicarboxylate. To an nmr tube were added controlled amounts of **2a** or **2b**, DMAD, and C_6D_6. C_6H_6 was used as an internal standard with the total volume being recorded. (The initial concentration of reactants was approximately 1 *M*.) The tube was flushed with nitrogen, sealed under vacuum, and maintained at the appropriate temperature (±0.1°) in an oil bath. Determinations for **2a** were made at 70.5, 80.7, and 91.4° while for **2b** determinations were made at 106.3, 113.6, and 120.9°. The disappearance of **2a** was monitored by periodic integration of the upfield endo cyclopropyl peak in the nmr spectrum of the reaction mixture. The disappearance of **2b** was followed by periodic integration of the cyclopropyl proton at position 5 in **2b**. Second-order rate constants and activation energies were obtained by least-squares fitting.

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Registry No.—**2a**, 31709-40-7; **2b**, 25088-90-8; **4**, 31709-41-8; **5**, 941-69-5; **6**, 51869-43-3; **7**, 51898-46-5; **8**, 51869-44-4; **9**, 31887-68-0; **11**, 51911-67-2; **12a**, 51869-45-5; **12b**, 51869-46-6; DMAD, 762-42-5; TCNE, 670-54-2.

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(16) Melting points are uncorrected. The microanalyses were performed by either Galbraith Laboratories, Knoxville, Tenn., or A. Bernhardt Microanalytisches Laboratorium, 5251 Elbach uber Engelskirchen, West Germany. The infrared spectra were recorded using a Perkin-Elmer 257. The nmr spectra were recorded using a Varian A-60 spectrophotometer.

Reactions of *N*-Aryl Nitrogen Oxides. 1. Selective Ortho Chlorination in the Reactions of Aryl Nitrones and Amine Oxides with Thionyl Chloride or Phosgene

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N-Aryl nitrones react rapidly with phosgene or thionyl chloride to produce ring-chlorinated imine hydrochlorides in high yield. Ring chlorination is shown to proceed exclusively on the aryl system adjacent to the nitrogen atom. The generality of this reaction with other *N*-aryl nitrogen oxides is discussed and a mechanism based upon the experimental observations is proposed.

The classes of *N*-aryl nitrogen oxides which are of current interest in this laboratory include, *inter alia*, *N*-aryl nitrones, *N*-aryl tertiary amine *N*-oxides, *N,N'*-diarylazoxy compounds, nitroaromatic compounds, and *N*-aryl-*N*-nitroso dimers. A few of the above have been reported to react with acid chlorides and anhydrides to yield ring-substituted products. For example, in an investigation of the Polonovski reaction, Huisgen, *et al.*,[1] have observed the production of small to moderate amounts of ortho-acetylated *N,N*-dimethylanilines when ring-substituted *N,N*-di-