Thermally Promoted Cleavage Reactions of *anti*-Tricyclo[3.2.0.0^{2,4}]heptanes. The Influence of 2,4 Substitution on Competitive Bond Scission Processes

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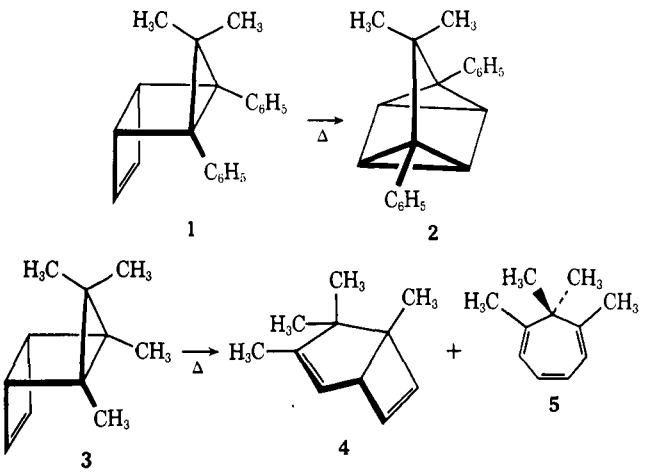
Received October 16, 1973

anti-Tricyclo[3.2.0.0^{2,4}]heptane and several derivatives of this ring system have been prepared and subjected to thermal activation. When positions 2 and 4 carry phenyl groups, pyrolysis occurs to give exclusively ethylene and the corresponding cyclopentadiene. Suitable deuterium substitution at C_6 and C_7 revealed that the production of ethylene takes place with a marked stereoselectivity for the [$\sigma 2_s + \sigma 2_s$] mode. When the phenyl substituent at C_2 was replaced by methyl, extrusion of ethylene comprised only 55% of the total product profile. In actual fact, 1,4-cycloheptadiene and 4-methylenecycloheptene formation was found to become competitive. Also, the latter mechanistic atlernatives became predominant when the remaining phenyl was replaced by methyl. The parent hydrocarbon afforded only 1,4-cycloheptadiene. Possible mechanisms are discussed.

Thermal cleavage reactions of internal carbon–carbon bonds in polycyclic hydrocarbons are now assumed to occur along a reaction coordinate involving rotation of the relevant atomic orbitals with respect to one another rather than mere in-plane stretching of the C–C linkage.[2] This so-called electrocyclic bond rupture can occur with particular ease in two different modes depending upon whether there are $4n$ (conrotatory) or $4n + 2$ (disrotatory) electrons in the ring-opened conjugated π system. However, when no associated π electron framework exists, bond reorganization frequently proceeds less readily and the intermediacy of steady-state singlet diradical intermediates has been postulated in such cases.[3] The isomerization and rearrangement reactions of bicyclo[2.1.0]pentanes[4] and bicyclo[2.2.0]hexanes[4b,g,5] are prototype processes for which the intervention of 1,3 and 1,4 diradicals, respectively, has been proposed. However, the very short lifetimes of such elusive species customarily preclude their direct observation[6] and necessitate an indirect assessment of their formation; stereochemical studies and product analyses are the tools most frequently utilized for this purpose. Although such data have proven consistent with the operation of two-step mechanisms, they do not require the intercession of diradicals. As a consequence, this long-respected rationale has recently been questioned on theoretical grounds. Hoffmann, using an extended Hückel approach, has constructed an energy profile for the thermal fragmentation of cyclobutane and has found no minimum in the potential energy surface to correspond to the tetramethylene diradical.[7] Rather, a broad, flat region of coordinate space was seen near the transition state. Similarly, in his examination of cyclopropane geometrical isomerization by *ab initio* methods, Salem noted no potential energy minimum for the singlet rearrangement.[8] The suggestion was advanced that geometric inversion may consist of a smooth one-step process involving bond-stretched species which lose configuration without becoming *bona fide* intermediates.

Consequently, the question of whether singlet nonstabilized diradicals exist as true intermediates or as transition states is currently unresolved.[9] Despite these existing differences in interpretation, we have sought to design strained polycyclic systems, cleavage of a key internal bond in which would initiate a secondary reaction of synthetic and/or mechanistic significance. Previously, the ready quantitative conversion of *anti*-tricyclo[3.2.0.0^{2,4}]-hept-3-ene (1) to quadricyclane 2 at 100° has been described.[10] That the 2 and 4 substituents play a key role in the chemical reactivity of such tricyclic molecules was attested to, for example, by the thermal behavior of tetramethyl derivative 3. No quadricyclane formation was observed, 4 (38%) and 5 (62%) resulting instead.[10b] This paper reports the results of a thermochemical investigation of several *anti*-tricyclo[4.1.0.0^{2,5}]heptanes and describes *inter alia* the first example of highly stereoselective [$\sigma 2_s + \sigma 2_s$] cycloreversion of a cyclobutane ring to olefinic products as the result of the suprafacial fragmentation of a third proximate σ bond.[11]

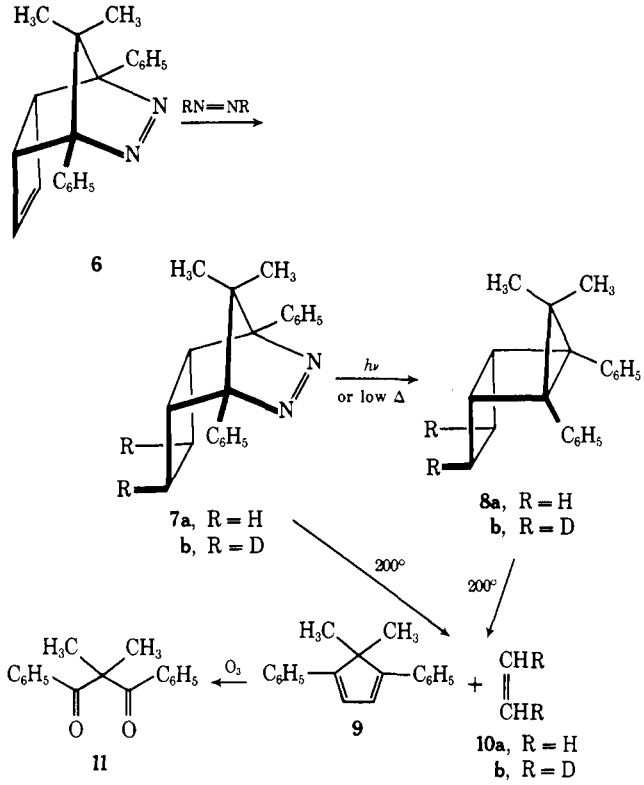


Results

2,4-Diphenyl Substitution. The readily accessible azo compound **6**, obtainable through reaction of cyclobutadiene with 3,3-dimethyl-2,4-diphenylisopyrazole,[10] could be conveniently reduced with diimide. Although a large excess (20–100-fold) of this reagent was necessary to realize a maximum yield (90%) of **7a** no competitive reduction of the azo linkage was observed. Photolysis of **7a** in Pyrex vessels resulted in efficient conversion to **8a**, the anti stereochemistry of which was established by similar reduction of **1** whose configuration had been proven earlier.[10] An identical preparation of **8b** starting with dideuteriodiimide proceeded with equal efficiency.

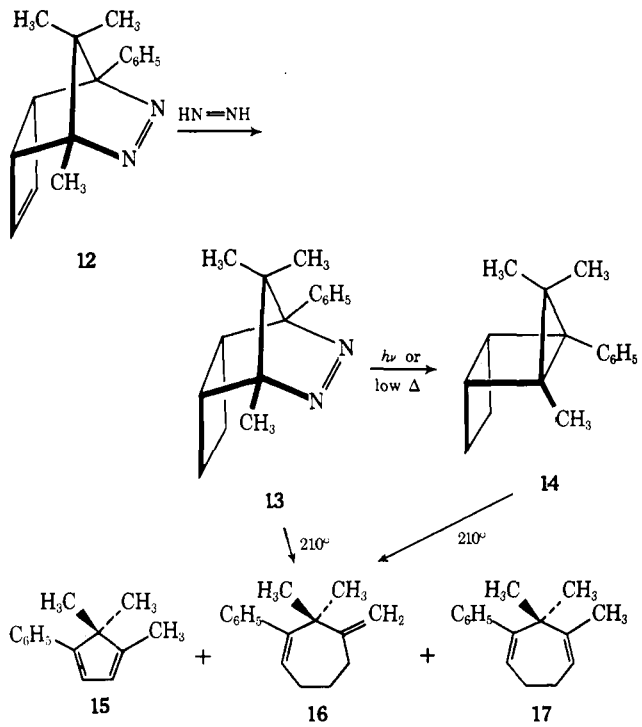
Thermolysis of **7a** in degassed deuteriochloroform solution could be conveniently monitored by nmr spectroscopy. After 5 hr at 140°, extrusion of nitrogen with quantitative formation of **8a** was observed. Further heating at 210° for 3 hr caused **8a** to experience fragmentation exclusively to 5,5-dimethyl-1,4-diphenylcyclopentadiene (**9**) and ethylene (**10a**). Indicative of its highly extended conjugation, **9** displays a blue fluorescence and ultraviolet maxima (isooctane solution) at 232 nm (ϵ 9000) and 330 (15,400). In agreement with the formal loss of ethylene from **8a**, the nmr spectrum of **9** (in $CDCl_3$) consists of a ten-proton multiplet at δ 7.50, a singlet of area 2 at 6.77, and an upfield singlet (6 H) at 1.65. These data compare very favor-

ably with the spectral features of 1,4-diphenylcyclopentadiene, for which λ_{max} (C_2H_5OH) 232 nm (ϵ 12,300) and 346 nm (22,900) as well as δ 7.27-7.77 (10 H), 6.93 (2 H), and 3.75 (2 H) have been reported.[12] Ultimate confirmation of the structural assignment was obtained by ozonolysis to diketone 11 of unequivocal constitution.[6b]



At 200°, the 7a → 8a conversion is so rapid that the product mixture is independent of which of the two is utilized as reactant. The stereochemistry attending the production of ethylene was studied by pyrolysis of both **7b** and **8b** as neat samples in sealed tubes and the results are shown in Table I. The isotopically substituted ethylene mixtures were transferred from the individual reaction chambers by high-vacuum techniques to nmr tubes containing carbon tetrachloride-10% tetramethylsilane (0.3 ml) and the relative proportions of *cis*- and *trans*-**10b** were determined by deuterium-decoupled proton nmr spectroscopy. This facile and entirely reliable method of analysis, initially devised by Closs,[13] provides singlet absorptions for *cis*- and *trans*-1,2-dideuterioethylene at 532.1 and 532.7 Hz, respectively, downfield from TMS at 100 MHz with relative intensities relatable directly to the isomer ratio. Cis-trans isomerization of 1,2-dideuterioethylene has been shown previously not to operate at temperatures as high as 450° under similar conditions.[14a,b] That a minor amount of stereorandomization occurs in **7b** and **8b** during thermal activation cannot be summarily dismissed, although it is rather unlikely. At the experimental level, nmr monitoring of these reactions indicated that such interconversions, if operative at all, do not reach spectroscopically detectable levels. Consequently, the data collected in Table I are considered to reflect kinetically controlled product distributions which reveal that fragmentation of the *anti*-tricycloheptane nucleus occurs in highly stereoselective fashion with a preference for [$_{\sigma}2_s$ + $_{\sigma}2_s$] cleavage of approximately 9.5.

The 2-Methyl-4-phenyl Example. Preparation of **13** and **14** was modeled on the synthesis of **7a**. Treatment of **12** with diimide led in 95% yield to **13**, which upon photolysis in ether solution or upon controlled thermolysis at 140° gave the desired tricycloheptane derivative. When neat samples of either **13** or **14** were heated at 210° for 4 hr, cycloreversion to ethylene and phenyltrimethylcyclopentadiene (**15**) was again observed. However, this pathway now represented only 55% of the total reaction. There was also produced a difficultly separable mixture of **16** (~15%), **17** (~15%), and a third hydrocarbon which has not been characterized (~15%).



Diene **15** exhibits an nmr spectrum in which the two nonequivalent olefinic protons appear at δ 6.60 and 6.00, the sp^2-bound methyl group at 1.90, and the equivalent pair of methyl substituents at 1.19. Comparison of these data with those of **9** and **21** show **15** to be a composite of these fully characterized structures (see Experimental Section). The electronic spectra of the three cyclopentadiene derivatives also form a triad consistent with the gradual diminution of phenyl conjugation.

The presence of a downfield triplet (J = 7.2 Hz) at δ 5.42 in the nmr of **16** is consistent with a styrene part structure. The exocyclic methylene group is demanded by the appearance of somewhat broadened one-proton absorptions at δ 5.00 and 4.80, and accords with the observation that a methyl substituent in **13** and **14** has been chemically modified during conversion to **16**. From an intense six-proton singlet at δ 1.17, the remaining two methyls are seen to be rapidly equilibrating under the conditions of measurement.

Structural assignment to **17** is founded principally on nmr similarities with those of the symmetrical tetramethyldiene **23**. Its most relevant absorptions appear at δ 5.92 (1 H), 5.70 (1 H), 1.78 (3 H), and 1.14 (6 H).

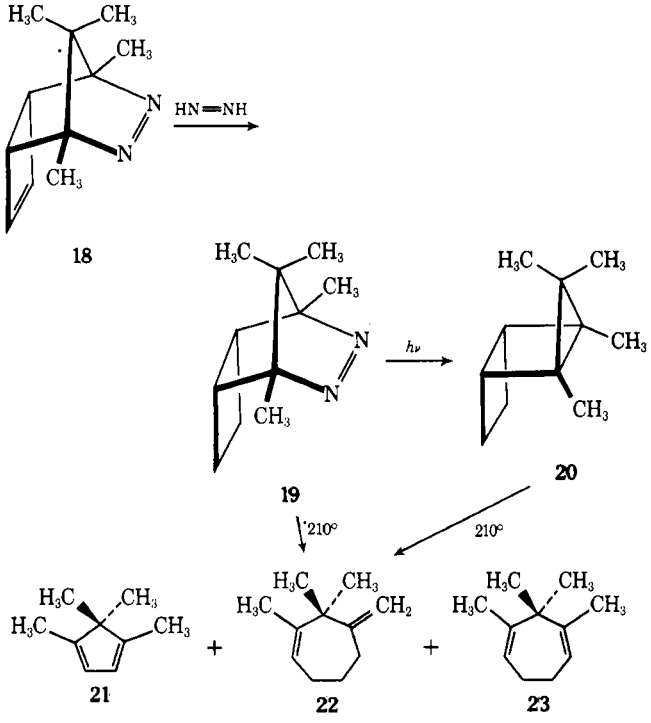
2,4-Dimethyl Substitution. The above observation that replacement of a 4-phenyl substituent by methyl caused pathways other than ethylene extrusion to gain importance suggested that replacement of the remaining phenyl group would cause a further decrease in the amount of cyclopentadiene produced. To this end, **20** was prepared as before. Thermal decomposition of **20** or its azo precursor **19** at 210° repeatedly led, in this instance, to partial recovery of the tricycloheptane (~30%) and the formation of three other hydrocarbons.

The minor component to be eluted first from an SE-30 vpc column was shown to be 1,4,5,5-tetramethylcyclopentadiene (**21**) by direct comparison of its nmr and electron-

Table I
Deuterated Ethylenes from Pyrolyses Conducted at 210°

		Products, % yield			
		Absolute		Relative	
Reactant	CH_2=CHD[a]	$\frac{D}{H}>C=C<\frac{D}{H}$	$\frac{D}{H}>C=C<\frac{H}{D}$	$\frac{D}{H}>C=C<\frac{D}{H}$	$\frac{D}{H}>C=C<\frac{H}{D}$
7b	10.2	82.1	7.7	91.4	8.6
7b	11.5	79.0	9.5	89.3	10.7
8b	9.8	82.0	8.2	90.9	9.1
8b	10.7	81.0	8.4	90.7	9.3

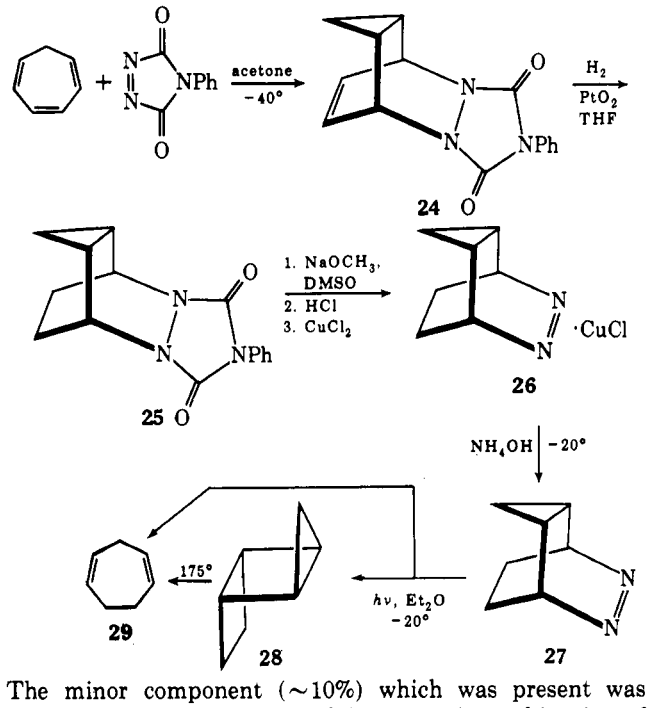
[a] Consistently, *ca.* 10% monodeuteration was encountered in the DN=ND reduction of **6** (mass spectral analysis of **7b** and **8b**). The ethylene analyses are in full agreement with the mass spectral data. The chemical shift for the protons in the CH_2=CHD (double irradiation conditions) is found at 533.4 Hz downfield from TMS at 100 MHz.



ic spectra with those of an authentic sample.[15] The nmr spectrum of the second product shows one endocyclic olefinic proton at δ 5.37, two exocyclic methylene hydrogens at δ 4.94 and 4.72, four allylic protons, and a nonconjugated methylene group. These data, in tandem with the presence of one sp^2-bound and two sp^3-bound methyl groups, are uniquely consistent with the methylenecycloheptene formulation **22** in which one of the four methyl substituents in **19** or **20** has been transmuted to an exocyclic methylene function. Structural assignment to the last component **23** was based chiefly upon the highly symmetrical nature of its nmr spectrum, which displayed resonances due to two equivalent olefinic protons (br m, δ 5.68), four allylic hydrogens (br m, δ 2.15), and two widely different pairs of methyl groups (s, δ 1.77 and 1.23).

The Parent System. *anti*-Tricyclo[3.2.0.0^{2,4}]heptane (**28**), the parent hydrocarbon of the series, has recently been prepared by Tanida and coworkers[16] and found by them to afford two products in a 10:1 ratio upon thermolysis. Although the major constituent was characterized as 1,4-cycloheptadiene (**29**), the minor component remained unidentified. Because the amount of cyclopentadiene produced is clearly dependent upon the ability of the 2,4 substituents to weaken the C_2–C_4 bond, interest was aroused in the question of whether two hydrogens at these sites would suffice to promote ethylene fragmentation. Accordingly, this question was investigated.

The sequence ultimately employed for the preparation of **28** represents a composite of the methods reported by the Tanida[16] and Roth[17] groups for the synthesis of azo compound **27** with several modifications (see Experimental Section). Because **27** suffers extrusion of nitrogen even at room temperature,[16-18] it becomes necessary to conduct all manipulations involving this material at temperatures below −20°. Upon pyrolysis of **28** (neat, 173° for 15 min), 1,4-cycloheptadiene was obtained as the only product.



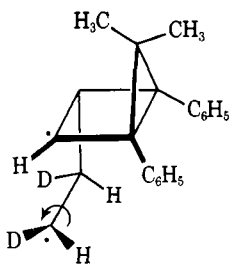
The minor component (~10%) which was present was found to be unreacted tricycloheptane. A combination of nmr and flame ionization vpc techniques gave no evidence for the formation of cyclopentadiene. Thus, hydrocarbon **28** fragments in a manner totally analogous to that followed by azo derivative **27** which likewise affords only **29**.[16-18]

Discussion

In our earlier study of the thermal rearrangement of tricyclo[3.2.0.0^{2,4}]hept-6-enes,[10] the experimental results denoted that the C_1–C_5 bond is intrinsically the weakest link in the system except when phenyl groups are situated at C_2 and/or C_4. Two corollaries of this position are that bicycloheptadiene (*e.g.*, **4**) and cycloheptatriene (*e.g.*, **5**) formation is triggered by initial homolysis at C_1–C_5 (and subsequent rupture between C_2–C_4) while quadricyclane production (*e.g.*, **2**) is the result of preferential bond weakening at C_2–C_4. In the latter instance, a distinction between a fully concerted ($\sigma 2_s + \sigma 2_s + \pi 2_s$) pathway or one involving singlet diradical intermediates was not possible. Prior rearrangement of **1** to the corresponding cis,syn,cis isomer[19] has been discounted,[9a,20] but the possible involvement of configuration interaction influences has recently been considered.[9a]

In the case of the tricycloheptane derivatives, removal of the π bond at C_6–C_7 was expected to render C_1–C_5 cleavage relatively more difficult. As a consequence of this structural alteration, the rates of cleavage of the C_1–C_5 and C_2–C_4 bonds were anticipated to be more equitable than observed in the unsaturated derivatives.

Fragmentation to Cyclopentadiene and Ethylene. The thermal cleavage of **7b** is seen to occur smoothly with a distinct preference for suprafacial cleavage of the two cyclobutane bonds [$(s + s)/(a + s) = 9.5$]. This ratio is substantially greater than those observed for the pyrolytic fragmentation of 7,8-*cis,exo*-dideuterio-*cis*-bicyclo[4.2.0]octane (0.75)[14] or the 11,12-*cis*-dideuteriopropella-2,4-dienes (2.0),[21] and is sufficient to dismiss the intervention of diradical intermediates such as **30** and **31**. The intermediacy of such species should under ordinary circumstances lead to extensive stereochemical scrambling (*cf.* arrows, no directional preference implied) since bond rotation and cleavage would be expected to be competitive.[22] Moreover, not only is initial C_5–C_6 fission not energetically economical, but the established need for phenyl substitution at C_2 and C_4 to promote ethylene formation likewise mitigates against the involvement of **30** and **31**.



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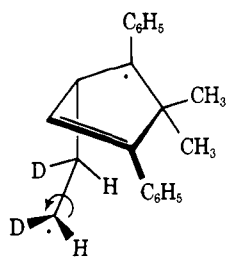

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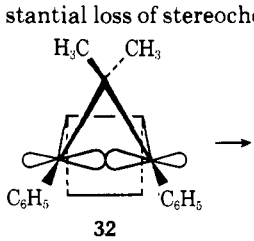
A more probable mechanistic interpretation is based upon stereoelectronic considerations which rationalize the role played by the phenyl groups. As fragmentation of the C_2–C_4 bond commences, rehybridization in the sp^2 direction to give maximum stabilization to the developing p orbitals takes place (**32** → **34**). It is not known whether the two cyclobutane bonds experience cleavage at that stage (**33**) where orbitals of the C_2–C_4 bond are well canted but not yet completely severed, or only after diradical **34** is formed. The first event would constitute a fully concerted process, whereas the latter is formally a stepwise pathway. The data require only that the two edge bonds of the four-membered ring break nearly simultaneously or at least in sufficiently rapid succession to preclude substantial loss of stereochemical configuration.



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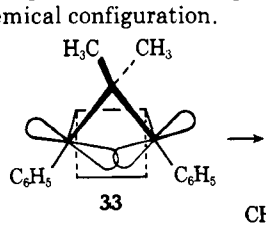

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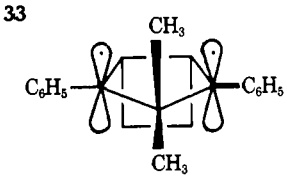

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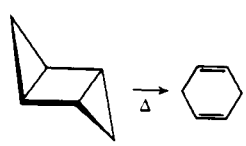
In either case, this particular fragmentation would appear to be the first instance in which highly stereoselective cycloreversion of a cyclobutane to olefinic products becomes energetically accessible as the direct result of suprafacial fragmentation of a third proximate σ bond. If operative, the concerted [$\sigma 2_s + \sigma 2_s + \sigma 2_s$] process is seen to contrast markedly with the severe distortions associated with the [$\sigma 2_s + \sigma 2_s$] pathway considered on theoretical grounds to be required of concerted cyclobutane fragmentations.[2,23]

Although the phenyl groups clearly weaken the C_2–C_4 bond, such substitution is seen to provide little overt acceleration to the fragmentation (estimated $\Delta H^* \cong 39$ kcal/mol for **8** → **9** + **10**).[24] Perhaps the full impact of maximum stabilization is not available at the rate-determining transition state owing to steric factors which preclude proper orientation of the phenyl rings with the developing p orbitals. Nevertheless, the requirement for aromatic substitution is clear from the rapid decrease in the amount of cyclopentadiene product as the series **14**, **20**, and **28** (55, 2.5, and 0%) is traversed.

Cycloheptadiene Formation. In a perhaps superficial sense, the tricycloheptane → cycloheptadiene reaction is analogous to the "high-energy" pathway for bicyclo[2.1.0]pentane decomposition[4] and to the bicyclo[2.2.0]hexane to 1,5-hexadiene rearrangements.[5] In the present examples, opening of the pair of internal carbon–carbon bonds follows, at least formally, the [$\sigma 2_s + \sigma 2_s$] mode.[25] This contrasts with the apparently general $s + a$ preferences of bicyclopentanes[4e] and bicyclohexanes,[5b,j] and could denote simply the controlling influence of ring strain in opening of the tricycloheptanes.

A suggestion that this need not be the case is available from quantitative analysis of the *anti*-tricyclo[3.1.0.$0^{2,4}$]-hexane (**35**) to 1,4-cyclohexadiene rearrangement.[26] In point of fact, the activation parameters for isomerization of **35** (log A = 13.7, E_a = 36.75 kcal mol^{-1})[26b] compare closely to those measured for the rearrangement of *exo*-2-methylbicyclo[2.1.0]pentane to its endo isomer (log A = 13.9, E_a = 38.65 kcal mol^{-1}),[4a] but differ significantly from those determined for the thermal cleavage of bicyclo[3.2.0]heptane (**36**)[27] and bicyclo[2.1.1]hexane (**37**).[28] These quantitative differences have prompted Baldwin[27b] to propose that the ring opening of **35** (in contrast to those of **36** and **37**) is a concerted process made possible by appreciable mixing of the two configurations of the opening bicyclopentane moiety to achieve formal orbital symmetry inversion.[9a]



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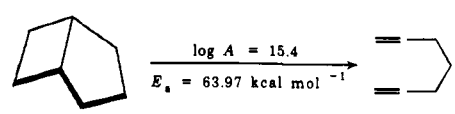

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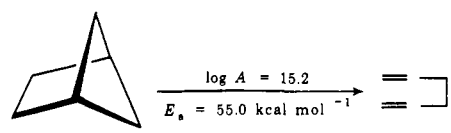

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We emphasize that the question of the concerted or diradical nature of the tricycloheptane → 1,4-cycloheptadiene isomerization remains unanswered. However, should an energetically concerted reaction profile be followed by **28**, our results would signify that the replacement of H_2 and H_4 by phenyl groups serves to cause a new reaction channel (the fragmentation of ethylene) to become competitive with the otherwise dominant pathway. In this connection, the recent suggestion of Andrist[29] which calls attention to the effects produced by large bulky groups

such as phenyl on the density of vibrational states with attendant enhancement of opportunities for diradical intervention is indeed relevant.

The 4-methylenecycloheptenes **16** and **22** could arise from protic shift in the diradicals (C_1–C_5 cleavage) initially produced. Bond reorganization would then lead to the observed dienes. The previous observations of Evnin and Arnold[30] parallel to some degree these findings. Most importantly, it should be noted that **16** and **22** do not result from further rearrangement of the 1,4-cycloheptadienes **17** and **23**, since the latter are stable to the reaction conditions employed. The dienes **16** and **22** are likewise resistant to further thermal rearrangement.

Experimental Section

Melting points are corrected. Proton magnetic resonance spectra were obtained with Varian A-60A and HA-100 spectrometers and apparent splittings are cited. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

endo-**7,8-Diaza-9,9-dimethyl-1,6-diphenyltricyclo[4.2.1.0^{2,5}]non-7-ene (7a).** To a magnetically stirred mixture of 12.93 g (66.6 mmol) of potassium azodicarboxylate and 1.00 g (3.33 mmol) of **6**[10] in 125 ml of absolute methanol contained in a round-bottom flask equipped with drying tube and serum cap was slowly injected 12.02 g (200 mmol) of glacial acetic acid in 2-ml portions over a 2-hr period. Upon disappearance of the yellow color (*ca.* 1 hr), the reaction mixture was poured into a separatory funnel, 250 ml of water was added, and the precipitated product was taken into ether by extraction (3 × 200 ml). The combined extracts were neutralized with saturated sodium bicarbonate solution, washed with saturated sodium chloride solution, and dried. Filtration, evaporation, and recrystallization from pentane gave 0.91 g (90%) of **7a** as a white powder: mp 101.5–103° dec; ir ($CHCl_3$) 2899, 1605, 1495, 1468, 1389, 1372, and 1022 cm^{-1}; λ_{max} (isooctane) 350 nm (sh, ϵ 100) and 362 (125); δ_{TMS} ($CDCl_3$) 7.38–8.00 (m, 10, aryl), 3.60 (m, 2), 1.82 (m, 4), 0.83 and 0.22 (s, 3 each, methyls).

Anal. Calcd for $C_{21}H_{22}N_2$: C, 83.40; H, 7.33. Found: C, 83.34; H, 7.31.

anti-**3,3-Dimethyl-2,4-diphenyltricyclo[3.2.0.0^{2,4}]heptane (8a). A. Photolysis of 7a.** A solution of 302.7 mg (1.001 mmol) of **7a** in 2 ml of ether contained in a quartz test tube was irradiated with a 200-W Hanovia lamp housed in a Pyrex cooling jacket. The progress of the reaction, monitored by thin layer chromatography, was deduced to be complete in 2.5 hr. Solvent removal followed by molecular distillation afforded 237 mg (86%) of **8a** as a viscous, colorless liquid: bp 75° (0.1 mm); ir (neat) 2865, 1603, 1490, 1441, 776, 747, and 702 cm^{-1}; δ_{TMS} ($CDCl_3$) 7.28 (br s, 10, aryl), 2.89 (m, 2), 2.12 (m, 4), 1.27 and 0.82 (s, 3 each, methyls).

Anal. Calcd for $C_{21}H_{22}$: C, 91.92; H, 8.08. Found: C, 91.98; H, 8.11.

B. Diimide Reduction of 1. To a magnetically stirred mixture of 2.13 g (11.0 mmol) of potassium azodicarboxylate and 150 mg (0.552 mmol) of **1**[10] in 40 ml of absolute methanol contained in a round-bottom flask equipped with a drying tube and serum cap was slowly injected 2.00 g (33.0 mol) of glacial acetic acid in 0.25-ml portions over a 1-hr period. Upon disappearance of the yellow color (*ca.* 1 hr) the reaction mixture was poured into a separatory funnel, 150 ml of water was added, and the product was taken into ether by extraction (3 × 200 ml). The combined ether extracts were neutralized with saturated sodium bicarbonate solution, washed with saturated sodium chloride solution, and dried. Filtration and evaporation followed by molecular distillation afforded 125 mg (82%) of **8a** which was identical with the material isolated above.

5,5-Dimethyl-1,4-diphenylcyclopenta-1,3-diene (9). Initial studies were performed with a 50-mg sample of **8a** in deuteriochloroform–TMS solution sealed in an evacuated nmr tube. After heating at 100° for 5 hr, partial conversion to **9** was observed; after heating at 140° for 3 hr, complete conversion to **9** was found. Subsequent heating of the tube at 210° for 3 hr revealed complete conversion to **9** and ethylene (**10a**).

In a typical preparative-scale experiment, 100 mg (0.331 mmol) of **8a** in 1.5 ml of tetrachloroethylene, sealed in an evacuated length of 12-mm Pyrex tubing, was heated at 209° for 7 hr. After cooling, the tube was opened, the solvent was removed at reduced pressure, and the residual solid was sublimed [57° (0.1 mm)] to give 68 mg (84%) of a yellow-white solid. Recrystallization from ether afforded pure product as long white needles: mp 96–98°; ir ($CHCl_3$) 1603, 1490, 1460, 1443, 850, and 693 cm^{-1}; λ_{max} (isooctane) 232 nm (ϵ 9000) and 330 (15,400); δ_{TMS} ($CDCl_3$) 7.50 (m, 10, aryl), 6.77 (s, 2, olefinic), and 1.65 (s, 6, methyls).

Anal. Calcd for $C_{19}H_{18}$: C, 92.63; H, 7.37. Found: C, 92.44; H, 7.41.

Ozonolysis of 9. A solution of 151 mg (0.614 mmol) of **9** in 200 ml of absolute methanol was ozonized at −70° until the uptake of ozone ceased. To the resulting solution was added a mixture of 4 ml of absolute methanol, 0.2 ml of glacial acetic acid, and 0.45 g of sodium iodide. Stirring for 4 hr was followed by dilution with 500 ml of water. Sodium bisulfite was added until the iodine color disappeared and sodium carbonate was next introduced to render the solution alkaline. Extraction with ether (3 × 250 ml) and drying of the combined extracts gave, after evaporation, 40 mg (26%) of crude diketone. Recrystallization from ethanol gave the pure product, mp 95–97°, which was found to be identical with **11**.[6b]

endo-**7,8-Diaza-9,9-dimethyl-1,6-diphenyltricyclo[4.2.1.0^{2,5}]non-7-ene-*cis,exo*-3,4-d_2 (7b).** Treatment of 1.00 g (0.00333 mol) of **6** in 100 ml of ethanol-*O*-*d* with potassium azodicarboxylate and acetic acid-*O*-*d* resulted in 80% conversion to product. This mixture was recycled; in all, a 110-fold excess of potassium azodicarboxylate was required. Work-up and recrystallization from pentane gave 0.740 g (73%) of **7b**: mp 102–104°; ir ($CHCl_3$) 2874, 2174, 1603, 1488, 1462, 1441, 1383, 1366, 1300, and 1018 cm^{-1}; δ_{TMS} ($CDCl_3$) 7.38–8.00 (br m, 10, aryl), 3.57 (m, 2), 1.73 (m, 2), 0.83 and 0.22 (s, 3 each, methyls). Analysis of the mass spectrum indicated 0% d_0, 9% d_1, and 91% d_2.

anti-**3,3-Dimethyl-2,4-diphenyltricyclo[3.2.0.0^{2,4}]heptane-*cis-exo*-6,7-d_2 (8b).** A solution of 200 mg (0.66 mmol) of **7b** in 3 ml of ether contained in a quartz test tube was photolyzed in a manner analogous to the diprotio compound. The reaction was terminated after 2.5 hr. Solvent removal and molecular distillation afforded 144 mg (79%) of **8b**: bp 75° (0.1 mm); ir (neat) 2865, 2174, 1603, 1490, 1441, 753, and 699 cm^{-1}; δ_{TMS} ($CDCl_3$) 7.25 (br s, 10, aryl), 2.90 (m, 2), 2.00 (m, 2), 1.27 and 0.80 (s, 3 each, methyls). Analysis of the mass spectrum indicated 0% d_0, 9% d_1, and 91% d_2.

Pyrolyses of 7b and 8b. In a typical experiment, *ca.* 50 mg of either **7b** or **8b** was placed in a pyrolysis apparatus fitted with a high-vacuum stopcock and an adjoining nmr tube. The apparatus was placed on a high-vacuum line and the valve was closed when the pressure was 0.2 μ. Placement of the pyrolysis chamber in an oven maintained at 210° for 4 hr was followed by removal, cooling, and addition of 0.3 ml of carbon tetrachloride–10% TMS to the nmr tube. The apparatus was again placed on the high-vacuum line and the resulting dideuterioethylene was vacuum transferred from the pyrolysis chamber to the nmr tube. The nmr tube was then sealed under vacuum prior to nmr analysis.

endo-**7,8-Diaza-1-phenyl-6,9,9-trimethyltricyclo[4.2.1.0^{2,5}]non-7-ene (13).** To a magnetically stirred mixture of 19.4 g (0.10 mol) of potassium azodicarboxylate and 1.19 g (0.005 mol) of **12**[10] in 250 ml of absolute methanol contained in a round-bottom flask equipped with drying tube and serum cap was slowly injected 18.0 g (0.30 mol) of glacial acetic acid in 1-ml portions over a 1-hr period. The reaction mixture was stirred for an additional 1 hr, after which time the yellow color had disappeared. The white suspension was poured into a separatory funnel, 250 ml of water was added, and the precipitated product was taken into ether by extraction (2 × 250 ml). The combined extracts were neutralized with saturated sodium chloride solution (2 × 250 ml), washed with saturated sodium chloride solution (2 × 250 ml), and dried. Filtration and solvent removal gave a white solid in a yellow oil. The oil was removed under high vacuum and the solid was sublimed [56° (0.05 mm)] to give 1.14 g (95%) of **13** as a white solid. Recrystallization of a small sample from hexane gave the pure compound: mp 72–74°; ir ($CHCl_3$) 2924, 1605, 1488, 1462, 1441, 1387, 1366, 1130, and 1013 cm^{-1}; λ_{max} (isooctane) 352 nm (sh, ϵ 78) and 363 (144); δ_{TMS} ($CDCl_3$) 7.30–7.92 (br m, 5, aryl), 3.08–3.63 (br m, 1), 2.53–3.00 (br m, 1), 1.66–1.88 (m, 4), 1.68 (s, 3, bridgehead methyl), 0.73 and 0.36 (s, 3 each, *gem*-dimethyl).

Anal. Calcd for $C_{16}N_{20}N_2$: C, 79.95; H, 8.39. Found: C, 79.83; H, 8.30.

anti-**2-Phenyl-3,3,4-trimethyltricyclo[3.2.0.0^{2,4}]heptane (14).** A solution of 140 mg (1.00 mmol) of **13** in 3 ml of ether contained in a quartz test tube was irradiated with a 200-W Hanovia lamp (Pyrex optics). After 2.5 hr, thin layer chromatography showed the absence of starting material. Solvent removal followed by molecular distillation afforded 185 mg (87%) of **14** as a colorless liquid: bp ambient temperature (0.04 mm); ir (neat) 2907, 1603, 1490, 1449, 1381, 1368, 764, and 698 cm^{-1}; δ_{TMS} ($CDCl_3$) 7.17 (br

s, 5, aryl), 1.67–2.83 (envelope, 6), 1.33 (s, 3, bridgehead methyl), 1.06 and 0.79 (s, 3 each, *gem*-dimethyl).

Anal. Calcd for $C_{16}H_{20}$: C, 90.50; H, 9.50. Found: C, 90.70; H, 9.46.

Pyrolyses of 13 and 14. Pilot nmr experiments performed on **13** provided the following information: 100°, 1 hr, no reaction; 140°, 3 hr, virtually completed conversion to **14**; 210°, 3 hr, several new products.

For preparative purposes, a sealed, evacuated tube containing 240 mg (1.00 mmol) of **13** was heated at 210° for 4 hr and the resulting product mixturewas subjected to vpc (150°, 10% SE-30 on Chromosorb W). The first fraction (80 mg, 55%) was found to be 1-phenyl-4,5,5-trimethylcyclopenta-1,3-diene (**15**): ir (neat) 3012, 2924, 1595, 1534, 1486, 1453, 1435, 1351, 1020, 826, 757, and 689 cm^{-1}; λ_{max} (isooctane) 222 nm (sh, ϵ 6000) and 306 (11,200); δ_{TMS} ($CDCl_3$) 7.08–7.65 (br m, 5, aryl), 6.60 (d, $J_{2,3}$ = 2.3 Hz, 1, H_2), 6.00 (dd, $J(CH_3\text{-}H)$ = 1.2 Hz, 1, H_3), 1.90 (d, 3, $=CCH_3$), and 1.19 (s, 6, *gem*-dimethyl).

Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.41; H, 8.72.

The second fraction (67 mg, 45%), obtained as an inseparable mixture, was found to contain **16** (~15%), **17** (~15%), and an unknown material (~15%). Although separable upon small-sized injections, these substances could not efficiently be separated when a preparative scale was employed. **16** had δ_{TMS} ($CDCl_3$) 5.42 (t, J = 7.2 Hz, 1, olefinic), 5.00 (br s, 1, exocyclic methylene), 4.80 (br s, 1, exocyclic methylene), and 1.17 (s, 6, *gem*-dimethyl). **17** had δ_{TMS} ($CDCl_3$) 5.92 (m, 1, olefinic), 5.70 (br m, 1, olefinic), 1.78 (br s, 3, $=CCH_3$), and 1.14 (s, 6, *gem*-dimethyl).

In a comparative experiment, nmr pyrolysis of **14** indicated the following: 100°, 1 hr, no reaction; 140°, 3 hr, no reaction; 210°, 3 hr, the same products as above.

***endo*-7,8-Diaza-1,6,9,9-tetramethyltricyclo[4.2.2.0^{2,5}]non-7-ene (19).** To a magnetically stirred mixture of 25 mg (0.128 mol) of potassium azodicarboxylate and 1.13 g (0.0064 mol) of crude 18[10] in 125 ml of absolute methanol contained in a round-bottom flask equipped with drying tube and serum cap was slowly injected 23.1 g (0.385 mol) of acetic acid in 2-ml portions over a 1-hr period. Upon disappearance of the yellow color, the reaction mixture was poured into a separatory funnel, 125 ml of water was added, and the product was taken into ether by extraction (3 × 125 ml). The combined extracts were neutralized with saturated sodium bicarbonate solution (2 × 125 ml), washed with water (2 × 125 ml) and saturated sodium chloride solution (2 × 125 ml), and dried. Filtration, followed by solvent removal by distillation through an efficient column, gave a concentrated ether solution of product. Preparative scale vpc purification (125°, 10% SE-30 on Chromosorb W) gave 606 mg (53%) of **19** as white crystals: mp 33.0–33.5°; ir ($CHCl_3$) 2890, 1462, 1437, and 1376 cm^{-1}; λ_{max} (isooctane) 347 nm (sh, ϵ 97) and 362 (246); δ_{TMS} ($CDCl_3$) 2.45–2.73 (br m, 2), 1.50–1.83 (br m, 4), 1.59 (s, 6, bridgehead methyls), 0.59 and 0.46 (s, 3 each, bridge methyls).

Anal. Calcd for $C_{11}H_{18}N_2$: C, 74.11; H, 10.18. Found: C, 74.20; H, 10.36.

***anti*-2,3,3,4-Tetramethyltricyclo[3.2.0.0^{2,4}]heptane (20).** A solution of 89 mg (0.50 mmol) of **19** in 1 ml of ether contained in a test tube was irradiated with a 200-W Hanovia lamp (Pyrex optics). After 3 hr, thin layer chromatography indicated the absence of starting material. Isolation by preparative-scale vpc (100°, 10% SE-30 Chromosorb W) furnished 47 mg (62%) of **20** as a highly volatile, colorless liquid: ir (neat) 2882, 1447, 1385, 1366, 1245, 1220, 1149, 1111, and 866 cm^{-1}; δ_{TMS} ($CDCl_3$) 1.83–2.50 (br m, 6), 1.02 (s, 6, bridgehead methyls), 0.94 and 0.87 (s, 3 each, *gem*-dimethyl).

Anal. Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.08. Found: C, 87.71; H, 11.96.

Pyrolysis of 19. A sealed, evacuated tube containing 147 mg (0.825 mmol) of **19** was heated in a furnace at 210° for 1.5 hr. The resulting product mixture was separated into its components by preparative-scale vpc (78°, 10% SE-30 on Chromosorb W).

The first fraction, present in small amounts, was found to be 1,4,5,5-tetramethylcyclopenta-1,3-diene (**21**) by comparison with the uv and nmr spectra of the known compound:[15] λ_{max} ($CDCl_3$) 259 nm; δ_{TMS} ($CDCl_3$) 5.87 (s, 2, olefinic), 1.85 (d, $J_{allylic}$ = 0.6 Hz, 6, $=CCH_3$), and 0.93 (s, 6, C_5 methyls).

The second fraction (22.4 mg, 29%) was recovered tricycloheptane **20**.

The third fraction (16.5 mg, 21%) was **22**: ir (neat) 2907, 1634, 1451, 1372, 1364, 1351, 1124, 1101, 855, 822, and 705 cm^{-1}; δ_{TMS} ($CDCl_3$) 5.37 (triplet with allylic coupling, J = 7.2, 1.2 Hz, 1, olefinic), 4.94 (d, J = 1.2 Hz, 1, exocyclic methylene), 4.72 (d, J = 1.2 Hz 1, exocyclic methylene), 1.37–2.50 (br m, 6, ring protons), 1.71 (d, 3, $=CCH_3$), and 1.18 (s, 6, *gem*-dimethyl).

Anal. Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.08. Found: C, 88.05; H, 12.18.

The fourth fraction (38.3 mg, 50%) was 2,3,3,4-tetramethylcyclohepta-1,4-diene (**23**): ir (neat) 2924, 1445, 1385, 1370, 1351, 1114, 1088, and 824 cm^{-1}; δ_{TMS} ($CDCl_3$) 5.68 (br m, 2, olefinic) 2.15 (br m, 4, allylic), 1.77 (br s, 6, $=CCH_3$), and 1.23 (s, 6, *gem*-dimethyl).

Anal. Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.08. Found: C, 88.01; H, 12.14.

Pyrolysis of 20. A sealed, evacuated tube containing 97.8 mg (0.651 mmol) of **20** was heated in a furnace at 210° for 1.5 hr. The resulting product mixture was separated into its components by preparative-scale vpc (78°, 10% SE-30 on Chromosorb W) and the product distribution was determined by planimetry of the vpc trace.

The first fraction (≤2.5%) was found to be **21**. The second fraction (≤0.8%) was not identifiable. The third fraction (≤8.4%) was unreacted starting material and the fourth fraction (≤2.0%) was **22**. The last fraction (≥86.4%) was **23**.

Thermal Stability of 23. In order to assess the thermal stability of **23**, a tetrachloroethylene solution of this hydrocarbon contained in a sealed nmr tube was heated at 208° for 5 hr. No rearrangement was observed.

4-Phenyl-2,4,6-triaza[5.3.2.0^{2,6}.0^{8,10}]quadricyclododec-11-ene-3,5-dione (24). Into a 1-l. three-necked flask equipped with magnetic stirrer, drying tube, and addition funnel were added 17.51 g (0.10 mol) of *N*-phenyltriazolinedione and 500 ml of acetone. The solution was cooled to −40° and 11.0 g (0.12 mol) of cycloheptatriene was added over 5 min. The deep red color disappeared after 0.5 hr and stirring was continued for an additional 1 hr. Solvent removal at reduced pressure followed by recrystallization from ethyl acetate gave 24.6 g (92%) of cycloadduct: mp 188–189° (lit.[31] mp 186–188°); ir ($CHCl_3$) 1761, 1706, 1493, 1397, 1238, 1133, 1053, 958, 915, and 868 cm^{-1}; δ_{TMS} ($CDCl_3$) 7.42 (br s, 5, aryl), 6.09 (t, J = 3.6 Hz, 2, olefinic), 5.21 (m, 2, bridgehead), 1.62 (m, 2, cyclopropyl), 0.70 and 0.35 (AB of ABM_2, J_{AB} = 6.8 Hz, J_{AM} = 6.8 Hz, J_{BM} = 3.2 Hz, 1 each, cyclopropyl methylene).

4-Phenyl-2,4,6-triaza[5.3.2.0^{2,6}.0^{8,10}]quadricyclododecane-3,5-dione (25). To a magnetically stirred solution of 6.10 g (0.0228 mol) of **24** in 600 ml of anhydrous tetrahydrofuran was added 0.700 g of platinum oxide and the mixture was hydrogenated at atmospheric pressure until the uptake of hydrogen ceased. Filtration through Celite to remove catalyst, followed by solvent removal and recrystallization from acetone, gave 5.4 g (89%) of **25**: mp 147.5–149° (lit.[31] mp 138–139°); ir ($CHCl_3$) 2941, 1757, 1695, 1401, 1274, 1126, 961, and 876 cm^{-1}; δ_{TMS} ($CDCl_3$) 7.27–7.75 (br m, 5, aryl), 4.61 (m, 2, bridgehead), 1.33–2.17 (br m, 6), and 0.75 (m, 2, cyclopropyl methylene).

***anti*-6,7-Diazatricyclo[3.2.2.0^{2,4}]non-6-ene Cuprous Chloride Adduct (26).** To a magnetically stirred solution of 2.00 g (0.00743 mol) of **25** in 30 ml of anhydrous dimethyl sulfoxide under nitrogen was slowly added 4.012 g (0.0743 mol) of sodium methoxide and the reaction mixture was heated at 87° for 14 hr. Upon cooling, the dark brown solution was slowly acidified to pH 4 with 1:1 hydrochloric acid (*ca.* 20 ml). A solution of cupric chloride dihydrate (5.0 g), water (100 ml), and 1:1 hydrochloric acid (2.0 ml) was then added over a 30-min period. The solution slowly turned dark red and stirring was continued for an additional 1.5 hr. Filtration, followed by washing with 30 ml each of water, acetone, and chloroform, gave 1.28 g (78%) of the red complex, mp 124° dec (lit.[16,17] mp 120° dec).

***anti*-Tricyclo[3.2.0.0^{2,4}]heptane (28).** To a flask containing 500 mg (2.26 mmol) of **26** in a bath maintained at −20° was added 30 ml of precooled (−20°) aqueous ammonia and the resultant mixture was swirled for 5 min. The liberated azo compound (**27**) was taken into cold ether (−20°) by extraction (5 × 5 ml) and dried. Filtration, followed by solvent removal through a short-path column at reduced pressure and temperature (−20°), gave a concentrated ethereal solution of azo compound. Immediate low-temperature (−20°) irradiation of this solution with a 450-W Hanovia lamp (Pyrex optics) for 3 hr followed by preparative-scale vpc (75°, 10% SF-96 on Chromosorb G) gave 10.2 mg (5%) of the desired tricycloheptane (**28**): δ_{TMS} π ($CDCl_3$) 2.38 (m, 4, H_6, H_7), 2.08 (m, $J_{1,3\text{-exo}}$ = 1.0 Hz, 2, H_1, H_5), 1.63 (d of t, $J_{2,3\text{-exo}}$ = 5.5, $J_{1,3\text{-endo}}$ = 1.8 Hz, 2, H_2 and H_4), 0.70 (dd, $J_{3\text{-exo},3\text{-endo}}$ = 4.2 Hz, 1, exo H_3), and 0.28 (d of t, 1, endo H_3).

The second component of the photolysis mixture, 44.0 mg (21%), was found to be 1,4-cycloheptadiene[32] (**29**): ir (neat) 2985, 2882, 2885, 1658, 1433, 824, and 682 cm^{-1}; δ_{TMS} ($CDCl_3$) 5.68 (m,

4, olefinic), 2.87 (m, 2, doubly allylic hydrogens), and 2.27 (m, 2, allylic hydrogens).

Pyrolysis of 28. An nmr tube containing 6 mg (0.064 mmol) of **28** which had been sealed *in vacuo* at −196° was placed in an oven maintained at 173° for 15 min. After the tube had been removed from the oven and allowed to cool, it was opened, deuteriochloroform–TMS was added, and the nmr spectrum was immediately recorded. Only cycloheptadiene (**29**) and a small amount of unreacted tricycloheptane (**28**) were found to be present (ratio of approximately 8:1). Flame-ionization vpc confirmed that these were the only components of the mixture.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for partial financial support of this work. The assistance of Professor G. Closs with the deuterium-decoupled proton nmr determinations is also deeply appreciated.

Registry No. **6**, 34783-14-7; **7a**, 33995-51-6; **7b**, 49586-94-9; **8a**, 33995-52-7; **8b**, 49586-96-1; **9**, 33930-83-5; **12**, 34780-54-6; **13**, 33995-53-8; **14**, 33995-55-0; **15**, 33930-85-7; **16**, 49585-76-4; **17**, 49585-77-5; **18**, 34780-61-5; **19**, 33995-54-9; **20**, 33995-56-1; **21**, 4249-11-0; **22**, 33930-86-8; **23**, 33930-84-6; **24**, 49587-03-3; **25**, 49587-04-4; **26**, 49587-05-5; **27**, 22144-75-8; **28**, 28102-61-6; *N*-phenyltriazolinedione, 4233-33-4; cycloheptatriene, 544-25-2.

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Dissolving Metal Reduction of *anti*-Tricyclo[3.2.0.0^{2,4}]heptanes and *anti*-Tricyclo[3.3.0.0^{2,4}]octanes. Intramolecular Epoxide Cleavage as a Route to Highly Strained Tricyclic Alcohols

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Received August 30, 1973

Reduction of epoxides derived from *anti*-tricyclo[3.2.0.0^{2,4}]hept-6-enes and *anti*-tricyclo[3.3.0.0^{2,4}]oct-6-enes with lithium in liquid ammonia affords exo tricyclic alcohols in high yield. The process involves initial reductive cleavage of the internal cyclopropane bond followed by back-side attack on the proximate C–O bond with formation of a new cyclopropane ring. The value of the synthetic method is revealed by the ready access which is gained to functionalized strained molecules inaccessible by other methods.

The relatively recent findings that phenyl substitution of cyclopropanes promotes their ready alkali metal cleavage and the intriguing stereoselectivity of these ring openings have stimulated considerable current interest.[2,3] Because the direction of cleavage of variously phenylated cyclopropane rings is minimally influenced by steric effects but markedly affected by electronic factors, a radical anion mechanism has been ascribed to the bond-breaking step. Subsequent events include addition of a second electron and ultimate protonation. In all likelihood, a range of mechanisms from purely radical anion to dianion is capable of operation depending upon the particular system