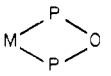
dominant exchange mechanism between the molybdenum and tungsten complexes. Pairwise exchange as observed for the tungsten complex is consistent with previously proposed idealized pathways based on the interconversion of pentagonal-bipyramidal, capped octahedral, and capped trigonal prismatic geometries.[43,44]

The Chelate $(CH_3O)_2POP(OCH_3)_2$ Ligand. To our knowledge, tetramethyl diphosphite has never been described in the literature either as the free molecule or as a ligand in a transition-metal complex although the closely related diphosphite $(C_2H_5O)_2PO-P(OC_2H_5)_2$ has been prepared and utilized to prepare transition-metal complexes in which the diphosphite serves as a bridging ligand between two metal atoms.[45-47] All the $(CH_3O)_2POP(OCH_3)_2$ derivatives of molybdenum, tungsten, and rhenium described in this article have been colored—brown for the first two metals and purple for $HRe[P(OCH_3)_3]_3[(CH_3O)_2POP(OCH_3)_2]$—whereas the strict "per" trimethyl phosphite analogues were colorless. Apparently, the presence of the four-membered cycle introduces electronic or steric features whereby electronically excited states are readily accessible by thermal activation.[48]



We presently seek a direct synthesis of the diphosphite to enable a more detailed study of the chelate chemistry.

Acknowledgment. This research was generously supported by the National Science Foundation. A sample of ammonium perrhenate was kindly provided by Dr. M. Lindner of the Lawrence Berkeley Laboratory. Analyses were performed by Mr. V. Tashinian of the U.C.B. Chemistry Department Microanalytical Laboratory and the mass spectrometric analyses performed by Ms. Sherry Ogden of the U.C.B. Mass Spectrometric Laboratory. E.L.M. is indebted to the Miller Institute for Basic Research in Science for a grant in the form of a Miller Professorship.

Registry No. $Mo[P(OCH_3)_3]_6$, 37478-27-6; $W[P(OCH_3)_3]_6$, 73411-63-9; $H_2Mo[P(OCH_3)_3]_5$, 79815-40-0; $H_4Mo[P(OCH_3)_3]_4$, 79803-06-8; $H_2W[P(OCH_3)_3]_5$, 73411-64-0; $H_4W[P(OCH_3)_3]_4$, 73460-89-6; $Mo[P(OCH_3)_3]_5(CO)$, 37478-26-5; $W[P(OCH_3)_3]_5(CO)$, 37478-28-7; *trans*-$Mo[P(OCH_3)_3]_4(CO)_2$, 79854-39-0; *trans*-$W[P(OCH_3)_3]_4(CO)_2$, 79854-40-3; *mer*-$Mo[P(OCH_3)_3]_3(CO)_3$, 15631-23-9; $Mo[P(OCH_3)_3]_4[(CH_3O)_2POP(OCH_3)_2]$, 79803-07-9; $W[P(OCH_3)_3]_4[(CH_3O)_2POP(OCH_3)_2]$, 79803-08-0; $Mo[P(OCH_3)_3]_5(NO)^+$, 79803-09-1; $Mo[P(OCH_3)_3]_3(NO)_2$, 79803-10-4; $\{W[P(OCH_3)_3]_5[P(OCH_3)_2]^+\}(CF_3COO^-)$, 79803-12-6; $HW[P(OCH_3)_3]_4(O_2CCF_3)$, 79815-39-7; $HW[P(OCH_3)_3]_6^+$, 79803-13-7; $H_2W[P(OCH_3)_3]_3[(CH_3O)_2POP(OCH_3)_2]$, 79803-14-8; $Re_2[(P(OCH_3)_3]_{10}$, 76281-32-8; $HRe[P(OCH_3)_3]_5$, 76428-28-9; $Re[P(OCH_3)_3]_5[P(O)(OCH_3)_2]$, 79815-41-1; $HRe[P(OCH_3)_3]_3[(CH_3O)_2POP(OCH_3)_2]$, 79803-15-9; $H_3Re[P(OCH_3)_3]_4$, 79803-16-0; $H_2Re[P(OCH_3)_3]_5^+$, 79803-17-1; $H_2Re[P(OCH_3)_3]_3(O_2CCF_3)$, 79803-18-2; *trans*-$HRe[P(OCH_3)_3]_4(CO)$, 79803-19-3; $MoCl_5$, 10241-05-1; WCl_6, 13283-01-7; $ReCl_5$, 13596-35-5; $MoOCl_3(NC_5H_5)_3$, 79803-20-6; $MoCl_4(OC_4H_8)_2$, 16998-75-7; $WOCl_3(NC_5H_5)_3$, 79803-21-7; $ReCl_4(NC_5H_5)_4$, 79803-22-8; $ReOCl_3(NC_5H_5)_2$, 18195-83-0; CF_3COOH, 76-05-1.

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(44) As discussed in ref 41, the geometry of the molybdenum complex can be considered as a hydride (equatorial) edge capped trigonal bipyramid if the trifluoroacetic ligand is treated as a unidentate ligand. In this structural approximation of a trigonal-bipyramidal pseudo-five-coordinate species with axial and equatorial sets of phosphorus ligands, the expected polytopal rearrangement involving a square-pyramidal intermediate or transition state would also be a pairwise exchange process.

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(48) A related diphosphite, $H_2P_2O_5^{2-}$, spans two closely set platinum atoms in $[K_4Pt_2H_8P_8O_{20}]\cdot 2H_2O$, a complex which is purple and intensely luminescent. The Pt–Pt interaction was proposed as the origin of the luminescence. Pinto, M. A. F. D. R.; Sadler, D. J.; Neidle, S.; Sanderson, M. R.; Subbiah, A.; Kuroda, R. *J. Chem. Soc., Chem. Commun.* **1980**, 13.

Reaction of Bicyclo[3.2.1]octa-2,6-diene with 1,2,4-Triazoline-3,5-diones: Competitive Dipolar and Homocycloaddition

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Abstract: The nonconjugated bicyclo[3.2.1]octa-2,6-diene (1) affords with 1,2,4-triazolin-3,5-diones the homocycloadducts **6**. An X-ray structure determination confirms cyclopropane formation as the preferred mode of homoreactivity. Dipolar cycloaddition takes place both at the C_2–C_3 and the C_6–C_7 sites, leading to the rearranged urazoles **7** and **8** (major product), respectively. As expected, attack at the more strained double bond (C_6–C_7 attack) predominates. Ene reactions and [2 + 2] cycloadditions are not observed. The urazoles **6–8** have been converted to their respective azoalkanes **10–12** via oxidative hydrolysis.

Bicyclo[3.2.1]octa-2,6-diene (**1**) should be an interesting and useful substrate for exploring competitive cycloaddition behavior in view of its great diversity in possible reaction modes with dienophiles. Although [2 + 4] cycloaddition is not possible since **1** is a nonconjugated diene, it could undergo [2 + 2], ene, homo, and dipolar reactions with suitable dienophiles (Figure 1). When triazolinediones (TAD) are used as dienophiles, these various cycloaddition modes would afford a maximum of nine products, i.e., urazoles **2–9**. For example, [2 + 2] cycloadditions[1] at the

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(1) (a) Seymour, C. A.; Greene, F. D. *J. Am. Chem. Soc.* **1980**, *102*, 6384. (b) Adam, W.; De Lucchi, O. *Tetrahedron Lett.* **1981**, *22*, 929.

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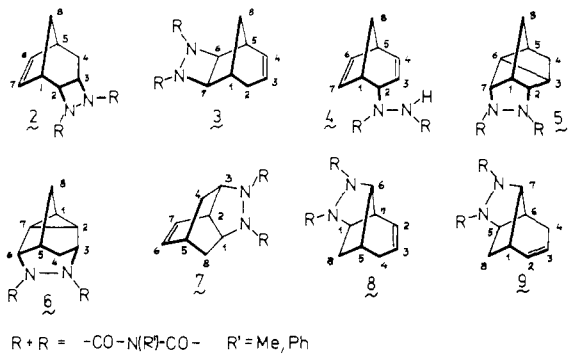


C_2–C_3 and C_6–C_7 double bonds would lead to the urazoles **2** and **3**, respectively, while ene reaction[1a,2] at C_4 would afford **4**. The two possible homocycloaddition modes[3] at the C_2–C_7 and C_3–C_6 sites would produce the urazoles **5** and **6**, respectively. On the other hand, dipolar cycloaddition[4] at the less strained C_2–C_3 double bond would give urazole **7**, resulting from attack at the C_3 position, while dipolar cycloaddition at the C_6 and C_7 positions of the more strained C_6–C_7 double bond would afford the urazoles **8** and **9**, respectively. Clearly, bicycloalkadiene **1** constitutes a choice substrate to assess its selectivity among these diverse cycloaddition modes. Consequently, it provides an excellent opportunity for probing the competitiveness of the various cycloaddition reactions. Such intramolecular competition studies appear not to have been reported for **1** and consequently we have investigated its cycloaddition behavior toward methyl- and phenyl-1,2,4-triazoline-3,5-diones, respectively MTAD and PTAD.

Results

Diene **1** is unreactive toward maleic anhydride and even singlet oxygen, while tetracyanoethylene leads to an intractable product mixture. However, on treatment with MTAD in CH_2Cl_2 at 25 °C for 48 h the diene **1** gave the urazoles **6–8** (R = Me) in 31, 11, and 37% yields, respectively. These were separated by means of silica gel chromatography using CH_2Cl_2 as eluant and purified by recrystallization (satisfactory elemental analyses). The ^1H and ^{13}C NMR and IR spectral data are summarized in Table I. Similarly, PTAD gave also the urazoles **6–8** (R = Ph) in 39, 11, and 33% yields, respectively.

Support in favor for the structure of urazole **6** rather than **5** as the homocycloaddition product was provided by the ^{13}C–H coupling constant, which is ca. 170 Hz. While this large coupling constant clearly implicates a cyclopropane rather than a cyclobutane ring, an unequivocal structure assignment was secured by means of X-ray analysis (Figure 2). Not even traces of urazole **5** with either MTAD or PTAD were produced, showing that cyclopropane formation to give urazole **6** is preferred over cyclobutane formation.

In regard to the structure elucidation of the rearranged urazoles **7** and **8**, produced by dipolar cycloaddition of MTAD or PTAD, the assignment of **7** (R = Me) was straightforward in view of its high degree of symmetry. The ^1H and ^{13}C NMR data (Table I) can only be reconciled in terms of structure **7** (R = Me). For example, the ^1H NMR spectrum of urazole **7** contains two symmetric multiplets at 6.00 and 6.60 ppm attributed to the two different olefinic protons H_7 and H_6, respectively. Each multiplet exhibits the mutual coupling between H_6 and H_7 ($J_{6,7}$ = 8.4 Hz) and with the adjacent ($J_{5,6}$ = 6.6 Hz; $J_{2,7}$ = 6.6 Hz) and the remote ($J_{2,6}$ = 1.5 Hz; $J_{5,7}$ = 1.5 Hz) bridgehead protons. Fortunately, the chemical shifts of the two bridgehead protons are sufficiently far apart, i.e., 3.10 and 2.72 ppm, respectively, to allow separate

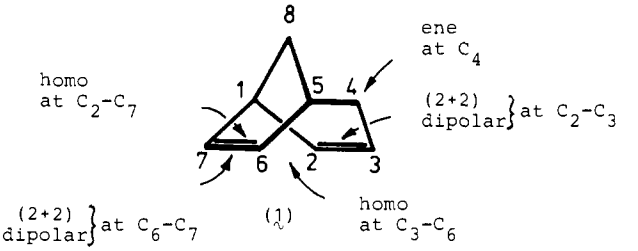


Figure 1. Possible cycloaddition modes of bicyclo[3.2.1]octa-2,6-diene (**1**) with TAD.

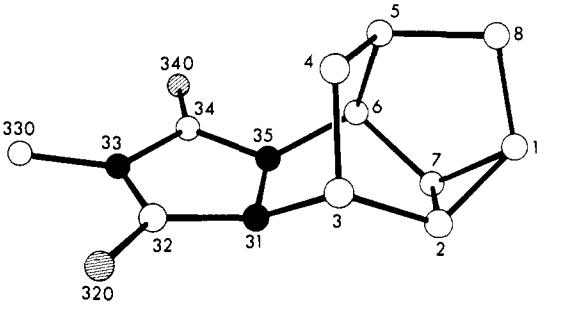
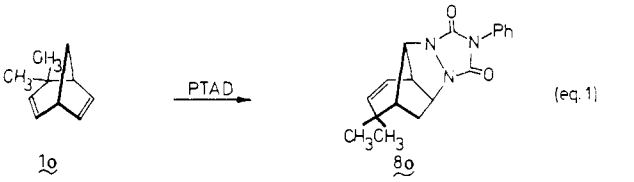


Figure 2. Perspective drawing of the urazole **6** with the labeling of the atoms corresponding to Tables III and IV. White, black, and hatched rings represent carbon, nitrogen, and oxygen atoms, respectively.

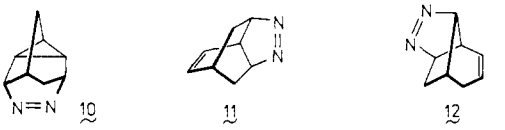
decoupling experiments on each. Thus irradiation of bridgehead proton H_2 at 3.10 ppm collapses the quartet of $H_{1,3}$ at 4.18 ppm into a triplet and the multiplets of H_6 and H_7 into a doublet of doublets and a doublet, respectively. Irradiation of the bridgehead proton H_5 at 2.72 ppm has a similar effect on the olefinic protons H_6 and H_7, does not affect the $H_{1,3}$ protons, but simplifies the multiplets for the $H_{4,8}$ protons. The ^{13}C NMR spectrum exhibits the expected six resonances for the symmetric bicyclic [2.2.2] skeleton.

An unequivocal assignment of the double-bond position in urazole **8** (R = Ph) was difficult on the basis of its spectral data (Table I). For this purpose we prepared urazole **8a** via the reaction of 4,4-dimethylbicyclo[3.2.1]octa-2,6-diene (**1a**) with PTAD (eq 1). Thus, the *gem*-dimethyl substitution simplified the ^1H NMR



spectrum sufficiently, so that at high field (400 MHz) analysis the double bond in **8a** and thus in **7a** could be placed with certainity.[5]

As chemical structure proof, the urazoles **6–8** were transformed into their azoalkanes **10–12**, respectively, via oxidative hydrolysis.[6]



Their spectral data are collected in Table II. While the azoalkanes **11** and **12** were stable compounds, azoalkane **10** lost nitrogen at 30 °C with a half-life of ca. 30 min, yielding diene **1** quantitatively. On photolysis of azoalkane **12** at 350 nm the known[7] tricyclo[3.2.1.$0^{7,8}$]oct-2-ene was obtained as major product,

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(4) Adam, W.; De Lucchi, O.; Erden, I. *J. Am. Chem. Soc.* **1980**, *102*, 4806.
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Table I. Spectral Data for Urazoles 6-8

urazole[a]	type	no. of H's	^{1}H NMR ($CDCl_3$, Me_4Si) δ[b]	pattern	J, Hz	^{13}C NMR ($CDCl_3$, Me_4Si), δ (multiplicity)	IR (KBr) ν cm^{-1}
6	$H_{1,2,4,7,8}$	7	1.30-2.20 (1.73-2.17)	m		155.80 (s, CO), 154.12 (s, CO), 57.89 (d), 50.09 (d), 33.78 (t), 33.59 (t), 31.12 (d), 25.18 (q), 19.57 (d), 16.73 (d), 16.50 (d)	3075, 3000, 2980, 2960, 2900, 1770, 1465, 1400, 1350, 1300, 1270, 1215, 1180, 1125, 1080, 1020, 1000, 940, 930, 870, 830, 790, 760, 720
	H_5	1	2.45 (2.52)	q	6		
	CHN	1	4.60 (4.68)	m			
	CHN	1	4.77 (4.85)	dd	3.6, 6		
	CH_3 (Ph)	3 (5)	3.10 (7.43)	s (m)			
7	$H_{4,8}$	4	1.70 (1.80)	m		156.71 (s, CO), 148.73 (d), 123.74 (d), 54.54 (d), 42.20 (d), 33.65 (d), 27.35 (t), 25.53 (q)	3035, 2970, 2940, 2860, 1765, 1700, 1450, 1400, 1360, 1220, 1100, 1070, 1010, 940, 910, 860, 810, 760, 700, 600
	H_5	1	2.72 (2.77)	br s			
	H_2	1	3.10 (3.20)	m	$J_{1,2} = 9.3$		
	$H_{1,3}$	2	4.18 (4.28)	q	$J_{1(3),4(8)} = 4.8$		
	H_7	1	6.00 (6.03)	m	$J_{6,7} = 8.4$, $J_{2,7} = 6.6$		
	H_6	1	6.60 (6.62)	m	$J_{2,6} = J_{5,7} = 1.5$, $J_{5,6} = 6.6$		
	CH_3 (Ph)	3 (5)	3.06 (7.50)	s (m)			
8	$H_{4,8}$	4	1.73-2.70 (1.78-2.53)	m		158.63 (s, CO), 158.34 (s, CO), 128.16 (d), 123.35 (d), 66.11 (d), 62.34 (d), 45.48 (d), 35.38 (t), 34.47 (d), 33.04 (t), 25.57 (q)	3040, 2945, 2900, 2840, 1765, 1700, 1450, 1390, 1360, 1260, 1200, 1150, 1085, 1050, 1030, 1020, 990, 770, 750, 690, 620
	$H_{7,5}$	2	2.68 (2.67)	br s			
	CHN	1	4.18 (4.28)	s			
	CHN	1	4.58 (4.70)	br s			
	$H_{2,3}$	2	5.68 (5.68)	m			
	CH_3 (Ph)	3 (5)	3.05 (7.47)	s (m)			

[a] Numbering is that of bicyclo[3.2.1]octa-2,6-diene (1). [b] Chemical shifts in parentheses are for PTAD (R = Ph); the others are for MTAD (R = Me).

Table II. Spectral Data for Azoalkanes 10-12

azoalkane[a]	type	no. of H's	^{1}H NMR (CCl_4, Me_4Si) δ	pattern	J, Hz	^{13}C NMR ($CDCl_3$, Me_4Si), (multiplicity)	IR (CCl_4) ν, cm^{-1}
10	$H_{1,2,4,5,7,8}$	8	0.38-2.20	m		13.47 (d), 20.54 (d), 23.63 (d), 25.62 (d), 30.92 (t), 34.68 (t), 63.17 (d), 68.69 (d)	
	CHN	1	5.37	m			
	CHN	1	5.55	m			
11	$H_{4,8}$	4	0.70-1.50	m		139.40 (d), 125.74 (d), 77.10 (d), 40.90 (d), 33.62 (d), 26.82 (t)	3060, 2980, 2950, 2860, 1530, 1450, 1440, 1370, 1320, 1250, 990, 860, 830, 695
	H_5	1	2.67	br s	$J_{5,7} = 1.5$		
	H_2	1	2.90	dd	$J = 10.8$, 5.4		
	$H_{1,3}$	2	4.37	dd	$J = 8.1$, 5.2		
	H_7	1	6.12	m	$J_{6,7} = 7.8$, $J_{2,7} = 6.6$		
	H_6	1	6.54	m	$J_{5,6} = 6.6$, $J_{2,6} = 1.2$		
12	H_8-exo	1	0.92	A part of AB system	$J_{AB} = 12$	127.33 (d), 125.20 (d), 82.82 (d), 79.04 (d), 48.58 (d), 33.91 (t), 28.39 (d), 26.77 (t)	3050, 3010, 2960, 2910, 2850, 1700, 1450, 1285, 1250, 865, 690
	H_8-endo	1	1.27	B part of AB system			
	H_1 or H_5	1	1.77	br s			
	H_1 or H_5	1	1.92	br s			
	H_4-exo	1	2.13	A part of AB system	$J_{AB} = 18$		
	H_4-endo	1	2.47	B part of AB system			
	CHN	1	4.60	br s			
	CHN	1	4.97	br s			
	$H_{2,3}$	2	5.62	m			

[a] Numbering is that of the bicyclo[3.2.1]octa-2,6-diene (1).

whose identity was established by comparison of capillary GC retention times with those of authentic material. This provides additional chemical proof of the location of the double bond in azoalkane **12** and urazole **8**.

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Discussion

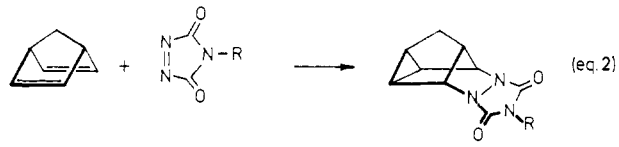
Of the four distinct cycloaddition modes that are possible, i.e., ene, [2 + 2], homo and dipolar reactions, the bicycloalkadiene **1** exhibits the latter two only. The homocycloaddition (minor path) leads exclusively to the cyclopropane product **6**, while dipolar rearrangement (major path) occurs predominantly at the C_6-C_7

double bond with exclusive attack on the C_6 position to give the rearranged urazole **8**. Attack at the C_7 position apparently does not take place, since urazole **9** is not observed.

The lack of ene reactivity of diene **1** toward TAD is at first glance surprising since such reactions are abundantly documented.[8] Previously we observed[9] that the 6,7-dibenzo derivative of **1** also does not give an ene reaction with PTAD. It was recently demonstrated[1a] that the mechanism of the ene reaction of PTAD resembles that of singlet oxygen; i.e., an axial allylic hydrogen must be available.[10] Inspection of Dreiding models of diene **1** reveals that the allylic hydrogens at C_4 are not well aligned for an ene reaction. Consequently, alternative cycloaddition modes between bicycloalkadiene **1** and TAD are preferred.

The fact that the [2 + 2] cycloadducts **2** and **3** are not formed in the reaction of **1** with TAD suggests that this forbidden cycloaddition mode requires higher activation energies and is, therefore, not competitive. When other cycloaddition modes are prevented, e.g. as in adamantylideneadamantane[1a] and dibenzobarrelene,[1b] and only under more drastic conditions, then the [2 + 2] reaction does take place. Thus, for diene **1** homocycloadditions and dipolar cycloadditions suppress effectively the [2 + 2] mode.

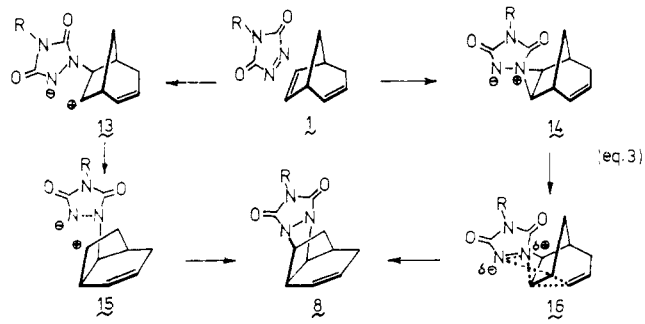
As to the homocycloaddition mode, the preference for cyclopropane (urazole **6**) vs. cyclobutane (urazole **5**) formation is not surprising; no examples of the latter appear to be documented.[6] Although Dreiding models suggest that the approach by TAD onto the C_2–C_7 site is sterically less encumbered than onto the C_3–C_6 site, the better overlap between the 2p orbitals at the C_2 and C_7 positions for cyclopropane formation seems to require C_3–C_6 attack by TAD. For example, in norbornadiene the geometry is so optimal for homocycloaddition that it is the exclusive route and no dipolar rearrangement is observed (eq 2).[3] The additional



(eq 2)

methylene unit in bicycloalkadiene **1** distorts the geometry of the diene moiety sufficiently to diminish homocycloaddition, so that dipolar rearrangement is the preferred reaction path.

Of the two dipolar cycloaddition alternatives, i.e., attack at the C_2–C_3 vs. attack at C_6–C_7 double bonds, clearly the more strained one predominates, so that the rearranged urazole **8** is the major product of the reaction of bicycloalkadiene **1** with TAD. Whether to formulate the initial TAD attack in the form of a two-center process[4] leading to the open dipolar intermediate **13** or in terms of the three-center process[1a] affording the closed dipolar intermediate **14** (eq 3) is mechanistic conjecture at this time. Both



(eq 3)

routes, i.e., via **13** and **15** vs. via **14** and **16**, will lead to the rearranged product **8**; however, the first route might procede stepwise via the rearranged open dipole **15**, while the second route might take place concertedly via the activated complex **16**. Of course, the closed dipole **14**, presumably formed in the rate-determining step,[1a] could open up into dipole **13**, which then rearranges via **15** into urazole **8**. Mechanistic experiments are in progress to elucidate the nature of the initial dipolar attack by TAD in such rearrangements.

Irrespective of the mechanism, the attack of the TAD dienophile must take place from the exo face of the C_6–C_7 double bond, as was confirmed for benzobicyclo[2.2.2]octa-2,6-diene.[4] Therefore, the migrating σ bond, i.e., the C_1–C_2 single bond, lies on the opposite side of the incoming dienophile. Consequently, the possibility of transposing **13** or **14** into the homocycloadduct **6** is impossible because bond formation between C_3 and the negatively charged nitrogen is for geometrical reasons prevented.

This strongly implies that the homocycloadditions and dipolar cycloadditions are mechanistically distinct events and not connected via a common intermediate, i.e., neither **13** nor **14**. The product distribution between the homocycloadducts and dipolar cycloadducts reflects, therefore, the selectivity of the bicycloalkadiene **1** toward these two cycloaddition modes. As already stated, the distorted geometry of the dienic system disfavors homocycloaddition but does not affect significantly the dipolar process, so that the latter can compete effectively.

In conclusion, dienic substrates like bicyclo[3.2.1]octa-2,6-diene (**1**), which are potentially capable of reacting via several cycloaddition modes, provide an excellent opportunity to assess their selectivity among ene, [2 + 2], homo, and dipolar reactions. From the product distributions of such intramolecular competition studies we expect to gain valuable mechanistic information on cycloaddition behavior. Relatively little work along these lines appears to be available as yet to recognize general reactivity patterns.

Experimental Section

Melting points were taken on a Reichert Thermovar Kofler apparatus. Melting points and boiling points are uncorrected. Infrared spectra were measured on a Beckman Acculab 4 or on a Perkin-Elmer 157G spectrophotometer and ^{1}H NMR spectra on Varian T-60 or Hitachi Perkin-Elmer R-24B instruments. Low-temperature ^{1}H NMR spectra were performed on a 90-MHz Bruker HFX 10 spectrometer. ^{13}C NMR spectra were kindly run for us by Dr. D. Scheutzow on a Bruker 4.22T at 45.28 MHz or on a Bruker WH-90 at 23.6 MHz. Combustion analyses for elemental composition were run in house and were within accepted limits, i.e., ±0.3%. Commercial reagents and solvents were purified to match reported physical and spectral data. Known compounds used in this research were either purchased from standard chemical suppliers or prepared according to literature procedures and purified to match the reported physical and spectral data.

Reaction of Bicyclo[3.2.1]octa-2,6-diene (1) with 4-Methyl-1,2,4-triazoline-3,5-dione (MTAD). A sample of 3.0 g (28.2 mmol) of bicyclo[3.2.1]octa-2,6-diene (**1**) was dissolved in ca. 70 mL of CH_2Cl_2 and placed into a 250-mL, round-bottomed flask. MTAD (3.5 g, 31 mmol) was added in one portion. The solution was stirred magnetically at room temperature while being protected from light until the red color of the MTAD had completely faded (ca. 36–48 h); a light yellow solution resulted. The solution was concentrated by rotary evaporation [25 °C (15 torr)] and chromatographed on a short (ca. 10:1 adsorbant: substrate) silica gel (70–230 mesh) column, with CH_2Cl_2 elution, to remove polymeric material. The eluate, 4.9 g (79% yield), consisted of a mixture of the urazoles **6**, **7**, **8** in a relative ratio of 4:1:5 (by ^{1}H NMR). Careful chromatography on 70–230 mesh silica gel (ca. 40:1 weight ratio of adsorbant to substrate), with CH_2Cl_2 elution, afforded 1.2 g (19% yield) of the rearranged urazole (**8**) as first product, mp 90–91 °C (needles from ether); satisfactory elemental composition by combustion analysis was obtained. As second product, 250 mg (4% yield) was eluted the rearranged urazole (**7**), mp 143–144 °C (needles from ether); satisfactory elemental composition on combustion analysis was obtained. As last product, 890 mg (14% yield), the Diels–Alder homoadduct (**6**) was eluted, mp 156.5–157 °C (prisms from EtOH); satisfactory elemental composition by combustion analysis was obtained.

Reaction of Bicyclo[3.2.1]octa-2,6-diene (1) with 4-Phenyl-1,2,4-triazoline-3,5-dione (PTAD). The cycloaddition with PTAD was conducted identically as described for MTAD. The three urazoles eluted in the same order, i.e., urazole **8** (33% yield), mp 168–170 °C (needles from EtOH), urazole **7** (11% yield), mp 217–218 °C (needles from EtOH), and urazole **6** (39% yield), mp 187–188 °C (prisms from EtOH). Satisfactory elemental composition by combustion analysis was obtained for the three urazoles.

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Table III. Positional and Thermal Parameters of the Atoms of Urazole 6 ($Å^2$)[a]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	0.0148 (4)	0.3547 (2)	−0.0839 (4)	0.045 (1)	0.047 (1)	0.045 (1)	0.017 (1)	0.004 (1)	0.014 (1)
C(2)	−0.0014 (3)	0.2541 (2)	0.0075 (4)	0.032 (1)	0.043 (1)	0.049 (1)	0.017 (1)	0.007 (1)	0.003 (1)
C(3)	0.1418 (3)	0.1691 (2)	−0.0354 (4)	0.034 (1)	0.032 (1)	0.038 (1)	0.010 (1)	0.000 (1)	−0.001 (1)
C(4)	0.2976 (4)	0.2013 (2)	−0.1757 (4)	0.051 (1)	0.042 (1)	0.038 (1)	0.010 (1)	0.013 (1)	0.011 (1)
C(5)	0.3536 (4)	0.3333 (2)	−0.0940 (4)	0.040 (1)	0.045 (1)	0.048 (1)	0.020 (1)	0.016 (1)	0.004 (1)
C(6)	0.3282 (3)	0.3770 (2)	0.1587 (4)	0.037 (1)	0.029 (1)	0.043 (1)	0.011 (1)	0.003 (1)	0.003 (1)
C(7)	0.1020 (4)	0.3726 (2)	0.1513 (4)	0.040 (1)	0.040 (1)	0.040 (1)	0.009 (1)	0.006 (1)	0.013 (1)
C(8)	0.1869 (4)	0.3759 (2)	−0.2091 (4)	0.053 (2)	0.054 (2)	0.049 (1)	0.026 (1)	0.008 (1)	0.008 (1)
N(31)	0.2545 (3)	0.1845 (2)	0.1888 (3)	0.035 (1)	0.032 (1)	0.040 (1)	0.013 (1)	0.002 (1)	−0.001 (1)
C(32)	0.3719 (3)	0.1070 (2)	0.2213 (4)	0.041 (1)	0.036 (1)	0.036 (1)	0.016 (1)	0.005 (1)	0.001 (1)
N(33)	0.5529 (3)	0.1725 (2)	0.3427 (3)	0.038 (1)	0.034 (1)	0.038 (1)	0.014 (1)	0.001 (1)	0.005 (1)
C(34)	0.5657 (3)	0.2883 (2)	0.3619 (4)	0.037 (1)	0.034 (1)	0.031 (1)	0.007 (1)	0.006 (1)	0.006 (1)
N(35)	0.3799 (3)	0.2967 (2)	0.2753 (3)	0.034 (1)	0.029 (1)	0.040 (1)	0.009 (1)	0.000 (1)	0.001 (1)
O(320)	0.3212 (3)	0.0028 (1)	0.1619 (3)	0.055 (1)	0.035 (1)	0.064 (1)	0.023 (1)	−0.005 (1)	−0.005 (1)
C(330)	0.7169 (4)	0.1256 (2)	0.4231 (5)	0.052 (2)	0.045 (1)	0.055 (2)	0.018 (1)	−0.007 (1)	0.012 (1)
O(340)	0.7101 (3)	0.3660 (1)	0.4472 (3)	0.039 (1)	0.039 (1)	0.059 (1)	0.008 (1)	−0.006 (1)	−0.001 (1)

[a] The form of the thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots 2U_{12}hka^*b^* + \ldots)]$.

Table IV. Bond Lengths (pm) and Angles (deg) for the Urazole 6

Bond Lengths

C(1)-C(2)	152.0 (4)	C(3)-C(4)	152.4 (3)	C(6)-C(7)	152.4 (3)	N(33)-C(330)	145.3 (4)
C(1)-C(7)	148.6 (4)	C(3)-N(31)	149.1 (3)	C(6)-N(35)	147.0 (3)	C(34)-N(33)	139.4 (3)
C(1)-C(8)	150.4 (4)	C(4)-C(5)	153.5 (3)	C(32)-N(31)	138.8 (3)	C(34)-N(35)	136.0 (3)
C(2)-C(3)	152.4 (3)	C(5)-C(6)	156.0 (3)	C(32)-N(33)	138.0 (3)	C(34)-O(340)	121.7 (2)
C(2)-C(7)	149.7 (3)	C(5)-C(8)	153.5 (4)	C(32)-O(320)	121.6 (3)	N(35)-N(31)	143.3 (2)

Angles

C(2)-C(1)-C(7)	59.7 (2)	C(5)-C(6)-C(7)	103.3 (2)	C(3)-N(31)-C(32)	121.7 (2)
C(2)-C(1)-C(8)	118.2 (2)	C(5)-C(6)-N(35)	111.5 (2)	C(3)-N(31)-N(35)	109.9 (2)
C(7)-C(1)-C(8)	107.5 (2)	C(7)-C(6)-N(35)	106.8 (2)	C(32)-N(31)-N(35)	106.9 (2)
C(1)-C(2)-C(3)	122.6 (2)	C(1)-C(7)-C(2)	61.3 (2)	C(32)-N(33)-C(34)	111.5 (2)
C(1)-C(2)-C(7)	59.0 (2)	C(1)-C(7)-C(6)	107.8 (2)	C(32)-N(33)-C(330)	124.3 (2)
C(3)-C(2)-C(7)	112.6 (2)	C(2)-C(7)-C(6)	107.4 (2)	C(34)-N(33)-C(330)	124.0 (2)
C(2)-C(3)-C(4)	110.6 (2)	C(1)-C(8)-C(5)	101.9 (2)	C(6)-N(35)-N(31)	113.8 (2)
C(2)-C(3)-N(31)	105.6 (2)	N(31)-C(32)-N(33)	106.1 (2)	C(6)-N(35)-C(34)	128.0 (2)
C(4)-C(3)-N(31)	106.5 (2)	N(31)-C(32)-O(320)	126.5 (2)	N(31)-N(35)-C(34)	109.6 (2)
C(3)-C(4)-C(5)	106.5 (2)	N(33)-C(32)-O(320)	127.3 (2)		
C(4)-C(5)-C(6)	108.0 (2)	N(33)-C(34)-N(35)	105.4 (2)		
C(4)-C(5)-C(8)	106.5 (2)	N(33)-C(34)-O(340)	127.1 (2)		
C(6)-C(5)-C(8)	103.3 (2)	N(35)-C(34)-O(340)	127.5 (2)		

Preparation of 4,5-Diazatetracyclo[4.2.1^{3,7}.0^{2,9}]dec-2-ene (10). The same procedure as described for azoalkane **12** was employed in this case for the preparation of the copper complex. The destruction of the copper complex and the isolation of the azoalkane had to be carried out at subambient temperature due to the thermal lability of the azoalkane. For example, the red complex was destroyed with ice-cold 2 N ammonium hydroxide and extracted with cold CH_2Cl_2 (3 × 30 mL), washed with ice–water, and dried over anhydrous Na_2SO_4. Filtration and rotary evaporation [0 °C (14 torr)] of the solvent afforded 128 mg (82% yield) of white solid, which denitrogenated already at ca. 30 °C with a half-life of ca. 30 min, affording quantitatively bicyclo[3.2.1]octa-2,6-diene (**1**), as confirmed by comparison of ^{1}H NMR and GC spectra with those of an authentic sample.

Preparation of 2,3-Diazatricyclo[4.3.1.0^{4,9}]deca-2,7-diene (11). The same procedure as described for azoalkane **12** was used, affording 51% yield of pure azoalkane **11** as waxy solid, mp 84 °C, after sublimation [65 °C (15 torr)]; satisfactory elemental composition by combustion analysis was obtained.

Preparation of 9,10-Diazatricyclo[4.4.0.0^{2,8}]deca-3,9-diene (12). The sample of 560 mg (2.55 mmol) of rearranged urazole **8** was dissolved in 5 mL of reagent grade methanol, and ca. 700 mg of KOH was added in one portion to the stirred solution and refluxed overnight. The reaction mixture turned yellow at reflux and soon began to thicken due to precipitation of a white solid, indicating that saponification was taking place. The yellow supernatant liquid was then decanted from the salt and thoroughly triturated with 3 × 2 mL portions of MeOH. The alcohol was removed from the combined triturates by rotary evaporation [ca. 50 °C (14 torr)] and the residual oil was treated with water (ca. 5 mL) and carefully neutralized with 2 N HCl. More water (ca. 30 mL) was added, the aqueous mixture was extracted with 3 × 40 mL of CH_2Cl_2, and the solvent was rotary evaporated [25 °C (15 torr)] and treated with a solution of 600 mg of $CuCl_2 \cdot 2H_2O$ in 3 mL of water. After stirring for 1 h, the red copper complex was collected by filtration. To the filtrate more $CuCl_2 \cdot 2H_2O$ was added, the pH adjusted to pH 4–5, and the additional precipitate was gathered and combined with the first portion of copper complex. The combined precipitates were washed with water, treated with 2 N NH_4OH to solubilize the copper, extracted with 3 × 30 mL of CH_2Cl_2, washed with 3 × 30 mL of water, dried over anhydrous Na_2SO_4, and rotary evaporated [20 °C (14 torr)] to give the crude azoalkane **12** as a colorless oil. Purification was achieved by sublimation [60–80 °C (14 torr)], affording 193 mg (56% yield) of pure **12** as waxy solid, mp 40–42 °C; satisfactory elemental composition by combustion analysis was obtained. Photolysis of 10 mg (0.07 mmol) of azoalkane **12** in pentane at 350 nm in a Rayonet photoreactor afforded as main product (80% yield) tricyclo[3.2.1.0^{7,8}]oct-2-ene. The identity of this tricyclooctene was established by comparison of GC retention times with those of the authentic material on a 50-m OV-101 capillary glass column, operated at a column temperature of 70 °C and a carrier gas flow of 2 mL/min.

X-ray Crystallography of Urazole 6. A clear colorless crystal of dimensions 0.4 × 0.4 × 0.15 mm was optically centered on a SYNTEX $P\bar{1}$ four-circle diffractometer. The orientation matrix and the cell parameters were determined on the basis of 15 reflections. The intensities of 2352 *hkl* reflections were measured according to the ω method (Mo Kα, graphite monochromator) using a scan range of 1° and a scan speed between 0.5 and 24.0° min^{-1} as a function of the intensities of the reflections. In the range between $3.0° \leq 2\theta \leq 55.0°$, 1966 reflections were obtained which were applied for the structure determination. For the evaluation the SHELXTL System on an Eclipse S250 at the Max-Planck-Institut für Festkörperforschung was employed. The structure was solved by direct phase determination. The phases of 45 strong reflections were determined, and on the resulting *E* map approximate positions of all C, N, O atoms could easily be determined. Positional and thermal parameters could be refined by anisotropic least-squares cycles to $R = 0.057$. The positions of the hydrogen atoms were calculated geometrically and considered isotropically in all refinements. We have omitted the presentation of the structure factors, which can be obtained upon request.

Urazole **6** crystallizes triclinically in the space group $P\bar{1}$ with a = 679.1 (4) pm, b = 1241.1 (8) pm, c = 632.0 (4) pm, α = 107.53 (5)°, β = 95.30 (5)°, and γ = 98.82 (5)°. The unit cell contains Z = 2 formula units; the density was calculated to be 1.466 mg m^{-3}. All atomic parameters are listed in Table III. The labeling of the atoms can be seen in Figure 2. Bond distances and bond angles are summarized in Table IV.

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Registry No. 1, 4096-95-1; **6** (R′ = Me), 79769-95-2; **6** (R′ = Ph), 79769-96-3; **7** (R′ = Me), 79769-97-4; **7** (R′ = Ph), 79769-98-5; **8** (R′ = Me), 79769-99-6; **8** (R′ = Ph), 79770-00-6; **10**, 79770-01-7; **11**, 79770-02-8; **12**, 79770-03-9; MTAD, 13274-43-6; PTAD, 4233-33-4; tricyclo[3.2.1.0^{7,8}]oct-2-ene, 15128-95-7.

Asymmetric Synthesis of (*S*)- and (*R*)-Malic Acid from Ketene and Chloral

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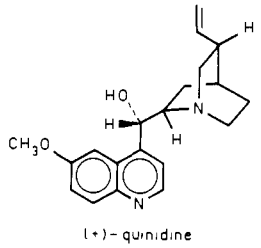
Abstract: Quinidine (**5**) catalyzes the addition of ketene (**1**) to chloral (**2**) at −50 °C in toluene. The β-(trichloromethyl)-β-propiolactone **3** is formed virtually optically pure (98% enantiomeric excess). A mechanism for this reaction, accounting for the high enantiomeric excess, is proposed. Known hydrolytic procedures convert the lactone **3** to malic acid (**6**). By proper choice of catalyst both (*R*)- and (*S*)-malic acid can be obtained optically pure.

"Rarest among efficient asymmetric synthesis is carbon–carbon bond formation with the simultaneous creation of a new chiral center".[1] With this statement A. I. Meyers and co-workers introduce the subject of the asymmetric synthesis of chiral alkanoic acids. If the type of synthesis referred to in that publication[1] is rare, a further severe restriction is introduced if we limit the asymmetric syntheses to those performed with chiral catalysts only, adding a further parameter by requiring an enantiomeric excess better than 80%. Important recent examples are the (*S*)-proline catalyzed intramolecular aldol condensation[2] (ee ~95%), the chiral cobalt and copper complex catalyzed carbene addition reaction[3] (ee ~88%), and the quinine catalyzed Michael reaction[4] (ee 99%). Our successful experiences with the use of cinchona alkaloids in base-catalyzed 1,4-addition reactions led us to reexamine the base-catalyzed 2 + 2 cycloaddition reaction between ketene (**1**) and chloral (**2**) to form β-(trichloromethyl)-β-propiolactone (**3**) as reported first by Borrmann and Wegler.[5]

We have now found that by using 1–2 mol % of quinidine (**5**)

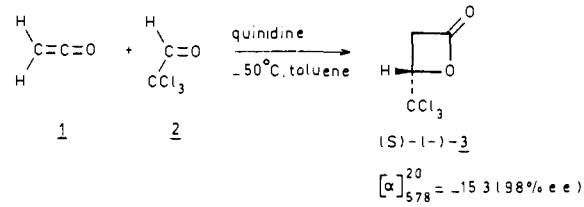


(+)-quinidine

5

in toluene at −50 °C the β-lactone **3** can be isolated in virtually quantitative chemical and optical yield (95%, Scheme I). By use of diastereomeric cinchona alkaloids (e.g., quinine) either enantiomer of the β-lactone can be obtained. The lactone **3** is readily crystallized from methylcyclohexane to complete optical purity and has an absolute rotation of $[\alpha]^{20}_{578}$ −15.6° (*c* 1, cyclohexane), mp 51–52 °C (lit. for racemic lactone mp 36–37 °C[5]). Mild acid hydrolysis of the β-lactone to the known[6] trichloromethyl hydroxy acid **4** can be used to correlate both the absolute configuration of **3** [*S*(−) and *R*(+)] and its optical purity. As check upon the reported values we prepared the diastereomeric esters of **4** using Mosher's reagent.[7] The integrated ^{19}F NMR values confirm the enantiomeric purity assignment. Careful basic hydrolysis of the trichlorohydroxy acid **4** to malic acid (**6**) by slight modification of published procedures[6] thus furnishes the natural (*S*)-(−)- and the rare (*R*)-(+)-malic acids. Under optimum conditions the optically pure malic acids can be obtained in an overall yield of 79%. This compares favorably with the elegant route of Seebach

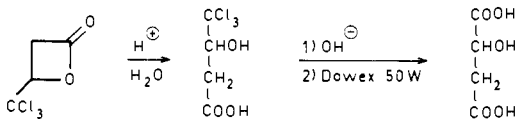
Scheme I



1 **2** (S)-(−)-**3**

$[\alpha]^{20}_{578}$ = −15.3 (98% e e)

Scheme II



3 **4** **6**

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