Synthesis and Reactions of Tetracyclo[4.2.0.0²,⁴.0³,⁵]octanes

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Tetracyclo[4.2.0.0²,⁴.0³,⁵]oct-7-ene (I) was prepared in four steps, starting with benzvalene. The adduct (V), which forms readily by addition of dichloroketene to benzvalene, was dehalogenated with triphenyltin hydride, and the resulting ketone (VII) was converted into I by the reaction of its p-toluenesulfonylhydrazone (X) with lithium 2,2,6,6-tetramethylpiperidide. Isomerization of I to cyclooctatetraene occurs thermally, photochemically, and in a silver ion catalyzed reaction. Reaction of I with N-phenyltriazolinedione yields the hexacyclic adduct (XII); reaction of I with hexafluoro-2-butyne yields a mixture of products, two of which were found to interconvert via a Cope rearrangement under the reaction conditions used. The preparation and pyrolysis of the parent tetracyclo-[4.2.0.0²,⁴.0³,⁵]octane (XIX) are described. Reaction of V with nitrogen nucleophiles gives 3,4-disubstituted tricyclo[3.1.0.0²,⁶]hexanes by a very facile ring cleavage. ¹³C NMR spectra are tabulated for most of the compounds encountered in this study.

Our incursion into the tetracyclo[4.2.0.0²,⁴.0³,⁵]octane system, and particularly the synthesis of tetracyclo-[4.2.0.0²,⁴.0³,⁵]oct-7-ene (I),[2] was prompted by a desire to use these compounds as precursors for tricyclo[5.1.0.0²,⁸]octa-3,5-diene ("octavalene", II). Earlier unsuccessful approaches

I   II
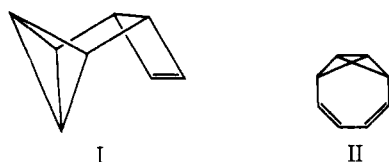
to the synthesis of II involved carbenoid species generated from different ring systems. Zimmerman and Sousa, for example,[3] subjected cycloheptatrienyldiazomethane (III) to thermal and photochemical reactions which yielded a variety of products:


III
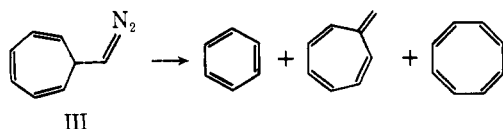
In these laboratories, Meinwald and van Vuuren treated 8,8-dibromobicyclo[5.1.0]octa-2,4-diene (IV) with methyllithium and obtained a labile mixture of dihydropentalenes; use of the tricarbonyliron complex of IV gave an unexpected insertion product; a more recent study has been carried out by Baird and Reese.[4] While II has not yet been prepared, the chemistry of I and its precursors has been sufficiently explored to justify presentation in its own right.

The "ready-made" bicyclobutane moiety in benzvalene, which is readily prepared by the method of Katz and coworkers,[5] made it an attractive starting point for our work. In
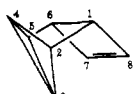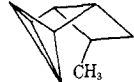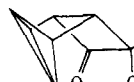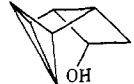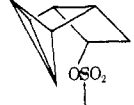
initial attempts to exploit benzvalene by additions to the double bond, reactions with ozone, with ethyl diazoacetate, and (photochemically) with maleic anhydride were explored. While reactions related to the first two of these have been carried out successfully by Christl and Brüntrup,[6] in our particular cases conveniently usable adducts were not obtained; nor was the reaction with maleic anhydride of any use. The reagent which did give useful results was dichloroketene.

The [2 + 2] cycloadditions of ketenes to olefins have received much attention, most extensively by Brady and coworkers, as well as by Ghosez and others.[7] The olefin most commonly used for these investigations has been cyclopentadiene, usually used in excess, to give yields ranging from very good to very poor based on a variety of ketenes generated in situ. Dichloroketene's combination of high reactivity for such cycloadditions and its relative stability made it the most attractive choice for the reaction with benzvalene. Yields in this step proved gratifyingly high: after correcting for unconsumed (and recoverable, if aqueous workup is avoided) benzvalene, adduct V could be isolated in 86% yield. Even without this

V
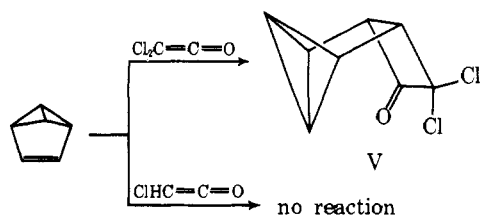
correction, 70% yields of V are obtained routinely if one is careful to use scrupulously pure starting materials. While one might expect that other ketenes might add comparably well to the highly reactive double bond of benzvalene, attempts to

Table I. ^{13}C NMR Data on Compounds in the Tetracyclo[4.2.0.0^{2,4}.0^{3,5}]octane Series[a]

| Compd	C-1	C-2	C-3 (syn)	C-4 (anti)	C-5	C-6	C-7	C-8	Other
	47.7	37.2	−0.7	16.2			139.4		
	37.1 (d, 145)	39.8 (d, 170)	−0.6 (d, 215)	7.0 (d, 210)			21.4 (tr, 135)		
	29.6*	39.5	−0.1	7.4	34.4	46.4*	38.9*	29.7*	22.1 (methyl)
	53.6 (d, 155)	36.9 (d, 170)	0.4 (d, 220)	9.8 (d, 215)	33.9 (d, 170)	63.7 (d, 150)	194.9 (s)	84.0 (s)	
	39.7 (d, 150)	35.1 (d, 170)	−0.4 (d, 215)	8.6 (d, 215)	33.7 (d, 170)	59.0 (d, 150)	204.4 (s)	64.0 (d, 145)	
	29.2 (d, 150)	39.1 (d, 165)	−2.0 (d, 215)	10.5 (d, 215)	33.4 (d, 170)	66.1 (d, 145)	209.1 (s)	45.8 (tr, 135)	
	30.6 (d, 140)	40.4 (d, 170)	−0.5 (d, 215)	4.8 (d, 210)	32.7 (d, 170)	46.0 (d, 140)	63.8 (d, 150)	34.4 (tr, 135)	
	31.4 (d, 145)	39.9 (d, 165)	0.0 (d, 210)	5.4 (d, 210)	33.4 (d, 170)	45.0 (d, 140)	71.7 (d, 150)	31.2 (tr, 135)	36.7 (q, 140, methyl)

[a] All samples were run in CDCl$_3$ on a Bruker HX-90 in the FT mode, both with and (sample size permitting) without broad-band proton decoupling. Assignments were based on shift, multiplicity, J_{C-H} (noted under each value in hertz, in parentheses), and internal consistency, and are reported in δ (Me$_4$Si) taking the center of the CDCl$_3$ triplet as δ 76.9. Values for J_{C-H} are generally ±5 Hz. Asterisks indicate uncertainty in assignments.

generate an adduct by addition of monochloroketene to benzvalene failed dismally.

It should be mentioned that some of the "unexpected" additions that benzvalene has been shown to undergo[8] made the course of this ketene reaction less than entirely certain. However, the carbonyl stretching frequencies in V and the ketones derived from it gave convincing initial evidence[7,9] that the cycloaddition had gone as desired. Later, ^{13}C NMR measurements further verified these structures—characteristic in this regard are particularly the pair of upfield signals associated with the bicyclobutane bridge, as well as the multiplicities and coupling constants which identify the other atoms in the tetracyclic framework. In these assignments, references by Christl,[10] Grover et al.,[11] and Levy and Nelson[12] were helpful. A summary of data for the tetracyclic derivatives appears in Table I.

With V in hand, a mild method for reductive dehalogenation was desired. Possible methods included use of a hydrogen radical donor, a hydride donor, or dissolving metal reduction. Of these, the first seemed by far the gentlest, and in retrospect is probably the only method that could have worked while keeping the ring structure intact, as a later section of this discussion will illustrate. While dehalogenation by tributyltin hydride is probably more commonly carried out, we chose to use triphenyltin hydride.[7a,b,13] The reasons for this choice were its higher reactivity, allowing for milder reaction conditions, and its much higher molecular weight, facilitating distillative purification of the product. The desired reduction products were in fact obtained readily. The monochloroketone VI could be obtained using 1 equiv of reducing agent in up to 87% yield,

while the parent ketone VII could be prepared in ca. 95% yield when 2 equiv of reductant was used. The endo stereochemistry of VI, expected from the reduction mechanism, is supported
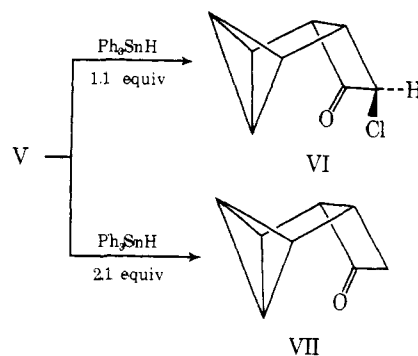

by the NMR pattern of the downfield α hydrogen, which appears as a doublet of doublets (J = 8 and 3 Hz), exhibiting both vicinal and transannular coupling.[7f]

A method for converting VII to I was now sought. In initial attempts, sodium borohydride reduction of VII to the endo alcohol VIII, followed by conversion of VIII to its tosylate (IX)
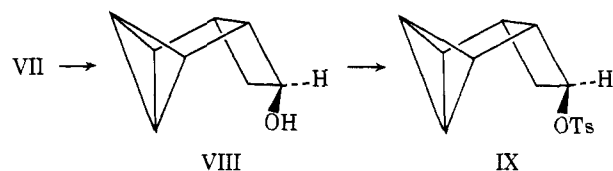
and subsequent treatment with base, failed to yield I even under increasingly vigorous conditions.[14] A milder and more generally effective method for olefin formation uses the Bamford–Stevens reaction of tosylhydrazones with strong bases (usually alkyllithium reagents).[15] This approach appeared especially appropriate because of a recently reported gentle method for preparing tosylhydrazones.[16] There was some difficulty at first in obtaining a crystalline tosylhydrazone (X) from VII. However, through use of very concentrated

VII → → I (35–55%)

X
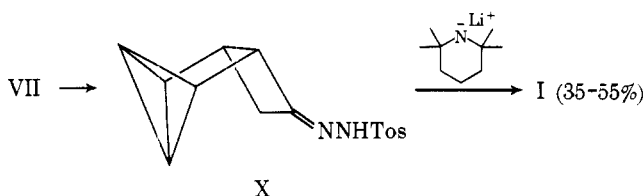
solutions, crystallization was usually observed within a few hours or overnight at room temperature. (It is convenient to carry out this reaction in small vials to allow centrifugal removal of the mother liquor; yields as high as 85% have been obtained. It is important to note that use of VII which was not of high purity, or use of more than a slight excess of tosylhydrazide, gave mixtures which would not crystallize; these mixtures usually performed poorly in the subsequent elimination step.)

The catalog of bases tried for the elimination need not be reiterated here,[2] but can be summarized by noting that the desired elimination was unexpectedly difficult to achieve. An initial attempt using methyllithium in ether gave a product whose mass spectrum (and eventual more thorough characterization) showed it to be the methylation product (XI).[17]

XI (40%)
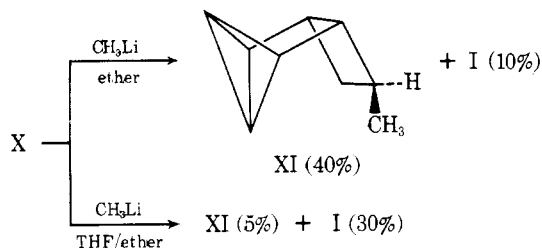
(Mechanistic considerations suggest that XI is the endo derivative. ^{1}H and ^{13}C NMR indicate that only one isomer is present.) Reaction of X with lithium tetramethylpiperidide in THF/ether gave yields of I as high as 55%, however. Use of lithium diisopropylamide as base gave ca. 20% yield; it was found later that methyllithium in THF/ether (where X is completely dissolved rather than reacting as a slurry) gives about 30% yield of I as well.

The properties of I are unexceptional. In addition to a very simple ^{1}H NMR spectrum (in which the only pronounced coupling appears in the "AB" pattern of the bicyclobutane bridge protons), a ^{13}C NMR spectrum which shows the expected five signals in places appropriate to the structure, and not very informative infrared and mass spectra,[2] the Raman spectrum of I was taken. This shows a strong double-bond stretching frequency at 1550 ± 2 cm^{-1}, which agrees with expectations for a somewhat strained cyclobutene ring.[18]

The chemistry of I was limited to some extent by its high stability, a stability doubtless due to the "forbiddenness" of all the thermal paths by which it might otherwise shed most of the roughly 100 kcal/mol of strain energy that it has been estimated to carry.[19] Vapor and solution phase pyrolyses were carried out both with and without added trapping reagents. Of these, the latter two yielded the more interesting, if originally unlooked for, results.

Some examples of vapor-phase cyclobutene pyrolyses which provided good precedents were carried out several years ago

by Dauben and Cargill, as well as by Chapman et al.[20] These used very brief contact times in an evacuated heated tube with a trap at its exit. One might imagine a variety of C_8H_8 isomers forming from I under such conditions; in fact, the only product found, in a very clean conversion which did not occur much below 250 °C and which was not complete until the tube approached 500 °C, was cyclooctatetraene. Given the severity of the conditions used, it is not surprising that possible intermediates such as the presumably unstable II were not observed here. In solution, similar results were obtained. At 140 °C in chloronaphthalene, conversion to cyclooctatetraene and traces of another C_8H_8 isomer proceeded with a half-life of about a day. Since I underwent little or no isomerization in benzene at 140 °C even after 2 days, it is probable that something in the chloronaphthalene catalyzed the isomerization. This still seemed a reasonable choice of conditions for the first solution trapping experiment, however, since the dienophile we wished to use, 4-phenyl-1,2,4-triazoline-3,5-dione,[21] is not stable above 140 °C. Other dienophiles considered included maleic anhydride (rejected because of its relatively low reactivity) and tetracyanoethylene (not used because of its low solubility and the low solubility of its adducts).
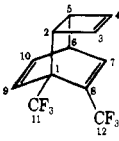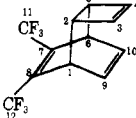
Reaction of I at 140 °C in the presence of the triazolinedione gave a major product (44%) whose identity was deduced on spectral grounds to be 4-phenyl-2,4,6-triazahexacyclo[7.4.0.0^{2,6}.0^{8,10}.0^{7,12}.0^{11,13}]trideca-3,5-dione (XII), and confirmed by comparison with an authentic sample.[22] Traces of two other 1:1 adducts were found. One of these was identified as 4-phenyl-2,4,6-triazapentacyclo[7.4.0.0^{2,6}.0^{8,10}.0^{7,13}]tridec-11-ene-3,5-dione (XIII) by an NMR shift reagent experiment. This was confirmed by comparison of XIII's NMR spectrum with published NMR descriptions of the analogous systems XIV and XV.[23] The other trace adduct was

XII   XIII (trace)

XIV   XV
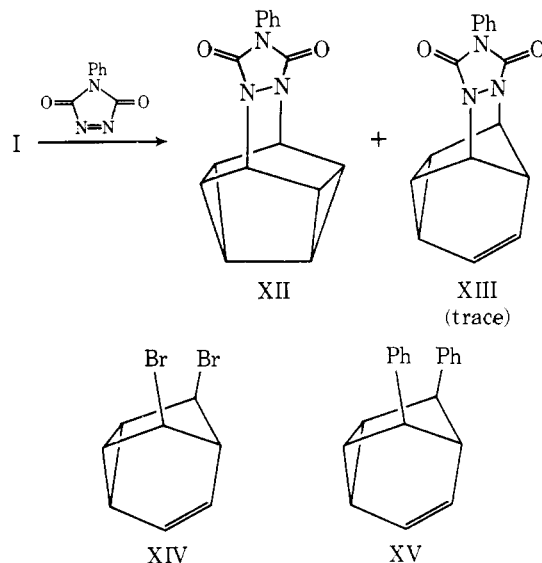
not identified, but by inspection of the rather low quality NMR spectrum obtained, the two cyclooctatetraene adducts of the triazolinedione could definitely be excluded.

The striking rearrangement required by the formation of XII raises questions about what might have happened "in transit". One might imagine various possibilities, including trapping of a semibullvalene intermediate by a homo-Diels–Alder reaction,[24] polar attack at the double bond, or polar attack at the bicyclobutane moiety. In an attempt to gain some insight into this process, the triazolinedione addition was repeated using I that had been labeled with deuterium in the 3 and 4 positions by treatment with butyllithium followed by quenching with deuterium oxide.[8a,25] The product was then analyzed by ^{1}H NMR to determine the deuterium position.

Table II. ^{13}C NMR on Compounds XVIII, XVII, and XVI[a]

Compd	Shift, δ	Mult	J_{C-H}, Hz	Assignment
	37.5	d	135	2,5,6[b]
	43.2	d	140	
	43.6	d	140	
	120.9	q	$J_{C-F} = 270$	11,12
	124.9	q	$J_{C-F} = 275$	
	129.2	d	175	3,4,9,10[c]
	134.1	d	175	
	137.5	d	175	
	138.4	d	170	7
	41.8	d	140	1,2,5,6
	43.4	d	145	
	121	q	$J_{C-F} = 265$	11,12
	129.4	d	165	3,4
	138.8	d	170	9,10[d]
	122	$(J_{C-F} = 270)$		7,8[e]
	127			5,4
	131			3,6

[a] All samples were run in CDCl$_3$, using the solvent triplet at δ 76.9 as internal reference. [b] The signals at 43.2 and 43.6 merged in the coupled spectrum. [c] From its intensity, the peak at δ 137.5 contains the two isochronous signals. Carbons 1 and 8 were not visible. [d] Carbons 7 and 8 could not be found with certainty. [e] Carbons 7 and 8 were visible as the central pair of a presumed quartet. Carbons 1 and 2 could not be found with certainty.

The "a" and "b" sets of protons have isochronous shifts, but can be separated by addition of "Resolve-Al EuFOD" (Al-


drich) shift reagent. Within the few percent uncertainty of repeated integrations, using both undeuterated and deuterated XII, all the deuterium was found to be at the "b" positions. Other (but ultimately superfluous) evidence for the deuterium location came from examining the splitting pattern of the "c" protons (90 MHz): undeuterated material showed a pentuplet, deuterated material a triplet ($J = 3$ Hz for each).
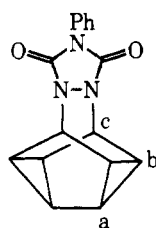
This result is compatible with the route shown in Scheme I, involving attack at the double bond, and appears to exclude the other possibilities mentioned above. The sequence of intermediates, cyclobutyl cation/cyclopropylcarbinyl cation/doubly cyclopropylcarbinyl cation/closure also seems plausibly "downhill" energetically. Inspection of models shows that the second bond migration could be facile because of the compact structure of the molecule; initial attack on the bicyclobutane moiety should be unfavorable in any case, since endo attack is thought to be the preferred mode.[26]

The suggested trapping of a semibullvalene intermediate was to some degree a "straw man", because semibullvalene was never isolated as a pyrolysis product. However, this does raise the queston of whether this might not still be a genuine trapping experiment rather than a simple attack on I by the triazolinedione. Since it was later found that the same reaction occurs readily in benzene at room temperature, where I is indefinitely stable, the former is also excluded. Adduct XIII is formed in about 5% yield in the room temperature reaction. Although no scheme will be proposed for its formation, it may be noted in passing that it is at least formally related to XII by a cyclopropylcarbinyl–homoallyl rearrangement.

The vapor-phase pyrolysis and trapping attempt was carried out using hexafluoro-2-butyne as dienophile; this re-

Scheme I
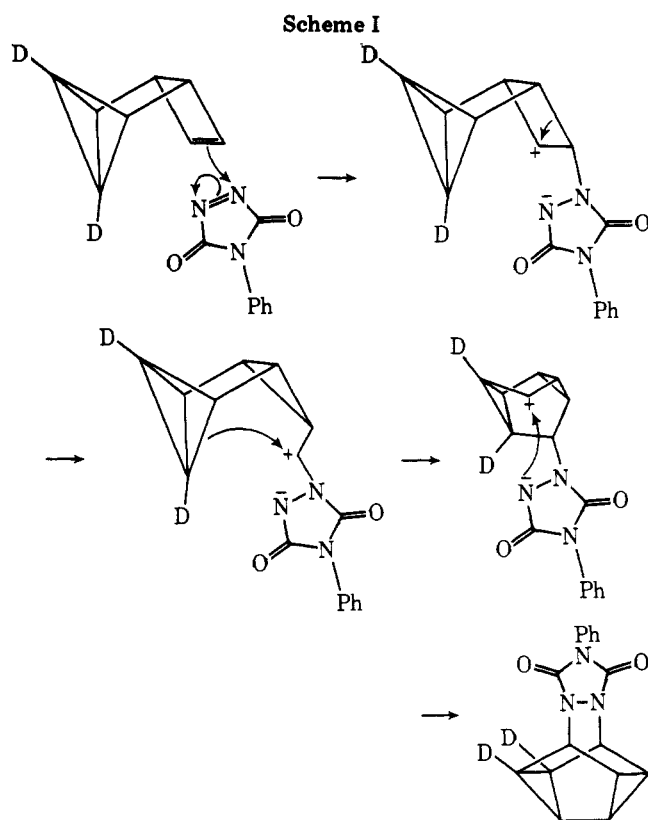
agent's thermal stability, high reactivity, volatility, and general reluctance to engage in polar or radical reactions[27] all seemed desirable. Attempted reaction at 175 °C gave very little conversion even after 7 h; however, reaction at 190–200 °C for 24 h consumed all the starting I and resulted in a mixture of three products isolable by GC, as summarized below. Of these, compound XVII was readily identifiable by its NMR spectrum.[28] The structure of XVI was strongly suggested by its mass spectrum and by its relatively short GC retention time. The identity of compound XVIII was less readily apparent. ^{1}H NMR spectra indicated a low symmetry structure wth five olefinic hydrogens, two of which were strongly (7 Hz) coupled to a one-proton multiplet upfield. Its ^{19}F NMR spectrum showed two quartets ($J = 10$ Hz), indicating the

4-5%
XVI

21%
XVII

21%
XVIII
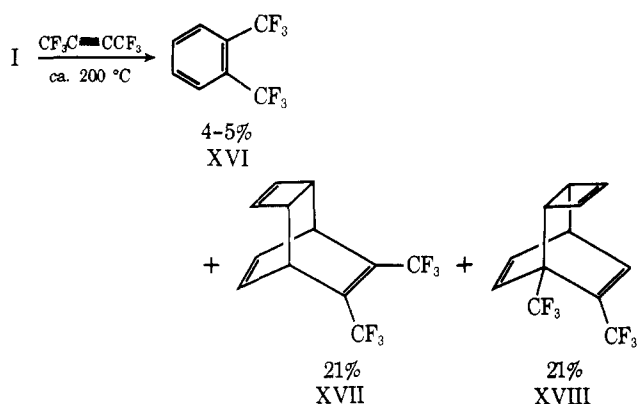
presence of vicinal trifluoromethyl groups; both EI and CI mass spectra were strikingly similar to those of XVII. The UV spectra of XVII and XVIII were also similar. In preparing an authentic sample of XVII (from the addition of hexafluoro-2-butyne to cyclooctatetrane in a sealed tube at 180 °C), it was found that the sample contained trace impurities at the GC retention times of XVI and XVIII; increased heating (190–200 °C) produced both these products in isolable amounts. ^{1}H NMR spectroscopy now confirmed the structure of XVI, and a ^{13}C NMR spectrum that of XVIII. Carbon-13 data for all three compounds appears in Table II.

While both XVII and XVIII are stable below about 180 °C, it was found that they do equilibrate to the same mixture when heated to around 200 °C overnight. A search of the literature showed that of the many pyrolytic studies of tricyclo-[4.2.2.0^{2,5}]deca-3,7,9-triene derivatives that have been undertaken, most were carried out under very severe (300–400 °C) conditions[29] and yielded benzene, naphthalene, and/or dihydronaphthalene derivatives, and sometimes butadiene as well. A more recent study by Masamune and co-workers,[30] however, showed an analogous rearrangement, under similar conditions, of a dideuterio derivative of the parent tricyclo-decatriene ("Nenitzescu's hydrocarbon"). Evidently, the equilibration of XVII and XVIII occurs via the cycle of Cope rearrangements shown in Scheme II.
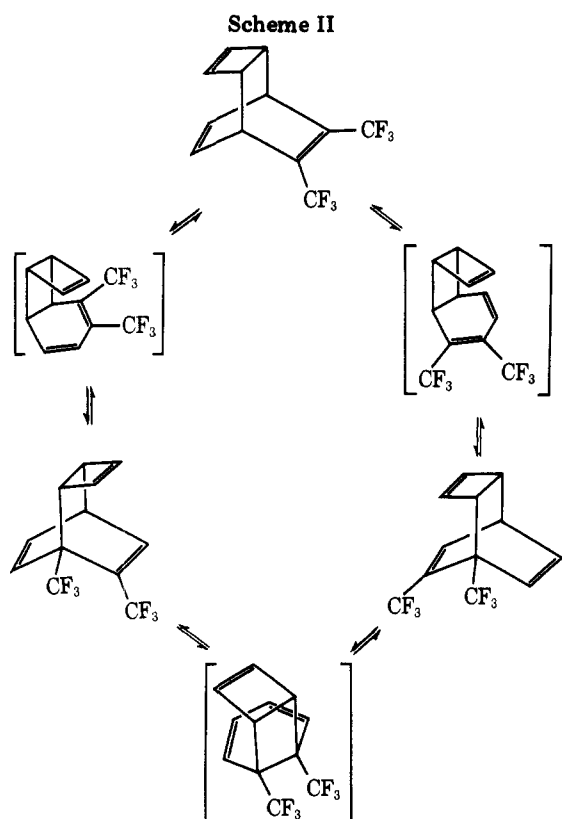
Scheme II

The stereochemistry shown for XVIII was assigned on assumption of the above scheme. Structures of the bracketed type are known to be unstable and to undergo rapid Cope rearrangement on gentle heating,[31] so it is not remarkable that they were not found in the mixture. On a purely statistical basis, one would expect XVII and XVIII to occur in a 1:2 mixture at equilibrium; in actuality, the ratio is about 1:6. This represents such a small energy difference that rationalization of its origin would be idle speculation.

It seems appropriate at this point to digress to the pyrolytic behavior of the parent tetracyclo[4.2.0^{2,4}.0^{3,5}]octane, XIX.
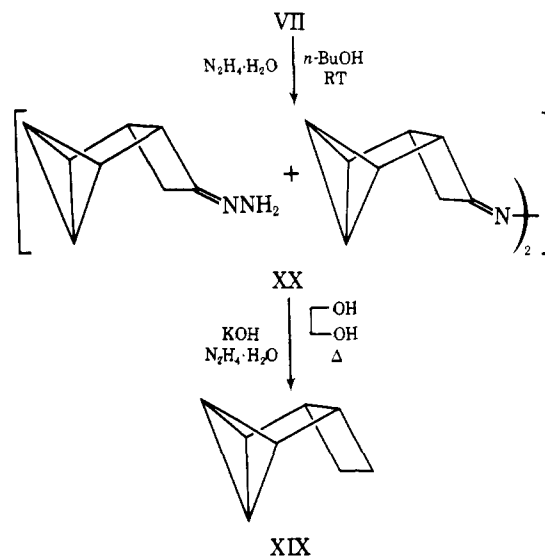
This compound was prepared by Wolff–Kishner reduction of the hydrazone and azine mixture (XX) obtained from VII, under conditions allowing XIX to distill into a trap as it formed. The conditions used were not entirely orthodox,[32] but the yield obtained (61% after preparative GC) was nonetheless acceptable.

Vapor-phase pyrolysis of XIX was carried out in a manner analogous to that used with I. At ca. 480 °C, XIX gave clean and complete conversion to two products; the minor one was benzene. The major one, on the basis of microhydrogenation and microozonolysis, appeared to be 1-vinylcyclohexadiene (XXI); this was confirmed by comparing its spectral proper-

ties with published NMR and IR data.[33a] Brief pyrolysis at a somewhat lower temperature (ca. 430 °C) gave a complex mixture of many products in roughly equal amounts, which were separable by preparative GC. The structures of XXII and XXIII were assigned by comparison of their NMR and IR spectra to published data;[33] that of XXIV was confirmed by its known IR spectrum and by its hydrogenation
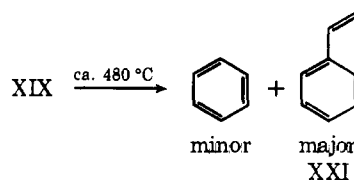
Table III. ^{13}C NMR Data on Compounds in the Tricyclo[3.1.0.0^{2,6}]hexane Series[a]

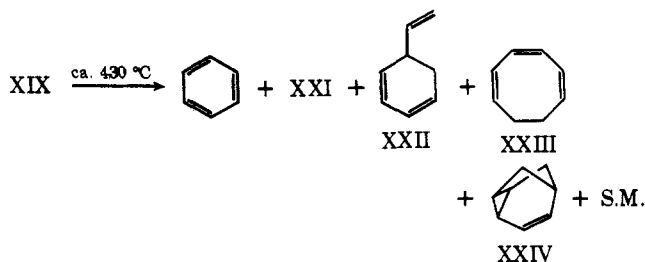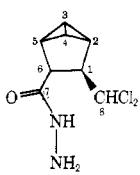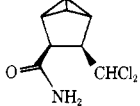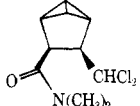| Compd	C-1	(C-2 and C-5)[b]	C-3 (syn)	C-4 (anti)	C-6	C-7	C-8[c]	Other	Solvent[d]
	46.1 (d, 145)	37.6 (d, 170)	38.3 (d, 180)	2.3 (d, 220)	4.0 (d, 220)	57.2 (d, 140)	171.0 (s)	75.4 (d, 180)		Me$_2$SO-d_6
	47.2	37.3	38.7^e	2.1	3.8	57.1	173.8	73.2		Me$_2$SO-d_6
	42.4 (d, 130)	36.9 (d, 160)	37.6 (d, 160)	1.6 (d, 217)	3.5 (d, 214)	56.6 (d, 136)	171.4 (s)	74.0 (d, 177)	34.5, 36.4^f (N-methyl)	CDCl$_3$

[a] Nonstandard numbering used to facilitate comparisons with Table I. [b] Not individually assignable. [c] Cf. ref 40. [d] Center of Me$_2$SO-d_6 multiplet taken as δ 39.6 relative to Me$_4$Si. [e] Superimposed on a peak of the solvent multiplet, but recognizable by the resulting intensity enhancement. [f] Assignment of coupling constants to the N-methyl groups is not definite owing to the complex appearance of this part of the coupled spectrum, but seems not inconsistent with quartets with J_{C-H} of ca. 135 Hz.

to bicyclo[3.2.1]octane.[34] In hindsight, this pyrolysis yielded few surprises. It is interesting that the reaction goes so cleanly at the higher temperature, but it has been known for several years that any of the compounds XXI, XXII, XXIII, or XXIV equilibrate above 200 °C to mixtures containing all four.[33,34] The complexity of this situation accordingly renders moot any specific discussion of how XIX comes unglued on heating.

The photochemistry of I can be summarized briefly. Some sensitized irradiations through Pyrex failed to generate useful results; irradiation through quartz produced cyclooctatetraene. While photochemical conversion of I to II is an allowed process, so is II's conversion to cyclooctatetraene. The difficulty in detecting II, even if it were an intermediate in this photolysis, is therefore apparent. An attempt at trapping II by irradiation through quartz in the presence of maleic anhydride yielded only artifacts from the anhydride.

The facile reactions of small-ring compounds with transition-metal catalysts are extensively documented.[35] It seemed certain, for example, that silver ion would readily "unzip" I to form cyclooctatetraene. In fact, such treatment did result in such conversion; yields were not very high, but no other volatile products were observed even after treatment with aqueous ammonia or sodium chloride. A few other similar

$$I \xrightarrow[\text{or Ag}^+]{h\nu} \text{(cyclooctatetraene)}$$
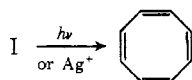
reactions of I were also examined. Cuprous chloride in dimethyl sulfide/hexane left I unaffected even after 3 days at room temperature. Benzylideneacetoneiron tricarbonyl,[36] which has been used as a trapping reagent for labile dienes,[37] failed to react with I in hexane at room temperature. In benzene at 65 °C overnight, it completely destroyed the starting olefin, but no volatile products were found in solution or were liberated by oxidation of the residue with ceric ammonium nitrate. μ-Dichlorotetraethylenedirhodium(I)[38] reacted rapidly in benzene at room temperature, again to consume I without the generation of other volatile material. The use of transition metals appeared increasingly less interesting and was terminated at this point.

Finally, some attempts to study further reactions of the dichloro ketone (V) led us to a brief examination of active metal reduction and Wolff–Kishner reduction conditions. Reaction of V with hydrazine hydrate in butanol[39] or, more

cleanly, in glyme gave a high yield of crystalline product whose elemental analysis, CI mass spectrum, and ^{13}C NMR spectrum (Table III)[10,40] conclusively showed it to be the ring-opened hydrazide XXV. Reactions of V with ammonia and with dimethylamine gave the analogous products XXVI and XXVII.
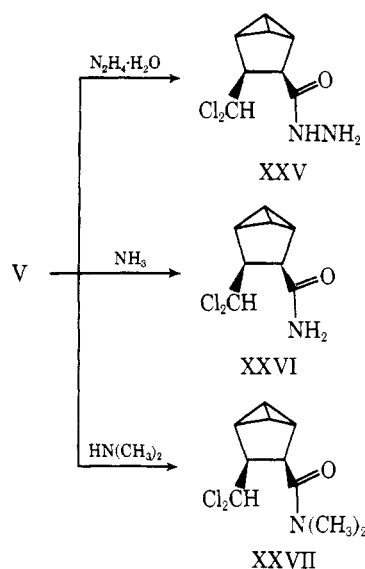
In all three cases, the product is evidently the result of nucleophilic attack at the carbonyl, followed by ring opening and proton transfer; with nucleophiles, there is well-established precedent for this type of reaction.[7d,41] While the formation of XXV, XXVI, and XXVII represents an easy route to 3,4-disubstituted tricyclo[3.1.0.0^{2,6}]hexanes, our particular interests lay elsewhere and our foray into this field went no further.

Experimental Section

preparative GC using a Varian 200 instrument; glass columns were used throughout.

8,8-Dichlorotetracyclo[4.2.0.0^{2,4}.0^{3,5}]octan-7-one (V). After a solution of benzvalene (2.42 g, 31 mmol) in ether (ca. 55 ml) had been cooled to 0 °C under nitrogen (a dry ice condenser was used to avoid losses due to evaporation), excluding moisture, a portion (ca. 0.5 ml) of a solution of triethylamine (3.45 g, 34 mmol) in ether (5 ml) was added. Freshly distilled dichloroacetyl chloride (4.58 g, 31 mmol) was then added to the stirred solution. With the temperature being maintained at 0 °C, the remainder of the solution of triethylamine was added dropwise to the rapidly stirred mixture over a period of 30 min. After the mixture had been stirred at 0 °C for a further 2.5 h, it was kept overnight at −15 °C. It was then allowed to warm to room temperature and the precipitate of triethylammonium chloride was removed by filtration. The ether was carefully removed at ambient temperature in vacuo (water pump) and was collected at −78 °C. (Using *N,N*-dimethylformamide as internal standard, the ether distillate was shown by NMR spectroscopy to contain 460 mg of benzvalene.) There remained a dark brown residue which yielded a pale yellow distillate (48 mg) on distillation at 24 °C (0.1 mm). Further distillation at bath temperature 24–110 °C gave a colorless distillate (4.42 g), bp 51–53 °C (0.08 mm), which turned brown on being kept overnight at 0 °C under nitrogen. Redistillation gave a pale yellow liquid (4.1 g, 86% based on consumed benzvalene). GC analysis (5% phenyldiethanolamine succinate column) showed the compound to be of high purity: MS (EI) *m/e* (rel intensity) 192 (very small), 191 (very small), 190 (1), 189 (very small), 188 (1), 187 (very small), 162 (5), 161 (7), 160 (8), 159 (11), 153 (9), 127 (32), 126 (9), 125 (100), 99 ([2(= 9] (9), 89 (36), 78 (40), 73 (8), 63 (18), 52 (11), 51 (13), 50 (10). Other data appear in ref 2.

8-Chlorotetracyclo[4.2.0.0^{2,4}.0^{3,5}]octan-7-one (VI). To 19.0 g (49 mmol) of triphenyltin hydride in 20 ml of AR cyclohexane in a 250-ml flask with reflux condenser, under nitrogen, was added 8.4 g (44 mmol) of V in 10 ml of cyclohexane. A few milligrams of azobis-isobutyronitrile were added and the mixture was refluxed for 0.5 h. After cooling, GC analysis (6% OV-1 column) showed that the reaction was complete. After storage at −20 °C overnight, the mixture was filtered, evaporated, and vacuum distilled to give 5.94 g (87%) of colorless liquid: bp 45–49 °C (0.1 Torr); IR (neat) 3150 vw, 3070 w, 2990 w, 1790 vs, 1380 w, 1295 w, 1120 m, 760 s, 720 cm^{-1} m; NMR δ 2.0–2.6 (m, 4 H), 3.05 (br "tr", "*J*" = 7–8 Hz, 1 H), 3.40–3.65 (m, 1 H), 4.62 (d of d, *J* = 8, 3 Hz, 1 H); MS (EI) *m/e* (rel intensity) 156 (1.5), 154 (4.5), 128 (2), 126 (7), 125 (4), 119 (18), 118 (16), 92 (8), 91 (100), 90 (16), 89 (20), 79 (6), 78 (87), 77 (17), 65 (28), 63 (21). Anal. Calcd for C$_8$H$_7$ClO: C, 62.15; H, 4.57. Found: C, 61.95; H, 4.39.

Tetracyclo[4.2.0.0^{2,4}.0^{3,5}]octan-7-one (VII). A solution of V (3.68 g, 18.4 mmol), triphenyltin hydride (15.2 g, 43 mmol), and azobis-isobutyronitrile (50 mg) in AR cyclohexane (20 ml) was stirred under nitrogen at 83 °C for 1 h. Additional azobisisobutyronitrile (20 mg) was then added to the mixture, which was then stirred at 83 °C for a further 3 h. (GC analysis now showed the absence of both V and VI.) Distillation of the mixture gave three fractions, each of which was collected in a dry ice cooled receiver. The first fraction (ambient temperature, water-pump pressure) was concentrated carefully to 1.18 g by removal, at atmospheric pressure, of most of the cyclohexane through a 20-cm column packed with glass rings. GC and NMR analysis showed the presence of 0.4 g of VII. The second fraction (ambient temperature, 0.1 Torr) (0.38 g) contained 0.19 g of VII. The third fraction [bp 30–35 °C (0.1 Torr)] contained 1.90 g of almost colorless VII, contaminated by several percent of cyclohexane. The total yield of VII was thus ca. 2.3 g, or over 95%. Spectral data appear in ref 2.

Tetracyclo[4.2.0.0^{2,4}.0^{3,5}]octan-7-one *p*-Toluenesulfonylhydrazone (X). To a warm (50–60 °C) solution of 12.4 g of *p*-toluenesulfonylhydrazide (recrystallized Aldrich material) in 18 ml of absolute ethanol was added 7.1 g of VII. The resulting solution was allowed to stand at room temperature for 20 h. The resulting mass of white crystals was separated from the mother liquor by centrifugation and dried at 0.05 Torr for several hours. The yield was 13.0 g (76%). Spectral and other characterization appears in ref 2. The ^{13}C NMR spectrum (CDCl$_3$) of X included δ −1.5, 9.6, 9.9 (bicyclobutane bridge), and 161.6 and 161.8 (C-7).

Tetracyclo[4.2.0.0^{2,4}.0^{3,5}]oct-7-ene (I). Into a dry flask, under nitrogen, was injected 1.60 ml (9.5 mmol) of 2,2,6,6-tetramethylpiperidine (Aldrich, 99+%). This was followed by injection (2 min) of methyllithium in diethyl ether (4.40 ml, Foote, 5.38%; 7.2 mmol). After the vigorous bubbling had ceased, 1 ml of dry, degassed THF was injected to dissolve the resulting yellow precipitate, giving 5 ml of dark amber solution. Into a flask fitted with septum, magnetic stirrer, and vacuum/nitrogen inlet was placed 0.58 g (2.0 mmol) of X. The flask

was evacuated to 0.03 Torr, then refilled with nitrogen. The solid was dissolved by injection of 3 ml of dry, degassed THF. The flask was chilled with dry ice, and 4.0 ml of base solution added (ca. 5 min); up to 2.0 ml, the base color faded to yellow, but then remained dark. After 10 min, the flask was allowed to warm to room temperature, and stirring was continued for a further 8 h. The flask was chilled with dry ice and 5 ml of water was injected dropwise; the mixture rapidly turned from very dark to yellow. The mixture was diluted with a few milliliters of *n*-pentane and the organic phase was separated and dried over anhydrous potassium carbonate. Analysis by GC (6% OV-1 column), using cumene as internal standard, showed ca. 50% yield of I. Further details of isolation and characterization appear in ref 2. Raman (neat, in capillary, using a Spex "Ramalog" instrument, using the 19 435-cm^{-1} line of an Ar laser; calibration of scale from the 1649-cm^{-1} stretch of cyclohexene) included 3140 s, 3120 s, 3050 vs, 2950 s, 1550 s, 1170 cm^{-1} vs.

Reaction of X with Methyllithium in Ether. X (0.51 g, 1.77 mmol) was placed in a 50-ml flask with magnetic stirrer and nitrogen/vacuum/septum adapter. The solid was dried by gentle warming under vacuum, and the flask then filled with nitrogen. Anhydrous ether (15 ml) was injected, and stirring begun to give a white suspension. An ice bath was placed around the flask, and 2.3 ml of methyllithium in ether (Ventron, 2.0 M) was injected (10 min). After 10 more min, the ice bath was removed. After 18 h, the brown suspension was treated with 15 ml of water. The turbid yellow aqueous layer was syringed away from the clear yellow ether layer, and the wash was repeated. After drying over ptassium carbonate, transferral to another flask, and slow evaporation to less than 1 ml (through a 6-in. Vigreux column), benzene (0.100 ml) was added as internal standard. NMR analysis showed about 40% yield of 7-methyltetracyclo[4.2.0.0^{2,4}.0^{3,5}]octane (XI) and a much smaller amount (possibly 10%) of I. These were collected from preparative GC (6% SE-30 column; the peak for XI was ca. three times the area of that for I), and XI was characterized: IR (vapor, 10-cm cell) 3160 vw, 3070 m, 2980 s, 2960 s, 2890 w, 1450 w, 1380 w, 1120 w, 775 cm^{-1} m; NMR complex pattern from δ 1.0–2.3, showing a three-proton doublet at 1.08 (*J* = 6 Hz) and strong broadened "singlets" at 1.85 and 2.15; MS (EI) *m/e* (rel intensity) 120 (3), 106 (1), 105 (10), 92 (6), 91 (13), 79 (14), 78 (100), 77 (15), 52 (10), 51 (14), 41 (9); MS (CI) *m/e* 135 (M + 15, 3), 121 (7), 119 (16), 107 (6), 105 (30), 93 (52), 91 (29), 80 (8), 79 (100), 78 (19).

Vapor-Phase Pyrolysis of I. A 1-cm o.d. Pyrex tube, packed with 20 cm of small Pyrex rings (washed with aqueous ammonia, then dried), was placed in a vertical tube furnace, topped with a septum, and with a small trap and outlet to vacuum at the bottom. The apparatus was evacuated (ca. 0.03 Torr) and a bleed valve, improvised from a 10-μl syringe needle, used to provide a 2–5 Torr nitrogen pressure to sweep samples through the tube. Injections of 0.1 ml of I in pentane (7 mg/ml) were passed through the tube and collected in the cold (liquid nitrogen) trap at the outlet. After 5 min, the system was filled with nitrogen, the trap allowed to warm to room temperature, and the contents analyzed. The sole significant product of the pyrolyses was cyclooctatetraene, as shown by coinjection with an authentic sample on 6% Carbowax 20M, 6% OV-1, and 10% QF-1 columns, and by comparison of the product's mass spectrum with that of authentic cyclooctatetraene. Pyrolyses were carried out at several temperatures ranging from 260 °C (<10% conversion) to ca. 450–500 °C (complete conversion). In no case was any discoloration of the column observed.

Reaction of I with *N*-Phenyltriazolinedione at 140 °C. In a Pyrex tube containing a small stirring bar were placed 110 mg (1.06 mmol) of I, 350 mg (2.0 mmol) of triazolinedione, and 3 ml of chloronaphthalene (Eastman, vacuum distilled). The tube was chilled and sealed under vacuum, then heated in a bath of refluxing xylene for 52 h in the dark. After cooling, the tube was opened and the contents were removed. After evaporation (high vacuum, gentle warming), the dark solid product was subjected to preparative TLC (silica gel, ether) to give the fractions listed below. (1) R_f 0: the mass spectrum of this dark, immobile fraction indicated the presence of diadduct(s), and this fraction was not characterized further. (2) R_f 0.1, ca. 10 mg of yellowish solid. The mass spectrum indicated this to be a 1:1 adduct; NMR showed the *N*-phenyl moiety. (3) R_f 0.45, 126 mg (44%) of material identified as XII by the near-perfect match of its IR spectrum, NMR spectrum (90 MHz), and melting point to those of an authentic sample.[22] (4) R_f 0.8, ca. 10 mg of yellowish solid; NMR and mass spectra were obtained. This fraction was later shown to be XIII by comparison with a pure sample obtained and characterized in a later experiment.

Deuteration of I. Single Treatment. I (150 mg) in 1.2 ml of anhydrous ether was dripped into 4 ml of 1.6 M *n*-butyllithium in hexane (Aldrich) at room temperature under nitrogen, and stirred for 1 h. The

Table IV

Initial spectrum	Final spectrum	Shift, ppm
1.86 (broadened s, 3 H)	2.7 (d, $J \simeq 5$ Hz, 1 H)	0.8
	5.4 (d, $J \simeq 6$ Hz, 2 H)	3.5
3.01 (d, $J \simeq 7$ Hz, 1 H)	5.7 (d, $J \simeq 7$ Hz)	2.7
4.15 (broadened s, 2 H)	8.2 (s)	4.1
5.68 ("tr", $J \simeq 7$ Hz, 1 H)	6.2 ("tr", $J \simeq 7$ Hz)	0.5
6.25 (m, 1 H)	6.7 ("tr", $J \simeq 7$ Hz)	0.4
7.4 (m, 5 H, aromatic)	7.8 (m, 3 H)	0.4
	12.9 (d, $J \simeq 7$ Hz, 2 H)	5.5

flask was then chilled in dry ice, and 1.0 ml of deuterium oxide was injected dropwise; the dry ice was then removed. The water was pipetted from the flask, and the remaining solution was dried over anhydrous potassium carbonate. Preparative GC (6% SE-30 column) gave ca. 100 mg of hydrocarbon. NMR of this indicated ca. 33% deuteration of the bicyclobutane bridgehead (positions 3 and 4); it also showed ca. 10% contamination by n-octane (from the butyllithium).

Deuteration of I. Repeated Treatment. I (0.251 g, 2.4 mmol) in 1.2 ml of anhydrous ether was placed in a dry, nitrogen-filled 25-ml flask with a magnetic stirrer and a septum/nitrogen inlet. n-Butyllithium (1.6 M in hexane, 2.5 ml, 4.0 mmol) was injected and the solution was left to stir at room temperature for 3 h. The flask was chilled in dry ice and 0.075 ml (4.2 mmol) of deuterium oxide injected. The dry ice was then removed, and after 15 min 4.0 ml (6.4 mmol) of n-butyllithium in hexane was injected. After 5.5 h more, the flask was again chilled, and 0.110 ml of deuterium oxide (6.1 mmol) was injected. The dry ice was removed, and 5.0 ml (8.0 mmol) of n-butyllithium in hexane injected. After a final 12-h wait, the flask was chilled again and 1.0 ml of deuterium oxide injected dropwise. Potassium carbonate was added after several minutes to take up excess moisture; preparative GC gave 0.164 g of material. NMR analysis showed this to be a mixture of 0.10 g of deuterated I and 0.06 g of n-octane. Integration of the NMR spectrum showed that the former was 75% deuterated at the 3 and 4 positions.

Reaction of 3,4-Dideuteriotetracyclo[4.2.0.0²,⁴.0³,⁵]oct-7-ene with *N*-Phenyltriazolinedione at 140 °C. This reaction was carried out as previously described, using 0.10 g of deuterated I (75% in the 3 and 4 positions) and 330 mg of triazolinedione. Reaction was continued for 24 h, and the product, deuterated XII, was isolated as before, and in the same yield: NMR δ 2.05 (4.5 H), 5.1 (2 H), 7.5 (5 H); at 90 MHz, the central two-proton signal shows as a triplet, $J = 3$ Hz; MS (EI) m/e (rel intensity) 282 (21), 281 (100), 280 (40), 120 (44), 119 (57), 118 (20), 106 (24), 105 (47), 104 (30), 93 (42), 92 (32), 91 (32). Shift reagent experiment: 24 mg of compound, in 0.3 ml of CDCl₃, was treated with weighed increments of solid "resolve-Al EuFOD" (Aldrich) until the "b" (see Discussion) proton set was clearly separated from the "a" set (40 mg of shift reagent). At this point, the spectrum was δ 2.5 (2 H), 2.8 (2.5 H), 7.9 (2 H), 7.1 (3 H), 10.0 (2 H). Confirmation of the first two signals as the respective sets noted above was accomplished by an identical experiment using undeuterated XII.

Reaction of I with *N*-Phenyltriazolinedione in Benzene at 23 °C. I (48 mg, 0.46 mmol) in 1.2 ml of benzene was added to 122 mg (0.7 mmol) of triazolinedione in a tube with a small stirring bar. The mixture was closed and allowed to stir at room temperature in the dark for 24 h. Preparative TLC gave two fractions, as listed below: (1) 58 mg (46%) of XII; (2) 8 mg (6%) of solid, mp 180–200 °C (201–204 °C after recrystallization from hexane/chloroform; IR and NMR spectra were virtually unchanged by this however). IR (KBr) 3100 vw, 3080 w, 3030 vw, 1775 m, 1705 vs, 1630 w, 1595 w, 1560 w, 1500 m, 1415 s, 1360 w, 1320 w, 1275 w, 1255, 1235 w, 1140 m, 1070 m, 775 m, 750 m, 720 cm⁻¹ m. For NMR (taken as a 3% solution in CDCl₃, with total added "Resolve-Al EuFOD" of 0, 2, 7, 12, 18, 26, and 36 mg), see Table IV. MS (EI) m/e (rel intensity) 280 (12), 279 (78), 227 (10), 177 (18), 160 (24), 119 (82), 118 (42), 117 (92), 104 (26), 103 (44), 91 (100), 90 (58), 78 (44), 77 (45). High-resolution MS calcd for $C_{16}H_{13}N_3O_2$, 279.1008; found, 279.1012. On the basis of this data, the structure XII was assigned to this compound.

Pyrolysis of I in the Presence of Hexafluoro-2-butyne. This experiment was carried out using a manifold of known volume. Into a 0.5-in. o.d. heavy-wall Pyrex tube (ammonia washed, then dried) were transferred, under vacuum by liquid nitrogen trapping, 0.104 g (1.0 mmol) of I and 0.36 g (2.2 mmol) of hexafluoro-2-butyne (Peninsular Chemical Research, Inc. This reagent came in a cylinder under pressure. Fitting the cylinder with an additional valve adapted

to a glass joint allowed small increments of gas to be introduced into the manifold via the two valves). The tube (8-in. section) was sealed under vacuum, padded with glass wool, and placed inside a copper pipe which in turn was heated in a tube furnace to 190–200 °C for 24 h. The tube was then cooled in dry ice, opened, and allowed to warm to room temperature (in the hood). The weight of brown oil obtained was 0.288 g; GC analysis of the mixture showed three major components (approximate ratio, in order of retention time, of 0.2:1:1), and a few small peaks at longer retention time. The products were identified by matching their properties with those of more thoroughly characterized samples prepared from cyclooctatetraene. The first component was identified as XVI by its CI mass spectrum and its GC behavior. The other two components were isolated by preparative GC (6% SE-30 column). This gave 55 mg of the second component, which was identified as XVII by its ¹H NMR spectrum, its IR spectrum, and its EI and CI mass spectra; the ¹⁹F NMR noted under the full characterization was also taken on this sample. The third component was isolated in 56-mg amount, and identified as XVIII by the same series of spectral methods; the ¹⁹F NMR and the proton decoupling experiment noted below were also performed on this sample.

Preparation of 1,2-Bis(trifluoromethyl)benzene) (XVI), 7,8-Bis(trifluoromethyl)tricyclo[4.2.2.0²,⁵]deca-3,7,9-triene (XVII), and 1,8-Bis(trifluoromethyl)tricyclo[4.2.2.0²,⁵]deca-3,7,9-triene (XVIII). Cyclooctatetraene (0.5 ml, 4.4 mmol) was placed in a 0.5-in. o.d. heavy-walled Pyrex tube, and an equal volume of hexafluoro-2-butyne was transferred in under vacuum. The tube was sealed and the mixture then heated to ca. 200 °C for 24 h. Preparative GC gave the three products, as described below. (1) 0.112 g (11%), identified as XVI: IR (neat) includes 1310 s, 1160 s, 1125 cm⁻¹ s; NMR symmetrical multiplet (collapsed A_2B_2 pattern) centered on δ 7.73; MS (EI) m/e (rel intensity) 214 (45), 195 (38), 164 (18), 145 (100), 125 (14), 95 (16), 75 (26), 69 (15), 50 (19); MS (CI) 215 (2.4), 214 (3.9), 196 (19), 195 (100), 194 (18), 193 (5). (2) 0.345 g (30%), identified as XVII: IR (neat) 1670 m, 1360 m, 1315 s, 1295 vs, 1250 s, 1185 vs, 1150–1140 vs, 1030 m, 1010 m, 780 m, 710 cm⁻¹ m; NMR matched that previously reported;²⁸ ¹⁹F NMR 45 ppm from CFCl₃ capillary (s); MS (EI) m/e (rel intensity) 227 (3), 196 (3), 195 (5), 178 (3), 177 (11), 145 (12), 128 (9), 77 (4), 75 (8), 53 (6), 52 (100), 51 (14), 50 (10); MS (CI) m/e (rel intensity) 295 (M + 29, 2), 268 (4), 267 (28), 266 (4), 248 (23), 247 (93), 246 (12), 228 (12), 227 (31), 183 (5), 93 (5), 79 (4), 67 (16), 53 (14), 52 (100), 51 (27), 50 (10); UV (isooctane) end absorption (ϵ_{210} 700), λ_{max} 221 nm (ϵ 700). (3) 0.459 g (39%), characterized as XVIII: IR (neat) 3140 vw, 3070 vw, 3000 vw, 2960 w, 1645 w, 1595 w, 1555 vw, 1360 m, 1330 s, 1285 s, 1180 vs, 1160–1150 s, 1055 m, 1030 m, 1015 m, 775 m, 740 w, 695 cm⁻¹ m; ¹H NMR δ 2.8 (narrow m, 2 H), 3.55 (m, 1 H), 6.1 (broadened s, 2 H), 6.45 (m, 3 H, containing a one-proton doublet, $J = 7$ Hz), 6.8 (d, $J = 7$ Hz, 1 H); a decoupling experiment showed that the multiplet at δ 3.55 was coupled to the multiplet at δ 2.8 and to the doublets at δ 6.45 and 6.8; ¹⁹F NMR 46 and 51 ppm from CFCl₃ capillary (equal quartets, $J = 10$ Hz); MS (EI) m/e (rel intensity) 227 (2), 197 (2), 196 (2), 195 (3), 177 (6), 151 (3), 145 (7), 128 (5), 75 (5), 69 (2), 53 (4), 52 (100), 51 (8), 50 (6); MS (CI) m/e (rel intensity) 295 (M + 29) (2), 268 (2), 267 (12), 249 (3), 248 (33), 247 (100), 246 (13), 228 (9), 227 (21), 81 (5), 79 (3), 67 (5), 53 (9), 52 (57), 51 (16), 50 (6); UV (isooctane) end absorption (ϵ_{210} 1100), λ_{max} 223 nm (ϵ 1100), λ_{max} 271 nm (ϵ 80). Anal. Calcd for $C_{12}H_8F_6$: C, 54.14; H, 3.03. Found: C, 53.94; H, 2.95.

Thermal Equilibration of XVII and XVIII. A sample of each isomer (ca. 30 mg) was sealed under vacuum into its own Pyrex tube, and both tubes were heated to 200 °C for 24 h. The NMR spectrum of each mixture was then taken and the two spectra were found to be nearly identical. From the integration, the XVIII:XVII ratio was about 6:1. Analysis by GC confirmed the near identity of the mixtures, and gave a similar ratio of XVIII to XVII. The GC trace also showed a peak at shorter, and two peaks at longer retention time than either starting material; from the NMR, these (minor) products appeared to be aromatics, but were not characterized further.

Tetracyclo[4.2.0.0²,⁴.0³,⁵]octane (XIX). In a 50-ml flask with magnetic stirring bar were placed 1.18 g of VII, 17 ml of AR 1-butanol, and 1.0 ml of 99% "hydrazine hydrate" (Baker). The flask was stoppered and stirring continued for 16 h; then the mixture was evaporated to give 1.23 g of a colorless, viscous mixture of hydrazone and azine (XX): IR (neat) 3360 w (broad), 3220 (broad), 3130 vw, 3060 w, 2970 m, 1685 m, 1615 w, 1400 w, 1110 m, 745 cm⁻¹ s; NMR δ 1.8–3.3 (m) and 4.82 (s, removable by D₂O), in area ratio 12:1; ¹³C NMR complex, but included δ −1.7 (d, 215), 8.7 and 8.9 (d, 210), 152.4 and 169.6 (s). Used for the reduction was a 50-ml flask with stirring bar and fitted with adapters leading to a trap cooled in ice. In the flask were placed 1.23 g of mixed hydrazone and azine, 13 ml of AR ethylene glycol, 1.5 g of potassium hydroxide, and 0.7 ml of hydrazine hydrate. After the hy-

droxide was dissolved by gentle warming and stirring, the apparatus was completed as noted, and the flask was heated by an oil bath to 180–185 °C for 2 h, after which two layers were visible in the trap. The flask was then brought to 200–210 °C for 2 h, by which time very little additional material was distilling over. After brief cooling, 2 ml of *n*-pentane was added to the pot and distilled over to rinse out droplets still in the adapters. The lower layer was pipetted from the trap, and the pentane solution dried over anhydrous potassium carbonate. Preparative GC (6% SE-30 column) gave 0.632 g of unpleasant-smelling, colorless XIX (61% from VII): IR (vapor, 10-cm cell) 3170 vw, 3060 m, 2960 s, 2870 w, 1440 w, 1380 w, 1290 w, 1230 w, 1165 w, 1120 m, 745 cm⁻¹ s; NMR δ 1.2–2.4, complex m, containing two major, roughly equal "peaks" at 1.85 and 2.15; MS (EI) *m/e* (rel intensity) 106 (21), 105 (11), 104 (6), 103 (7), 92 (3), 91 (41), 79 (21), 78 (100), 77 (25), 65 (10), 52 (12), 51 (21), 50 (11), 41 (6); MS (CI) *m/e* (rel intensity) 107 (15), 105 (28), 93 (6), 91 (12), 80 (6), 79 (100), 78 (10). Anal. Calcd for C_8H_{10}: C, 90.50; H, 9.50. Found: C, 89.69; H, 9.68. For ¹³C NMR data, see Table I.

Pyrolysis of XIX, ~480 °C. The apparatus used in this experiment was a modified version of that used for the vapor-phase pyrolysis of I. The pyrolysis tube and the trapping arrangement were the same, but the column was topped by an apparatus allowing a capillary containing the reactant to be opened under vacuum by rotating a stopcock. The furnace was heated to ca. 480 °C, a sealed capillary containing ca. 30 mg of XIX was placed in the apparatus, and the whole apparatus was then evacuated (0.05 Torr). The trap was cooled in liquid nitrogen and the capillary was opened. After 5 min, the apparatus was filled with nitrogen, the trap was allowed to warm to room temperature, and the small amount of yellow, foul-smelling liquid product was separated by preparative GC (6% SE-30 column) into its two components. The first component was identified as benzene by its NMR and mass spectra. The second was identified as XXI by its IR and NMR spectra.³³ᵃ The identity of XXI was confirmed by its conversion to ethylbenzene on treatment with hydrogen and 10% Pd/C catalyst, and by its conversion to dimethyl succinate by ozonolysis (−78 °C, methanol/ether) followed by oxidation (hydrogen peroxide/formic acid, brief reflux) and subsequent diazomethane treatment. From the NMR spectrum of the crude mixture, the molar ratio of benzene to XXI was 1:2.7.

Pyrolysis of XIX, ~430 °C. Apparatus and method were the same as for the higher temperature reaction, except that the furnace was set to ca. 430 °C and ca. 40 mg of XIX was used. GC analysis of the product showed six components, in about equal amounts (proportions varied significantly in the two times that this experiment was carried out, but all were present in isolable amounts both times). Preparative GC gave the components, which are listed in order of retention time (6% SE-30 column). NMR and IR were obtained of all, in CDCl₃ solution: (1) identified as benzene; (2) identified as XXII by comparing its NMR and IR spectra with published descriptions;³³ (3) identified as starting XIX; (4) on the basis of its IR spectrum and its hydrogenation (ether, 0 °C, 1 atm, 1 h, 10% Pd/C catalyst) to bicyclo-[3.2.1]octane,³⁴ this fraction was identified as XXIV; (5) identified as XXI; (6) identified as XXIII by its IR and NMR spectra.³³

Irradiation of I through Quartz. A solution of I in hexane (1 ml, containing several milligrams of I) was placed in a quartz tube fitted with a stopcock, along with 10 μl of 0.1% 2,6-di-*tert*-butyl-4-methylphenol in pentane. After four freeze–pump–thaw cycles at ca. 0.01 Torr, the tube was filled with nitrogen and the stopcock closed. The sample was irradiated at ca. 20 °C for 5.5 h using a 450-W Hanovia mercury lamp. After irradiation, the yellow, foul-smelling solution was analyzed by GC, which showed a roughly 1:1 mixture of I and a product whose retention time matched that of cyclooctatetraene on both a 6% OV-1 and a 6% Carbowax 20M column. The identities both of recovered I and of the product were also confirmed by their mass spectra.

Treatment of I with Silver Ion. Solutions of silver tetrafluoroborate (D. F. Goldsmith Chemical and Metal Corp.) and of silver perchlorate (Alpha) were made up both in acetone and in THF, to ca. 0.04 M concentration. To 0.2-ml portions of these solutions were added 1-drop portions of I in CDCl₃ (containing 1–2 mg of I), and the mixture was analyzed by GC (6% OV-1 column) after 1, 15, and 30 min. At 30 min, the mixture was quenched by addition of 1 ml of saturated aqueous sodium chloride, and the organic layer again analyzed. In all cases, there was observed rapid formation of a small to moderate proportion of a single product with retention time identical with that of cyclooctatetraene.

(4-Dichloromethyl)-3-tricyclo[3.1.0.0²,⁶]hexanecarboxylic Acid Hydrazide (XXV). To 1.437 g (7.6 mmol) of V in 50 ml of glyme was added 0.50 ml (10 mmol) of hydrazine hydrate, with stirring. After 1.5 h of stirring at room temperature, the resulting slurry was evap-

orated, then dried at 0.1 Torr overnight to give 1.618 g (96%) of cream-colored, finely crystalline solid. This substance was stable indefinitely in the solid state, but soon turned brown in Me₂SO solution; when heated, it turned black in the range 100–200 °C, without melting. IR (KBr) 3340 s, 3050 w, 2940 w, 1625 vs, 1525 m, 1390 w, 1325 w, 1265 m, 1225 w, 1195 w, 1130 w, 1065 w, 1010 w, 940 w, 885 w, 800 w, 770 w, 730 cm⁻¹ m; NMR (Me₂SO-d_6) 2.0–2.35 (m, 4 H), 2.35–2.65 (m, 2 H), 3.3–5.1 (broad, 3 H), 5.9–6.3 (symmetrical m, 1 H); MS (CI) *m/e* (rel intensity) 251 (1) and 249 (2) (M + 29), 225 (5), 224 (3), 223 (28), 222 (5), 221 (43), 188 (3), 187 (32), 186 (10), 185 (100), 149 (9), 137 (8), 133 (7), 127 (8), 125 (7), 121 (8), 95 (4), 91 (18), 79 (4). Anal. Calcd for $C_8H_{10}N_2Cl_2O$: C, 43.46; H, 4.56; N, 12.67; Cl, 32.07. Found: C, 42.49; H, 4.46; N, 13.30; Cl, 31.80. For ¹³C NMR data, see Table III.

(4-Dichloromethyl)-3-tricyclo[3.1.0.0²,⁶]hexanecarboxamide (XXVI). Into a dry, nitrogen-filled 50-ml three-necked flask with septum, dry ice cold finger condenser topped with a stopcock, and an inlet tube were condensed a few milliliters of ammonia. Anhydrous ether (20 ml) was injected, followed by 0.447 g (2.52 mmol) of V in 1 ml of ether (dropwise over 1 min). After 1 h, a stream of nitrogen was passed through the flask until the solvent had evaporated, leaving a white deposit. This was dried overnight at 0.1 Torr at room temperature to give 0.38 g (73%) of product: mp 123–124.5 °C dec; IR (KBr) 3400 s, 3190 m, 2860 vw, 1650 vs, 1620 m/s, 1430 m, 1295 m, 1285 m, 1265 w, 1220 w, 1140 w, 1125 m, 980 w, 805 w, 760 m, 745 cm⁻¹ m; NMR (Me₂SO-d_6) δ 2.1–2.4 (m, 4 H), 2.62 (broadened s, 1 H), 2.71 (broadened s, 1 H), 6.23 (pentuplet, J = 5 Hz, 1 H), 6.8 (br, 1 H), 7.4 (br, 1 H); ms (CI) *m/e* (rel intensity) 210 (6), 209 (3), 208 (31), 207 (4), 206 (49), 172 (34), 170 (100), 134 (9), 127 (20), 122 (20), 91 (46), 79 (10); MS (EI) *m/e* (rel intensity) 172 (1), 170 (3), 127 (16), 125 (43), 123 (20), 122 (82), 92 (6), 91 (57), 90 (7), 89 (18), 85 (17), 83 (27), 80 (10), 79 (98), 78 (16), 77 (35), 65 (19), 63 (15), 52 (13), 51 (17), 44 (100). Anal. Calcd for $C_8H_9Cl_2NO$: C, 46.62; H, 4.40; Cl, 34.41; N, 6.80. Found: C, 46.81; H, 4.42; Cl, 34.62; N, 6.86.

***N,N*-Dimethyl-(4-dichloromethyl)-3-tricyclo[3.1.0.0²,⁶]hexanecarboxamide (XXVII).** A dry, 50-ml, three-necked flask was set up with cold finger condenser with bubbler outlet, septum/stopcock inlet, stopper, and magnetic stirrer. After flushing with nitrogen, the flask was chilled in dry ice and the condenser filled with dry ice. Several milliliters of dimethylamine (Matheson) were condensed in via the stopcock; this was withdrawn as completely as possible with a chilled syringe, and 2 ml was returned to the flask. Next, 15 ml of anhydrous ether was injected and stirring commenced. V (0.814 g, 2.32 mmol) was syringed in (5 min), then after another 5 min the dry ice bath was removed and the solution allowed to come to room temperature. After 4 h at room temperature, the light yellow solution was evaporated to give 1.01 g of light yellow oil (99%). IR, NMR, and GC analysis indicated that starting V was absent. The product turned black and viscous at room temperature after a few days in chloroform-*d* solution; GC analysis (6% OV-1 column) was unsuccessful. IR (neat) 3140 w, 3050 w, 2990 w, 2950 m, 1660 s, 1490 m, 1410 m, 1395 m, 1255 w, 1145 m, 1115 m, 760 m, 735 cm⁻¹ m; NMR δ 1.90–2.55 (m, 4 H), 2.55–3.39 (m, 2 H), 2.91 (s, 3 H), 3.10 (s, 3 H), 5.95 (d, J = 9 Hz, 1 H); MS (CI) *m/e* (rel intensity) 238 (10), 237 (8), 236 (62), 235 (18), 234 (100), 233 (11), 200 (28), 199 (12), 198 (85), 180 (23), 162 (23), 150 (22), 72 (89). For ¹³C NMR data, see Table III.

Registry No.—I, 35434-65-2; V, 54220-48-3; VI, 61076-11-7; VII, 54220-49-4; VIII, 61076-12-8; VIII mesylate, 61076-13-9; X, 54220-50-7; XI, 61117-20-2; XII, 30114-59-1; XIII, 61104-53-8; XVI, 433-95-4; XVII, 59905-85-0; XVIII, 61076-14-0; XIX, 36328-44-6; XX hydrazone, 61076-15-1; XX azine, 61076-16-2; XXV, 61076-17-3; XXVI, 61076-18-4; XXVII, 61076-19-5; benzvalene, 659-85-8; dichloroacetyl chloride, 79-36-7; *N*-phenyltriazolinedione, 4233-33-4; hydrazine hydrate, 10217-52-4; ammonia, 7664-41-7; dimethylamine, 124-40-3; *p*-toluenesulfonylhydrazide, 1576-35-8; hexafluoro-2-butyne, 692-50-2.

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