endo acetate, **55**, and 0.056 g (12%) of the exo acetate, **38**. Exo acetate:[46] ir (neat) 3.31 (s), 3.42 (w), 5.71 (s), 6.90 (w), 7.28 (m), 7.96 (s), 8.06 (s), 9.56 (w), 9.80 (m), and 10.32 (m) μ; nmr (CCl_4) τ 5.23 (d, 1 H, J = 4 Hz), 7.66–8.66 (m, 9 H), 8.07 (s, 3 H), and 8.88 (s, 3 H). Endo acetate:[46] $n^{24.5}$D 1.4501; ir (neat) 3.33 (s), 3.44 (m), 5.72 (s), 6.89 (w), 7.25 (m), 7.90 (s), 8.05 (s), 8.22 (m), and 9.60 (s) μ; nmr (CCl_4) τ 5.41 (complex q, 1 H, J = ~9 Hz), 7.70–8.70 (m, 9 H), 8.03 (s, 3 H), and 8.82 (s, 3 H).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: (exo) C, 71.02; H, 9.57; (endo) C, 70.90; H, 9.63.

Acknowledgment. We are indebted to the National Science Foundation and to the Petroleum Research Fund, administered by the American Chemical Society, for grants which partially supported this study.

New Synthetic Methods. A Rational Synthesis of 7,8-Diazatetracyclo[3.3.0.0^{2,4}.0^{3,6}]oct-7-ene[1]

Barry M. Trost,*[2] Robert M. Cory,[3] and (in part) Paul H. Scudder and Hans B. Neubold

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received May 12, 1973*

Abstract: Alkylation of sodium cyclopentadienide with *N*-(bromomethyl)benzamide followed by Diels–Alder addition of dimethyl azodicarboxylate generated dimethyl 7-*anti*-benzamidomethyl-2,3-diazabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate. Nitrosation followed by base converted the benzamido group to a diazo grouping. Quenching of this diazo compound with acetic acid produced the 7-*anti*-acetoxymethyl-2,3-diazabicyclo[2.2.1]-hept-5-ene-2,3-dicarboxylate also available by an analogous alkylation Diels–Alder route using bromomethyl acetate. This quench served to allow assignment of stereochemistry at C-7. Carbene generation by photolysis of the diazo compound led by double bond insertion to dimethyl 7,8-diazatetracyclo[3.3.0.0^{2,4}.0^{3,6}]octane-7,8-dicarboxylate. Hydrolysis, decarboxylation, and oxidation by cupric chloride generated the title compound. The flexibility of the approach should permit applicability to the all carbon system as well.

A continuing challenge for synthetic organic chemistry resides in the construction of the valence tautomers of cyclic polyenes. Among the unlimited number of candidates having the formula $(CH)_n$, the isomers of benzene, $(CH)_6$, and cyclooctatetraene, $(CH)_8$, hold special interest. In spite of the great stability of benzene and the high degree of strain embodied in its valence tautomers, two of the four possible isomers, namely Dewar benzene[4] (**1**) and benzvalene[4b,5] (**2**), had been synthesized at the initiation of our work. Although substituted derivatives of all four were known,[6] the parent prismane[7] (**3**) and 3,3′-biscyclopropenyl[8] (**4**) remained undetected in several attempts at their generation.[9] Similarly, many of the 18 possible[10] $(CH)_8$ isomers have been prepared, but the most highly strained member of this series, tetracyclo[3.3.0.0^{2,4}.0^{3,6}]oct-7-ene (**5**), is known only in the form of derivatives.[11]

Encouraged by the then recent synthesis of Dewar benzene,[4a] we were led in 1965 to attempt a synthesis of the parent prismane molecule. In the course of this

(1) (a) A preliminary report of a portion of this work has appeared: B. M. Trost and R. M. Cory, *J. Amer. Chem. Soc.*, **93**, 5572 (1971); (b) also see B. M. Trost, R. M. Cory, P. H. Scudder, and H. B. Neubold, to be submitted for publication; (c) for a parallel and independent investigation see T. J. Katz and N. Acton, *ibid.*, **95**, 2738 (1973).

(2) Henry and Camille Dreyfus Teacher-Scholar Grant Recipient.

(3) National Science Foundation and National Institutes of Health Predoctoral Fellow.

(4) (a) E. E. van Tamelen and S. P. Pappas, *J. Amer. Chem. Soc.*, **85**, 3297 (1963); (b) H. R. Ward and J. S. Wishnok, *ibid.*, **90**, 1085 (1968); (c) E. E. van Tamelen, S. P. Pappas, and K. L. Kirk, *ibid.*, **93**, 6092 (1971); (d) E. E. van Tamelen and D. Carty, *ibid.*, **93**, 6102 (1971).

(5) (a) K. E. Wilzbach, J. S. Ritscher, and L. Kaplan, *ibid.*, **87**, 4004 (1965); (b) T. J. Katz, E. J. Wang, and N. Acton, *ibid.*, **93**, 3782 (1971).

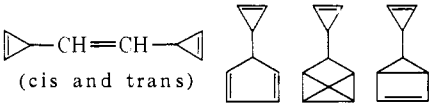
(6) For reviews of the chemistry of the valence tautomers of aromatic compounds, see E. E. van Tamelen, *Angew. Chem., Int. Ed. Engl.*, **4**, 738 (1965); L. B. Jones and V. K. Jones, *Fortschr. Chem. Forsch.*, **13**, 322 (1969); E. D. Bergmann, *J. Chim. Phys. Physicochim. Biol.*, **67**, 649 (1970).

(7) (a) K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, **87**, 4004 (1965); (b) R. Criegee and R. Askani, *Angew. Chem., Int. Ed. Engl.*, **5**, 519 (1966); (c) D. M. Lemal and J. P. Lokensgard, *J. Amer. Chem. Soc.*, **88**, 5934 (1966); (d) W. Schäfer, R. Criegee, R. Askani, and H. Grüner, *Angew. Chem., Int. Ed. Engl.*, **6**, 78 (1967); (e) J. F. M. Oth, *ibid.*, 7, 646 (1968); (f) *Recl. Trav. Chim. Pays-Bas*, **87**, 1185 (1968); (g) R. Criegee and H. Güner, *Angew. Chem., Int. Ed. Engl.*, **7**, 467 (1968); (h) R. Criegee, H. Grüner, D. Schönleber, and R. Huber, *Chem. Ber.*, **103**, 3696 (1970); (i) L. A. Paquette, G. R. Krow, J. M. Bollinger, and G. A. Olah, *J. Amer. Chem. Soc.*, **90**, 7147 (1968); (j) H. Hogeveen and H. C. Volger, *Chem. Commun.*, 1133 (1967); (k) M. G. Barlow, R. N. Hazelline, and R. Hubbard, *ibid.*, 202 (1969); (l) *J. Chem. Soc. C*, 1232 (1970); (m) D. M. Lemal, J. V. Staros, and V. Anstel, *J. Amer. Chem. Soc.*, **91**, 3373 (1969); (n) E. D. Clifton, W. T. Flowers, and R. N. Haszeldine, *Chem. Commun.*, 1216 (1969); (o) M. G. Barlow, J. G. Dingwall, and R. N. Haszeldine, *ibid.*, 1580 (1970).

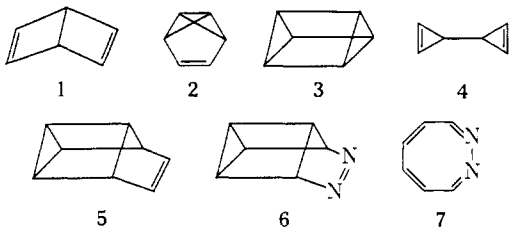
(8) A recent attempt to prepare **4** was not successful: G. H. Wahl, Jr., and K. Weiss, *J. Org. Chem.*, **35**, 3902 (1970). For the 3,3′-dimethyl derivative, see W. H. de Wolf, W. Stol, I. J. Landheer, and F. Bickelhaupt, *Recl. Trav. Chim. Pays-Bas*, **90**, 405 (1971).

(9) For the results of photolyses of benzene under various conditions, see ref 4b. The photolysis of quadricyclanone gives only a small amount of benzene in addition to tars: D. M. Lemal and K. S. Shim, *Tetrahedron Lett.*, 2779 (1965). Other efforts have so far met without success: (a) E. H. Farmer, *J. Chem. Soc., London, Trans.*, 3332 (1923); (b) J. P. Lokensgard, Ph.D. Thesis, University of Wisconsin, 1967; (c) R. J. Lorence, Ph.D. Thesis, State University of New York, Buffalo, N. Y., 1969.

(10) Calculations of thermodynamic properties for "all possible" $(CH)_8$ isomers have recently been published: H. Iwamura, K. Morio, and T. L. Kunii, *Chem. Commun.*, 1408 (1971). However, these authors omitted at least four, which, for the record, are shown below.



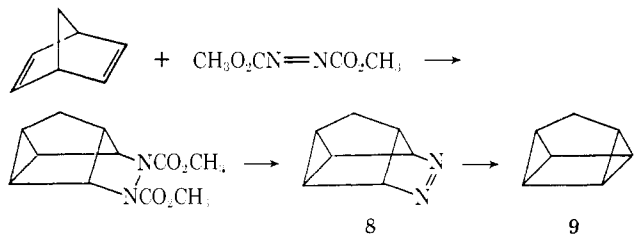
(11) (a) W. H. F. Sasse, P. J. Collin, and G. Sugowdy, *Tetrahedron Lett.*, 3373 (1965); (b) G. W. Klumpp, W. G. J. Rietman, and J. J. Vrielink, *J. Amer. Chem. Soc.*, **92**, 5266 (1970).



1 2 3 4 5 6 7

investigation, we have developed a simple approach to 7,8-diazatetracyclo[3.3.0.0^{2,4}.0^{3,6}]oct-7-ene (**6**), a heterocyclic $(CH)_6N_2$ analog of the $(CH)_8$ hydrocarbon, **5**, which should be applicable to the all carbon system as well. This compound has now served as a valuable synthetic intermediate to prismane[1b,c] and 1,2-diaza-2,4,6,8-cyclooctatetraene (**7**).

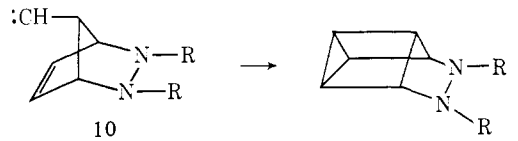
In 1963 Moriarty reported that photolysis of azo compound **8**, readily available from norbornadiene, gave quadricyclane (**9**) in 35% yield.[12] Thus, the conversion of azo compound **6** to prismane seemed a reasonable approach. Furthermore, one might envision a pathway to **6** analogous to that for **8**, starting



8 9

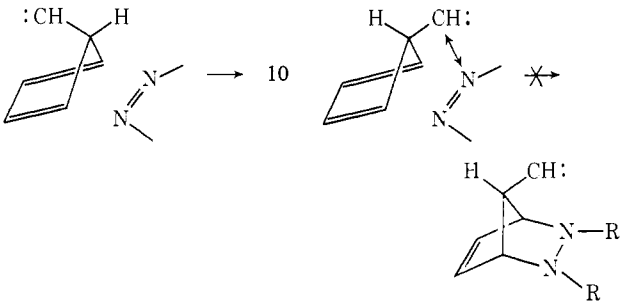
from Dewar benzene. However, Lemal and Lokensgard had already been frustrated at the beginning of that very route.[4c,9b] Not only was Dewar benzene not available in preparatively useful quantities, but its hexamethyl derivative suffered extensive rearrangement upon reaction with an azo dienophile.

An alternative approach for the construction of the tetracyclic framework centered on the most direct method of constructing cyclopropanes, carbene addition to a double bond. Of the various possibilities, carbene **10**, which would create the requisite carbon



10

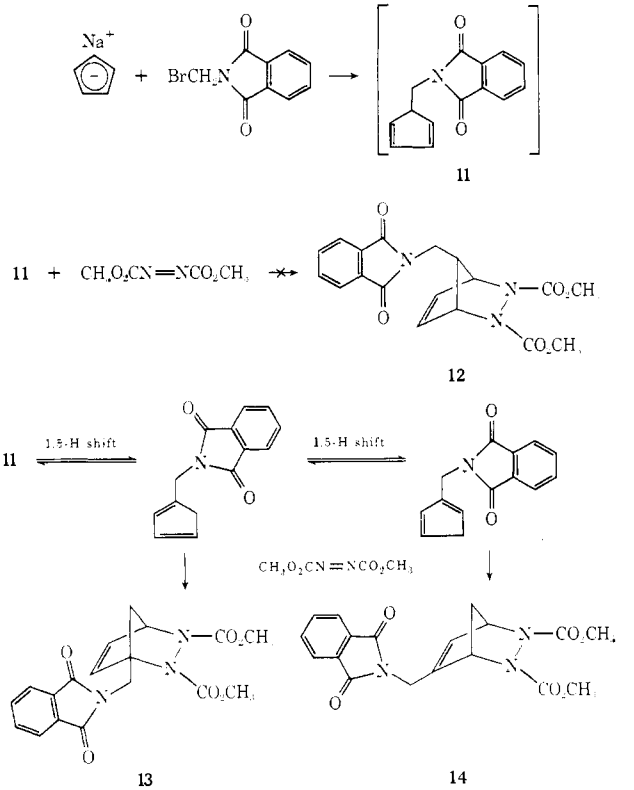
skeleton by intramolecular addition to the double bond, appeared to be the most accessible.[13] Conceptually, the simplest approach to **10** would start with a 5-monosubstituted cyclopentadiene. Diels–Alder addition might be anticipated to occur from the sterically more accessible face of the cyclopentadiene to generate the requisite stereochemistry. Disfavoring this idea were the instability of 5-monosubstituted cyclopentadienes relative to the 1 and 2 isomers and obtention of the undesired stereochemistry in some of the reported



Diels–Alder adducts.[14] However, as we indicated in a prior publication,[15] alternative starting materials comprising cyclopentadienone ketals and fulvenes gave adducts with azo compounds which could not be converted to intermediates necessary for the formation of carbene **10**. The success of an analogous Diels–Alder reaction to that proposed above in a synthesis of prostaglandins encouraged us to attempt the direct approach.[16]

Assuming that an aminomethyl group would constitute a suitable precursor to a diazo group, the immediate precursor to a carbene, the sequence outlined in Scheme I was investigated. Alkylation of sodium

Scheme I. Alkylation–Diels–Alder Sequence with *N*-Bromomethylphthalimide



11 12 13 14

cyclopentadienide with *N*-bromomethylphthalimide in THF at −30° followed by addition of excess dimethyl azodicarboxylate led to two 1:1 adducts in 65 and 35% yields, neither of which was the desired adduct **12**. The major adduct identified as **13** showed only one bridgehead proton as a multiplet at δ 5.18, two broad

(12) R. M. Moriarty, *J. Org. Chem.*, 28, 2385 (1963). Later, two groups were unable to reproduce this result: R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, *J. Chem. Soc. C*, 1905 (1967); J. K. Harrington, Ph.D. Thesis, University of Colorado, Boulder, Colo., 1970.

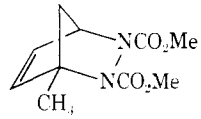
(13) See, for example, (a) D. M. Lemal, F. Menger, and G. W. Clark, *J. Amer. Chem. Soc.*, **85**, 2529 (1963); (b) D. M. Lemal and K. S. Shim, *Tetrahedron Lett.*, 3231 (1964); (c) G. L. Closs and R. B. Larrabee, *ibid.*, 287 (1965); (d) M. Schwarz, A. Besold, and E. R. Nelson, *J. Org. Chem.*, **30**, 2425 (1965).

(14) (a) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Amer. Chem. Soc.*, 77, 4183 (1955); (b) S. McLean and P. Haynes, *Tetrahedron Lett.*, 2313 (1965).

(15) B. M. Trost and R. M. Cory, *J. Org. Chem.*, 37, 1106 (1972).

(16) E. J. Corey, N. M. Weinshenker, T. K. Schaaf, and W. Huber, *J. Amer. Chem. Soc.*, **91**, 5675 (1969).

doublets at δ 1.64 and 1.83 (J = 9 Hz) assignable to the two methylene protons in the 7 position, two sharp doublets at δ 4.22 and 5.12 (J = 14 Hz) for the two protons in the NCH_2 grouping adjacent to an asymmetric carbon, and a pattern for the two olefinic protons almost identical with that for the corresponding methyl derivative, **15**.[17] In contrast, the minor adduct **14**



15

showed only one vinyl proton as an unresolved multiplet at δ 6.20, an unresolved multiplet at 1.82 for the two 7 protons, a closely spaced doublet (J = 1.5 Hz) at 4.51 assignable to the NCH_2 protons coupled with the vinyl proton, and an unresolved multiplet for the two bridgehead protons at 5.10. These data strongly suggested the structures depicted for **13** and **14**.

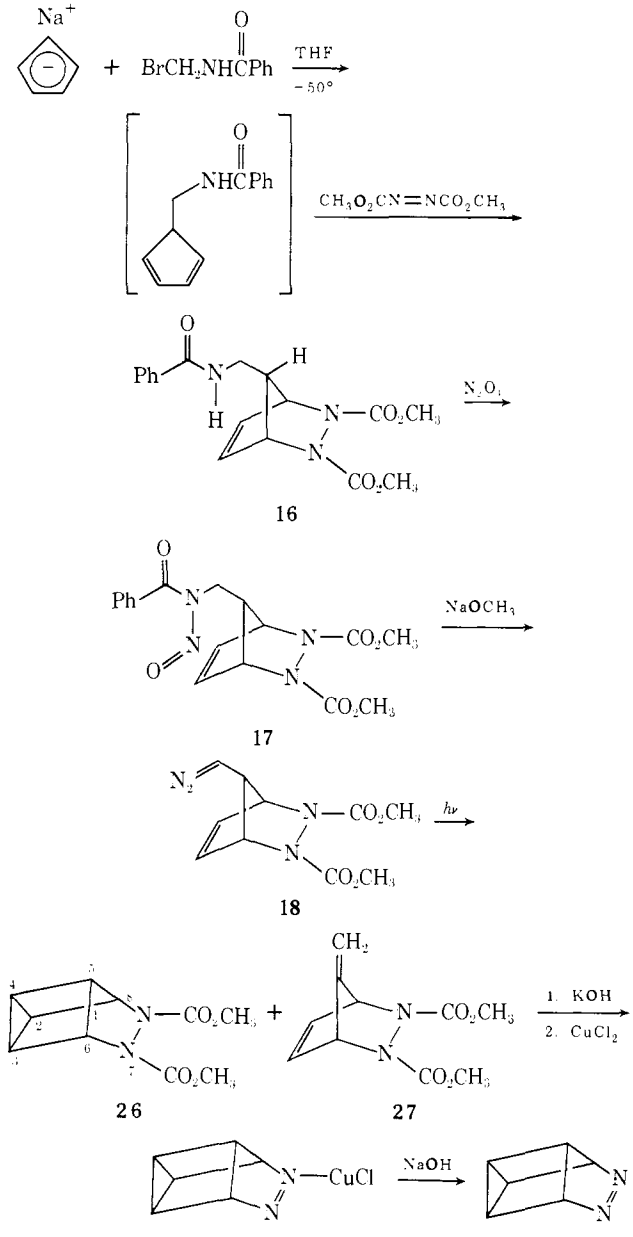
Reasoning that the steric bulk of the phthalimido group slowed the 4 + 2 cycloaddition sufficiently to allow 1,5-H shift to compete favorably, we turned to the use of a smaller alkylating agent *N*-bromomethylbenzamide which was available in essentially quantitative yield by a slight modification of the literature procedure (see Experimental Section).[18] Treatment of sodium cyclopentadienide with an excess of this alkylating agent in THF at −50° followed by addition of an excess of dimethyl azodicarboxylate and warming to 0° produced a 78% yield of a homogeneous 1:1 adduct **16** (see Scheme II). That the amidomethyl group was bonded to C-7 was immediately apparent from the nmr spectrum in which the protons on the bicyclic nucleus gave rise to absorption strikingly different from those of **13** and **14**. The two olefinic protons appeared as a pseudotriplet (J = 2 Hz) at δ 6.49 and the two bridgehead protons as an unresolved multiplet at δ 4.98, typical of symmetrical 2,3-diazabicyclo[2.2.1]hept-5-enes. The single 7 proton, showing a broadened triplet (J = 7 Hz) at δ 2.48, was coupled with the NCH_2 protons, which were also split by the NH proton. The assignment of anti stereochemistry to **16** was established at a later stage of the synthesis of **6** and by the ultimate success of the synthetic plan.

The transformation of benzamide **16** to the corresponding nitrosamide, **17**, proceeded smoothly, provided great care was taken to exclude moisture. Treatment of a solution of **16** in methylene chloride in the presence of an excess of sodium acetate at 0° with dinitrogen tetroxide in methylene chloride for 20 min produced an excellent yield of **17**. Although the crude material was reasonably pure, and suitable for conversion to the diazo compound **18**, it could be further purified by tlc. However, one attempt to chromatograph a larger sample on Woelm neutral alumina led to the disappearance of the yellow band as it traveled down the column. After elution with a more polar solvent and additional chromatography on

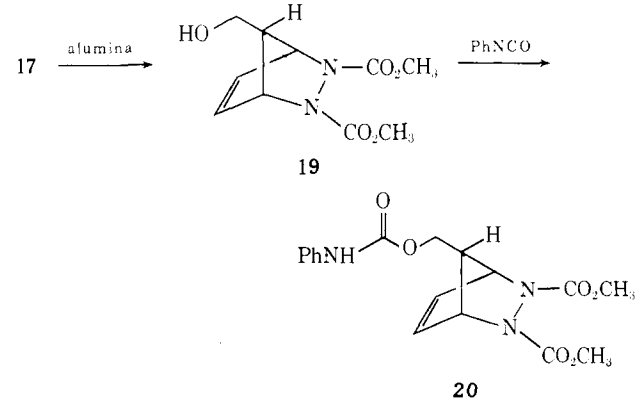
(17) J. Wagner, W. Wojnarowski, J. E. Anderson, and J. M. Lehn, *Tetrahedron*, **25**, 657 (1969).

(18) H. Böhme, R. Broese, A. Dick, F. Eiden, and D. Schünemann, *Chem. Ber.*, **92**, 1599 (1959). These authors reported *N*-bromomethylbenzamide, but gave no experimental details for its preparation. We found that it could not be purified without a certain amount of decomposition, but the crude bromide was suitable for the alkylation of cyclopentadienide anion.

Scheme II. Synthesis of 7,8-Diazatetracyclo[3.3.0.0^{2,4}.0^{3,6}]oct-7-ene



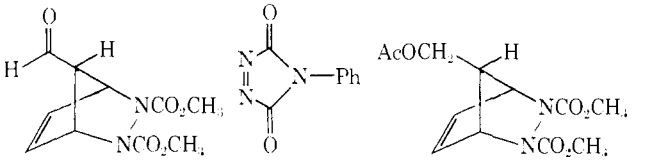
Florisil, a 37% yield of the alcohol **19** could be isolated. Although neither this compound nor its precursors, **16** and **17**, could be obtained in crystalline form, being hard gums, a solid phenylurethane (**20**)



was formed on reaction of **19** with phenyl isocyanate.

While conversion of nitrosamide **17** to the diazo com-

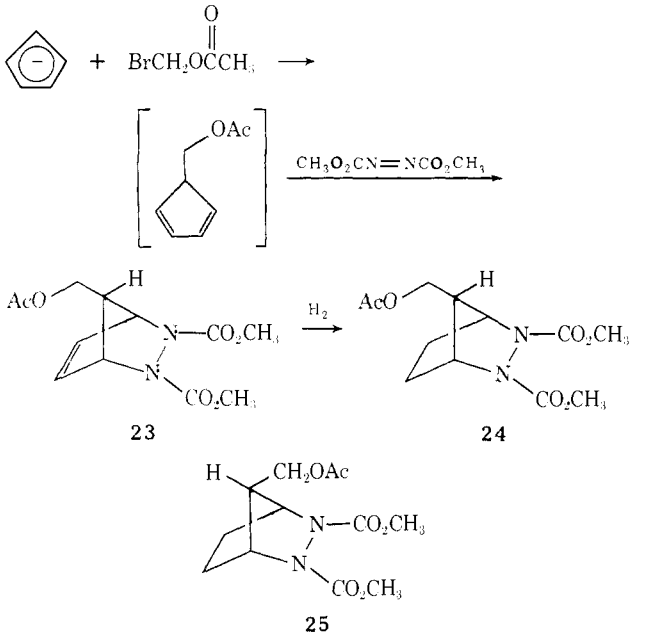
pound **18** and the decomposition of the latter were being studied, attempts were made to oxidize the alcohol **19** to the corresponding aldehyde **21**. The latter



21 22 23

could presumably serve as a source of the carbene **10** *via* its tosylhydrazone. In every case but one, only starting material could be recovered. Reagents investigated included Collins reagent[19] (dipyridinechromium(VI) oxide) in methylene chloride, phenyltriazolinedione (**22**) in benzene,[20] Jones reagent, and lead tetraacetate in pyridine.[21] The last method gave, in addition to starting **19**, a 21% yield of the corresponding acetate, **23**. This product was also prepared in 50% yield from cyclopentadienylsodium, bromomethyl acetate, and dimethyl azodicarboxylate under the same conditions as for amide **16**. Again, none of the syn isomer could be detected, and only the 7-substituted isomer was observed. Furthermore, **23** could be hydrogenated to the saturated acetate **24** which was shown to be distinct from the previously obtained syn isomer **25**.[15] The $AcOCH_2$ doublet in the nmr spectrum of **25** was 5 Hz

Scheme III. Independent Synthesis of **23**



upfield from that in the nmr spectrum of **24**. The resistance of alcohol **19** to oxidation remains unexplained, but may be related to the inductive effect of the carbamate groups.[22]

Under a variety of strongly basic conditions, the nitrosamide **17** was converted in part to the diazo compound **18** characterized in crude form in solution by a strong band in the ir spectrum at 2070 cm^{-1}, and nmr absorptions at δ 2.89 (doublet of multiplets, J = 7 Hz) for the 7 proton and δ 3.34 (doublet, J = 7 Hz) for the diazomethyl proton (N_2CH). This assignment was confirmed by treatment of the crude product with sodium acetate in acetic acid, which resulted in the isolation of an acetate identical with the *anti*-acetate **23**. This correlation establishes the stereochemistry of the diazo compound and thus adduct **16**.

As the yield of **18** was moderate to poor, the product mixtures always containing a collection of extraneous materials, some effort was made to find optimum conditions. The best conditions developed involve addition of sodium methoxide to a solution of nitrosamide **17** in slightly wet tetrahydrofuran at 0° (optimum appears to be about a 1:1.6 molar ratio of methoxide to water) and led *directly* to a 60% yield (not isolated) of diazo compound **18**. Surprisingly, only a very small amount of methyl benzoate was formed, and a fair yield of sodium benzoate was obtained upon filtration of the reaction mixture. It was also noted that there is an apparent induction period of variable time before any band is observed at 2070 cm^{-1} in the infrared.

When a crude, dilute solution of the diazo compound **18** in methylene chloride was irradiated at −78° by a 450-W mercury vapor lamp through a Pyrex filter, two products whose molecular formulas corresponded to loss of nitrogen from **18** could be isolated by careful chromatography. The major one (28% from nitrosamide **17**) was a crystalline solid purifiable by sublimation. That this compound, **26**, had the desired tetracyclic framework present in azo compound **6** was proven by spectral means. Its nmr spectrum showed, in addition to a singlet at δ 3.78 for the methyl ester protons, four multiplets in a ratio of 2:1:1:2. The two protons on carbon bonded to nitrogen give rise to a broadened doublet at δ 5.00, and the remaining three multiplets appeared between δ 2 and 3. The splitting patterns were analyzed with the aid of a computer leading to the assignments in Table I. The mass spectral fragmentation pattern was fully consistent.[23]

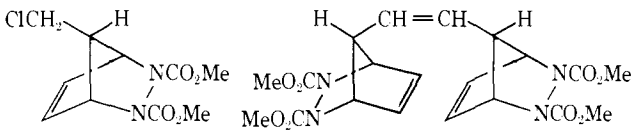
Table I. Nmr Data for the Tetracyclic Carbamate, **26**, and for the Azo Compound, **6**

Protons	**26** Shift, δ, $CDCl_3$	Coupling	J, Hz	**6** Shift, δ, $CFCl_3$
1,6	5.00	1,5	4.7	5.74
		1,2	2.0	
2,3	2.23	1,3	1.0	2.19
		1,4	0.0	
4	2.53	1,6	0.2	2.19
		2,5	4.7	
5	2.96	2,4	3.3	2.79
		2,3	5.5	
		4,5	0.8	

The minor isomer of **26** produced (15% yield from nitrosamide **17**) in the photolysis of diazo compound **18** was identical in all respects with the adduct, **27**, of fulvene with dimethyl azodicarboxylate.[16] In the present instance, it must result from intramolecular insertion of the carbene **10** (R = CO_2CH_3) into the α-CH bond. In addition, if great care was not taken to purify and dry the methylene chloride used as solvent

(19) J. C. Collins, W. W. Hess, and F. J. Frank, *Tetrahedron Lett.*, 3363 (1968).
(20) R. C. Cookson, I. D. R. Stevens, and C. T. Watts, *Chem. Commun.*, 744 (1966).
(21) R. E. Partch, *Tetrahedron Lett.*, 3071 (1964).
(22) For a related case, see E. L. Allred, C. L. Anderson, and R. L. Smith, *J. Org. Chem.*, **31**, 3493 (1966).
(23) R. Cory, Ph.D. Thesis, University of Wisconsin, 1971; H. Hart and J. L. Brewbaker, *J. Amer. Chem. Soc.*, **91**, 706 (1969).

in the photolysis, a comparable amount of the chloride, **28**, was produced at the expense of **26** and **27**. Pre-

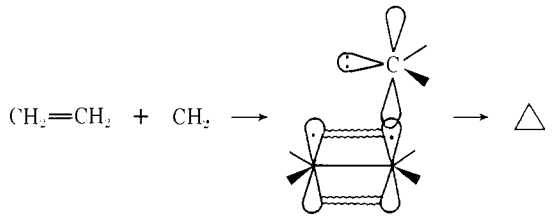


28 **29**

sumably, **28** is formed by reaction of the diazo compound with hydrogen chloride. To obviate this problem, subsequent photolyses were carried out in tetrahydrofuran in which the tetracyclic compound **26** could be isolated in yields up to 44% (overall yield from **17**).

Although photolysis was not the only method investigated for the conversion of the diazo compound, **18**, to the tetracyclic carbamate ester, **26**, other procedures did not result in the formation of the latter. Treatment of a crude solution of **18** in toluene with a catalytic amount of tetrakis[iodo(tri-*n*-butylphosphine)-copper(I)] gave a small yield of olefin, tentatively assigned structure **29**, which appeared to be a mixture of *Z* and *E* isomers. No other products would be identified. In contrast, when the decomposition of **18** in ether was catalyzed by cupric sulfate, the only product isolated, in very small yield, was tentatively characterized as the aldehyde, **21**. The latter compound apparently arose by reaction of the diazo compound with oxygen or peroxides in the solvent.

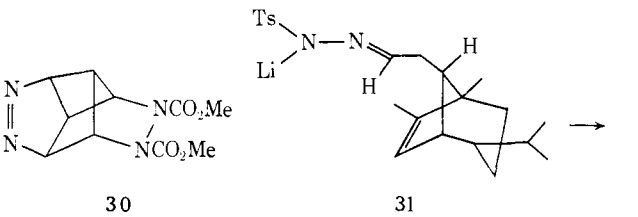
The success of the photolysis of **18** in producing **26** should be commented upon, in light of a recent article by Hoffmann[24] in which he calculated that the most favorable geometry for addition of singlet methylene to ethylene is such that the p orbital overlaps in a σ manner with *one end* of the ethylene π bond. This lopsided configuration is unattainable in carbene **10**, with-



out severely twisting the rigid bicyclic framework. It may be, then, that **26** arises from a triplet state of the carbene, **10**, or that yet another mechanism is operative here. For instance, initial 1,3-dipolar addition of the diazo group to the double bond would produce pyrazoline **30**, and extrusion of nitrogen from the latter could give **26**. This process has, in fact, recently been observed in a similar system,[25] namely the conversion of tosylhydrazone salt **31** to the tetracyclic hydrocarbon, **32**. In the latter case, however, the intermediate pyrazoline was isolated in good yield by *pyrolysis* of **31**, and **32** was produced by photolysis of the purified pyrazoline.

The tetracyclic carbamate ester, **26**, was smoothly saponified by methanolic potassium hydroxide at room temperature. Upon neutralization and addition of

(24) R. Hoffmann, *ibid.*, **90**, 1475 (1968).
(25) E. Piers, R. W. Britton, R. J. Keziere, and R. D. Smillie, *Can. J. Chem.*, **49**, 2623 (1971).



30 **31**

32

aqueous cupric chloride, a 90% yield of a brick red complex precipitated and was collected. Without further purification the latter was suspended in methylene chloride and treated with aqueous sodium hydroxide, giving a 75% yield (from **26**) of a low melting solid. As deduced from its derivation from **26** and fully consistent spectral data, this product was undoubtedly the penultimate goal of our synthesis, azo compound **6**. In contrast to the carbamate **26** in which the nmr absorptions of the 4 proton were completely separated from those of the 2 and 3 protons, the corresponding three protons in **6** appeared coincidentally as a single multiplet. Thus, the nmr spectrum consisted of three multiplets in a ratio of 2:1:3 at δ 5.74, 2.79, and 2.19, respectively (Table I). A sharp band in the infrared at 1493 cm^{-1} and ultraviolet maxima in the region of 360–380 nm were also observed, very similar to the absorptions of azo compound **8**.[12] In conjunction with the mass spectrum which established the formula $C_6H_6N_2$ and the mode of synthesis, structure **6** can be conclusively assigned. The advantage of this, in essence, five-step synthesis is the flexibility to apply it to variously substituted systems as well as its applicability to the all carbon system.

Experimental Section

Melting points were taken on a Thomas-Hoover melting point apparatus and are corrected. Infrared spectra were determined on a Beckman IR-8 spectrophotometer and ultraviolet spectra were recorded on Cary Model 11 and Model 15 spectrophotometers. Nmr spectra were determined on a Varian Associates Model A-60A spectrometer fitted with a variable-temperature probe. Chemical shifts are given in δ units, ppm relative to TMS as an internal standard. Mass spectra were taken on a CED 103 C or a MS-902 mass spectrometer at an ionizing current of 40 mA and ionizing voltage of 70 V. Analyses were performed by Spang Microanalytical Laboratory.

All reactions were carried out under nitrogen. Thick-layer chromatography (tlc) was performed on 20 × 20 cm × 1.5 mm or 20 × 40 cm × 1.5 mm layers of silica gel PF-254 (E. Merck AG Darmstadt).

Phthalimides 13 and 14: Respectively Dimethyl 1-Phthalimidomethyl-2,3-diazabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate and Dimethyl 5-Phthalimidomethyl-2,3-diazabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate. To a suspension of 0.985 g (4.1 mmol) of *N*-(bromomethyl)phthalimide (Aldrich Chemical Co.) in 2.0 ml of anhydrous tetrahydrofuran, cooled to −30° by a freezing 65:35 mixture of *o*- and *m*-xylene, was added 2.0 ml (*ca.* 3.6 mmol) of an 18% solution of sodium cyclopentadienide in tetrahydrofuran (Eastman) in 15 min. The orange mixture was stirred at −30° for 40 min. An additional 0.5 ml of tetrahydrofuran was added to decrease the viscosity of the thick suspension, and stirring was continued for a total of 2 hr. Then 0.993 g (6.8 mmol) of dimethyl azodicarboxylate in 1.5 ml of tetrahydrofuran was added in 10 min, the mixture was stirred for a few minutes at −30°, and the xylene was replaced by an ice bath. The mixture was stirred for 4.5 hr at 0°, then 14 hr at room temperature. The bulk of the tetrahydrofuran was evaporated under aspirator pressure, and 5 ml of methylene chloride

was added. After the mixture had stirred for a few minutes, 0.5 ml of water and 5 ml of saturated sodium chloride were added. The organic layer was separated and the aqueous layer was washed three times with 10 ml of methylene chloride. The combined organic extracts were dried over sodium sulfate and evaporated to an orange gum. Preparative tlc on a portion of this gave two bands (eluting with 1:1 ether–methylene chloride) very close together. The one with higher R_f value (0.49) yielded a gum which crystallized partially on standing in the refrigerator overnight. Trituration with carbon tetrachloride and recrystallization from the same solvent gave white microcrystals, mp 181–182°, of compound **13**. Nmr showed the presence of a small amount of the simple cyclopentadiene adduct in the mother liquor. On the basis of this sample, the total yield of **13** from this experiment was calculated to be 0.85 g (65% from sodium cyclopentadienide): nmr ($CDCl_3$) 1.64 and 1.83 (bd's, 2 H, J = 9 Hz, 7-CH_2), 3.79 (s, 6 H, OCH_3), 4.42 (d, 1 H, J = 14 Hz, NC*H*H), 5.12 and 5.18 (d, J = 14 Hz, NCH*H*, and unresolved m, bridgehead CH, respectively, 2 H), 6.38 (dd, 1 H, J = 6 and 3 Hz, 5-vinyl H), 6.75 (dd, 1 H, J = 6 and 1 Hz, 6-vinyl H), 7.81 (m, 4 H, ArH); ir ($CHCl_3$) 1779 (w sh), 1721 (s), cm^{-1}; ms *m/e* (%), 59 (100, $^+CO_2CH_3$), 76 (36), 77 (61), 78 (100, fulvene), 80 (40), 118 (30), 120 (29), 161 (91, phthalimidomethyl$^+$), 225 (25, M − dimethyl azodicarboxylate and/or M − phthalimidyl), 226 (78), 371 (26, M); exact mass determination, 371.11271 ± 0.003 (calcd for $C_{18}H_{17}N_3O_6$, 371.11173); uv (ethanol) λ_{max} 218 nm (log ϵ 4.66), 241 (3.98), 294 (3.30).

The other tlc band (R_f 0.35) was rechromatographed to give pure isomer **14**, mp 119–121° (from methylene chloride–ether–pentane). The total yield of **14** was calculated to be *ca.* 0.5 g (30–40%): nmr ($CDCl_3$) 1.82 (m, 2 H, 7-CH_2), 3.75 and 3.80 (s's, 6 H, OCH_3), 4.51 (d, 2 H, J = 1.5 Hz, NCH_2), 5.10 (unresolved m, 2 H, bridgehead CH), 6.20 (unresolved m, 1 H, vinyl H), 7.79 (m, 4 H, ArH); ir ($CHCl_3$) 1718 (s) cm^{-1}; ms *m/e* (%) 59 (40, $^+CO_2CH_3$), 78 (100, fulvene), 160 (61, phthalimidomethyl$^+$), 225 (81, phthalimidomethylcyclopentadiene), 371 (12, M); exact mass determination, 371.11502 ± 0.005 (calcd for $C_{18}H_{17}N_3O_6$, 371.11173); uv (ethanol) λ_{max} 221 nm (log ϵ 4.67), 238 (4.02), 293 (3.25).

***N*-(Bromomethyl)benzamide.** To a solution of phosphorus pentabromide[26] (167.40 g, 0.389 mol) in 160 ml of diethyl ether (distilled from sodium benzophenone ketyl) at 0° in vigorously dried equipment was added over 10 min 58.00 g (0.384 mol) of *N*-(hydroxymethyl)benzamide.[27] The orange slurry was stirred at 0° for 2 hr and then at 25° for 3 hr and filtered. The yellow solid was washed with hexane and commercial anhydrous ether until off-white and then dried in a vacuum desiccator to give 82.78 g (quantitative yield), mp 119–121° (lit.[18] mp 105–107°). It appeared to be pure by nmr (when impure, an additional multiplet at δ 8.1–8.3 apparently due to a polymeric substance appears) and was used without purification in further reactions, since recrystallization caused considerable loss due to decomposition. It may be recrystallized from chloroform–petroleum ether (bp 60–68°): nmr ($CDCl_3$) 5.53 (d, 2 H, J = 8 Hz, CH_2), 7.3–8.05 (m, 6 H, ArH and NH); ir ($CHCl_3$) 3472 (w), 1675 (s), 1511 (s), 1488 (s) cm^{-1}.

Benzamide 16: Dimethyl 7-*anti*-Benzamidomethyl-2,3-diazabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate. To 1.76 g (8.2 mmol) of *N*-(bromomethyl)benzamide in 8.0 ml of anhydrous tetrahydrofuran, cooled to −50° by a freezing 1:1 mixture of *o*- and *m*-xylene, was added 3.3 ml (*ca.* 6.6 mmol) of an 18% solution of sodium cyclopentadienide in tetrahydrofuran (Eastman) in 15 min. The dropping funnel was rinsed with 1.0 ml of tetrahydrofuran, and the resulting suspension was stirred at −50° for 2 hr. To the thick suspension at −50° was then added 1.83 g (12.5 mmol) of dimethyl azodicarboxylate in 4.0 ml of tetrahydrofuran in 15 min. The dropping funnel was washed with 0.5 ml of tetrahydrofuran, and the mixture was stirred at −50° for 20 min. It was then warmed to 0° with an ice bath, stirred for 0.5 hr, and placed in the refrigerator at 0° for 19 hr. After it had been allowed to warm to room temperature, the bulk of the solvent was evaporated under aspirator pressure. The residue was taken up in 20 ml of methylene chloride, and 1.6 ml of water and 10 ml of saturated sodium chloride were added. The water layer was washed with methylene chloride and the combined organic extracts were dried over sodium sulfate and evaporated. The residual reddish gum was purified by preparative tlc on four 20 × 40 cm plates eluting twice with 1:1 ether–methylene chloride to give 0.3 g of the simple cyclopentadiene adduct, R_f 0.7, 0.10 g (R_f 0.53) and 0.13 g (R_f 0.40) of unidentified compounds, and 1.75 g (78%) of the desired amide, **16**, R_f 0.27. Crystalline white product, mp 141–143°, is obtained by dissolving the amide in ether, and allowing the ether to slowly evaporate: nmr ($CDCl_3$) 2.48 (bt 1 H, J = 7 Hz, 7-CH), 3.34 (bt, 2 H, J = 7 Hz, NCH_2), 3.75 (s, 6 H, OCH_3), 4.98 (m, 2 H, bridgehead CH), 6.49 (t, 2 H, J = 2 Hz, vinyl H), 6.97 (bt, 1 H, J = 7 Hz, NH), 7.3–7.9 (m, 5 H, ArH); ir ($CHCl_3$) 3472 (w), 1715 (sb), 1664 (s) cm^{-1}; ms *m/e* (%) 59 (12, $^+CO_2Me$), 65 (4, $C_5H_5^+$), 77 (33, Ph^+), 78 (18, fulvene), 105 (100, $PhCO^+$), 121 (5, $PhCONH_2$), 134 (7, $PhCONHCH_2^+$), 199 (12, benzamidomethylcyclopentadiene), 224 (15, M − $PhCONH_2$), 286 (1, M − 59), 345 (2, M); exact mass determination, 345.13247 ± 0.003 (calcd for $C_{17}H_{19}N_3O_5$, 345.13247); uv (EtOH) λ_{max} 227 nm (log ϵ 4.06).

Nitrosamide 17: Dimethyl 7-*anti*-*N*-Nitrosobenzamidomethyl-2,3-diazabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate. To 0.134 g (0.39 mmol) of the benzamide, **16**, in 1.5 ml of methylene chloride over 0.153 g (1.86 mmol) of sodium acetate at −78° was added 1.5 ml (0.87 mmol) of a 0.58 *M* solution of dinitrogen tetroxide in methylene chloride at −20°. The mixture was allowed to warm to 0° and stirred for 25 min, during which it became deep yellow. It was then poured into 5 ml of ice–water, and the reaction flask was washed with methylene chloride. The organic phase was washed with methylene chloride. The organic phase was washed twice with 5% aqueous sodium bicarbonate and twice with saturated sodium chloride. The yellow solution was dried over sodium sulfate at 0° and evaporated to give 0.138 g (95%) of the nitrosamide, **17**, a yellow amorphous solid. Although the product was shown by nmr to be essentially pure, it could be further purified by preparative tlc (R_f 0.51) (eluting with 1:1 ether–methylene chloride): nmr ($CDCl_3$) 2.28 (bt, 1 H, J = 7 Hz, 7-CH), 3.73 (s, 6 H, OCH_3), 3.84 (d, 2 H, J = 7 Hz, NCH_2), 4.83 (m, 2 H, bridgehead CH), 6.52 (t, 2 H, J = 2 Hz, vinyl H), 7.2–7.9 (m, 5 H, ArH); ir (CCl_4) 1712 (sb) cm^{-1}; ms *m/e* (%) 59 (47, $^+CO_2CH_3$), 77 (58, Ph^+), 78 (68, fulvene), 105 (100, $PhCO^+$), 122 (23, $PhCO_2H$), 165 (6, 224 − 59), 224 (19, 346 − 122), 287 (2, 346 − 59), 346 (M − N_2), 374 (0.05, M).

Alcohol 19: Dimethyl 7-*anti*-Hydroxymethyl-2,3-diazabicyclo-[2.2.1]hept-5-ene-2,3-dicarboxylate. To 5.0 g (14.5 mmol) of benzamide **16** and 5.0 g (61 mmol) of sodium acetate in 50 ml of methylene chloride at −70° was added 50 ml (29 mmol) of a 0.58 *M* solution of dinitrogen tetroxide in methylene chloride kept at −70° by means of a Dry Ice jacketed dropping funnel. The addition required 15 min, and the white suspension was then allowed to warm to 0° by placing the flask in an ice bath. The mixture began to turn yellow as it warmed, and after it had stirred for 30 min at 0° it was poured into 250 ml of ice–water. The organic layer was washed twice with cold 5% aqueous sodium bicarbonate and twice with cold saturated sodium chloride. The yellow solution was dried in the cold over sodium sulfate and evaporated to give 5.03 g (93%) of almost pure nitrosamide **17** (by nmr).

This crude product was chromatographed on 500 g of activity II Woelm alumina, eluting with ether. Bubbles of gas began to be evolved immediately upon application of the material to the top of the column, and by the time it had traveled half way down the column, the yellow band had all but disappeared. The major fraction (1.8 g) was eluted with ethyl acetate continuously added to the ether. This material was rechromatographed on 200 g of Florisil by elution of 1:1 ether–ethyl acetate. There was obtained 1.2 g (37%) of alcohol **19** as a colorless gum: nmr ($CDCl_3$) 2.51 (bt, 1 H, J = 7 Hz, 7-CH), 2.63 (bs, 1 H, chemical shift concentration dependent, OH), 3.56 (bd, 2 H, J = 7 Hz, OCH_2), 3.83 (s, 6 H, OCH_3), 5.08 (m, 2 H, bridgehead CH), 6.54 (t, 2 H, J = 2 Hz, vinyl H); ir ($CHCl_3$) 3636 (w), 3509 (w, b), 1718 (s, b) cm^{-1}; ms *m/e* (%) 49 (54), 59 (100, $^+CO_2CH_3$), 78 (21, fulvene), 79 (24, $C_6H_7^+$), 96 (56), 165 (3, 224 − 59), 183 (4, M − 59), 211 (9, M − CH_2OH), 224 (3, M − H_2O), 242 (32, M); exact mass determinations, 242.086413 ± 0.002 (calcd for $C_{10}H_{14}N_2O_5$, 242.09025).

Phenylurethane 20: Dimethyl 7-*anti*-(*N*-Phenylcarbamatomethyl)-2,3-diazabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate. To 54.9 mg (0.227 mmol) of alcohol **19** in 0.6 ml of deuteriochloroform in an nmr tube was added 30 μl (*ca.* 0.277 mmol) of phenyl isocyanate and the reaction was followed by nmr. After 24 hr at room temperature the tube was warmed to 50° for 24 hr and finally allowed to stand at room temperature for 3 days. The product was purified by preparative tlc (eluting with 1:1 ether–ethyl acetate) giving 97.3 mg of a gum (R_f 0.46) which solidified on trituration with carbon

(26) C. E. Kaslow and M. M. Marsh, *J. Org. Chem.*, **12**, 456 (1947).

(27) A. Einhorn, E. Bischkopff, C. Ladish, T. Mauermayer, G. Schupp, E. Sprögerts, and B. Szelinski, *Justus Liebigs Ann. Chem.*, **343**, 207 (1905).

tetrachloride. The white solid was washed with carbon tetrachloride and dried under aspirator pressure, giving 72.2 mg (88%): mp 148.2–149.6° (hot stage); nmr ($CDCl_3$) 2.56 (bt, J = 7 Hz, 7-CH), 3.75 (s, 6 H, OCH_3), 4.03 (d, 2 H, J = 7 Hz, OCH_2), 5.02 (m, 2 H, bridgehead CH), 6.47 (t, 2 H, J = 2 Hz, vinyl H), 6.8–7.6 (m, 6 H, ArH + NH); ir ($CHCl_3$) 3460 (w), 1724 (s, b), 1605 (m), cm^{-1}; uv (ethanol) λ_{max} 236 nm (log ϵ 4.25), 273 (2.89), 281 (2.78); ms *m/e* (%) 59 (73, $^+CO_2CH_3$), 65 (14, $C_5H_5^+$), 77 (16, Ph^+), 78 (28, fulvene), 79 (26, $C_6H_7^+$), 91 (40, PhN), 93 (6, $PhNH_2$), 96 (29, hydroxymethylcyclopentadiene), 119 (100, PhNCO), 137 (20, $PhNHCO_2H$), 211 (3, M − $PhNHCO_2CH_2$), 224 (10, M − 137), 242 (9, M − 119, alcohol 100), 361 (2.5, M); exact mass determination, 361.12739 ± 0.005 (calcd for $C_{17}H_{19}N_3O_6$, 361.12737).

Acetate 23: Dimethyl 7-*anti*-Acetoxymethyl-2,3-diazabicyclo-[2.2.1]hept-5-ene-2,3-dicarboxylate. To 0.562 g (3.67 mmol) of bromomethyl acetate[28] in 2.0 ml of dry tetrahydrofuran at −50° was added rapidly 1.7 ml (3.5 mmol) of an 18% solution of cyclopentadienylsodium in tetrahydrofuran (Eastman). A precipitate formed immediately and the tan mixture was stirred for 1 hr at −50°. To it was then added 0.969 g (6.63 mmol) of dimethyl azodicarboxylate in 1.0 ml of tetrahydrofuran. After another 25 min of stirring at −50° the mixture was allowed to warm to 0° and placed in the refrigerator (0°) for 18 hr. It was then allowed to warm to room temperature and let stand for 4 hr. The bulk of the solvent was evaporated under aspirator pressure and 8 ml of methylene chloride and 0.8 ml of water were added. When the sodium bromide had dissolved, 1 ml of saturated sodium chloride was added, the organic phase was separated, and the aqueous layer was washed with 3 × 5 ml of methylene chloride. The combined organic extracts were dried over sodium sulfate and evaporated to an orange gum, which was purified by preparative tlc, eluting twice with ether. The two major bands were just barely separated: R_f 0.50, 0.291 g of the adduct of dimethyl azodicarboxylate with cyclopentadiene, dimethyl 2,3-diazabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate, nmr identical with that of an authentic sample;[29] R_f 0.39, 0.298 g (50%) of acetate **23**; nmr ($CDCl_3$) 2.03, (s, 3 H, CH_3CO), 2.51 (bt, 1 H, J = 7 Hz, 7-CH), 3.78 (s, 6 H, OCH_3), 3.96 (d, 2 H, J = 7 Hz, OCH_2), 5.01 (m, 2 H, bridgehead CH), 6.49 (t, 2 H, J = 2 Hz, vinyl H); ir (CCl_4) 1751 (s), 1718 (s) cm^{-1}; ms *m/e* (%) 43 (66, Ac^+), 59 (35, $^+CO_2CH_3$), 78 (100, fulvene), 138 (3, acetoxymethylcyclopentadiene), 165 (2, 224 − 59), 224 (7, M − AcOH), 225 (2, M − 59), 284 (3, M); exact mass determination, 284.08763 ± 0.008 (calcd for $C_{12}H_{16}N_2O_6$, 284.10083).

Reaction of Alcohol 19 with Lead Tetraacetate. To 55.8 mg (0.23 mmol) of the alcohol, **19**, in 1.0 ml of anhydrous pyridine in an nmr tube was added 106.5 mg (0.24 mmol) of lead tetraacetate. The contents of the tube were mixed thoroughly, giving a very dark red solution. No reaction was evident by nmr after 21 hr standing at room temperature, so the tube was placed in a steam bath at 95–100° for 40 min. At this point the red color had become lighter, and nmr showed starting material and the corresponding acetate, **23**. After another hour at 100° the mixture had become darker and more greenish, and the solvent was evaporated. The residue was taken up in methylene chloride and subjected to preparative tlc (eluting with 1:1 ethyl acetate–ether) giving 13.6 mg (21%) of acetate **23**, nmr identical with that of an authentic sample prepared from acetoxymethylcyclopentadiene and dimethyl azodicarboxylate as described above, and 37 mg (R_f 0.17) of the starting alcohol, **19** (66% recovery). The yield of the acetate on the basis of unrecovered alcohol was thus 62%.

Saturated *anti*-Acetate 24: Dimethyl 7-*anti*-Acetoxymethyl-2,3-diazabicyclo[2.2.1]heptane-2 3-dicarboxylate. After 29.5 mg of 10% palladium-on-charcoal in 3 ml of ethyl acetate had been equilibrated under 1 atm of hydrogen for 5 hr, 91 mg (0.32 mmol) of acetate **23** in 1.5 ml of ethyl acetate was added. Most of the hydrogen was taken up within 3 min; after 20 min the reaction was complete, 7.7 ml (0.27 mmol) of hydrogen having reacted. The mixture was filtered, and the filtrate was evaporated to a colorless gum, which was purified by preparative tlc (ether elution) to give 90 mg (98%) of the saturated acetate, **24** (R_f 0.16). On molecular distillation (135° (0.01 mm)) and trituration with carbon tetrachloride the compound crystallized. Two recrystallizations from benzene–cyclohexane gave an analytical sample: mp 102.5–103.5°; nmr (CCl_4) 1.82 (bs, 4 H, bridge CH_2), 2.03 (s, 3 H, CH_3CO), 2.25 (t, 1 H, J = 8 Hz, 7-CH), 3.73 (s, 6 H, OCH_3), 4.01 (d, 2 H, J = 8 Hz, OCH_2), 4.36 (unresolved m, 2 H, bridgehead CH); ir (CCl_4) 1748 (s), 1715 (s) cm^{-1}; ms *m/e* (%) 43 (94, Ac^+), 59 (52, $^+CO_2CH_3$), 95 (71), 139 (100), 183 (33), 227 (28, M − 59), 286 (89, M); exact mass determination, 286.11648 ± 0.003 (calcd for $C_{12}H_{18}N_2O_6$, 286.11648).

Anal. Calcd for $C_{12}H_{18}N_2O_6$: C, 50.35; H, 6.34; N, 9.79. Found: C, 50.33; H, 6.27; N, 9.76.

Dimethyl 7-*anti*-Diazomethyl-2 3-diazabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (18). To 0.348 g (0.93 mmol) of the nitrosamide, **17**, in 7.0 ml of freshly distilled tetrahydrofuran at 0° was added 54.5 mg (1.01 mmol) of sodium methoxide. The mixture was stirred at 0° until no further increase in the intensity of the ir band at 2070 cm^{-1} was observed between 1.5 and 2 hr. The bulk of the THF was evaporated at 0°, 8 ml of methylene chloride was added, and the mixture was stirred at 0° for 15 min. Filter aid was added and the suspension was filtered through more filter aid. The dark reddish-brown filtrate was dried over sodium sulfate at −20° overnight and filtered again. Nmr integration, using cyclohexane as an internal standard, indicated an approximate yield of 130 mg (60%). This solution of crude diazo compound **18** was diluted with methylene chloride and used without purification for subsequent reactions: nmr ($CDCl_3$) 2.89 (d of m's, 1 H, J = 7 Hz, 7-CH), 3.34 (d, 1 H, J = 7 Hz, N_2CH), 3.79 (s, 6 H, OCH_3), 5.02 (m, 2 H, bridgehead CH), 6.48 (t, 2 H, J = 2 Hz, vinyl H); ir (CH_2Cl_2) 2070 cm^{-1} (s).

Reaction of the Diazo Compound 18 with Acetic Acid. To 87 mg (<0.23 mmol) of the crude nitrosamide, **17**, in 2.0 ml of toluene at −20° was added 0.20 ml (*ca.* 0.59 mmol) of a solution made by dissolving 0.164 g of sodium hydroxide in 1.4 ml of methanol. After 4 hr of stirring at −20°, the mixture was warmed to 0° and extracted with 2 × 2 ml of ice-cold 15% sodium hydroxide. The light yellow toluene layer was dried over potassium hydroxide pellets at −20° and showed a strong band in the ir at 2070 cm^{-1}.

The above solution of **18** was decanted into a flask containing 56 mg of sodium acetate, and 0.10 ml of glacial acetic acid saturated with sodium acetate was added with stirring. During this addition a gas was evolved, and at its conclusion the solution was colorless. The mixture was washed three times with 5% sodium bicarbonate and once with saturated sodium chloride. The toluene layer was dried over sodium sulfate.

Meanwhile, the above sodium hydroxide extracts were extracted twice with ice-cold methylene chloride. The resulting organic layers showed a strong diazo band in the ir. Thus, they were extracted twice with 15% sodium hydroxide and dried over potassium hydroxide pellets at −20° overnight. The yellow solution was treated as before with 68 mg of sodium acetate and 0.10 ml of glacial acetic acid saturated with sodium acetate. The resulting methylene chloride solution was combined with the above toluene solution and evaporated to a gum. Tlc of this material gave 21 mg (35%) of the acetate, **23**.

Tetracyclic Carbamate Ester 26: Dimethyl 7,8-Diazatetracyclo-[3.3.0.$0^{2,4}$.$0^{3,6}$]octane-7,8-dicarboxylate. Method A. A solution of the crude diazo compound **18** (prepared from 0.205 g, 0.55 mmol, of nitrosamide **17**) in *ca.* 100 ml of methylene chloride (freshly distilled from calcium hydride and stored over molecular sieves) was purged with a stream of nitrogen for 30 min in a photolysis well. The solution was then cooled to −78° by means of a Dry Ice–isopropyl alcohol bath and irradiated through a Pyrex filter sleeve with a Hanovia 450-W mercury vapor lamp cooled by methanol at −78° circulating through the lamp insert. The reaction was followed by ir, and after 3 hr the band at 2070 cm^{-1} could no longer be detected. The solution was allowed to warm to room temperature and evaporated to a brown gum. Tlc (elution with 1:1 ether–ethyl acetate) separated this into at least five bands. The first (R_f 0.63) was found to contain 16 mg of methyl benzoate. Two of the other bands could not be identified, but the remaining two gave 18 mg (15% from **17**) of the olefin **27** (R_f 0.46), and 35 mg (28% from **17**) of **26** (R_f 0.36, detectable on the tlc plate only with iodine, not by uv). Recrystallization from cyclohexane gave an off-white solid: mp 100.5–102.5°; nmr ($CDCl_3$) 2.23 (m, 2 H, J = 5.5, 4.7, 3.3, 2.0, and 1.0 Hz, 2- and 3-CH), 2.53 (t of d, 1 H, J = 3.3 and 0.8 Hz, 4-CH), 2.96 (t of t of d, 1 H, J = 4.7, 4.7, and 0.8 Hz, 5-CH), 3.78 (s, 6 H, OCH_3), 5.00 (d of m, 2 H, J = 4.7, 2.0, 1.0, and 0.2 Hz, NCH); ir (CCl_4) 1748 (s), 1709 (s), 1437 (s), 1348 (s), 1323 (s) 1304 (s), 1272 (s), 1120 (s) cm^{-1}; ms *m/e* (%) 39 (30), 59 (100, $^+CH_2CH_3$), 77 (41), 78 (37), 80 (31), 94 (51), 105 (84), 138 (39), 165 (10, M − 59), 224 (13, M); exact mass determination, 224.07970 ± 0.002 (calcd for $C_{10}H_{12}N_2O_4$, 224.07970).

It was later found convenient to filter the crude product through

(28) L. H. Ulrich and R. Adams, *J. Amer. Chem. Soc.*, **43**, 660 (1921).

(29) A. Rodgmann and G. F. Wright, *J. Org. Chem.*, **18**, 465 (1953).

a short column of Woelm alumina I in methylene chloride before tlc, although this procedure seemed to destroy the olefin, **27**. The thus purified **26** from tlc (elution with 4:1 methylene chloride–ether, R_f 0.33) could be sublimed at 80° (0.01 mm).

In one case a comparable yield of the chloride, **28**, was also obtained. This product could not be separated from **27**, but nmr and mass spectrometry of the mixture confirmed the structure: nmr ($CDCl_3$) 2.55 (bt, 1 H, J = 8 Hz, 7-CH), 3.40 (d, 2 H, J = 8 Hz), CH_2Cl), 3.75 (s, 6 H, OCH_3), 5.00 (m, 2 H, bridgehead CH), 6.50 (t, 2 H, J = 2 Hz, vinyl H); ms *m/e* 114 (chloromethylcyclopentadiene), 201 (M − CO_2CH_3), 225 (M − Cl), 260 (M); exact mass determination, 260.06049 ± 0.003 (calcd for $C_{10}H_{13}ClN_2O_4$, 266.05637).

Method B. To 6.7 g (17.9 mmol) of the nitrosamide in 100 ml of tetrahydrofuran (used without purification) at 0° were added 1.52 g (28.1 mmol) of sodium methoxide and 5 drops (*ca.* 0.1 ml) of water. The reaction flask was kept in the dark and stirred at 0° until no further increase in the ratio of the infrared band at 2070 cm^{-1} compared to the carbonyl band was observed (between 7.5 and 8.0 hr). The reaction mixture was then filtered through a sintered glass filter in the dark and the precipitate was washed with dry tetrahydrofuran. The filtrate was poured into a photolysis well fitted with a Pyrex filter and 1 l. of additional dry tetrahydrofuran added. The photolysis unit was immersed in a Dry Ice–isopropyl alcohol bath. After purging the solution with a stream of dry nitrogen, irradiation commenced and continued until the disappearance of the infrared band at 2070 cm^{-1}. The solution was allowed to warm to room temperature and the solvent evaporated. The crude product was purified by column chromatography utilizing 400 g of silica gel and eluting with 10% ether in hexane to give 1.6 g (40% overall from **17**) of pure compound identical in all respects with the previously obtained sample.

Decomposition of the Diazo Compound 18 with Tetrakis[iodo(tri-*n*-butylphosphine)copper(I)]. To 0.206 g (0.55 mmol) of crude nitrosamide, **17**, in 4.0 ml of toluene at 0° was added 0.20 ml of 40% aqueous potassium hydroxide. The mixture was stirred at 0° for 8 hr, near the end of which no further increase in the ir band at 2070 cm^{-1} was observed. The reaction was worked up with 15% sodium hydroxide.

Half (*ca.* 6 ml) of the above toluene solution of **17** was added to 6.6 mg of the copper compex,[30] $[CuI[(n\text{-}Bu)_3]]_4$, in 3 ml of toluene in 20 min. After 1 hr of stirring at room temperature ir showed the absence of a band at 2070 cm^{-1}. The solution was then stirred vigorously in succession with 5 ml of saturated sodium chloride, 3 ml of water, and 5 ml of saturated sodium chloride again, and was then dried over sodium sulfate. Evaporation of the solvent and tlc of the gummy residue (eluting with 1:1 ether–methylene chloride) gave 9.8 mg (from **17**, 8%), R_f 0.45, of the olefin, **34**, 1,2-bis(dimethyl-2,3-diazabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate-7-yl)ethene, as the only identifiable product: nmr ($CDCl_3$) 2.8 (m, 2 H, 7-CH), 3.77 nd 3.72 (singlets, 12 H, OCH_3), 4.90 (m, 4 H, bridgehead CH), 5.2 (m, 2 H, vinyl H), 6.44 (m, 4 H, bridge vinyl H); ms *m/e* (%) 59 (100, $^+CO_2CH_3$), 77 (44), 91 (56), 95 (39), 105 (95), 389 (16, M − 59), 448 (12, M); ir ($CHCl_3$) 1715 (s, b), 1439 (s), 1333 (s, b) cm^{-1}; exact mass determination, 448.15940 ± 0.004 (calcd for $C_{20}H_{24}N_4O_8$, 448.15940).

Decomposition of the Diazo Compound 18 with Cupric Sulfate. A solution of crude **18** in *ca.* 11 ml of toluene, obtained as described in the previous experiment from 0.198 g (0.53 mmol) of the nitrosamide, **17**, was added to a stirred suspension of 0.214 g (1.34 mmol) of anhydrous cupric sulfate in 50 ml of ether. The addition was spread out over 7 hr, and the mixture was then allowed to stir for 14 hr. It was then filtered, and the filtrate was evaporated to a yellowish gum. It showed no band at 2070 cm^{-1}. Tlc, eluting with 1:1 ether–methylene chloride, gave 7.2 mg (R_f 0.19) of what appeared to be a 50:50 mixture of the aldehyde, **21**, dimethyl 7-*syn*-formyl-2,3-diazabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate, and an unidentified compound: nmr of **21** ($CDCl_3$) 2.95 (m, 1 H, 7-CH), 3.79 (s, 6 H, OCH_3), 5.32 (m, 2 H, bridgehead CH), 6.55 (t, 2 H, J = 2 Hz, vinyl H), 9.41 (d, 1 H, J = 2 Hz, CHO); ir ($CHCl_3$) 1721 (b) cm^{-1}; ms *m/e* (%) 59 (100, $^+CO_2Me$), 94 (12, formylcyclopentadiene), 181 (2, M − 59), 211 (3, M − CHO), 240 (5, M).

Azo Compound 6: 7,8-Diazatetracyclo[3.3.0.$0^{2,4}$.$0^{3,6}$]oct-7-ene. In 1.0 ml of absolute methanol which had been degassed by several pump–nitrogen flush cycles was dissolved 0.102 g (0.45 mmol) of the tetracyclic carbamate, **26**. To the colorless solution was added 0.329 g (5.9 mmol) of potassium hydroxide, and the mixture was stirred for 3 hr. To the resulting tan suspension was added 2.0 ml of water, and the mixture was stirred until a light brown solution had formed. This was then neutralized to litmus with dilute hydrochloric acid (1 ml of concentrated acid to 9 ml of water), followed by the addition of 2 *M* aqueous cupric chloride solution dropwise until gas ceased to be evolved and no further precipitate was formed (0.40 ml, 0.8 mmol). The suspension was stirred for 30 min and filtered by suction in a sintered glass funnel, and the dark reddish-brown cake was washed with minimum amounts of water, ethanol, and methylene chloride. A second crop was precipitated by addition of more cupric chloride solution to the filtrate and collected in the same way. The combined yield of the air-dried complex was 83 mg (90%).

To 0.45 g of the crude copper complex, obtained from 0.404 g (1.80 mmol) of the tetracyclic carbamate, **26**, as described above, in 8.0 ml of methylene chloride was added 4.0 ml (15 mmol) of 15% aqueous sodium hydroxide. The mixture was stirred vigorously for 20 min. The methylene chloride layer was separated from the green aqueous sludge and filtered by gravity. The aqueous phase was washed with 4 × 10 ml of methylene chloride, filtering each extract and combining it with the others. The combined organic layers were dried over sodium sulfate and potassium hydroxide pellets at 0°, filtered, and evaporated at ~10°. The residual oil was reevaporated once with pentane, and the resulting solid was extracted with pentane, filtering each extract through a cotton plug. The combined pentane solutions were cooled to −78° under nitrogen and allowed to stand at −78° until crystallization was complete. The mother liquor was pipetted into another flask under nitrogen, and the light yellowish crystals were dried by applying aspirator pressure and allowing the material to warm briefly to room temperature. In this manner, 0.130 g of the azo compound, **6**, was collected. A second crop was obtained by concentrating the mother liquor, 12.5 mg. The yield of **6** was thus 0.143 g (75% from the tetracyclic carbamate, **26**). The product appeared to be hygroscopic, and was stored in a desiccator under nitrogen in the freezer (−15°). For the latter reason, a melting point could not be determined: nmr ($CDCl_3$) 2.19 (m, 3 H, cyclopropyl H), 2.79 (m, 1 H, 5-CH), 5.74 (m, 2 H, NCH); ir (CCl_4) 3040 (s), 1493 (m), 1230 (s) cm^{-1}; uv (cyclohexane) λ_{max} *ca.* 357 nm sh (log ϵ 2.37), 363 (2.46), 368 (2.46), 372 (2.49), 381 (2.40); exact mass determination 106.05288 (calcd for $C_6H_6N_2$, 106.05306).

Acknowledgment. We wish to thank the National Science Foundation for their generous support of our program. We also thank the Foundation for their contribution toward the establishment of our spectroscopic instrumentation center.

(30) G. B. Kauffman and L. A. Teter, *Inorg. Syn.*, 7, 12 (1963).