

Direct and Indirect Trapping of Isomeric Monosubstituted Bicyclo[4.2.0]octadienes with Triazolinediones. Photocyclization and Ag⁺-Catalyzed Rearrangement of the Derived Adducts as a Route to Functionalized 9,10-Diazasnoutanes¹

Leo A. Paquette,* Donald R. James,^{2a} and Gary H. Birnberg^{2b}

Contribution from the Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210. Received May 21, 1974

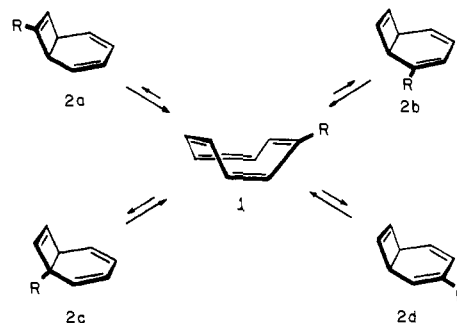
Abstract: The direct cycloaddition of triazolinediones to cyclooctatetraene and a number of its monosubstituted derivatives produces tricyclic adducts resulting from dipolar addition to the monocyclic ring system and/or tetracyclic adducts arising from $\pi 4_s + \pi 2_s$ bonding to the bicyclo[4.2.0]octatriene valence tautomers. Controlling factors appear to be the polarizability and electron density inherent in the [8]annulene, the facility with which valence isomerism proceeds, and the relative ordering of the rates of bicyclo[4.2.0]octatriene formation (k_1) and the subsequent Diels-Alder reaction (k_2). In the case of monoalkyl substitution, $k_2 > k_1$, and closure to the 7-substituted bicyclic valence tautomer is kinetically favored such that a single tetracyclic adduct can be obtained. The presence of halogens and electron-withdrawing groups reverses the kinetic order ($k_1 > k_2$) such that a wider array of tetracyclic adducts is produced. By prior bromination of the cyclooctatetraene, reaction with the triazolinedione, and subsequent debromination with zinc-copper couple, the undesired formation of tricyclic adducts is completely arrested, and access to a wider variety of substituted tetracyclic adducts is gained. In several cases, all four possible isomeric addition compounds have been isolated by judicious manipulation of these two sets of reaction conditions. Sensitized irradiation of the dienes leads to variously monosubstituted 9,10-diazabasketanes in all cases except for the bromo derivatives where decomposition was witnessed. These cubyl systems produce 9,10-diazasnoutanes upon Ag⁺-catalyzed rearrangement. This reaction is sensitive to the nature and position of substitution, particularly when this group is cyano. A general overview of substituent effects on the $\pi 2_s + \pi 2_s$ photocyclization and the transition metal catalyzed bond reorganization is given.

Recently, we have described a convenient procedure for the transformation of the cyclooctatetraene (COT) nucleus into the semibullvalene ring system on a preparative scale.³ This involved bromination of COT, reaction with *N*-phenyltriazolinedione (PTAD), subsequent debromination, photocyclization, Ag⁺-catalyzed rearrangement, and elimination of the latent azo functionality. As a further test of the generality of this synthetic method, we have now investigated its application to the preparation of various monosubstituted semibullvalenes. This study was prompted by the extensive theoretical interest which has been directed to an *a priori* assessment of the equilibrium displacements which would arise from framework substitution of this twofold degenerate system.⁴ Monofunctionalized semibullvalenes hold particular fascination, because the double degeneracy of the parent hydrocarbon eliminates the cumbersome feature of preferential ground-state weighting toward one of the constituent isomers as seen, for example, in cycloheptatriene-norcaradiene⁵ and cyclooctatriene-bicyclo[4.2.0]octadiene valence isomerizations.⁶ Also, the activation energy for Cope rearrangement in semibullvalene is less than 6 kcal/mol⁷ so that equilibration between the pair of isomers occurs very readily.

In seeking to extend the scope of the synthetic sequence to monosubstituted COT's, we were immediately drawn to consider three important factors: (a) control of positional selectivity; (b) minimization of 1,4-cycloaddition to the monocyclic COT nucleus; and (c) elucidation of the effects of various substituents on the photochemical $\pi 2_s + \pi 2_s$ closure and transition metal catalyzed $\sigma 2_a + \sigma 2_a$ rearrangement. This report documents the search for and discovery of methodology for the controlled synthesis of monosubstituted 9,10-diazabasketanes. Intriguing findings relating to point c are also detailed. The ensuing paper⁸ addresses itself to the ultimate generation of the semibullvalenes, their variable-temperature pmr features, and the equilibrium imbalances which are observed.

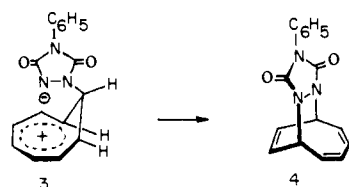
Results and Discussion

Direct Addition. The tub conformation of the cyclooctatetraene ring (**1**) deters attainment of planarity by neighboring double bonds. Because of this, the [8]annulene framework does not provide a conjugated diene unit properly aligned for effective participation in the Diels-Alder reaction. Rather, disrotatory ring closure to bicyclo[4.2.0]octatriene (**2**, R = H) frequently precedes $\pi 4_s + \pi 2_s$ cycloaddition. This occurs despite the requisite surmounting of an energy barrier greater than 20 kcal/mol⁹ because the bicyclic intermediate affords a quasi-planar diene system which greatly facilitates capture by the dienophile.

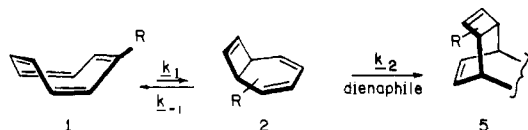


In contrast to most dienophiles, PTAD exhibits a predilection for 1,4-cycloaddition to the monocyclic ring system.¹³⁻¹⁵ Such behavior has been attributed to the high reactivity of the azo compound and particularly to its ability to enter into dipolar reactions. As noted by Huisgen,¹⁵ the incursion of this pathway is the likely result of homotropylum zwitterion (**3**) intervention and its subsequent intramolecular charge annihilation to give **4**. Ample analogy exists to support this hypothetical scheme.¹⁶ For the present purposes, this reaction mode is undesirable. However, if the polarizability and electron density of the COT nucleus lends

itself to such 1,4-cycloaddition,¹⁷ one might expect ring substituents to play a significant role in directing the cycloaddition chemistry. This has been found to be the case (*vide infra*).

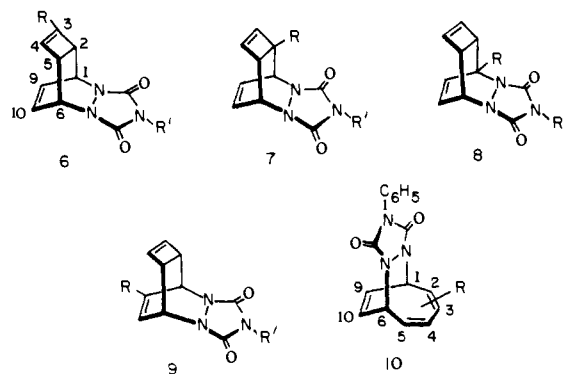


As concerns the prior valence isomerization of a mono-substituted cyclooctatetraene, the possibility exists that four structurally different bicyclo[4.2.0]octatrienes (**2a-d**) can be formed. This potentially complicating feature is compounded further by a subtle mechanistic changeover as the nature of the R group is altered. In those cases where R is methyl, ethyl, or phenyl, ring closure to **2** is recognized to be rate determining, *i.e.*, $k_2 > k_1$.^{10b,14,18} Intriguingly, closure to 7-substituted bicyclo[4.2.0]octatriene **2a** is kinetically favored in these examples, and it is this isomer which is trapped predominantly or exclusively by the dienophile as rapidly as it is formed. Highly regioselective or fully regio-specific adduct formation is observed. In contrast, halogeno-, cyano-, and carbomethoxycyclooctatetraene undergo rate-determining cycloaddition ($k_1 > k_2$) with little interference from competing homotropylium ion formation, experience disrotatory closure to a greater variety of bicyclo[4.2.0]octatrienes (*vide infra*), and consequently give rise in certain cases (*viz.*, when the dienophile is highly reactive and nondiscriminating) to a broader spectrum of adducts.



In any event, the need existed to establish that substitution by different R groups is a sufficient perturbation to modify the reactivity of monofunctionalized COT's toward triazolinediones. To this end, phenylcyclooctatetraene was allowed to react with *N*-methyltriazolinedione (utilized in place of PTAD in this instance to enhance the solubility of the adducts) in refluxing ethyl acetate; the adduct **6-C₆H₅** could be isolated in 84% yield after column chromatography. Its ultraviolet maxima (in ethanol) at 248 (ϵ 20,000) and 282 nm (450) accord well with the presence of a styrene chromophore. That the phenyl substituent resides on the cyclobutene double bond is firmly established by the strong differential shielding of H₂ and H₅ (δ 3.62 and 3.28, see Experimental Section) and the appearance of the remaining cyclobutene olefinic proton (H₄) as a singlet at δ 6.10. Careful processing of the mother liquors obtained from the recrystallization (2-propanol) of **6-C₆H₅** led to the isolation of an isomeric adduct identified as **8-C₆H₅** (<1% yield). The fact that this crystalline solid exhibits an olefinic/methine proton ratio of 4:3 and displays a single bridgehead absorption unambiguously rules out the possibility that it be formulated as **7** or **9**.

Methyl-, acetoxymethyl-, and methoxymethylcyclooctatetraene comprise an interesting set of compounds. In experiments comparable to that described above, methylcyclooctatetraene underwent cycloaddition with PTAD to give adduct **6-CH₃** in low (11%) yield. Accompanying this substance was a mixture of two isomeric tricyclic adducts **10-CH₃** formed likewise in 11% yield. These latter substances were not separated, although one isomer was noted to be enriched upon fractional recrystallization. The com-



bined pmr spectrum shows a broad olefinic signal of area 5 at δ 5.63–6.27, a multiplet at δ 4.83–5.18 for the two bridgehead protons, and two broadened singlets for the environmentally different methyl groups at δ 2.18 (30% of 3 H) and 1.93 (70%). Like its phenyl counterpart, **6-CH₃** has a pmr spectrum consisting of only three olefinic protons, one of which is a somewhat broadened singlet because of its unique position as the sole cyclobutene hydrogen. It is probable that the diminished yields in this instance arise as a result of the concomitant involvement of PTAD in the ene reaction. We have been unable to establish this point, however, perhaps because of further cycloadditions to the new tetraene with formation of high molecular weight products.

Acetoxymethylcyclooctatetraene exhibited behavior rather comparable to that of the methyl compound. In addition to the expected formation of **6-CH₂OAc** (32%), a mixture of three isomers of **10-CH₂OAc** was successfully isolated in 10% yield. Somewhat surprisingly in view of these findings, methoxymethylcyclooctatetraene in the presence of PTAD afforded not only **6-CH₂OCH₃** (42%), but **7-CH₂OCH₃** (14%) and **8-CH₂OCH₃** (7.5%) as well. These products were characterized primarily by pmr spectroscopy, and the relative amounts of each isomer were obtained after lengthy chromatographic separation. Isomer **7-CH₂OCH₃** shows relevant signals at δ 5.95–6.42 (m, 4, olefinic), 4.92–5.20 (m, 2, bridgehead), and 2.95 (d, $J = 5$ Hz, H₅) in addition to the other requisite peaks. Adduct **8-CH₂OCH₃** is similarly characterized by the presence of four olefinic protons (m, δ 5.85–6.20); however, it differs spectrally from its congeners by virtue of its single bridgehead proton (m, δ 4.95–5.20) and the ubiquity of H₂ and H₅ (d, $J = 2.5$ Hz, δ 3.33). Also isolated from this reaction mixture were two isomers of **10-CH₂OCH₃** (17%); these were not examined further because of their tangential relationship to the title goal. This abrupt changeover in product distribution was not entirely expected for methoxymethylcyclooctatetraene although comparable involvement of several isomeric bicyclo[4.2.0]octatrienes (**2**) has been noted in other examples to be discussed. It might be thought that replacement of a methyl hydrogen by OAc and OCH₃ groups would not eventuate in widely differing imbalances in either k_1 , k_2 , or the capability for valence isomerization to **2a**, **2b**, and **2c**. Yet, for reasons which remain unclear, acetoxymethylcyclooctatetraene is aligned closely to methylcyclooctatetraene in reactivity toward PTAD, while methoxymethylcyclooctatetraene is not.

The widely differing electronegativities of the halogen atoms do affect the valence isomerization tendencies of the halocyclooctatetraenes, and this is reflected chiefly in the relative rates at which the respective monocyclic and bicyclic forms react with PTAD. F-COT is transformed in 95% yield exclusively to **7-F**.¹⁹ The product composition obtained by comparable reactions of Cl-COT consists of **6-Cl** (27%) and **7-Cl** (30%).¹⁴ When the transition is made to the bromo derivative, adducts of type **6** (12%) and **7** (25%) are

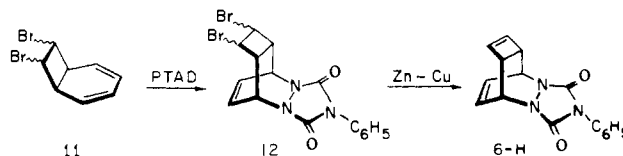
still encountered, but direct competition from the open cyclooctatetraene now operates, and 10% of **10** (as the 9-bromo isomer) is also isolated.¹⁴ This latter situation is also the case for I-COT which at 80° in ethyl acetate gives 13% of **6-I** together with 2-iodo **10** (5.0%) and 9-iodo **10** (3.5%).¹⁵

The exclusive formation of **7-F** from F-COT is not paralleled by electron-withdrawing, but conjugatively interactive groups, such as carbomethoxy and cyano. When carbomethoxycyclooctatetraene was allowed to react with PTAD and the unpurified product mixture was examined by pmr spectroscopy, the presence of multiple products was clearly denoted. Careful chromatographic separation afforded pure **6-COOCH₃** (8%) whose structure was soundly related to those adducts of similar substitution plan by appropriate spectral comparison (see Experimental Section). Also isolated were the isomeric adducts **8-COOCH₃** (27%), **9-COOCH₃** (2%), and **10-COOCH₃** (8%). The latter was a single compound, but efforts were not made to establish the specific site of substitution. The pmr spectrum of **8-COOCH₃** shows five aromatic protons at δ 7.40, olefinic protons in the ratio of 1:3 at δ 6.75 and 6.10, one bridgehead hydrogen at δ 5.05, a methyl singlet at δ 3.92, and two aliphatic hydrogen atoms, one at δ 3.65 and the other at 3.45. By way of comparison, **9-COOCH₃** exhibits pmr features confirming the presence of three olefinic protons, one appearing as a doublet of doublets substantially downfield shifted (δ 7.06) and the other two as a sharp singlet at δ 6.00. The pair of bridgehead hydrogens are also rather widely separated (mult at δ 5.58 and 5.18). It follows that the cyclobutene double bond is unsubstituted, and that the carbomethoxy group is positioned at a bicyclooctene trigonal center.

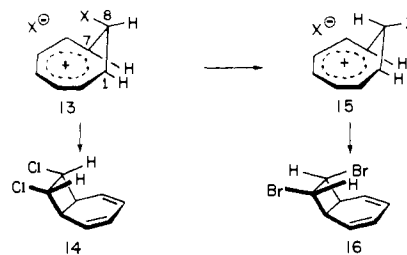
PTAD reacts with CN-COT to give all four possible tetracyclic adducts: **6-CN** (26%), **7-CN** (24%), **8-CN** (31%), and **9-CN** (2-4%). The formation of tricyclic adduct was not detected. The pmr features of the individual isomers are detailed in the Experimental Section. Owing to the presence of **9-CN** in low concentration levels, its isolation in highly purified form was not possible by this route. However, utilization of the indirect method provides **9-CN** as the major product. Full characterization of this isomer was consequently made feasible under the latter conditions. We consider it noteworthy that carbomethoxycyclooctatetraene finds it possible to experience competitive direct addition to its monocyclic form to the extent of at least 10%, whereas CN-COT exhibits no such behavior. We offer no explanation of these findings at this time but note only that, in line with the assumption that polarizability and electron density considerations encourage direct attack of PTAD upon an [8]annulene, MeO-COT affords in 60% yield two tricyclic adducts of type **10** but no tetracyclic products. The appreciably enhanced reactivity of MeO-COT toward electrophilic reagents has previously been demonstrated^{16a,17} and is further supported by the present demonstration of its susceptibility for direct 1,4-addition to PTAD.

Indirect Addition. Huisgen and his coworkers have showed that cyclooctatetraene resides chiefly (99.99%)^{10b} in its monocyclic form even when heated to 100°. However, its products of chlorination and bromination, the 7,8-dihalo-1,3,5-cyclooctatrienes, enjoy far less impedance to valence isomerization. In fact, the cis and trans forms of these dihalides are appreciably more bicyclic (as in **11**) than monocyclic at room temperature.^{6a,20} Such substantially increased levels of bicyclo[4.2.0]octadiene tautomers, in conjunction with the practical feasibility of dehalogenative reintroduction of the cyclobutene double bond, have led earlier investigators to adopt this method for the efficient indirect construction of bicyclo[4.2.0]octatriene cycload-

ducts.²¹ High yield sequences of this type, adopted also by us for the preparation of **6-H** in our original semibullvalene synthesis,^{3a} bypass entirely the sometimes complicating feature of direct 1,4-attack by PTAD on the eight-membered ring. The behavior of COT in this latter respect is particularly disadvantageous.¹³



At the mechanistic level, the halogenation of COT is now recognized to proceed by initial bonding of chlorine or bromine with generation of an *endo*-8-halohomotropylum ion (**13**).^{16b,c,22} This may be preceded by transient intervention of the tub-shaped classical cation, a low-energy conformational change which occurs readily to develop 1,7-interaction and gain access to homoaromatic delocalization.^{16a} Passage to cis dihalide **14** occurs by exclusive *endo* attack of the halide gegenion at C₁ as a consequence of electron density factors existent in the orbital construct of the C₁C₇ bond.^{16b} The incursion of trans product **16** seemingly results because of isomerization of **13**, presumably by ring inversion, prior to covalent bonding to the second halide ion.^{16,22}



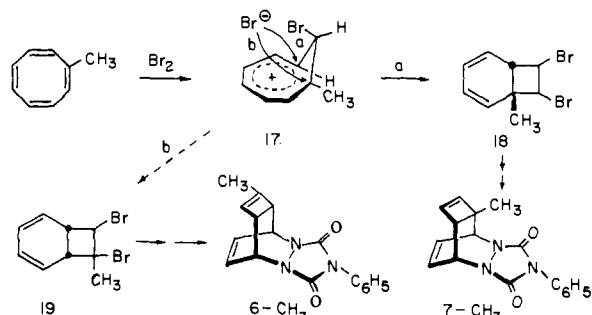
The presence of a substituent on the COT ring will unquestionably control the energetics of initial bromine attack, but it was unclear to what extent and, in some cases, in what direction this effect would operate. Moreover, given that selectivity did arise in the generation of the four possible *endo*-8-bromo-*x*-substituted homotropylum ions, little information was available on the consequences of the resulting dissymmetry (in three of the four cations) upon competitive bromide ion capture at C₁ and C₇.²³ The situation is illustrated below for Me-COT. If, as with chlorosulfonyl isocyanate,^{16a} electrophilic attack operates predominantly at C₂ because of incipient charge stabilization by the methyl group, intermediate **17** will obtain. Irrespective of the question relating to retention or loss of configuration at C₈, covalent bonding of bromide ion can in principle occur to give **18**, **19**, or the pair of dibromides. Subsequent reaction with PTAD and debromination with zinc-copper couple should eventuate in the formation of **6-CH₃** and **7-CH₃**. When Me-COT was treated under these conditions, **7-CH₃** was the only product isolated (30%). It is important to recall that there was no indication of this particular isomer in the direct addition experiments. If such impressive crossover in positional selectivity is intrinsically associated with the indirect addition method, the possibility of controlled accessibility to certain of the various isomers **6-9** could be realized.

In agreement with this favorable augury, investigation of a number of additional examples vindicated the utility of the process. The data are summarized in Table I. We wish to direct attention specifically to the striking contrasts realized in the phenyl, acetoxymethyl, cyano, and bromo studies. Whereas PTAD reacts with Ph-COT to provide **6-C₆H₅**

Table I. Results of Direct and Indirect Addition of PTAD to Various Monosubstituted Cyclooctatetraenes

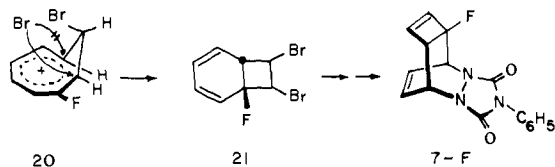
R	Mode of addition	Adducts, %				
		6	7	8	9	10
C ₆ H ₅	Direct	84		~1		
	Indirect		6		9	
CH ₃	Direct	11				11 ^a
	Indirect		30			
CH ₂ OAc	Direct	32				10 ^b
	Indirect		10	35	10	
CH ₂ OCH ₃	Direct	42	14	7.5		17 ^a
	Indirect		23	32		
COOCH ₃	Direct	8		27	2	10 ^c
	Indirect			31		
CN	Direct	26	24	31	2-4	
	Indirect		12	9	49	
F	Direct		95			
	Indirect		90			
Cl	Direct ^d	27	30			
	Indirect		25			10 ^c
Br	Direct	12				
	Indirect				28	
I	Direct ^e	13				8.5 ^a

^a Two isomers present. ^b Three isomers formed. ^c A single isomer detected. ^d See ref 14. ^e See ref 15.



and trace amounts of 8-C₆H₅, the bromination-debromination sequence furnishes the remaining two isomers 7-C₆H₅ and 9-C₆H₅. Similarly, in the related case of AcOMe-COT where direct addition affords 6-CH₂OAc, the alternative route furnishes 7- (10%), 8- (35%), and 9-CH₂OAc (10%) in good overall yield. As already pointed out, the product distribution from CN-COT is such that the formerly elusive 9-CN is isolated at the 49% level. The bromo derivative is roughly comparable in that it also reacts so as to provide synthetic entry to 9-Br (28%) (see Table II).

F-COT proved to be a source of disappointment in that both methods led only to 7-F. Should this electronegative substituent, as anticipated, deter formation of the 1-fluoro-endo-8-bromohomotropylum ion intermediate (compare 17), our findings suggest that this adduct arises from regio-specific carbon-bromine bonding in cation 20. This course of events isolates the fluorine atom from the conjugated diene unit in 21 such that it can affect only indirectly the ensuing cycloaddition and debromination steps.

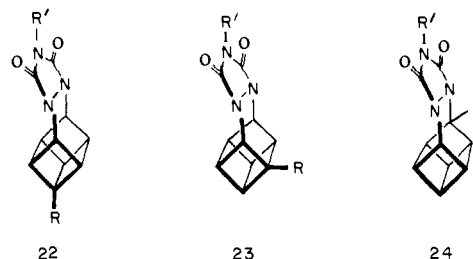


Photocyclization Reaction. Following the discovery by Schenck and Steinmetz²⁴ of the sensitized intramolecular photocyclization of dicyclopentadiene to pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{5,8}]decane, a number of types of polycyclic cage hydrocarbons have been synthesized by this technique.²⁵ Notably lacking in more recent studies was an examination of the effect of varying electronic features at ei-

ther double bond upon the reaction course. Environmental alternatives such as this usually involve changes in the nature and location of one or more substituents. Owing to the wide range of compounds made available by the preceding cycloaddition studies and our need for suitably functionalized 9,10-diazabasketanes, an investigation of adduct triplet excited-state photochemistry was undertaken in an effort to gain information about the generality of such a process within a given structural type.

Acetone-sensitized photocyclization of 6-H resulted in smooth conversion to 4-phenyl-2,4,6-triazahexacyclo[5.4.2.0^{2,6}.0^{8,11}.0^{9,13}.0^{10,12}]tridecane-3,5-dione (22-H) in 84% yield.^{21c,26} The characterization of 22-H is founded on its pmr spectrum which consists of a multiplet (5 H) centered at δ 7.45, a septet (2 H) at 5.08, and quintets at 3.78 (4 H) and 3.20 (2 H).

Each of six 3-substituted tetracyclic adducts 6 was similarly irradiated on a preparative scale through Vycor or Corex under nitrogen in acetone or acetone-benzene solvent systems.²⁷ It was immediately clear from inspection of the photochemical reaction mixtures that with but one exception closure to the related 9,10-diazabasketane 22 had occurred. These substances are quite stable and may be purified without undue difficulty by standard column chromatographic techniques. Isolated yields ranged from 24% in the case of 22-CH₂OCH₃ to 92% for 22-CN. In most instances, this photochemical step was repeated several times; however, we do not yet consider the yields optimized.²⁷ The results are collected in Table III.



The exception is 6-Br whose chemical response to photoinduced sensitization under a variety of conditions is to suffer gradual decomposition with production of an amorphous black material. This behavior was also noted for 7-Br and 9-Br. No evidence for $\pi_2s + \pi_2s$ closure was obtained, suggesting that the bromine substituent, regardless of its position, is capable of effectively deterring such C-C bond formation.

The same reaction conditions were applied to six 2-substituted adducts of type 7, exclusive of the bromo derivative. Once again, ready closure to the basketanes was observed, and conversions in the order of 34-93% were realized. It is of some interest that the photocyclization is not affected by the presence of a fluorine substituent at C₂, as 23-F was isolated in 56% yield. Since those tetracyclic adducts which possess an R group at C₉, *i.e.*, 9, are likewise subject to photochemical isomerization to basketane 23, a comparison of the relative efficiencies of the two pathways was made in the phenyl series. In our hands, the conversion of 7-C₆H₅ to 23-C₆H₅ (42%) was exactly twice as good as the process beginning with 9-C₆H₅ (21%). For reasons of convenience, 7-CH₂OAc and 9-CH₂OAc were invariably handled as a mixture. In this instance, 23-CH₂OAc was obtained in 72% yield, and the two dienes gave qualitative indication of comparable reaction rates.

When samples of 8-CH₂OAc, -CH₂OCH₃, -COOCH₃, and -CN were irradiated in comparable fashion, conversion to a single photoproduct was observed without exception in yields ranging from 35 to 70%. From the absence of olefinic

Table II. Physical Data for the 7,8-Diazatricyclo[4.2.2.0^{2,5}]deca-3,9-diene-7,8-dicarboximides

Compd	Pmr (δ , CDCl ₃ , 60 or 100 MHz)	Analysis, %	
		Calcd	Found
6-C ₆ H ₅	7.33 (s, 5, phenyl), 6.21 (s, 1, H ₁), 5.86-6.36 (m, 2, H ₉ and H ₁₀), 4.87-5.36 (br m, 2, H ₁ and H ₆), 3.62 (t, $J = 4$ Hz, 1, H ₂), 3.28 (t, $J = 4$ Hz, 1, H ₃), and 3.04 (s, 3, methyl) ^a	For C ₁₇ H ₁₅ N ₃ O ₂ : C, 69.61; H, 5.15; N, 14.33	C, 69.36; H, 5.29; N, 14.48
7-C ₆ H ₅	7.19-7.60 (m, 10, phenyl), 5.99-6.63 (br m, 4, olefinic), 4.86-5.33 (br m, 2, H ₁ and H ₆), and 3.57 (d, $J = 4.5$ Hz, 1, H ₃) ^a	For C ₂₂ H ₁₇ N ₃ O ₂ : C, 74.35; H, 4.82; N, 11.82	C, 74.26; H, 4.98; N, 11.89
8-C ₆ H ₅	7.32-7.64 (m, 5, phenyl), 6.64 (d, $J = 8$ Hz, 1, H ₉), 6.20 (dd, $J = 6$ and 8 Hz, 1, olefinic), 6.02 (d, $J = 3$ Hz, 1, olefinic), 5.82 (d, $J = 3$ Hz, 1, olefinic), 5.04 (dd, $J = 4$ and 6 Hz, 1, H ₆), 3.32-3.48 (m, 2, H ₂ and H ₃), and 2.90 (s, 3, methyl) ^b	For C ₁₇ H ₁₅ N ₃ O ₂ : C, 69.61; H, 5.15; N, 14.33	C, 69.29; H, 5.35; N, 14.12
9-C ₆ H ₅	7.36 (m, 10, phenyl), 6.28 (dd, $J = 2$ and 6 Hz, H ₁₀), 5.98 (d, $J = 3$ Hz, 1, H ₃ or H ₄), 5.86 (d, $J = 3$ Hz, 1, H ₃ or H ₄), 5.36-5.46 (m, 1, H ₁), 5.08 (dd, $J = 4$ and 6 Hz, 1, H ₆), and 3.26-3.50 (m, 2, H ₂ and H ₃) ^b	For C ₂₂ H ₁₇ N ₃ O ₂ : C, 74.35; H, 4.82; N, 11.82	C, 74.27; H, 5.17; N, 11.91
6-CH ₃	7.40 (br s, 5, phenyl), 6.05-6.30 (m, 2, H ₉ and H ₁₀), 5.60-5.75 (m, 1, H ₁), 4.98 (pent, $J = 4$ Hz, 2, H ₁ and H ₆), 2.98-3.25 (m, 2, H ₂ and H ₃), and 1.57 (s, 3, methyl) ^a	For C ₁₇ H ₁₅ N ₃ O ₂ : C, 69.61; H, 5.15; N, 14.33	C, 69.30; H, 5.12; N, 14.24
7-CH ₃	7.42 (s, 5, phenyl), 5.85-6.50 (m, 4, olefinic), 4.66 and 5.05 (m, 1 H each, H ₁ and H ₆), 2.88 (d, $J = 4$ Hz, 1, H ₃), and 1.50 (s, 3, methyl) ^a	For C ₁₇ H ₁₅ N ₃ O ₂ : C, 69.61; H, 5.15; N, 14.33	C, 69.44; H, 4.94; N, 14.48
6-CH ₂ OAc	7.42 (m, 5, phenyl), 6.02-6.32 (m, 2, H ₉ and H ₁₀), 5.83 (br s, 1, H ₁), 4.70-5.25 (m, 2, H ₁ and H ₆), 4.41 (s, 2, -OCH ₂ -), 3.05-3.45 (m, 2, H ₂ and H ₃), and 2.02 (s, 3, methyl) ^b	For C ₁₉ H ₁₇ N ₃ O ₄ : C, 64.95; H, 4.88; N, 11.96	C, 64.64; H, 4.98; N, 11.99
7-CH ₂ OAc } 9-CH ₂ OAc }	7.31 (s, 5, phenyl), 5.80-6.28 (m), 5.88 (s, H ₃ and H ₄), 4.78-5.10 (m), 4.30-4.65 (m), 3.20-3.40 (m), 2.90-3.05 (d with fine splitting), 2.07 and 2.03 (s, methyls) ^c	For C ₁₉ H ₁₇ N ₃ O ₄ : <i>m/e</i> 351.1219	<i>m/e</i> 351.1224
8-CH ₂ OAc	7.43 (s, 5, phenyl), 6.1-6.3 (m, 2, H ₉ and H ₁₀), (s, 2, H ₃ and H ₄), 4.80-5.20 (m, 1, H ₆), 4.91 (s, 2, -OCH ₂ -), 3.20-3.52 (m, 2, H ₂ and H ₃), and 2.10 (s, 3, -CH ₃) ^a	For C ₁₉ H ₁₇ N ₃ O ₄ : C, 64.95; H, 4.88; N, 11.96	C, 64.66; H, 4.79; N, 12.09
6-CH ₂ OCH ₃	7.40 (m, 5, phenyl), 6.08-6.20 (m, 2, H ₉ and H ₁₀), 5.82 (br s, 1, H ₁), 4.86-5.14 (m, 2, H ₁ and H ₆), 3.76 (m, 2, -OCH ₂ -), 3.27 (s, 3, methoxyl), and 3.06-3.40 (m, 2, H ₂ and H ₃) ^b	For C ₁₈ H ₁₇ N ₃ O ₃ : C, 66.86; H, 5.30; N, 13.00	C, 66.53; H, 5.33; N, 12.92
7-CH ₂ OCH ₃	7.48 (m, 5, phenyl), 5.95-6.42 (m, 4, olefinic), 4.92-5.20 (m, 2, H ₁ and H ₆), 3.75 (center of AB, $J_{AB} = 9$ Hz, 2, -OCH ₂ -), 3.43 (s, 3, methoxyl), and 2.95 (d, $J = 5$ Hz, 1, H ₃) ^a	For C ₁₈ H ₁₇ N ₃ O ₃ : C, 66.86; H, 5.30; N, 13.00	C, 66.56; H, 5.29; N, 12.99
8-CH ₂ OCH ₃	7.42 (m, 5, phenyl), 5.85-6.20 (m, 4, olefinic), 4.95-5.20 (m, 1, H ₆), 4.18 (center of AB, $J_{AB} = 11$ Hz, 2, -OCH ₂ -), 3.45 (s, 3, methoxyl), and 3.33 (d, $J = 2.5$ Hz, 2, H ₂ and H ₃) ^a	For C ₁₈ H ₁₇ N ₃ O ₃ : C, 66.86; H, 5.30; N, 13.00	C, 66.74; H, 5.39; N, 13.22
7-F	7.20 (br s, 5, phenyl), 5.75-6.35 (m, 4, olefinic), 4.80-5.10 (m, 2, H ₁ and H ₆), and 3.32 (dd, $J = 4$ and 5 Hz, 1, H ₃) ^a	See ref 19	
6-CN	7.34 (s, 5, phenyl), 6.73 (s, 1, H ₁), 6.28 (t, $J = 4$ Hz, 2, H ₉ and H ₁₀), 5.00-5.24 (m, 2, H ₁ and H ₆), 3.64 (t, $J = 4$ Hz, 1, H ₂ or H ₃), and 3.45 (t, $J = 4$ Hz, 1, H ₂ or H ₃) ^b	For C ₁₇ H ₁₂ N ₄ O ₂ : C, 67.09; H, 3.98; N, 18.41	C, 67.01; H, 3.97; N, 18.66
7-CN	7.36 (s, 5, phenyl), 6.00-6.28 (m, 4, olefinic), 5.02-5.24 (m, 2, H ₁ and H ₆), and 3.68 (d with fine coupling, $J = 5$ Hz, 1, H ₃) ^a	For C ₁₇ H ₁₂ N ₄ O ₂ : C, 67.09; H, 3.98; N, 18.41	C, 66.78; H, 4.14; N, 18.61
8-CN	7.44 (s, 5, phenyl), 6.36 and 6.30 (two s, 1 H each, H ₉ and H ₁₀), 6.13 (s, 2, H ₃ and H ₄), 5.12 (q with fine coupling, $J = 4$ Hz, 1, H ₆), and 3.40-3.73 (m, 2, H ₂ and H ₃) ^a	For C ₁₇ H ₁₂ N ₄ O ₂ : C, 67.09; H, 3.98; N, 18.41	C, 67.22; H, 4.09; N, 18.52
9-CN	7.34 (s, 5, phenyl), 6.82 (dd, $J = 2$ and 6 Hz, 1, H ₁₀), 5.98 (AB q, $J = 4$ Hz, 2, H ₃ and H ₄), 5.10 (m, 2, H ₁ and H ₆), and 3.38 (m, 2, H ₂ and H ₃) ^b	For C ₁₇ H ₁₂ N ₄ O ₂ : C, 67.09; H, 3.98; N, 18.41	C, 67.03; H, 4.12; N, 18.56
6-COOCH ₃	7.40 (s, 5, phenyl), 6.63 (s, 1, H ₁), 6.10-6.30 (m, 2, H ₉ and H ₁₀), 4.90-5.40 (m, 2, H ₁ and H ₆), 3.72 (s, 3, methyl), and 3.20-3.65 (m, 2, H ₂ and H ₃) ^a	For C ₁₈ H ₁₅ N ₃ O ₄ : C, 64.09; H, 4.48; N, 12.46	C, 64.36; H, 4.58; N, 12.37
8-COOCH ₃	7.40 (s, 5, phenyl), 6.62-6.85 (m, 1, H ₉ or H ₁₀), 5.88-6.30 (m, 3, olefinic), 4.95-5.20 (m, 1, H ₆), 3.92 (s, 3, methyl), and 3.36-3.75 (m, 2, H ₂ and H ₃) ^a	For C ₁₈ H ₁₅ N ₃ O ₄ : C, 64.09; H, 4.48; N, 12.46	C, 63.96; H, 4.58; N, 12.30
9-COOCH ₃	7.40 (m, 5, phenyl), 7.06 (dd, $J = 2$ and 6 Hz, H ₁₀), 6.00 (s, 2, H ₃ and H ₄), 5.18 and 5.58 (m, 1 each, H ₁ and H ₆), 3.76 (s, 3, methyl), and 3.27-3.58 (m, 2, H ₂ and H ₃) ^a	<i>d</i>	
9-Br	7.43 (s, 5, phenyl), 5.95-6.18 (m, 1, H ₁₀), 5.99 (s, 2, H ₃ and H ₄), 4.88-5.23 (m, 2, H ₁ and H ₆), and 3.15-3.45 (m, 2, H ₂ and H ₃) ^a	For C ₁₈ H ₁₂ BrN ₃ O ₂ : <i>m/e</i> 357.0113	<i>m/e</i> 357.0119

^a 60-MHz spectrum. ^b 100-MHz spectrum. ^c Not separated and used subsequently as a mixture. ^d Insufficient quantity for further characterization.

Table III. Physical Data for the 9,10-Diazabasketanes

Starting diene (g)	Solvent (ml)	Filter	Time, hr	9,10-Diazabasketane	Yield, %	Mp, °C	Pmr (δ , CDCl ₃ , 60 or 100 MHz)	Anal. data
6-C ₆ H ₅ (5.73)	Acetone (450)	Corex	37	22-C ₆ H ₅	30	146 dec ^a	6.95–7.46 (m, 5), 4.88–5.30 (m, 2), 3.33–3.83 (m, 5), and 3.02 (s, 3) ^e	Calcd for C ₁₇ H ₁₅ N ₃ O ₂ : C, 69.61; H, 5.15; N, 14.33. Found: C, 69.44; H, 5.22; N, 14.46
7-C ₆ H ₅ (0.090)	Acetone (10)	Corex	22	23-C ₆ H ₅	42	Glassy	7.08–7.64 (m, 5), 5.00–5.24 (m, 2), 3.64–3.80 (m, 3), 3.40–3.56 (m, 1), and 3.16–3.32 (m, 1) ^b	Calcd for C ₂₂ H ₁₇ N ₃ O ₂ : <i>m/e</i> 355.1321. Found: 355.1323
9-C ₆ H ₅ (0.10)	Acetone (10)	Corex	41	23-C ₆ H ₅	21	As above	As above	As above
6-CH ₃ (0.27)	Acetone (50)	Vycor	32	22-CH ₃	72	219.5–220.5 ^b	7.20–7.72 (m, 5), 4.86–5.19 (t, <i>J</i> = 6 Hz, 2), 2.82–3.77 (m, 5), and 1.21 (s, 3) ^e	Calcd for C ₁₇ H ₁₅ N ₃ O ₂ : C, 69.61; H, 5.15; N, 14.33. Found: C, 69.46; H, 5.25; N, 14.32
7-CH ₃ (0.33)	Acetone (50)	Vycor	24	23-CH ₃	93	182–184 ^b	7.30–7.72 (m, 5), 4.6–5.3 (m, 2), 2.85–3.90 (m, 5), and 1.39 (s, 3) ^e	Calcd for C ₁₇ H ₁₅ N ₃ O ₂ : C, 69.61; H, 5.15; N, 14.33. Found: C, 69.56; H, 5.05; N, 14.06
6-CH ₂ OAc (0.50)	Acetone– benzene, 1:1 (350)	Corex	6	22-CH ₂ OAc	82	159–160 ^c	7.25–7.70 (m, 5), 4.9–5.2 (m, 2), 4.12 (s, 2), 3.40–3.75 (m, 4), 3.0–3.3 (m, 1), and 2.07 (s, 3) ^e	Calcd for C ₁₉ H ₁₇ N ₃ O ₄ : C, 64.95; H, 4.88. Found: C, 64.81; H, 4.84
7-CH ₂ OAc: 9-CH ₂ OAc (1:1, 0.50)	Acetone– benzene, 1:1 (300)	Corex	3	23-CH ₂ OAc	72	94–95 ^c	7.2–7.68 (m, 5), 4.76–5.12 (m, 2), 4.23 (AB, <i>J</i> _{AB} = 12 Hz, 2), 3.23–3.7 (m, 3), 2.95–3.18 (m, 2), and 2.00 (s, 3) ^e	Calcd for C ₁₉ H ₁₇ N ₃ O ₄ : C, 64.95; H, 4.88; N, 11.96. Found: C, 64.97; H, 5.26; N, 12.09
8-CH ₂ OAc (1.17)	Acetone– benzene, 1:1 (350)	Corex	7	24-CH ₂ OAc	70	170–171 ^c	7.2–7.75 (m, 5), 4.90–5.25 (m, 1), 4.75 (br s, 2), 3.40–3.90 (m, 4), 3.0–3.4 (m, 2), and 2.10 (s, 3) ^e	Calcd for C ₁₉ H ₁₇ N ₃ O ₄ : C, 64.95; H, 4.88; N, 11.96. Found: C, 64.84; H, 4.78; N, 12.14
6-CH ₂ OCH ₃ (1.11)	Acetone (500)	Vycor	24	22-CH ₂ OCH ₃	24	156–156.5 ^e	7.2–7.75 (m, 5), 4.85–5.25 (m, 2), 3.4–3.8 (m, 4), 3.42 (s, 2), 3.32 (s, 3), and 3.0–3.35 (m, 2) ^e	Calcd for C ₁₈ H ₁₇ N ₃ O ₂ : C, 66.86; H, 5.30; N, 13.00. Found: C, 66.42; H, 5.33; N, 12.86
7-CH ₂ OCH ₃ (0.71)	Acetone (350)	Vycor	3	23-CH ₂ OCH ₃	34	76.5–77.5 ^e	7.25–7.70 (m, 5), 4.88–5.25 (m, 2), 3.4–3.85 (m, 3), 3.54 (s, 2), 3.37 (s, 3), and 3.07–3.28 (m, 2) ^e	Calcd for C ₁₈ H ₁₇ N ₃ O ₂ : C, 66.86; H, 5.30; N, 13.00. Found: C, 66.79; H, 5.40; N, 13.05
8-CH ₂ OCH ₃ (0.90)	Acetone (300)	Vycor	12	24-CH ₂ OCH ₃	64	145–146 ^c	7.25–7.70 (m, 5), 4.9–5.25 (m, 1), 4.04 (s, 2), 3.5–3.80 (m, 4), 3.47 (s, 3), and 2.03–2.4 (m, 2) ^e	Calcd for C ₁₈ H ₁₇ N ₃ O ₂ : C, 66.86; H, 5.30; N, 13.00. Found: C, 66.73; H, 5.36; N, 12.97
8-COOCH ₃ (1.00)	Acetone (300)	Vycor	48	24-COOCH ₃	35	202.5–203.5 ^b	7.2–7.6 (m, 5), 4.9–5.18 (m, 1), 3.89 (s, 3), 3.5–4.15 (m, 4), and 3.05–3.42 (m, 2) ^e	Calcd for C ₁₈ H ₁₅ N ₃ O ₄ : C, 64.09; H, 4.48; N, 12.46. Found: C, 64.36; H, 4.76; N, 12.40
6-CN (0.30)	Acetone (350)	Vycor	9	22-CN	92	236–238 dec ^d	7.28 (s, 5), 5.18 (t, <i>J</i> = 5 Hz, 1), 4.96 (t, <i>J</i> = 5 Hz, 1), and 3.40–4.05 (m, 5) ^f	Calcd for C ₁₇ H ₁₂ N ₄ O ₂ : C, 67.09; H, 3.98; N, 18.41. Found: C, 66.78; H, 4.08; N, 18.71
7-CN (0.30)	Acetone (400)	Vycor	4	23-CN	80	211–217 dec ^d	7.64 (m, 5), 4.93–5.40 (m, 2), and 3.12–3.93 (m, 5) ^f	Calcd for C ₁₇ H ₁₂ N ₄ O ₂ : C, 67.09; H, 3.98; N, 18.41. Found: C, 66.78; H, 4.14; N, 18.46
8-CN (0.30)	Acetone (450)	Vycor	113	24-CN	50	224–228 dec ^d	7.18–7.54 (m, 5), 4.93 (t with fine splitting, <i>J</i> = 5 Hz, 1), and 3.0–4.05 (m, 6) ^e	Calcd for C ₁₇ H ₁₂ N ₄ O ₂ : C, 67.09; H, 3.98; N, 18.41. Found: C, 66.90; H, 4.18; N, 18.55
7-F (1.45)	Acetone (275)	Vycor	34	23-F	56	167.5–168 ^a	7.25–7.73 (m, 5), 4.90–5.32 (m, 2), and 2.91–4.09 (m, 5) ^e	Calcd for C ₁₆ H ₁₂ FN ₃ O ₂ : C, 64.64; H, 4.07; N, 14.14. Found: C, 64.36; H, 4.16; N, 14.15

The following recrystallization solvents were employed: ^a 2-propanol; ^b benzene–hexane; ^c ethanol; ^d 2-propanol–acetonitrile. ^e Determined at 60 MHz. ^f 100-MHz spectrum.

pmr absorptions, the presence of a single α -imido proton, and the obvious similarity of the remainder of the spectra to that of **22-H**, the structural assignment **24** can be inferred. Further consideration of the structural features of **22-24** reveals that such molecules possess four proximal cubyl positions and two distal cubyl sites. The pmr absorptions of these two groups of protons exhibit chemical shifts sufficiently different such that monosubstitution at one of these sites is quickly recognized by simple integration of these regions. Consequently, the three possible positional isomers may be distinguished from each other with particular ease.

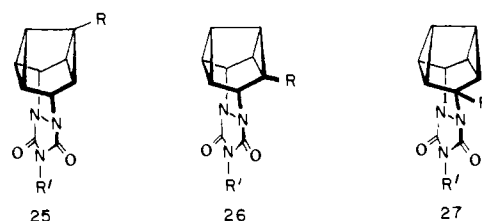
Ag⁺-Catalyzed Rearrangements. Since its discovery in 1970,²⁸ the Ag⁺-catalyzed skeletal rearrangement of cubyl systems has been the focus of several investigations but continues to remain, at least with respect to its mechanistic definition, the subject of dispute.^{28a,29} Although small incremental strain differences such as found in stereoisomeric *seco*-cubyl diesters have little kinetic consequence,³⁰ electronic effects exert wide variations in rate.³¹ Initial reversible metal ion-carbon σ -bond complexation has been demonstrated,^{31b} but little work has been carried out on such molecules having a substituent positioned other than at a distal carbon.³²

With these considerations in mind, we undertook a study of the rearrangement of the three sets of 9,10-diazabasketanes **22-24** which incorporate not only the intriguing feature of groups predisposed at all three possible sites, but also rather wide differences in the electronic nature of these substituents. In our initial experiments with **22-H**, dilute chloroform solutions of this diazabasketane were heated at reflux for 5-7 days with intermittent introduction of small quantities of silver fluoroborate. After removal of the silver salts by filtration through silica gel and recrystallization from ethanol, the 9,10-diazasnoutane **25-H**³³ was consistently obtained in 81% yield. In the pmr, this product showed resonances at δ 7.20-7.70 (m, 5), 4.90-5.25 (m, 2), and 1.73-2.22 (m, 6) in agreement with the anticipated upfield shifting of the six newly formed cyclopropyl protons.

Despite the quite good yield of this conversion, reaction times were long, and we therefore sought to accelerate the reaction. If the behavior of **22-H** compares with that of other cubyl systems which have been examined kinetically, then its rearrangement to **25-H** should obey the second-order catalytic rate law $-\frac{d[\mathbf{22-H}]}{dt} = k_{Ag}[\mathbf{22-H}][Ag^+]$.³¹ That is to say that the rate of disappearance of **22-H** is related directly to the level of silver salt present in solution. Since AgBF₄ is only slightly soluble in chloroform and suffers some decomposition upon prolonged heating in this medium, this phenomenon was considered to be a factor responsible for the relatively slow isomerization. Further difficulties arising from complexation of the small amount of available Ag⁺ with the electron-rich urazole ring in **22-H** were almost certainly present as well. This problem was partly resolved by making recourse to three different sets of conditions, the choice of which was dictated chiefly by the nature of the R group, its sensitivity to the reaction parameters, and the relative ease or difficulty in effecting the rearrangement. The silver salt-solvent systems selected were: (a) silver nitrate in aqueous methanol; (b) silver perchlorate in benzene or toluene; and (c) silver nitrate in acetonitrile. We were particularly gratified to observe that the use of silver nitrate in methanol did not effect solvent incorporation or result in autocatalytic acid production as it does with bicyclo[1.1.0]butanes.³⁴

For the purpose of comparison, specific attention is called to the behavior of **22-CH₃**, **23-CH₃**, **22-C₆H₅**, and **23-C₆H₅** whose rearrangements were effected under roughly comparable conditions utilizing excess silver nitrate in methanol-water (4:1) at reflux in the absence of light. The lengths of

time required to achieve essentially complete (tlc analysis) conversion to the respective substituted snoutanes were: 60 hr, 72 hr, 20 hr, and 19 days. The yields realized were: **25-CH₃** (97%), **26-CH₃** (74%), **25-C₆H₅** (96%), and **26-C₆H₅** (72%).



In the acetoxymethyl, methoxymethyl, and cyano series, all three diazabasketane isomers were available in quantities sufficient for continuation of the synthetic sequence. As Table IV shows, no complications were encountered with either of the first two groups of compounds other than the fact that some attention to solvent was required. For example, the acetoxymethyl derivatives could not be effectively rearranged in aqueous methanol because of competing aqueous hydrolysis and acetyl transfer to the methanol. Consequently, silver perchlorate in benzene was employed. The electronic characteristics of this side chain are such that reaction times of 7-8 days were required to achieve complete isomerization. Our data reveal a somewhat comparable rate-retarding effect for the methoxymethyl group, the rearrangements of **22-**, **23-**, and **24-CH₂OCH₃** in aqueous methanol containing excess silver nitrate requiring 7, 8, and 10 days, respectively, for total conversion. Treatment of **23-CN** with silver nitrate in refluxing aqueous methanol led unexpectedly to the rearranged carboxamido derivative **26-CONH₂** in 29% yield. When **23-CN** was exposed instead to the catalytic effect of silver nitrate in acetonitrile, skeletal bond reorganization with formation of **26-CN** now occurred in 75% yield over a 6.3-day period. When the cyano group is positioned at a distal carbon as in **22-CN**, rearrangement to the diazasnoutane could not be effected. When subjected to similar rearrangement conditions (AgNO₃, CH₃CN), no evidence could be found for its isomerization after 11 days at the reflux temperature; **22-CN** was returned in good yield. Neither rearrangement nor hydrolysis to the carboxamidobasketane was observed with silver nitrate in refluxing aqueous *n*-butyl alcohol or methanol. Silver fluoroborate in chloroform was equally ineffective, while silver perchlorate in refluxing benzene or toluene brought about gradual decomposition of the cubyl framework. The third isomer **24-CN** was less exhaustively studied. However, like **22-CN** it failed to show any indication of conversion to snoutane **27-CN** after prolonged heating with silver nitrate in acetonitrile.

It might be thought that the unreactivity of **22-CN** is a result of strong electron withdrawal from the σ orbital or orbitals involved in the initial complexation, such that the relevant σ bond cannot experience cleavage.^{31b} Strong coordination of Ag⁺ to the nitrile group is also highly probable. This latter phenomenon may underlie the inability of **24-CN** to isomerize, particularly in view of the relative ease with which **24-COOCH₃** undergoes the desired transposition of carbon atoms. Lastly, we note that the conversion of **23-F** to **26-F** proceeded smoothly, albeit that somewhat more elevated temperatures (refluxing toluene) were required to effect complete isomerization in a reasonable time.

Inasmuch as all the diazabasketanes in the absence of Ag⁺ ion were completely stable to the reaction conditions employed, effective transition metal catalysis is seen to be operational. Every diazasnoutane prepared herein has ex-

Table IV. Physical Data for the Diazasnoutanes

9,10-Diazabasketane (mmol)	Catalyst (mmol)	Solvent systems (ml)	Time, days	Diazasnoutane	Yield, %	Mp, °C	Pmr (δ , CDCl ₃ , 60 or 100 MHz)	Anal. data
22-H (34)	AgBF ₄ (17) ^a	CHCl ₃ (100)	7	25-H	81	183–184 ^b	7.20–7.70 (m, 5), 4.90–5.25 (m, 2), and 1.73–2.22 (m, 6) ^o	Calcd for C ₈ H ₁₃ N ₃ O ₂ : C, 68.80; H, 4.69; N, 15.05. Found: C, 68.75; H, 4.69; N, 15.06
22-C₆H₅ (5.1)	AgNO ₃ (75)	CH ₃ OH–H ₂ O (4:1, 200)	0.85	25-C₆H₅	96	166.5–167.5 ^c	7.0–7.34 (m, 5), 4.97–5.22 (m, 2), 3.04 (s, 3), and 1.95–2.47 (m, 5) ^o	Calcd for C ₁₇ H ₁₃ N ₃ O ₂ : C, 69.61; H, 5.15; N, 14.33. Found: C, 69.47; H, 5.29; N, 14.43
23-C₆H₅ (1.2)	AgNO ₃ (18)	CH ₃ OH–H ₂ O (4:1, 60)	19	26-C₆H₅	72	166–167 ^c	7.02–7.66 (m, 10), 5.14–5.47 (m, 2), and 1.96–2.60 (m, 5) ^o	Calcd for C ₂₂ H ₁₇ N ₃ O ₂ : C, 74.35; H, 4.82; N, 11.82. Found: C, 74.06; H, 5.03; N, 11.68
22-CH₃ (0.68)	AgNO ₃ (10)	CH ₃ OH–H ₂ O (4:1, 15)	2.5	25-CH₃	97	165.5–166.5 ^d	7.15–7.65 (m, 5), 4.98–5.20 (m, 2), 1.60–2.12 (m, 5), and 1.28 (s, 3) ^o	Calcd for C ₁₇ H ₁₃ N ₃ O ₂ : C, 69.61; H, 5.15; N, 14.33. Found: C, 69.63; H, 5.13; N, 14.37
23-CH₃ (4.5)	AgNO ₃ (66)	CH ₃ OH–H ₂ O (4:1, 100)	3	26-CH₃	74	146.5–147.5 ^c	7.25–7.75 (m, 5), 4.80–5.29 (m, 2), 1.70–2.15 (m, 5), and 1.23 (s, 3) ^o	Calcd for C ₁₇ H ₁₃ N ₃ O ₂ : C, 69.61; H, 5.15; N, 14.33. Found: C, 69.86; H, 5.11; N, 14.75
22-CH₂OAc (4.0)	AgClO ₄ (30)	C ₆ H ₆ (150)	7	25-CH₂OAc	95	147–148 ^b	7.20–7.60 (m, 5), 4.90–5.20 (m, 2), 4.16 (s, 2), 2.02 (s, 3), and 1.87–2.15 (m, 5) ^o	Calcd for C ₁₉ H ₁₇ N ₃ O ₄ : C, 64.95; H, 4.88; N, 11.96. Found: C, 64.64; H, 4.88; N, 12.05
23-CH₂OAc (0.65)	AgClO ₄ (5)	C ₆ H ₆ (25)	7	26-CH₂OAc	75	Oil	7.25–7.70 (m, 5), 4.90–5.30 (m, 2), 4.03 (AB, J _{AB} = 12.5 Hz, 2), 1.95 (s, 3), and 1.85–2.30 (m, 5) ^o	(Molecular ion too weak for accurate mass determination)
24-CH₂OAc (2.3)	AgClO ₄ (10)	C ₆ H ₆ (50)	8	27-CH₂OAc	91	153–154 ^b	7.20–7.65 (m, 5), 5.00–5.30 (m, 1), 4.88 (s, 2), 2.11 (s, 3), and 1.80–2.30 (m, 6) ^o	Calcd for C ₁₉ H ₁₇ N ₃ O ₄ : C, 64.95; H, 4.88; N, 11.96. Found: C, 64.72; H, 5.01; N, 12.18
22-CH₂OCH₃ (1.4)	AgNO ₃ (59)	CH ₃ OH–H ₂ O (4:1, 75)	7	25-CH₂OCH₃	40	112–113 ^b	7.17–7.67 (m, 5), 4.90–5.25 (m, 2), 3.49 (s, 2), 3.32 (s, 3), and 1.85–2.25 (m, 5) ^o	Calcd for C ₁₈ H ₁₇ N ₃ O ₃ : C, 66.86; H, 5.30; N, 13.00. Found: C, 66.73; H, 5.33; N, 13.05
23-CH₂OCH₃ (2.0)	AgNC ₃ (88)	CH ₃ OH–H ₂ O (4:1, 75)	8	26-CH₂OCH₃	82	Oil	7.20–7.70 (m, 5), 4.80–5.25 (m, 2), 3.34 (AB, J _{AB} = 10.5 Hz, 2), 3.25 (s, 3), and 1.80–2.25 (m, 5) ^o	Calcd for C ₁₈ H ₁₇ N ₃ O ₃ : m/e 323.1270. Found: 323.1276
24-CH₂OCH₃ (1.8)	AgNO ₃ (70)	CH ₃ OH–H ₂ O (4:1, 50)	10	27-CH₂OCH₃	67	97–98 ^b	7.14–7.60 (m, 5), 4.90–5.20 (m, 1), 4.16 (s, 2), 3.48 (s, 3), and 1.80–2.20 (m, 6) ^o	Calcd for C ₁₈ H ₁₇ N ₃ O ₃ : C, 66.86; H, 5.30; N, 13.00. Found: C, 66.71; H, 5.58; N, 12.72
24-COOCH₃ (3.7)	AgClO ₄ (20)	C ₆ H ₆ (100)	8	27-COOCH₃	88	158–159 ^d	7.27–7.68 (m, 5), 5.03–5.26 (m, 1), 3.91 (s, 3), and 1.83–2.60 (m, 6) ^o	Calcd for C ₁₈ H ₁₅ N ₃ O ₄ : C, 64.09; H, 4.48; N, 12.46. Found: C, 64.06; H, 4.58; N, 12.19
23-CN (0.33)	AgNO ₃ (5)	CH ₃ OH–H ₂ O (4:1, 10)	2	26-CONH₂	27	242–242.5 ^c	Insoluble	Calcd for C ₁₇ H ₁₄ N ₃ O ₃ : C, 63.35; H, 4.38; N, 17.38. Found: C, 62.99; H, 4.41; N, 17.61
23-CN (0.32)	AgNO ₃ (5)	CH ₃ CN (10)	6.3	26-CN	75	225–236 dec ^f	7.28–7.68 (m, 5), 5.16–5.36 (m, 2), and 1.96–2.84 (m, 5) ^h	Calcd for C ₁₇ H ₁₂ N ₃ O ₂ : C, 67.09; H, 3.98; N, 18.41. Found: C, 66.68; H, 4.03; N, 18.40
23-F (4.7)	AgClO ₄ (48)	Toluene (100)	4	26-F	93	177.5–178.5 ^c	7.0–7.58 (m, 5), 5.00–5.55 (m, 2), and 1.70–2.75 (m, 5) ^o	Calcd for C ₁₆ H ₁₂ N ₃ O ₂ : C, 64.64; H, 4.07; N, 14.14. Found: C, 64.47; H, 4.16; N, 14.56

^a Added in incremental amounts (see Experimental Section). The following recrystallization solvents were employed: ^b ethanol; ^c 2-propanol; ^d benzene–cyclohexane; ^e acetonitrile; ^f 2-propanol–acetonitrile. ^o Spectrum obtained at 60 MHz. ^h At 100 MHz.

hibited good shelf-life stability and, with the exception of 26-CH₂OAc, is nicely crystalline. Since these substances are but one synthetic manipulation removed from the thermal- and acid-sensitive semibullvalenes,^{3,8} they represent attractive penultimate precursors to these interesting fluxional molecules.

Experimental Section

Melting points are corrected and boiling points are uncorrected. Proton magnetic resonance spectra were obtained on Varian A-60-A, Varian HA-100, and Jeolco MH-100 spectrometers; apparent splittings are given in all cases. Infrared spectra were determined on Perkin-Elmer Model 137 and 467 instruments. Mass spectra were recorded on a AEI-MS9 spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Direct Addition of *N*-Methyltriazolinedione to Phenylcyclooctatetraene. Generalized Procedure. A solution of 8.25 g (45.8 mmol) of phenylcyclooctatetraene³⁵ in 400 ml of ethyl acetate was heated to reflux with stirring, while a solution of 5.18 g (45.8 mmol) of freshly sublimed *N*-methyl-1,3,4-triazoline-2,5-dione³⁶ in 400 ml of the same solvent was added dropwise during 1 hr. Discharge of the red color of the dienophile was almost immediate and a pale yellow color persisted. The solvent was removed *in vacuo* to leave a yellow-orange oil which was chromatographed on neutral activity III alumina. Ether elution returned 2.15 g of phenylcyclooctatetraene and also yielded 8.34 g (84%) of white crystalline adduct. Recrystallization from 2-propanol furnished pure 6-C₆H₅, mp 192–194° dec; λ_{max} (C₂H₅OH) 248 (ε 20,000) and 282 nm (450).

When the mother liquors were subjected to preparative thick layer chromatography (silica gel, ether-hexane (1:1) elution), small amounts of 8-C₆H₅, mp 175.5–176.5° (from 2-propanol), could also be isolated.

3-Methyl-7,8-diazatricyclo[4.2.2.0^{2,5}]deca-3,9-diene-7,8-dicarboxylic Acid Phenylimide (6-CH₃). Treatment of a solution containing 1.0 g (8.49 mmol) of methylcyclooctatetraene³⁷ dissolved in ethyl acetate (40 ml) with 1.5 g (8.57 mmol) of freshly sublimed *N*-phenyl-1,3,4-triazoline-2,5-dione,^{36,38} followed by heating at reflux under nitrogen for 24 hr and chromatography on silica gel (200 g, methylene chloride elution), gave in the initial fractions 274 mg (11%) of 6-CH₃. Recrystallization from benzene-hexane gave the pure tetracyclic adduct as colorless crystals, mp 189.5–190°.

Later fractions consisted of 273 mg (11%) of a mixture of two tricyclic adducts in the form of a white solid: δ_{TMS} (CDCl₃) 7.42 (m, 5, aryl), 5.63–6.27 (br m, 5, olefinic), 4.83–5.18 (m, 2, bridgehead), 2.18 (br s, 30% of 3 H, methyl), and 1.93 (br s, 70% of 3 H, methyl).

3-Acetoxyethyl-7,8-diazatricyclo[4.2.2.0^{2,5}]deca-3,9-diene-7,8-dicarboxylic Acid Phenylimide (6-CH₂OAc). When 2.70 g (15.3 mmol) of acetoxyethylcyclooctatetraene³⁹ and 2.68 g (15.3 mmol) of PTAD dissolved in 250 ml of ethyl acetate was refluxed for 4.5 hr and the residue was chromatographed on Florisil (methylene chloride elution), there were obtained in the early fractions 0.10 g (4%) of recovered cyclooctatetraene and 1.70 g (32%) of 6-CH₂OAc, mp 108–108.5° (from ethanol).

The more polar fractions contained a mixture of three tricyclic adducts (pmr shows three distinct acetate methyl singlets at δ 2.11, 2.15, and 2.19 and three well defined -OCH₂- signals at 4.65, 4.77, and 4.88) which were not investigated further.

Methoxymethylcyclooctatetraene. To a stirred slurry of 4.0 g (95 mmol) of 57% sodium hydride dispersion (previously washed with pentane) in 100 ml of dry dimethylformamide was added dropwise a solution of cyclooctatetraenecarbinyl alcohol in 25 ml of the same solvent during 15 min. Upon completion of the addition, the mixture was brought to 40° for 10 min and then cooled in ice, while 28.4 g (0.19 mol) of methyl iodide was introduced in one portion. After 5 min, water (10 ml) was carefully introduced, and the reaction mixture was poured into 200 ml of water and 40 ml of pentane. The aqueous phase was separated and extracted with pentane, and the combined organic phases were washed with water and brine and dried. Distillation in a Kugelrohr apparatus at 115° (0.5 mm) gave 5.03 g (82%) of bright yellow oil. An analytical sample was obtained by preparative vpc isolation from a 6 ft × 0.25 in. 5% SE-30 column (Chromosorb G) operating at 100°:

δ_{TMS} (CDCl₃) 5.72 (pseudo-singlet, 7), 3.80 (s, 2), and 3.28 (s, 3).

Anal. Calcd for C₁₀H₁₂O: C, 81.04; H, 8.16. Found: C, 81.00; H, 8.34.

Direct Addition of PTAD to Methoxymethylcyclooctatetraene. A solution of 2.00 g (13.5 mmol) of methoxymethylcyclooctatetraene and 2.86 g (13.5 mmol) of PTAD in 300 ml of ethyl acetate was refluxed for 6 hr and evaporated, and the residue was subjected to silica gel chromatography. Elution with ether-hexane (1:3) afforded in the following order: fractions 6–7, 750 mg of unreacted cyclooctatetraene; fractions 19–24, 203 mg (7.5%) of 8-CH₂OCH₃, mp 146–146.5° (from ethanol); fractions 28–42, 324 mg (14%) of 7-CH₂OCH₃, mp 201–202° (from ethanol); fractions 46–90, 1.11 g (42%) of 6-CH₂OCH₃, mp 114–115° (from ethanol); fractions 95–140, 460 mg (17%) of two tricyclic adducts which were not further purified: δ_{TMS} (CDCl₃) (A) 7.18–7.70 (m, 5, phenyl), 5.76–6.44 (m, 5), 4.92–5.36 (m, 2), 3.80–4.22 (m, 2), and 3.28 (s, 3); (B) 7.12–7.70 (m, 5), 5.80–6.36 (m, 5), 4.88–5.24 (m, 2), 4.12 (AB q, J_{AB} = 13 Hz, 2), and 3.35 (s, 3).

2-Fluoro-7,8-diazatricyclo[4.2.2.0^{2,5}]deca-3,9-diene-7,8-dicarboxylic Acid Phenylimide (7-F). After heating a solution containing 1.60 g (13.1 mmol) of fluorocyclooctatetraene¹⁹ and 2.3 g (13.1 mmol) of PTAD in 40 ml of ethyl acetate at reflux for 2.5 hr, there was isolated after solvent evaporation and alumina chromatography (neutral, methylene chloride elution) 2.93 g (75%) of 7-F as a white flocculent solid, mp 204–205° (lit.¹⁹ mp 204–205°), after recrystallization from chloroform-ethanol.

Direct Addition of PTAD to Cyanocyclooctatetraene. Reaction of 4.0 g (31 mmol) of cyanocyclooctatetraene⁴⁰ with 5.42 g (31 mmol) of PTAD in 400 ml of ethyl acetate (reflux, 12 hr), followed by solvent removal *in vacuo*, gave an orange oil which was triturated with a small quantity of ethyl acetate. The crystalline white solid so obtained (2.06 g, 26%) was identified as 6-CN, mp 250° dec (from acetonitrile).

The remaining material (6.83 g) was chromatographed on silica gel (500 g). The collected fractions gave in order of elution 40 mg of recovered CN-COT, 2.37 g (31%) of 8-CN, mp 180–182° dec (from 2-propanol-acetonitrile), and 1.84 g (24%) of 7-CN, mp 214–218° dec (from 2-propanol-acetonitrile).

For 6-CN: λ_{max} (C₂H₅OH) 215 (ε 30,000) and 260 nm (4250). For 8-CN: λ_{max} (C₂H₅OH) 260 nm (ε 2000).

Direct Addition of PTAD to Carbomethoxycyclooctatetraene. An equimolar (26.4 mmol) mixture of carbomethoxycyclooctatetraene⁴¹ (4.38 g) and PTAD (4.36 g) dissolved in 200 ml of ethyl acetate was refluxed for 4.5 hr. The resulting mixture of adducts was chromatographed on Florisil (200 g). Elution with ether-hexane (1:9) gave 1.08 g of recovered carbomethoxycyclooctatetraene. A solvent polarity increase to 25% ether in hexane furnished 1.88 g (27%) of 8-COOCH₃, mp 176–177° (from benzene-hexane). Continued elution also afforded 0.14 g (2%) of slightly impure 9-COOCH₃, 0.55 g (8%) of 6-COOCH₃, mp 181–182° (from benzene-hexane), and 0.69 g (10%) of 10-COOCH₃. The pmr spectrum of the latter tricyclic substance indicated it to be a single isomer: δ_{TMS} (CDCl₃) 7.40 (s, 5, phenyl), 6.0–6.4 (m, 5, olefinic), 4.9–5.45 (m, 2, bridgehead), and 3.79 (s, 3, methyl).

7,8-Diazatricyclo[4.2.2.0^{2,5}]deca-3,9-diene-7,8-dicarboxylic Acid Phenylimide (6-H). General Procedure for Indirect Addition. A 30.0-g (0.288 mol) sample of cyclooctatetraene was dissolved in 300 ml of methylene chloride, and this solution was treated dropwise with bromine (46.1 g, 0.288 mol) at -78° during 30 min. The resultant solution was stirred for 15 min, and 50.4 g (0.288 mol) of freshly sublimed PTAD in 100 ml of the same solvent was added slowly. Stirring was maintained for 4 hr, while the red solution was allowed to warm to room temperature. Evaporation of the solvent and recrystallization of the residue from ethyl acetate gave 110 g (87%) of white crystalline dibromide, mp 253.5–257.5°.

Solid dibromide (110 g, 0.25 mol) was added to zinc-copper couple⁴² (20.0 g, 0.31 mol) stirred magnetically in refluxing dimethylformamide (800 ml). Refluxing was continued for 9 hr, and then the mixture was filtered hot. The light brown filtrate was concentrated *in vacuo* to give a wet crystalline mass. This was washed with 3 *N* sulfuric acid and water to yield 69.5 g (99%) of 6-H as a sparkling white solid. Recrystallization from carbon tetrachloride produced glistening plates, mp 216–217° (lit.²⁶ mp 216–217°).

Indirect Addition to Methylcyclooctatetraene. Treatment of 1.0 g (8.46 mmol) of Me-COT sequentially with 1.39 g (8.70 mmol) of bromine and 1.5 g (8.48 mmol) of PTAD gave a crimson oil which

was dissolved in 50 ml of absolute ethanol and heated at reflux with 5.3 g (81 mmol) of zinc-copper couple for 12 hr. Chromatography of the pale orange residue on silica gel (methylene chloride elution) afforded 691 mg (30%) of 7-CH₃ as white prisms, mp 184–185° (from 2-propanol).

Indirect Addition to Phenylcyclooctatetraene. Bromine (8.70 g, 54.3 mmol) was added to 9.78 g (54.3 mmol) of Ph-COT at –78° in methylene chloride solution, followed by 9.50 g (54.3 mmol) of PTAD. The resulting orange oil was taken up in 550 ml of absolute ethanol and heated at reflux with 16.3 g (0.25 mmol) of zinc-copper couple (12 hr). Chromatography on silica gel (ether-hexane elution) gave 1.74 g (9.1%) of 9-C₆H₅, mp 174.5–175° (from 2-propanol-acetonitrile), and 1.13 g (5.9%) of 7-C₆H₅, mp 222.5–223° dec (identical solvent mixture).

Indirect Addition of Acetoxymethylcyclooctatetraene. From 3.00 g (17.0 mmol) of AcOMe-COT, 2.73 g (17.0 mmol) of bromine, and 2.98 g (17.0 mmol) of PTAD, there was obtained after debromination an oil which upon trituration with ethanol afforded 3.10 g (35%) of 8-CH₂OAc as a white crystalline solid, mp 155–156° (from ethanol). The filtrate contained an equimolar mixture (pmr integration of methyl signals) of 7-CH₂OAc and 9-CH₂OAc. Because these two isomers afford the same cubyl photoproduct, further purification was not undertaken (1.23 g, 10% each of the two isomers).

Indirect Addition to Methoxymethylcyclooctatetraene. From 1.00 g (6.75 mmol) of MeOCH₂-COT, 1.14 g of bromine, and 1.25 g of PTAD with subsequent debromination and chromatography on silica gel (elution with 25% ether in hexane), there were isolated 693 mg (32%) of 8-CH₂OCH₃, mp 146–146.5° (from ethanol), 511 mg (23%), of 7-CH₂OCH₃, mp 201–202° (from ethanol), and 389 mg of an unknown substance.

Indirect Addition to Carbomethoxycyclooctatetraene. Reaction of 1.00 g (6.17 mmol) of carbomethoxycyclooctatetraene with 1.00 g of bromine and 1.10 g of PTAD, followed by debromination, gave 640 mg (31%) of 8-COOCH₃ as the only isolable product upon direct crystallization from ethanol.

Indirect Addition of Cyanocyclooctatetraene. When 1.0 g (7.74 mmol) of CN-COT was brominated (1.24 g of Br₂) at –78° in methylene chloride and subsequently treated with PTAD (1.35 g) and zinc-copper couple (2.29 g), there was obtained an orange oil. Chromatography on silica gel (300 g) and elution with ether-hexane gave three products; the initial fractions returned 580 mg of the COT, followed by 489 mg (49%) of 9-CN, mp 212–213° dec (from 2-propanol-acetonitrile), 86 mg (9%) of 8-CN, and lastly 120 mg (12%) of 7-CN.

Indirect Addition to Fluorocyclooctatetraene. Reaction of 1.0 g (8.19 mmol) of F-COT with 1.31 g of bromine and 1.43 g of PTAD afforded 3.39 g (91%) of a white powdery dibromide. A 3.39-g sample of this solid was debrominated with zinc-copper couple in absolute ethanol (100 ml, reflux 12 hr) to give 1.39 g (90%) of 7-F.

Indirect Addition to Bromocyclooctatetraene. From 1.00 g (5.46 mmol) of Br-COT, 0.88 g of bromine, and 0.96 g of PTAD with subsequent debromination and chromatography on silica gel (elution with methylene chloride), there was isolated 540 mg (28%) of 9-Br, mp 197–204° dec (from ethanol), as the only characterizable product.

4-Phenyl-2,4,6-triazahexacyclo[5.4.2.0^{2,6}.0^{8,11}.0^{9,13}.0^{10,12}]tridecane-3,5-dione (22-H). General Photocyclization Procedure. A solution of 10.0 g (35.8 mmol) of 6-H in 1000 ml of acetone was purged with nitrogen and irradiated through Vycor with a Hanovia 200-W lamp source with magnetic stirring. After 29 hr, the solvent was removed *in vacuo*, and the residual solid was washed with absolute ethanol and dried to give 8.4 g (84%) of 22-H, mp 193–194° (lit.²⁶ mp 193–194°).

As concerns the irradiation of 6-C₆H₅, 7-C₆H₅, and 9-C₆H₅, orange-red oils were obtained in each instance, and chromatography on silica gel (thick layer or column) was required in each instance. The isolation of 22-CH₃ was similarly effected, but 23-CH₃ was crystallized directly. In the case of the acetoxymethyl derivatives, chromatography of 22-CH₂OAc on silica gel (chloroform elution) was suitable; the isomeric diazabasketanes 23-CH₂OAc and 24-CH₂OAc were most satisfactorily purified by Florisil chromatography. The direct crystallization of 22-CH₂OCH₃ and 23-CH₂OCH₃ proved feasible, but it was necessary to process 24-CH₂OAc by chromatographic purification on silica gel. Ester 24-

COOCH₃ was obtained pure after elution chromatography on activity I alumina (methylene chloride elution). The efficient photocyclization of 6-CN lent itself to direct isolation of 22-CN by crystallization; however, the purification of 23-CN and 24-CN required chromatography on silica gel (elution with 10% ethyl acetate in ether) and Florisil (same elution solvent mixture), respectively. Finally, the isolation of 23-F was achieved by chromatography on activity I neutral alumina using 30% ether in methylene chloride as the eluent.

Ag⁺-Catalyzed Rearrangement of 22-H. A solution of 9.50 g (0.034 mol) of 22-H in 100 ml of chloroform was treated with 250 mg of anhydrous silver fluoroborate and the mixture was heated at reflux in the dark with magnetic stirring for 7 days. At approximately 12-hr intervals, additional 250-mg quantities of the silver salt were added to the reaction mixture. The cooled solution was passed through a silica gel column (elution with methylene chloride), and the resulting solid (7.73 g, 81.2%) was recrystallized from ethanol to give 25-H as colorless blades, mp 183–184°.

Ag⁺-Catalyzed Rearrangement of 23-C₆H₅. General Procedure for Silver Nitrate-Aqueous Methanol Reactions. A solution of 431 mg (1.21 mmol) of 23-C₆H₅ and 3.06 g (18 mmol) of silver nitrate in 60 ml of methanol-water (4:1) was heated at reflux in the dark for 19 days. The cooled solution was treated with 100 ml of water and extracted with an equal volume of methylene chloride. The organic phase was washed with water (3 × 100 ml), dried, and evaporated. The resulting orange residue was chromatographed on activity III neutral alumina (chloroform elution) to give 310 mg (72%) of 26-C₆H₅, mp 166.5–167.5°.

Ag⁺-Catalyzed Rearrangement of 22-CH₂OAc. General Procedure for Silver Perchlorate-Benzene Reactions. The reagent solution was prepared in the following manner. Silver perchlorate (G.F. Smith Co.) (100 g) was ground to a powder in a mortar and pestle and kept under high vacuum (0.005–0.01 mm) at room temperature for 3 days. Dry benzene (600 ml, freshly distilled from lithium aluminum hydride) was added, and dissolving was complete after 15 min at the reflux temperature. This solution was allowed to cool to room temperature, and aliquots were removed as needed. A 1.41-g (4.02 mmol) sample of 22-CH₂OAc in 150 ml of this solution (30 mmol of AgClO₄) was heated at reflux with protection from moisture in the dark for 7 days. The cooled reaction mixture was added to 1 l. of water, and the product was extracted with chloroform. The combined organic layers were dried and evaporated to give a solid residue, crystallization of which from ethanol gave 1.35 g (95%) of 25-CH₂OAc as white needles, mp 147–148°.

Ag⁺-Catalyzed Rearrangement of 23-CN. A. Aqueous Methanol. A solution of 100 mg (0.33 mmol) of 23-CN and 850 mg (5 mmol) of silver nitrate in 10 ml of methanol-water (4:1) was heated at reflux in the dark for 48 hr and processed as above to give 100 mg of a white solid. Preparative thick-layer chromatography on silica gel (development with ether) gave a low R_f component amounting to 29 mg (27%) of 26-CONH₂. This product was recrystallized from acetonitrile to give colorless blades, mp 242–242.5°: ν_{max} (KBr) 3400, 3300, 3170, 3080, 1760, 1685, 1620, 1500, 1410, 1280, 1150, 1130, 1000, and 880 cm⁻¹.

B. Acetonitrile Solution. A solution of 100 mg (0.33 mmol) of 23-CN and 850 mg (5 mmol) of silver nitrate in 10 ml of acetonitrile was heated at reflux in the dark for 152 hr. The solvent was evaporated, and the resultant oil was triturated with methylene chloride and filtered to remove the precipitated silver salts. The filtrate was washed with water (2 × 50 ml), dried, and evaporated to leave a light orange oil which was chromatographed on a thick-layer silica gel plate (development with 10% ethyl acetate in ether). Two major bands were obtained; these were extracted separately to give 34 mg of recovered 23-CN and 49 mg of 26-CN (75%), mp 225–236° dec: ν_{max} (KBr) 3070, 3000, 2235, 1760, 1685, 1600, 1495, 1405, 1295, 1180, 1120, and 765 cm⁻¹.

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References and Notes

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