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Cycloaddition Reactions of Triazolinediones to Tricyclo[4.1.0.0^{2,7}]hept-3-enes. Consequences of Charge Control as Compared to Frontier Orbital Control

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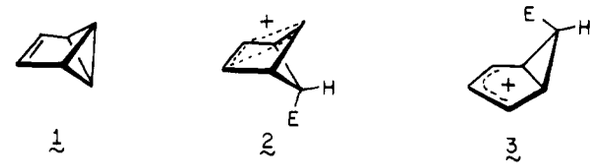
Tricyclo[4.1.0.0^{2,7}]hept-3-enes substituted with methyl groups at C_1, C_1–C_7, C_6, and C_1–C_6–C_7 react with *N*-phenyltriazolinedione to yield 2,4,6-triazapentacyclo[5.4.1.0^{2,6}.0^{8,10}.0^{9,12}]dodecane-3,5-diones. The cycloaddition proceeds with skeletal rearrangement of the strained hydrocarbon system. Through deuterium labeling, it was established that the C_1–C_6–C_7 cyclopropyl triad maintains its integrity. The regiospecificity of the reaction is believed to be a manifestation of charge control, with the triazolinedione attacking olefinic carbon C_4 and presumably generating a dipolar 7-norbornenyl intermediate. This reaction mode differs from that followed by H^+ or D^+, which attack an edge bicyclobutane bond under frontier orbital (HOMO–LUMO) control. The title reaction is somewhat sensitive to the locus and extent of alkyl substitution. Both 1,6-dialkyl derivatives examined suffered prior rearrangement to the related 1,2-disubstituted cycloheptatriene. Various mechanistic factors are considered.

One of the continuing and persistent questions in mechanistic organic chemistry concerns a priori knowledge of when perturbation HMO theory might apply to a chemical reaction and when it does not. The highly successful utilization of frontier orbital analysis in rationalizing the regioselectivity of Diels–Alder reactions,[2] 1,3-dipolar cycloadditions,[3] and a variety of other processes[4] attests to the impressive predictive powers of this theory. Such HOMO–LUMO control of reactivity is seemingly made feasible because of the reactant-like nature of the activated complex which precedes bond formation. When this condition does not apply and the original reactant structures become so greatly altered in the transition state that they no longer represent suitable models of the prevailing interactions, then some other factor, typically charge control, can be expected to gain importance. [2 + 2] cycloadditions, which customarily proceed with the endothermic production of zwitterions in late transition states, appear representative of this latter mechanistic category.[5]

Given the elegant studies alluded to above, there has been little attention directed to assessing the possible multifaceted reactivity of a *single* structural type. Molecules which we consider ideal for the evaluation of a crossover from orbital-controlled to charge-controlled behavior are those which have at least two sites of potential reactivity. An additional criterion necessary to the recognition of the desired mechanistic divergency is an abrupt change in regiospecificity (preferred) or regioselectivity with alteration in the governing reaction mode.

In the particular case of benzvalene (1),[6,7] whose geometry



1 2 3

(microwave spectroscopy[8]) and electronic character (PE measurements[9,10] and theoretical calculations[10–12]) have recently become available, there is seen a strikingly intense interaction between the $b_2(\pi)$ orbital of its double bond and the $b_2(\sigma)$ orbital of the neighboring bicyclobutane ring. Since the HOMO is predominantly π in character, those electrophilic reactions which proceed under frontier orbital control should occur at the double bond. The ground-state polarization does induce some measure of negative charge on the bicyclobutane moiety in **1**. Accordingly, when other factors are discounted,

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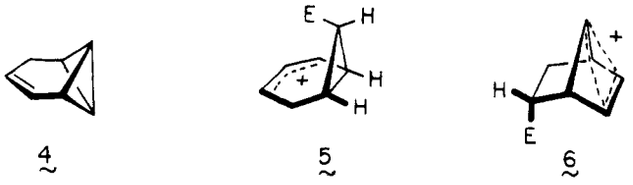
a charge-controlled reaction could be expected to attack the strained ring. However, this low-level polarization is seemingly inadequate to overcome the large stabilization energy available to cation **2**,[13] which is produced (after a 1,2-carbon shift) when the π bond is attacked. Only when the benzvalene ring system is heavily substituted is electrophilic capture (protonation) perhaps directed to central (→ **2**) or edge (→ **3**) bicyclobutane bonds.[14] Thus, it is now recognized that **1** reacts with such reagents as bromine,[15] *N*-phenyltriazolinedione,[16] chlorosulfonyl isocyanate,[17] benzenesulfenyl chloride,[17] Ag^+,[18] ozone,[19] 1,3 dipolarophiles,[20] dibromocarbene,[20] and mercuric acetate[21] by initial π-bond attack. A distinction between the two types of control is unfortunately not possible.

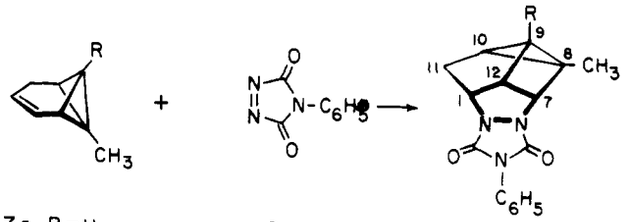
Recent photoelectron (PE) spectral studies of the readily available[22,23] homologous tricyclo[4.1.0.0^{2,7}]hept-3-ene system (**4**) have revealed the Walsh-type a_1 orbital of the bicyclobutane moiety to be the HOMO in this instance.[23] This finding contrasts with the orbital ordering previously established for **1** and speaks clearly to the large electronic perturbation which results when an insulating methylene group is inserted between the interacting systems. Since the σ level now resides above the π level, the expectation is that a frontier orbital controlled electrophilic reaction should be directed to the bicyclobutane moiety. Where H^+ and D^+ are concerned, regiospecific attack at a strained edge bond has indeed been demonstrated.[23] No definitive answer was realized with Ag^+; the ultimate departure of this electrophile from the intermediates prior to product formation (deargentation) foiled labeling studies.[23]



4 **5** **6**

In view of the polarization within **4** and the likelihood that electrophilic attack at the π bond could lead to the formation of stabilized 7-norbornenyl cations such as **6** (rather than the less thermodynamically favored **5**), we undertook an investigation of the cycloaddition of *N*-phenyltriazolinedione (PTAD) to various tricyclo[4.1.0.0^{2,7}]hept-3-enes. The extensively explored chemistry of PTAD has demonstrated its capability to enter into reactions with highly dipolar transition states,[24] a property we deemed highly conducive to charge-controlled behavior in the present circumstances.

In the first experiment, admixtures of equimolar amounts of the 1-methyl derivative **7a** and PTAD (**8**) in ethyl acetate



7a, R = H; **b**, R = D; **c**, R = CH_3 — **8** — **9a**, R = H; **b**, R = D; **c**, R = CH_3

or chloroform at room temperature resulted in colorless solutions. With ethyl acetate as solvent, fading of the red color required 6–8 h; the alternate use of chloroform caused the reactions to proceed at a considerably faster rate. Accordingly, $CHCl_3$ was employed as the solvent of choice in this study. The resulting crystalline solid was shown to be a 1:1 adduct by mass spectroscopy. Its ^1H and ^{13}C NMR spectra exhibited no evidence for the presence of an olefinic moiety in the molecule. In actuality, the 100 MHz ^1H NMR spectrum proved to be magnificently first order, with all nonaromatic protons being well separated and diagnostically spin coupled. The spectrum has been fully analyzed by double resonance techniques and is reproduced in Figure 1. The findings accord fully with the formation of a 2,4,6-triazapentacyclo[5.4.1.0^{2,6}.0^{8,10}.0^{9,12}]-dodecane-3,5-dione structure having a methyl substituent positioned at C_8 as depicted by **9a**.

For the purpose of more extensively mapping the course of the structural reorganization operative during the formation of **9a**, the monodeuterated derivative **7b** was synthesized. The resulting adduct was seen to lack the doublet of doublets centered at δ 2.05; in addition, the splitting patterns due to H_{10} (d, J = 2.7 Hz) and H_{12} (dd, J = 8.0 and 5.6 Hz) were modified

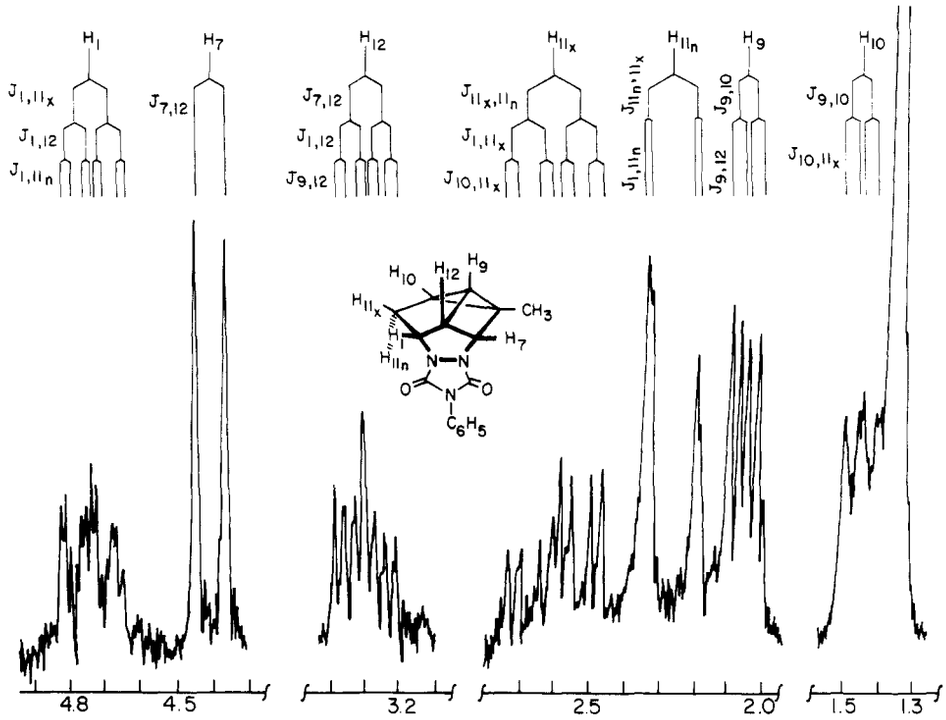


Figure 1. The 100 MHz ^1H NMR spectrum of **9a** ($CDCl_3$ solution) with an overlap showing the prevailing spin–spin interactions.

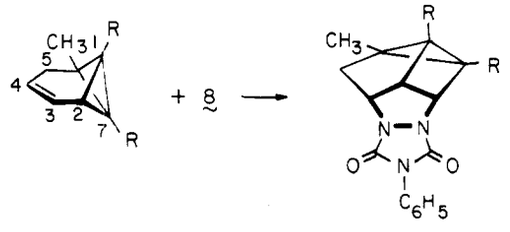
Table I. Partial ^{1}H NMR Spectral Data for the Substituted 4-Phenyl-2,4,6-triazapentacyclo[5.4.1.0^{2,6}.0^{8,10}.0^{9,12}]dodecane-3,5-diones (δ, $CDCl_3$, 100 MHz)

compd	H_1	H_7	H_{12}	H_{11x}	H_{11n}	H_9	H_{10}	H_8
9a	4.75 (d of d of d)	4.42 (d)	3.28 (d of d of d)	2.55 (d of d of d)	2.23 (d of d)	2.05 (d of d)	1.45 (d of d)	
9b	4.75 (d of d of d)	4.42 (d)	3.28 (d of d)	2.55 (d of d of d)	2.23 (d of d)		1.45 (d)	
9c	4.80 (d of d of d)	4.43 (d)	3.14 (d of d)	2.63 (d of d of d)	2.23 (d of d)		1.15 (d)	
11a	4.81 (d of d of d)	4.66 (d of d)	3.31 (d of d of d)	2.59 (d of d)	2.29 (d of d)	2.10–1.94[a] (m)		2.10–1.94[a] (m)
11b	4.81 (d of d of d)	4.66 (d)	3.31 (d of d)	2.59 (d of d)	2.29 (d of d)			
11c	4.74 (d of d of d)	4.43 (d)	3.13 (d of d)	2.51 (d of d)	2.21 (d of d)			

[a] Overlapping signals.

as expected for positioning of the isotopic label at C_9 as in **9b**. In common with **7a** and **7b**, the symmetrical 1,7-dimethyl derivative **7c** was converted to **9c** (see Table I for ^{1}H NMR data).

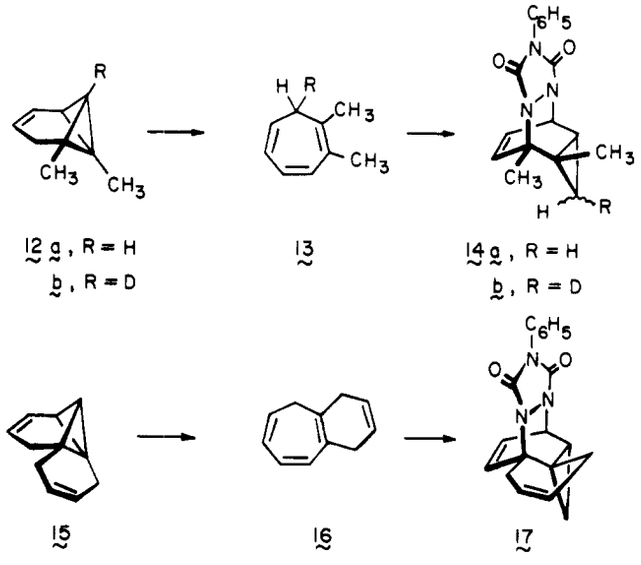
The reaction of PTAD with the 6-methyltricycloheptene **10a** proceeded rapidly in chloroform solution at room temperature to give a crystalline 1:1 adduct identified as **11a**. The



10a, R = H
b, R = D
c, R = CH_3

11a, R = H
b, R = D
c, R = CH_3

100 MHz ^{1}H NMR spectrum of this product proved to be similar in many respects with that of **9a** and, with the aid of spin-decoupling measurements, could also be fully interpreted (Table I). In the case of its dideuterated counterpart **10b**, the adduct was determined to be **11b**. While the prior conversion of **7b** to **9b** established that the integrity of the C_1–C_7 bond was preserved in the course of reaction, the findings with **10b** permit the conclusion that the entire C_1–C_6–C_7 cyclopropyl moiety remains intact. Furthermore, the presence of a triad of methyl groups at these three centers as in **10c** does not deter or alter the course of the cycloaddition. In this instance, **11c** was formed in essentially quantitative yield.



12a, R = H
b, R = D

13

14a, R = H
b, R = D

15 **16** **17**

Somewhat to our surprise, the reaction of PTAD with the 1,6-disubstituted tricycloheptenes **12** and **15** afforded adducts identical with those independently prepared from the corresponding 1,2-disubstituted cycloheptatrienes **13** and **16**, respectively.[25] In common with the other tricycloheptenes, both **12** and **15** are stable in $CHCl_3$ and $CDCl_3$ for periods of time greatly in excess of those utilized for the cycloadditions. Consequently, the possibility of solvent-promoted acid-catalyzed rearrangement can be dismissed. When $CDCl_3$ solutions of **12a** contained in an NMR tube were treated with portions of freshly sublimed PTAD and the tubes shaken, colorless solutions were maintained as the triazolinedione dissolved. Between additions of PTAD, the ^{1}H NMR spectra were recorded. The patterns due to **12a** were seen gradually to diminish in intensity as those of **14a** increased until at completion only those of **14a** were apparent. At no time was there any evidence for the transient formation of **13** (R = H).

When **15** was comparably treated, the concentration of **16** did become adequately high to be observable. However, the isomerization to **16** did not proceed to completion upon addition of only small amounts of PTAD. Rather, the conversion to **16** and then to **17** progressed in incremental fashion. As will be discussed below, these facts suggest that PTAD is itself acting as an electrophilic isomerization catalyst in these examples.

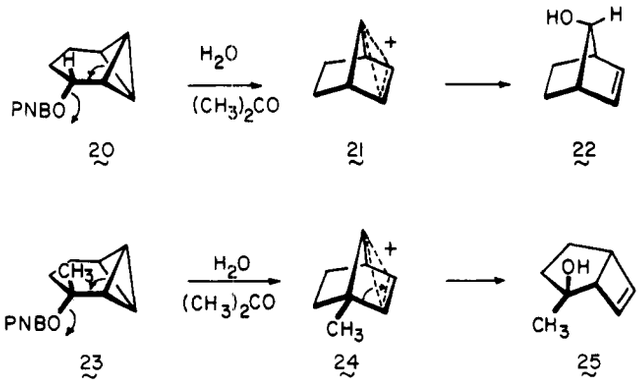
Discussion

The present investigation describes experimental tests which, when taken in conjunction with earlier protonation studies,[23] explicitly demonstrate an abrupt change in the regiospecificity of electrophilic attack on the tricyclo[4.1.0.0^{2,7}]hept-3-ene nucleus. The prior results observed with H^+ and D^+ conform to simple models involving bicyclobutane edge bond cleavage and formation of transient cations **18** (allylic) or **19** (homoallylic), depending upon the

18 **19**

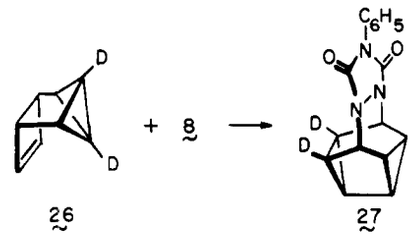
site(s) of alkyl substitution (R). Such mechanistic analysis conforms to expectations based upon orbital symmetry control as determined by PE spectroscopy.

The behavior of the same tricycloheptenes toward PTAD clearly does not conform to this precedent. Rather, π-bond attack is favored by this reagent. In the course of their investigation of the hydrolysis of *p*-nitrobenzoates **20** and **23**, Yano



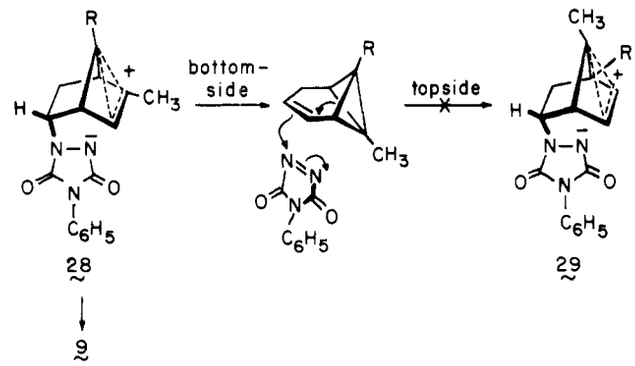
and Yoshida demonstrated the facility with which an edge bicyclobutane bond is capable of migrating (1,2 shift) to an adjacent electron-deficient center.[26] The effect of a methyl substituent at C_3 on the product-forming step is rather dramatic. Although speculation on mechanism does persist,[27] the intervention of 7-norbornenyl cation **24** and its electronic reorganization to the 2-methylbicyclo[3.2.0]hept-6-en-2-yl cation do provide one consistent explanation of the experimental findings.[28]

A more distant bicyclobutane edge bond migration (1,4 shift) has been invoked by Smith, Gream, and Meinwald to account for the conversion of **26** to **27** when treated with



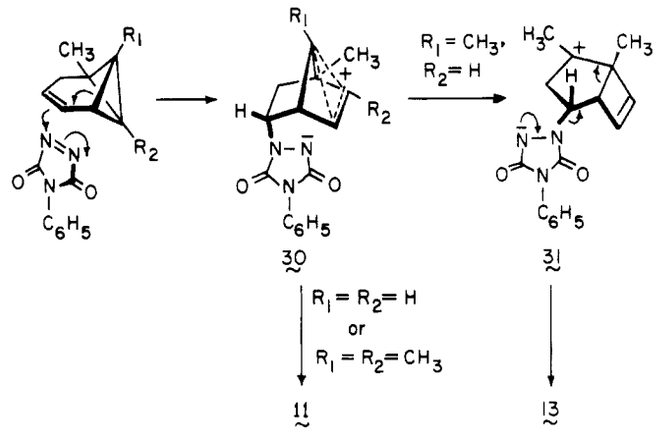
PTAD.[31]

Somewhat analogously, the conversion of tricycloheptenes **7** to adducts **9** can be explained in terms of initial C–N bond formation at C_4 with production of zwitterionic intermediates **28**, where molecular polarization and the stabilization normally accruing to 7-norbornenyl cations are taken advantage of (charge control). For **7a** and **7b** (**7c** is symmetrical about the horizontal plane), attack at the somewhat more sterically hindered bottomside surface operates to the exclusion of topside approach. This is considered to be due to energy differences in the respective transition states which reflect the relative abilities of the methyl groups in **28** and **29** to stabilize

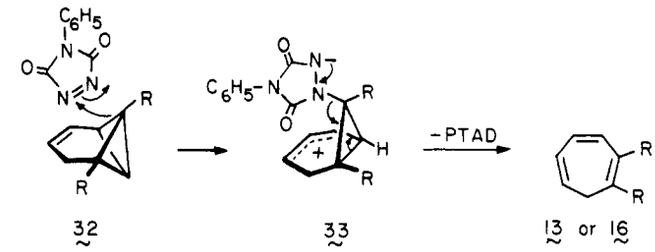


positive charge and (in **7a**) to relieve nonbonded steric interactions. Such regiospecificity is to be expected when charge control is the dominating reaction mode.

The sites of alkyl substitution in **10** preclude realization of the maximum stabilizing capacity of the methyl group(s) (see **30**). Nonetheless, the symmetrical 6-methyl (**10a**) and 1,6,7-trimethyl derivatives (**10c**) deliver products in a manner entirely comparable to the above. Consequently, the reaction



course chosen by these tricycloheptenes closely parallels that followed by benzvalene (**1**).[16] However, a delicate energetic balance apparently prevails, for when R_2 = H (as in **12** and **15**), attack from the less sterically hindered surface seemingly occurs to give **30**. In this fashion, the level of residual nonbonded steric strain is reduced to a minimum, since the 1-Me/7-Me interaction appears less severe than the 1-Me/6-Me option. Additional electronic reorganization within intermediate **30** can then produce **31** (compare **24** → **25**),[26,30] whose subsequent fragmentation to regenerate PTAD and the cycloheptatriene appears to be kinetically preferred to cyclization and formation of a highly strained adduct. Of course, this hypothetical mechanism warrants further scrutiny. In fact, an alternate scheme involving direct PTAD attack at a bicyclobutane edge bond (**32** → **33**) is not ruled out by our findings.



Such postulation of an entirely different regiospecificity is also not warranged. An advantage of the hypothetical **30** → **31** → **13** process is that it provides welcomed mechanistic consistency for the entire series.

In conclusion, the product structural considerations and deuterium labeling results observed for tricycloheptene–PTAD cycloadditions indicate that this strained carbocyclic framework does enter into charge-controlled reactions. In contrast, H^+ and D^+ electrophilic attacks are governed by the prevailing HOMO–LUMO interactions, with the consequences of frontier orbital control reflected in an entirely different regiospecificity and product profile.[23] Thus, it appears that the tricyclo[4.1.0.0^{2,7}]hept-3-ene ring system is capable of multifaceted reactivity. In the future, additional studies may well establish that all exothermic electrophilic additions will consistently opt for maximization of HOMO–LUMO stabilization and be guided to bicyclobutane edge bond cleavage, whereas those reactions which evolve substantial dipolar character and occur later in the reaction profile are governed by maximum charge stabilization and consequently directed to the olefinic site.

Experimental Section

The ^1H NMR spectra were obtained with Varian T-60 and HA-100 spectrometers, and apparent splittings are given in all cases. A Bruker 90 spectrometer was employed for the recording of ^{13}C NMR spectra. Mass spectral measurements were made on an AEI-MS9 spectrometer at an ionizing potential of 70 eV. Preparative VPC work was done on a Varian Aerograph A90-P3 instrument equipped with a thermal

conductivity detector. Microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Preparation of the Tricyclo[4.1.0.0^{2,7}]hept-3-enes. Hydrocarbons **7a, 10a,** and **12a** were prepared according to earlier procedures. The tetracyclic system **15** was made available from an independent study, the details of which will be published separately.[32]

1-Methyltricyclo[4.1.0.0^{2,7}]hept-3-ene-*7-d* (7b). To a stirred solution of tetramethylethylenediamine (3 mL) in pentane (50 mL) maintained under nitrogen at 0 °C was added a solution of *n*-butyllithium (3 mL of 1.6 M) in hexane. After the mixture was stirred for 30 min, a 200-mg (1.9-mmol) sample of **7a** was introduced dropwise via a syringe. The resultant solution was stirred at 0 °C for 3 h prior to quenching with excess deuterium oxide.

The solution was washed successively with saturated copper sulfate (4 × 30 mL) and sodium chloride (1 × 30 mL) solutions, and the organic layer was concentrated and subjected to preparative VPC (12 ft × 0.25 in. 10% QF-1 on 60–80 mesh Chromosorb G, 100 °C) to give pure **7b.** The ^{1}H NMR spectrum of **7b** indicated no evidence for the signal corresponding to the C_7 proton.

1,7-Dimethyltricyclo[4.1.0.0^{2,7}]hept-3-ene (7c). To a solution of tetramethylethylenediamine (2 mL) and *n*-butyllithium (2 mL of 1.6 M in hexane) in pentane (30 mL) maintained at 0 °C under nitrogen was introduced a 200-mg (1.89-mmol) sample of **7c.** After the mixture was washed with saturated copper sulfate and sodium chloride solutions, the organic phase was concentrated and subjected to preparative VPC (same above QF-1 column, 90 °C) to give pure **7c:** ^{1}H NMR ($CDCl_3$) δ 6.07–5.65 (m, 1), 5.40–5.00 (m, 1), 2.00 (m, 2), 1.84–1.50 (m, 2), and 1.24 (s, 6); MS *m/e* 120.0941 (calcd *m/e* 120.0939).

Anal. Calcd for C_9H_{12}: C, 89.94; H, 10.06. Found: C, 89.75; H, 10.14.

6-Methyltricyclo[4.1.0.0^{2,7}]hept-3-ene-*1,7-d*$_2$ (10b). To a pentane (50 mL) solution of tetramethylethylenediamine (2 mL) and *n*-butyllithium (2 mL of 1.6 M in hexane) was added 90 mg (0.85 mmol) of **10a.** After the resultant mixture had been stirred at 0 °C for 5 h, an excess of D_2O was introduced. Workup and VPC purification as above gave **10b,** the ^{1}H NMR spectrum of which provided no evidence for the signal corresponding to the C_1 and C_7 protons.

1,6,7-Trimethyltricyclo[4.1.0.0^{2,7}]hept-3-ene (10c). A 300-mg sample of **10a** (2.5 mmol) was dimethylated according to the above procedure. Comparable workup and purification furnished 174 mg (52%) of **10c:** ^{1}H NMR ($CDCl_3$) δ 6.07–5.73 (m, 1), 5.43–5.00 (m, 1), 2.03–1.87 (m, 2), 1.73 (m, 1), 1.37 (s, 6), and 1.02 (s, 3); MS *m/e* 134.1099 (calcd *m/e* 134.1095).

Anal. Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.15; H, 10.55.

Generalized PTAD Cycloaddition Procedure. To a stirred solution of **7a** (62 mg, 0.58 mmol) in chloroform at room temperature was added during 10 min a solution of *N*-phenyltriazolinedione (102 mg, 0.58 mmol) in chloroform (20 mL). The resulting colorless solution was evaporated to dryness, and the oily residue was triturated with ethanol. The solid product which formed quantitatively (in each case studied) was recrystallized from ethanol to give 8-methyl-4-phenyl-2,4,6-triazapentacyclo[5.4.1.0^{2,6}.0^{8,10}.0^{9,12}]dodecane-3,5-dione (**9a**) as off-white crystals: mp 116–118 °C; ^{1}H NMR ($CDCl_3$) δ 7.56–7.20 (m, 5), 4.75 (d of d of d, $J_{1,11x}$ = 8.0 Hz, $J_{1,12}$ = 5.6 Hz, $J_{1,11n}$ = 1.2 Hz, H_1), 4.42 (d, $J_{7,12}$ = 8.0 Hz, H_7), 3.28 (d of d of d, $J_{7,12}$ = 8.0 Hz, $J_{1,12}$ = 5.6 Hz, $J_{9,12}$ = 2.7 Hz, H_{12}), 2.55 (d of d of d, $J_{11x,11n}$ = 13.5 Hz, $J_{1,11x}$ = 8.0 Hz, $J_{10,11x}$ = 2.7 Hz, H_{11x}), 2.23 (d of d, $J_{11x,11n}$ = 13.5 Hz, $J_{1,11n}$ = 1.2 Hz, H_{11n}), 2.05 (d of d, $J_{9,10}$ = 5.0 Hz, $J_{9,12}$ = 2.7 Hz, H_9), 1.45 (d of d, $J_{9,10}$ = 5.0 Hz, $J_{10,11x}$ = 2.7 Hz, H_{10}), and 1.35 (s, 3); IR (KBr) ν_{max} 3050, 2960, 2925, 2865, 1775, 1720, 1602, 1505, 1420, 1342, 1280, 1253, 1133, 1081, 770, and 696 cm^{-1}; MS *m/e* 281.1169 (calcd *m/e* 281.1164); ^{13}C NMR ($CDCl_3$) 153.23 (s), 132.09 (s), 129.10 (d), 128.01 (d), 125.50 (d), 61.02 (d), 58.41 (d), 48.64 (d), 36.84 (t), 31.81 (s), 30.48 (q), 23.75 (d), and 17.31 (d) ppm.

Anal. Calcd for $C_{16}H_{15}N_3O_2$: C, 68.31; H, 5.38. Found: C, 67.90; H, 5.45.

Adduct **9b** was comparably prepared from 50 mg (0.47 mmol) of **7b** and 82 mg (0.47 mmol) of PTAD: ^{1}H NMR, see Table I; MS *m/e* 282.1232 (calcd *m/e* 282.1227). The ^{13}C NMR spectrum was the same as that for **9a** except for perturbation of the 23.75 ppm signal.

8,9-Dimethyl-4-phenyl-2,4,6-triazapentacyclo[5.4.1.0^{2,6}.0^{8,10}.0^{9,12}]dodecane-3,5-dione (9c). Reaction of **7c** (70 mg, 0.58 mmol) in chloroform (15 mL) with PTAD (102 mg, 0.58 mmol) in chloroform (25 mL) afforded **9c** as colorless needles: mp 148.5–149.5 °C (from ethanol); ^{1}H NMR ($CDCl_3$) δ 7.58–7.18 (m, 5), 4.80 (d of d of d, $J_{1,11x}$ = 8.8 Hz, $J_{1,12}$ = 5.3 Hz, $J_{1,11n}$ = 1.2 Hz, H_1), 4.43 (d, $J_{7,12}$ = 8.4 Hz, H_7), 3.14 (d of d, $J_{7,12}$ = 8.4 Hz, $J_{1,12}$ = 5.3 Hz, H_{12}), 2.63 (d of d of d, $J_{11x,11n}$ = 13.5 Hz, $J_{1,11x}$ = 8.8 Hz, $J_{10,11x}$ = 3.2 Hz, H_{11x}), 2.23 (d of d, $J_{11x,11n}$ = 13.5 Hz, $J_{1,11n}$ = 1.2 Hz, H_{11n}), 1.31 (s, 6), and 1.15 (d, $J_{10,11x}$ = 3.2 Hz, H_{10}); IR (KBr) ν_{max} 3015, 2935, 2915, 2860, 1765, 1710, 1599, 1494, 1407, 1345, 1281, 1255, 1122, 1071, 947, 795, 759, 691, and 635 cm^{-1}; MS *m/e* 295.1328 (calcd *m/e* 295.1321); ^{13}C NMR ($CDCl_3$) 154.37 (s), 132.06 (s), 129.05 (d), 127.92 (d), 125.43 (d), 61.18 (d), 57.87 (d), 53.03 (d), 36.67 (t), 34.49 (s), 30.44 (s), 14.65 (q), and 9.98 (q) ppm.

Anal. Calcd for $C_{17}H_{17}N_3O_2$: C, 69.13; H, 5.80. Found: C, 68.73; H, 5.89.

10-Methyl-4-phenyl-2,4,6-triazapentacyclo[5.4.1.0^{2,6}.0^{8,10}.0^{9,12}]dodecane-3,5-dione (11a). Reaction of **10a** (48 mg, 0.45 mmol) in chloroform (10 mL) with PTAD (80 mg, 0.45 mmol) in the same solvent (20 mL) gave **11a** as colorless needles: mp 165.5–167 °C (from ethanol); ^{1}H NMR ($CDCl_3$) δ 7.55–7.21 (m, 5), 4.81 (d of d of d, $J_{1,11x}$ = 9.0 Hz, $J_{1,12}$ = 5.6 Hz, $J_{1,11n}$ = 1.8 Hz, H_1), 4.66 (d of d, $J_{7,12}$ = 7.8 Hz, $J_{7,10}$ = 3.0 Hz, H_7), 3.31 (d of d of d, $J_{7,12}$ = 7.8 Hz, $J_{1,12}$ = 5.6 Hz, $J_{9,12}$ = 2.8 Hz, H_{12}), 2.59 (d of d, $J_{11x,11n}$ = 13.5 Hz, $J_{1,11x}$ = 9.0 Hz, H_{11x}), 2.29 (d of d, $J_{11x,11n}$ = 13.5 Hz, $J_{1,11n}$ = 1.8 Hz, H_{11n}), 2.10–1.94 (m, 2), and 1.12 (s, 3); IR (KBr) ν_{max} 3060, 3040, 2955, 2910, 2850, 1772, 1710, 1600, 1500, 1418, 1342, 1280, 1251, 1130, 837, 780, 765, 741, and 690 cm^{-1}; MS *m/e* 281.1170 (calcd *m/e* 281.1164); ^{13}C NMR ($CDCl_3$) 154.47 (s), 153.04 (s), 131.95 (s), 129.10 (d), 128.01 (d), 125.45 (d), 60.97 (d), 53.86 (d), 50.02 (d), 42.43 (t), 31.43 (s), 30.44 (d), 25.65 (d), and 16.83 (q) ppm.

Anal. Calcd for $C_{16}H_{15}N_3O_2$: C, 68.31; H, 5.38. Found: C, 68.13; H, 5.33.

Adduct **11b** was comparably prepared from 30 mg (0.28 mmol) of **10b** and 50 mg (0.28 mmol) of PTAD: ^{1}H NMR, see Table I; MS *m/e* 283.1296 (calcd *m/e* 283.1290). The ^{13}C NMR spectrum was the same as that for **11a** except for perturbation of the 30.44 and 25.65 ppm signals.

8,9,10-Trimethyl-4-phenyl-2,4,6-triazapentacyclo[5.4.1.0^{2,6}.0^{8,10}.0^{9,12}]dodecane-3,5-dione (11c). Reaction of **10c** (86 mg, 0.64 mmol) with PTAD (112 mg, 0.64 mmol) in 40 mL of chloroform at room temperature gave **11c** as colorless needles: mp 131–132 °C (from ethanol); ^{1}H NMR ($CDCl_3$) δ 7.55–7.22 (m, 5), 4.74 (d of d of d, $J_{1,11x}$ = 8.0 Hz, $J_{1,12}$ = 5.2 Hz, $J_{1,11n}$ = 1.8 Hz, H_1), 4.43 (d, $J_{7,12}$ = 8.2 Hz, H_7), 3.13 (d of d, $J_{7,12}$ = 8.2 Hz, $J_{1,12}$ = 5.2 Hz, H_{12}), 2.51 (d of d, $J_{11x,11n}$ = 13.5 Hz, $J_{1,11x}$ = 8.0 Hz, H_{11x}), 2.21 (d of d, $J_{11x,11n}$ = 13.5 Hz, $J_{1,11n}$ = 1.8 Hz, H_{11n}), 1.27 (s, 3), 1.16 (s, 3), and 1.02 (s, 3); IR (KBr) ν_{max} 3020, 2950, 2915, 2860, 1767, 1710, 1597, 1493, 1456, 1400, 1346, 1281, 1253, 1115, 1072, 793, 759, and 687 cm^{-1}; MS *m/e* 309.1484 (calcd *m/e* 309.1477); ^{13}C NMR ($CDCl_3$) 154.47 (s), 132.18 (s), 129.10 (d), 127.96 (d), 125.48 (d), 60.35 (d), 58.51 (d), 53.34 (d), 43.52 (d), 34.89 (s), 34.37 (s), 32.14 (s), 12.75 (q), 11.80 (q), and 6.78 (q) ppm.

Anal. Calcd for $C_{18}H_{19}N_3O_2$: C, 69.88; H, 6.19. Found: C, 69.78; H, 6.36.

Reaction of 1,6-Dimethyltricyclo[4.1.0.0^{2,7}]hept-3-ene (12a) with PTAD. To a solution of **12a** in either ethyl acetate or chloroform was added an equimolar quantity of freshly sublimed PTAD. After the reaction mixture was stirred at room temperature for 1 h, it was concentrated to dryness and the residual solid was recrystallized from ethyl acetate to give **14a** as colorless needles, mp 148–149 °C. This substance was spectroscopically identical with authentic **14a** obtained earlier by Diels–Alder cycloaddition of PTAD to 1,2-dimethylcycloheptatriene.[23]

Adduct **14b** was prepared comparably from **12b.** In the ^{1}H NMR spectrum the absorption at δ 0.54 was substantively diminished in intensity, while in the ^{13}C NMR spectrum the 15.39 ppm signal was perturbed.

12-Phenyl-10,12,14-triazapentacyclo[7.5.2.0^{1,6}.0^{6,8}.0^{10,14}]hexadeca-3,15-diene-11,13-dione (17). Reaction of **15** (100 mg, 0.69 mmol) with PTAD (122 mg, 0.69 mmol) in chloroform (35 mL) at room temperature gave **17** as tiny colorless needles: mp 129–130 °C (from ethyl acetate); ^{1}H NMR ($CDCl_3$) δ 7.32 (br s, 5), 6.00–5.70 (m, 4), 5.30–5.05 (m, 1), 4.05–3.60 (m, 1), 2.97–1.67 (br m, 3), 1.47–1.13 (m, 1), and 0.73–0.55 (m, 2).

Anal. Calcd for $C_{19}H_{17}N_3O_2$: C, 71.46; H, 5.37. Found: C, 71.06; H, 5.49.

Silver(I)-Catalyzed Rearrangement of 15. A solution of **15** (100 mg, 0.7 mmol) in benzene (10 mL) was treated with 1 mL of a 0.15 M solution of anhydrous silver perchlorate in dry benzene. After the mixture was allowed to stand at room temperature for 10 min, it was repeatedly washed with saturated sodium chloride solution, dried, and concentrated. The residual oil was purified by preparative VPC (6 ft × 0.25 in. 10% TCEP on 60–80 mesh Chromosorb W, 120 °C) to give 6,9-dihydrobenzocycloheptatriene (**16**) as the sole product: ^{1}H NMR ($CDCl_3$) δ 6.43–5.23 (m, 10), 2.88 (br s, 4), and 2.30 (d, J = 7 Hz, 2); MS *m/e* 144.0942 (calcd *m/e* 144.0939).

Anal. Calcd for $C_{11}H_{12}$: C, 91.61; H, 8.39. Found: C, 91.23; H,

8.51.

Diels–Alder Cycloaddition of PTAD to 16. To a stirred solution of 16 (56 mg, 0.39 mmol) in chloroform (10 mL) was added during 10 min a solution of PTAD (68 mg, 0.39 mmol) in chloroform (10 mL). The resulting colorless solution was triturated to dryness, and the residual gum was triturated with ethanol to give crystalline **17**, mp 129–130 °C (from ethyl acetate). This substance was identical in all respects with that isolated above.

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Steric Inhibition of a Silver(I)-Catalyzed 1,8-Bishomocubane–Snoutane Rearrangement[1]

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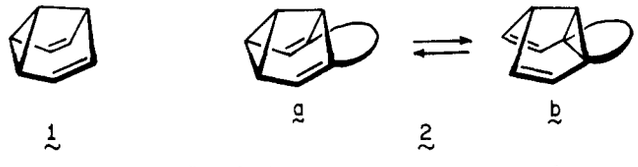
In an attempt to probe the effect of symmetrical bisannulation of the semibullvalene nucleus with trimethylene bridges as in **5,** a synthesis of the diazabishomocubane **3** was undertaken. Thus, Diels–Alder cycloaddition of cyclopentene-1,2-dicarboxylic anhydride to 1,2-dimethylenecyclopentane afforded a tetracyclic adduct (**8**) that could be transformed into the bridged sulfide **10** by standard methodology. Recourse to a Ramberg–Bäcklund ring contraction sequence provided the propelladiene **12,** from which the requisite triene **13** could be prepared. *N*-Phenyltriazolinedione addition to **13** gave rise to **14** which when irradiated in acetone–benzene (1:1) through Corex furnished the caged structure **3** of C_{2v} symmetry. Unlike all bishomocubanes previously examined, **3** was unreactive toward Ag^+ even under the most forcing conditions. This result is considered to be due to serious steric impediment and appears consistent with earlier mechanistic considerations.

Recent research activity in the area of semibullvalene chemistry has contributed to our understanding of the extraordinary ease of Cope rearrangement in this system ($\Delta G^{\ddagger}$ for **1** = 5.5 kcal/mol)[2,3] and to an appreciation of the pronounced sensitivity of its molecular framework to ground-state equilibrium displacements upon monosubstitution[4,5] or by bracketing by aliphatic[6] or heteroaliphatic chains[7] as in **2.** Particularly worthy of note is the behavior of the trimethylene-bridged hydrocarbon. Whereas tautomer **2b** predominates (57%) in CS_2 solution at room temperature, the concentration levels of **2a** and **2b** equalize at −29 °C, and **2a** dominates the equilibrium below this temperature.[6c] The



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