The Reactions of Medium-Membered-Ring Unsaturated Compounds with Iodine Azide[1]

TADASHI SASAKI,* KEN KANEMATSU, AND YUSUKE YUKIMOTO

Institute of Applied Organic Chemistry, Faculty of Engineering, Nagoya University, Chikusa, Nagoya, 464, Japan

Received July 29, 1971

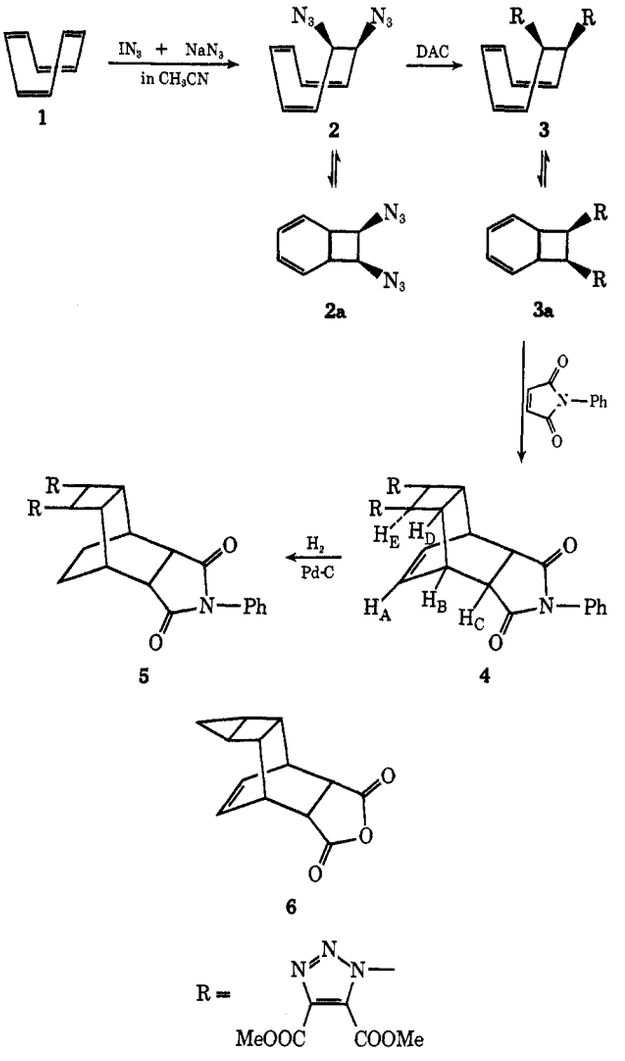
Reaction of some medium-membered-ring unsaturated compounds such as cyclooctatetraene, 1-ethoxycarbonyl-1(1*H*)-azepine, and tropone ethylene ketal with the IN_3 solution, a mixture of iodine azide and sodium azide, gave the bisazides. However, in the case of the reactions of cycloocta-1,3- and -1,5-dienes with the same mixture under the same conditions, only normal monoazides were obtained which were convertible to the corresponding bisazides with NaN_3 in DMF at 35–40°. The formation of these adducts was confirmed by spectral evidence of their triazolo derivatives prepared by the reactions of the adducts with dimethyl acetylenedicarboxylate.

The addition reactions of halogen azides to olefins provide a useful general method for the stereospecific and regiospecific introduction of an iodo azide function into organic molecules.[2] Although the reactions of numerous olefins with iodine azide (IN_3) have been examined, little is known about the similar reactions of cyclic conjugated polyolefins with the exception of cycloocta-1,3-diene.[3] In this paper we report the reactions of cyclooctatetraene (COT), 1-ethoxycarbonyl-1(1*H*)-azepine, and tropone ethylene ketal with IN_3 to give the bisazides **2**, **15**, and **18**, respectively.

Results and Discussion

Formation of the Bisazides. –The reaction of COT (**1**) with an IN_3 solution prepared *in situ* from excess sodium azide and iodine monochloride in acetonitrile[2] afforded an oily compound **2**. When an excess of NaN_3 was removed in the reaction, considerable amounts of tarry compounds were obtained, presumably because of unstable 1:1 IN_3 adduct initially formed (*cf.* Experimental Section, method B). Compound **2** showed a strong azide absorption at 2100 cm^{-1} in the ir spectrum and is negative to the Beilstein halogen test. Since the azide is quite explosive at room temperature, the structure determination was based on that of 1,3-dipolar cycloadduct; treatment of **2** with dimethyl acetylenedicarboxylate (DAC) gave a crystalline compound **3**. From the analytical data, the adduct **3** was determined to be a bistriazolo derivative. The nmr spectrum of **3** showed signals at τ 3.30 (2 H, dd, J = 4.0 and 2.5 Hz), 3.68 (2 H, dd, J = 8.2 and 4.0 Hz), 4.75 (4 H, complex multiplets), 6.05 (3 H, s, $COOCH_3$), and 6.10 (3 H, s, $COOCH_3$). From the spectrum, however, it is difficult to determine the positions of the triazolo groups whether at 1,2 or 1,4, because of the complexity of the signals centered at τ 4.75. Thus, the cycloaddition reaction of **3** with *N*-phenylmaleimide was attempted, which afforded a 1:1 adduct **4**; the nmr spectrum exhibited signals at τ 2.50–3.00 (m, C_6H_5), 4.00 (H_A, dd, J = 3.4 and 4.2 Hz), 6.05 (s, 4 $COOCH_3$), 6.45 (H_B, m), 6.87 (H_C, t, J = 1.5 Hz), 7.38 (H_E, m), and 8.26 (H_D, m). Double resonance experiments verified the assignments of H_A and H_B; on irradiation at τ 6.45 the double

SCHEME I



doublet signals at τ 4.00 were collapsed into a singlet. Furthermore, the spectrum pattern of **4** is quite similar to that of an endo cycloadduct (**6**)[4] of tricyclo[4.3.0.$0^{7,9}$]nona-2,4-diene to maleic anhydride. The signals at both τ 4.00 and 6.45 disappeared by the catalytic hydrogenation and new ones appeared at τ 8.2–8.6 (m, 6 H). These results indicate that the signal at τ 4.0 is due to the olefinic protons (H_A), and that at τ 6.45 is attributable to the methine proton (H_B) ad-

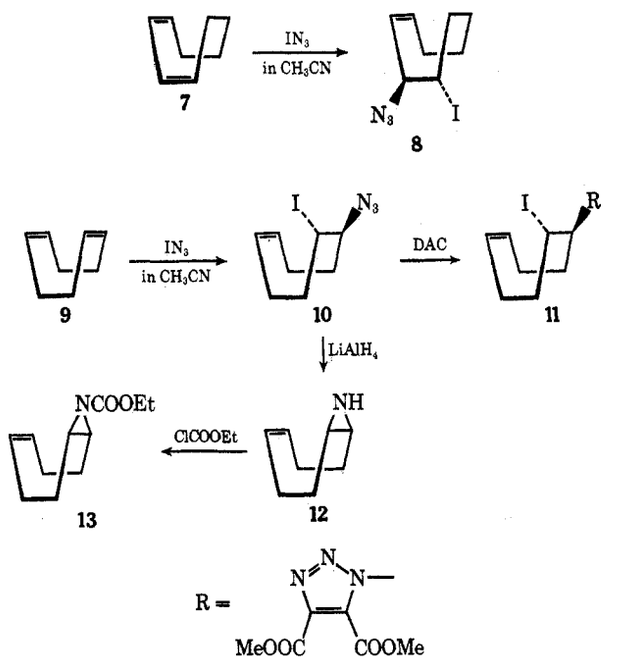
(1) Studies of Heteroaromaticity. Part LX. For Part LIX of this series, see T. Sasaki, K. Kanematsu, and K. Hayakawa, *J. Chem. Soc. C.* in press.

(2) A. Hassner, *Accounts Chem. Res.* **4**, 9 (1971).

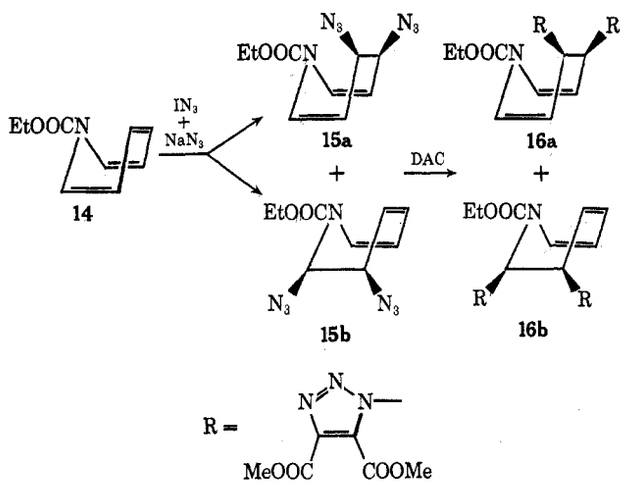
(3) F. W. Fowler, A. Hassner, and L. A. Levy, *J. Amer. Chem. Soc.*, **89**, 2077 (1967).

(4) W. H. Okamura and T. W. Osborn, *J. Amer. Chem. Soc.*, **92**, 1061 (1967).

SCHEME II



SCHEME III



jacent to the double bond. Thus, the adduct (**4**) is assigned as a (4 + 2) π cycloadduct of *N*-phenylmaleimide to 7,8-bistriazolobicyclo[4.2.0]octa-2,4-diene.

From these results, compound **3** could be assigned as 7,8-bistriazolobicyclo[4.2.0]octa-2,4-diene (**3a**) as depicted in Scheme I. Further structural confirmation of the adduct will be described below.

The reaction of cycloocta-1,3-diene (**7**) with IN_3 has been reported to give a normal 1:1 adduct (**8**).[2] We reinvestigated similar reactions of cycloocta-1,3- and -1,5-dienes with the IN_3 solution under the same conditions as described above to give 1:1 IN_3 adducts **8** and **10**. Compound **10** exhibited a strong azide absorption at 2100 cm^{-1} and is positive to the Beilstein halogen test. For the structural elucidation, the 1,3-dipolar cycloaddition reaction of **10** with DAC was also carried out and gave the cycloadduct **11** in 40% yield. Compound **10** was converted to the aziridine derivative **12** by lithium aluminium hydride.[5] Treatment of **12** with ethyl chloroformate afforded **13**, which was

(5) This reaction was studied in detail for the proof of anti addition of IN_3 to the olefin providing by $LiAlH_4$ reduction of the adducts; see ref 2.

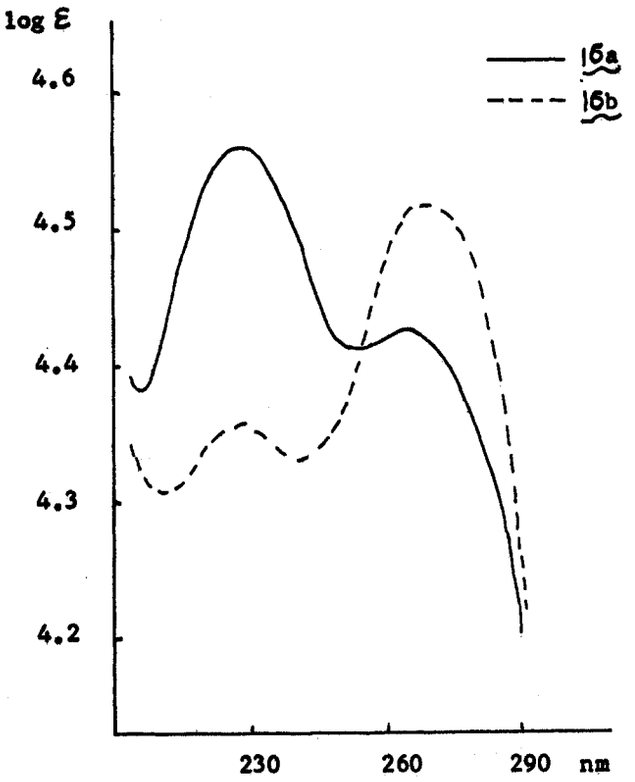


Figure 1.—Ultraviolet spectra of compounds **16a** and **16b** in MeOH.

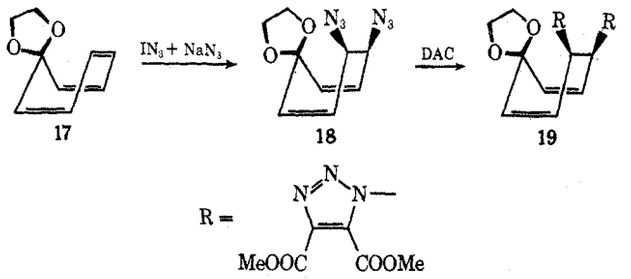
identical with an authentic sample prepared from the photochemical reaction of cycloocta-1,5-diene and ethyl azidoformate[6] (Scheme II).

Similar treatment of 1-ethoxycarbonyl-1(1*H*)-azepine (**14**) with the IN_3 solution gave a mixture of **15a** and **15b**, which was readily converted to the cycloadducts to DAC. The isomeric mixture was separated by column chromatography and recrystallized into **16a** and **16b** in the ratio of 10:1. The isomeric adducts were assigned on the basis of the spectral inspection. The ir and uv spectra (*cf.* Figure 1) of **16a** were quite similar to those of the 4,5-homoazepine derivative,[7] and the spectra of **16b** were similar to those of the 2,3-homoazepine isomer.[7]

The nmr spectrum of **16a** shows symmetrical patterns at τ 2.79 (H_A, d, J_{AB} = 9.0 Hz), 3.61 (H_C, d, J_{CB} = 6.0 Hz), 4.63 (H_B, dd, J = 9.0 and 6.0 Hz), the two methoxycarbonyl signals at τ 6.06 and 6.15, and the ethoxycarbonyl signals at τ 5.65 (OCH_2, q, J = 7.0 Hz) and 8.60 (CH_3, t, J = 7.0 Hz). The spectrum of **16b** exhibited the 1,3-diene ring proton signals at τ 3.10 (1 H, t, J = 6.0 Hz), 3.12 (1 H, d, J = 9.0 Hz), 3.85 (1H, d, J = 6.0 Hz), and 4.65 (1 H, dd, J = 6.0 and 9.0 Hz), the methine proton signals at τ 2.50 (1 H, d, J = 4.3 Hz) and 3.92 (1 H, d, J = 4.3 Hz), the two methoxycarbonyl signals at τ 6.06 and 6.15, and the ethoxycarbonyl signals at τ 5.65 (OCH_2, q, J = 7.0 Hz) and 8.60 (CH_3, t, J = 7.0 Hz). From the results, the structures of **16a** and **16b** were characterized as the 1-ethoxycarbonyl-4,5-*cis*-bistriazolo-4,5-dihydro-1(1*H*)-azepine derivative and the 2,3 isomer, respectively (Scheme III).

(6) S. Fujita, T. Hiyama, and H. Nozaki, *Tetrahedron*, **26**, 4347 (1970).
(7) W. H. Okamura and W. H. Snider, *Tetrahedron Lett.*, 3367 (1968).

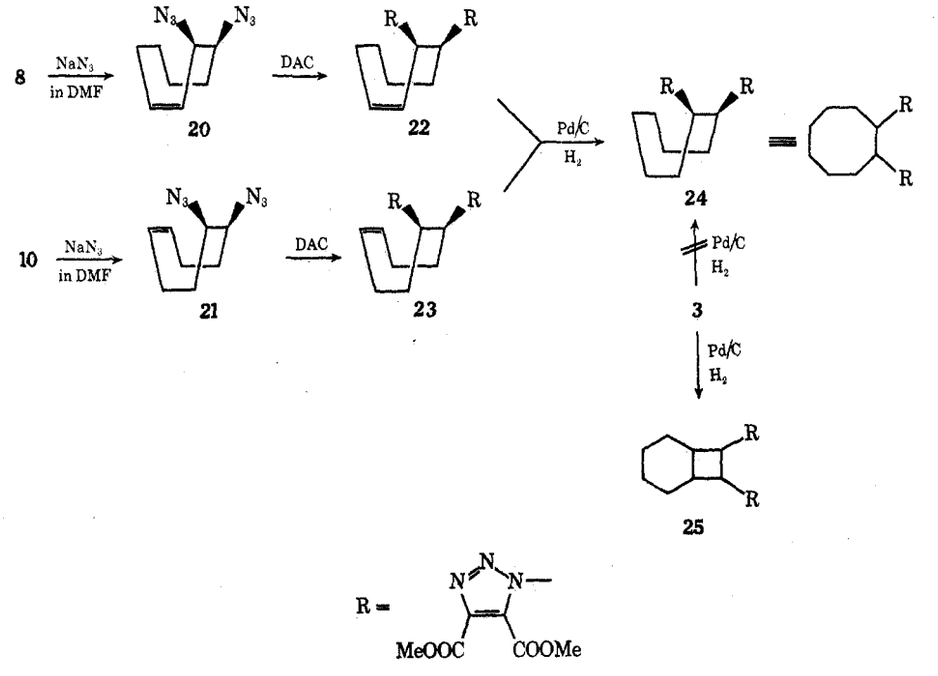
SCHEME IV



7.25. It should be mentioned that the reaction of the tropone ketal with the IN_3 solution is entirely similar to that of the azepine with the polyolefinic characters, although the tropone ethylene ketal is classified as a spiro-conjugated aromatic system from the calculated stabilization energy by Simmons and Fukunaga.[8]

Stereochemistry of the Bisazides.—For further structural elucidation, the stereochemistry of the bisazides was studied. The 1:1 adducts **8** and **10** to cycloocta-1,3- and -1,5-dienes were treated with NaN_3 in DMF at 30–40° for 10 hr to give the bisazides **20**

SCHEME V



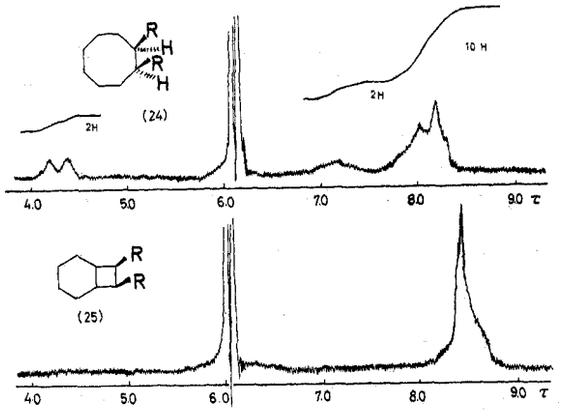


Figure 2.—Nmr spectra of compounds **24** and **25**.

Similar reaction of tropone ethylene ketal (**17**) with the IN_3 solution gave an oily compound (**18**), which was converted to the cycloadduct **19** with DAC (Scheme IV). The adduct **19** was also assigned as the *cis*-bistriazolo derviative from a completely symmetrical pattern of the nmr spectrum: it displayed four equivalent vinyl protons as a singlet at τ 3.75, two methine protons as a singlet at τ 3.80, two methyl protons of two methoxycarbonyl groups as two singlet patterns at τ 6.00 and 6.07, and two equivalent pairs of methylene protons ($-OCH_2CH_2-O-$) as doublets (J = 6.0 Hz) centered at τ 6.95 and and **21**, respectively, whose structual determinations were based on that of the corresponding 1,3-dipolar cycloadducts **22** and **23** to DAC. Catalytic hydrogenation of the cycloadducts **22** and **23** in ethanol over palladium on charcoal gave **24** (uptake 1 g-atom of H_2) in quantitative yield. However, the cycloadducts **3** absorbed only 2 g-atoms of hydrogen and afforded **25** (no olefinic protons by nmr) in quantitative yield (Scheme V). The difference in the nmr spectra of **24** and **25** suggested that **25** was not the trans isomer of **24** but a bicyclo[4.2.0]octane derivative. Compound **25** can be assigned the cis configuration because of the symmetrical pattern by nmr (*cf.* Figure 2).

Mechanisms for the Formation of the Bisazides.—As described above, the reactions of the conjugated cyclotetraene and trienes with the IN_3 solution gave readily the 1,2-cis bisazides, and those of the conjugated and nonconjugated cyclic dienes afforded only the 1:1 adducts. Further treatment of the 1:1 adduct with NaN_3 under the conditions as described above gave the bis adduct.

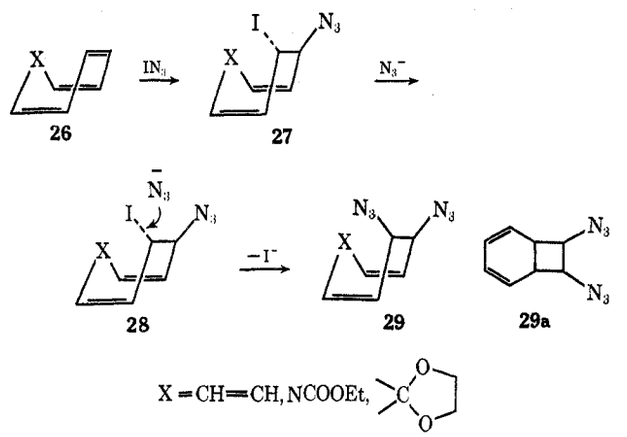
Based on these facts, we suggested that the adduct **27** where

$$X = NCOOEt, \overline{COCH_2CH_2OC}$$

(8) H. E. Simmons and T. Fukunaga, *J. Amer. Chem. Soc.*, **89**, 5208 (1967).

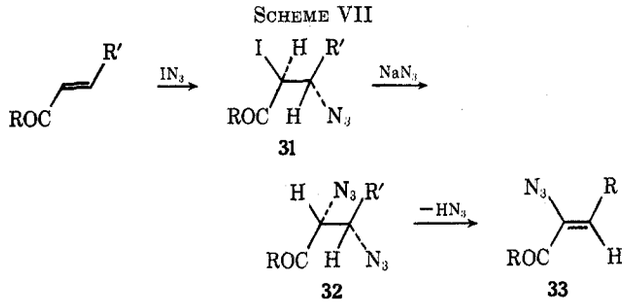
was initially formed in the reaction of **26** with IN_3, followed by the SN2 attack of the azide ion to give **29**, since the iodine group in **27** might be activated by the vinyl function rather than by the alicyclic group. In the case of COT (**25**, X = CH=CH), the monocyclic adducts were not isolated, which readily gave the bicyclic adduct **29a** through valence tautomerization (Scheme VI).

SCHEME VI



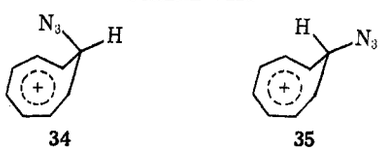
In these connections, Hassner, *et al.*,[9] recently suggested that the bisazides **32** might be formed by the SN2 attack of the azide ion on the iodine-bearing carbon of **31**, as shown in Scheme VII.

SCHEME VII



An alternative mechanism involving homotropylium ions **34** and **35** could be considered;[10,11] the former should lead to the cis azide, whereas the latter might be a precursor to the trans isomer (Scheme VIII).

SCHEME VIII



However, neither the 1,2-trans bisazide nor the 1,4 bisazide could be obtained in these reactions. Consequently, this mechanism might be deleted.

(9) G. Lábbé and A. Hassner, *J. Org. Chem.*, **36**, 258 (1971).

(10) We are grateful to a referee for a valuable suggestion.

(11) In these connections, the 1,4 cycloadduct rather than the 1,2 cycloadduct of COT to chlorosulfonyl isocyanate has been rationalized by the intervention of a dipolar homotropylium cation, followed by collapse of two intermediates *via* either one of two equivalent six-centered transition states; see L. A. Paquette, J. A. Malpass, and T. J. Barton, *J. Amer. Chem. Soc.*, **91**, 4714 (1969).

Experimental Section[12]

General Procedure for Iodine Azide Addition Reactions. A.—To 3.9 g (0.06 mol) of sodium azide in 25 ml of acetonitrile at −20° was added slowly 3.6 g (0.022 mol) of iodine monochloride over a period of 5–10 min. The reaction mixture was then stirred for an additional 5 min. After 0.02 mol of the unsaturated compound was added to the solution, the reaction mixture was allowed to stand at room temperature overnight. The red-brown slurry was poured into 50 ml of water, and the mixture was extracted with ether. The extract was washed with 40 ml of 5% aqueous sodium thiosulfate and then with water and dried over magnesium sulfate. Removal of the solvent under reduced pressure at room temperature produced yellow oily compounds **2**, **15**, and **18** in 80–90% yields, respectively. These compounds were used in the following reactions without further purification, since the azido functions in the adducts are quite explosive even under the reduced distillation.

B.—To a stirred slurry of 0.01 mol of sodium azide in 20 ml of acetonitrile in a methanol–ice cold bath was added slowly 0.011 mol of iodine monochloride over a period of 10–20 min. The reaction mixture was stirred for an additional 5 min. After excess insoluble sodium azide was removed by filtration, the filtered IN_3 solution was added to 0.01 mol of the olefin using a cooled addition funnel.[10] However, when treated with IN_3 and COT, considerable amounts of black tarry compounds were obtained.

1,3-Dipolar Cycloaddition of the Bisazides with DAC.—A solution of the bisazides **2**, **15**, and **18** (0.01 mol) and DAC (0.02 mol) in acetonitrile (40 ml) was refluxed for 12 hr. The solvent was removed under reduced pressure to give the cycloadducts as follows.

7,8-*cis*-Bis(4,5-dimethoxycarbonyl-1,2,3-triazolo)bicyclo[4.2.0]octa-2,4-diene (**3a**) was obtained as a crude colorless solid and recrystallized from methanol in 70% yield: mp 137–139°; ν_{max}^{KBr} 1720 (C=O) and 1570 cm^{-1} (C=C); τ ($CDCl_3$, both at 40 and 52°) 3.30 (2 H, dd, J = 4.0 and 2.5 Hz), 3.68 (2 H, dd, J = 8.2 and 4.0 Hz), 4.75 (4 H, m), 6.05 (3 H, s, COOMe), 6.10 (3 H, s, COOMe).

Anal. Calcd for $C_{20}H_{20}N_6O_8$: C, 50.85; H, 4.28; N, 17.79. Found: C, 51.01; H, 4.40; N, 17.59.

1-Ethoxycarbonyl-4,5-*cis*-bis(4,5-dimethoxycarbonyl-1,2,3-triazolo)-4,5- and -2,3-dihydro-1(1H)-azepines 16a and **16b** were obtained as a mixture in 80% yield. The mixture was purified by silica gel chromatography with methanol–benzene (3%) as an eluent to give **16a**, mp 149–151°, and **16b**, mp 152–155° (recrystallization from methanol).

16a: ν_{max}^{KBr} 1720 (C=O) and 1675 cm^{-1} (C=C); λ_{max}^{MeOH} 225 nm (log ϵ 4.57), 265 (ϵ 4.43); τ ($CDCl_3$) 2.79 (1 H), d, J = 9.0 Hz), 3.61 (1 H, d, J = 6.0 Hz), 4.63 (1 H, dd, J = 9.0 and 6.0 Hz), 6.06 (3 H, s, $COOCH_3$), 6.15 (3 H, s, $COOCH_3$), 5.65 (2 H, q, J = 7.0 Hz), 8.60 (3 H, t, J = 7.0 Hz).

16b: ν_{max}^{KBr} 1745 (shoulder), 1720 (C=O), 1650, 1615 cm^{-1} (C=C); λ_{max}^{MeOH} 225 nm (log ϵ 4.36), 268 (ϵ 4.52); τ ($CDCl_3$) 3.10 (1 H, t, J = 6.0 Hz), 3.12 (1 H, d, J = 9.0 Hz), 3.85 (1 H, d, J = 6.0 Hz), 4.65 (1 H, dd, J = 6.0 and 9.0 Hz), 2.50 (1 H, d, J = 4.3 Hz), 3.92 (1 H, d, J = 4.3 Hz), 6.06 (3 H, s, $COOCH_3$), 6.15 (3 H, s, $COOCH_3$), 5.65 (2 H, q, J = 7.0 Hz, OCH_2), 8.60 (3 H, t, J = 7.0 Hz, OCH_2CH_3).

Anal. Calcd for $C_{21}H_{23}N_7O_{10}$: C, 47.28; H, 4.35; N, 18.38. Found for **16a**: C, 47.16; H, 4.36; N, 18.21. Found for **16b**: C, 47.55; H, 4.41; N, 18.24.

4,5-*cis*-Bis(4,5-dimethoxycarbonyl-1,2,3-triazolo)-4,5-dihydrotropone ethylene ketal (**19**) was obtained as colorless prisms in 40% yield: mp 206–209°; ν_{max}^{KBr} 1730 (C=O) and 1565 cm^{-1} (C=C); τ ($CDCl_3$) 3.75 (4 H, s), 3.80 (2 H, s), 6.00 (3 H, s, $COOCH_3$), 6.07 (3 H, s, $COOCH_3$), 6.95 (2 H, t, J = 6.0 Hz), 7.25 (2 H, t, J = 6.0 Hz).

Anal. Calcd for $C_{21}H_{22}N_6O_{10}$ C, 48.65; H, 4.28; N, 16.21. Found: C, 48.63; H, 4.29; N, 16.19.

Cycloaddition of 3 with *N*-Phenylmaleimide.—A solution of **3** (2.4 g, 0.05 mol) and *N*-phenylmaleimide (1.7 g, 0.01 mol) in

(12) The melting points were measured with a Yanagimoto micromelting point apparatus and are uncorrected. Microanalyses were performed on a Perkin-Elmer 240 elemental analyzer. The uv spectra were determined with a JASCO Model ORD/UV-5 recorder. The nmr spectra were taken with a Model C-60-XL nmr spectrometer and with a Varian A-60 recording spectrometer with tetramethylsilane as an internal standard. The chemical shifts are expressed in τ values. The ir spectra were taken with a JASCO Model IR-S spectrophotometer.

toluene (100 ml) was refluxed for 3 days. The solvent was then removed under reduced pressure and the residue was recrystallized from benzene to give colorless needles of **4** (80%), mp 243–245°, ν_{max}^{KBr} 1730 and 1705 cm^{-1}.

Anal. Calcd for $C_{30}H_{27}N_7O_{10}$: C, 55.81; H, 4.22; N, 15.19. Found: C, 55.86; H, 4.25; N, 14.90.

Hydrogenation of 4.—A solution of **10** (1.0 g, 0.0015 mol) in 50 ml of acetone was hydrogenated over 10% Pd/C (0.1 g) for 12 hr at room temperature. The catalyst was then separated by filtration and the solvent was removed under reduced pressure. The residue was recrystallized from methanol to give colorless needles of **5** in a quantitative yield: mp 240–241°; ν_{max}^{KBr} 1730 and 1710 cm^{-1}; τ ($CDCl_3$) 2.5–3.0 (m, C_6H_5), 6.90 (m, 2 H), 7.32 (m, 2 H), and 8.2–8.6 (m, 8 H).

Anal. Calcd for $C_{30}H_{29}N_7O_{10}$: C, 55.64; H, 4.51; N, 15.14. Found: C, 55.63; H, 4.56; N, 14.91.

5-Azido-6-iodocyclooctene (**10**) was prepared from cycloocta-1,5-diene and the IN_3 solution as described in method A. This compound was obtained in 80% yield and was used in the following reactions without further purification.

1-(2-Iodocyclooct-5-enyl)-4,5-dimethoxycarbonyl-1,2,3-triazole (**11**) was prepared from **10** (2.77 g, 0.01 mol) and DAC (1.42 g, 0.01 mol) in 40% yield: mp 98–99.5° (from methanol); ν_{max}^{KBr} 1745 and 1720 cm^{-1}; τ ($CDCl_3$) 4.32 (m, 2 H), 4.40–4.92 (m, 2 H), 6.02 (s, OCH_3), 6.05 (s, OCH_3), 7.0–8.0 (m, 8 H).

Anal. Calcd for $C_{14}H_{18}N_3O_4I$: C, 40.11; H, 4.33; N, 10.02. Found: C, 40.37; H, 4.35; N, 10.28.

9-Azabicyclo[6.1.0]nona-4-ene (**12**).—To a stirred solution of 2.0 g of lithium aluminium hydride in 50 ml of anhydrous ether was added the iodo azide adduct **10** (5.5 g, 0.02 mol) in 15 ml of ether. The solution was stirred at room temperature and added with excess $LiAlH_4$ (1 g). The reaction mixture was then treated with 20% sodium hydroxide solution and extracted with ether. The extract was removed under reduced pressure to give **12** (50%) as a pale yellow oil, picrate mp 173–175° (from methanol).

Anal. Calcd for $C_{14}H_{16}N_4O_7$ (picrate): C, 47.73; H, 4.58; N, 1590. Found: C, 47.61; H, 4.51; N, 15.94.

9-Ethoxycarbonyl-9-azabicyclo[6.1.0]non-4-ene (**13**).—To 1.23 g (0.01 mol) of the aziridine **12** and 5 g of triethylamine in 70 ml of benzene was added 1.1 g (0.01 mol) of ethyl chloroformate at 0°. The reaction mixture was stirred for 5 hr at room temperature. The salts were filtered and the solution was removed under reduced pressure to give a pale yellow oil (**13**) (80%). Compound **13** shows identical spectroscopic properties with those of an authentic sample prepared from the photochemical reaction of ethyl azidoformate and cycloocta-1,5-diene.[6]

Reaction of the Iodine Azide Adducts with Sodium Azide.—The corresponding IN_3 adducts **8** and/or **10** were allowed to react with sodium azide (0.02 mol) in DMF (60 ml) at 30–40° for 15 hr. The solution was then poured into water and extracted with ether. The extract was washed with water and dried ($MgSO_4$). Removal of the solvent under reduced pressure at room temperature produced the corresponding bizazides **20** and/or **21** as a yellow oil in 30–40% yields. However, these compounds were explosive at room temperature and were used in the following reactions without further purification.

3,4-*cis*-Bis(4,5-dimethoxycarbonyl-1,2,3-triazolo)-1-cyclooctene (**22**) was obtained by the reaction of DAC and **20** as described above: mp 179–181°; colorless prisms; yield 50%; ν_{max}^{KBr} 1730 (C=O), cm^{-1} 1570 (C=C); τ ($CDCl_3$) 3.3–3.9 (3 H, m), 4.2–4.7 (1 H, m), 6.00 (3 H, s, $COOCH_3$), 6.10 (3 H, s, $COOCH_3$), 6.13 (3 H, s, $COOCH_3$), 6.30 (3 H, s, $COOCH_3$), 7.2–8.7 (8 H, m).

Anal. Calcd for $C_{20}H_{24}N_6O_8$: C, 50.42; H, 5.08; N, 17.64. Found: C, 50.50; H, 5.10; N, 17.60.

5,6-*cis*-Bis(4,5-dimethoxycarbonyl-1,2,3-triazolo)-1-cyclooctene (**23**) was obtained by the reaction of DAC and **21** as described above: mp 141–142°; colorless prisms; yield 20%; ν_{max}^{KBr} 1740 (C=O) and 1560 cm^{-1} (C=C); τ ($CDCl_3$) 4.0–4.5 (4 H, m), 6.10 (3 H, s, COOMe), 6.18 (3 H, s, COOMe), 6.5–8.5 (8 H, H, m).

Anal. Calcd for $C_{20}H_{24}N_6O_8$: C, 50.42; H, 5.08; N, 17.64. Found: C, 50.39; H, 5.03; N, 17.65.

Hydrogenation of 22 and 23.—A solution of **22** or **23** (0.1 g) in acetone (20 ml) was hydrogenated over 10% Pd/C (0.02 g) for 2 hr at room temperature. The catalyst was then separated by filtration and the solvent was removed under reduced pressure. The residue was recrystallized from methanol to give colorless needles (**24**) in quantitative yield: mp 158–160°; ν_{max}^{KBr} 1735 (C=O) and 1660 cm^{-1} (C=C); τ ($CDCl_3$) 4.28 (2 H, br d, J = 10.0 Hz), 7.15 (2 H, m), 7.5–8.3 (10 H, m).

Anal. Calcd for $C_{20}H_{26}N_6O_8$: C, 50.20; H, 5.48; N, 17.57. Found: C, 50.18; H, 5.50; N, 17.51.

Hydrogenation of 3.—A solution of **3** (0.94 g, 0.002 mol) in acetone (50 ml) was hydrogenated over 10% Pd/C (0.1 g) at room temperature. Uptake of hydrogen was complete after 2 hr and amounted to a total of 90 ml (0.004 mol). The catalyst was then separated by filtration and the solvent was removed under reduced pressure. The residue was recrystallized from methanol to give colorless needles (**25**) in quantitative yield: mp 145–147°; ν_{max}^{KBr} 1730 (C=O) and 1765 cm^{-1} (C=C); τ ($CDCl_3$) 6.00 (3 H, s, COOMe), 6.10 (3 H, s, COOMe), 8.1–8.8 (12 H, m).

Anal. Calcd for $C_{20}H_{24}N_6O_8$: C, 50.42; H, 5.08; N, 17.64. Found: C, 50.45; H, 5.10; N, 17.60.

Registry No.—**2**, 33224-25-8; **3a**, 33224-26-9; **4**, 33303-95-6; **5**, 33224-27-0; **11**, 33224-28-1; **12** picrate, 33224-29-2; **15a**, 33224-30-5; **15b**, 33224-31-6; **16a**, 33224-32-7; **16b**, 33264-04-9; **18**, 33224-33-8; **19**, 33224-34-9; **22**, 33303-96-7; **23**, 33224-35-0; **24**, 33224-36-1; **25**, 33224-37-2; cyclooctatetraene, 629-20-9; 1-ethoxycarbonyl-1(1*H*)-azepine, 2955-79-5; tropone ethylene ketal, 17637-62-6; cycloocta-1,3-diene (*Z*,*Z*), 3806-59-5; cycloocta-1,5-diene (*Z*,*Z*), 1552-12-1; iodine azide, 14696-82-3.