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The Chemistry of Polyunsaturated Bicyclo[4.2.2]decyl Systems

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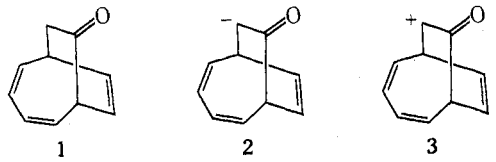
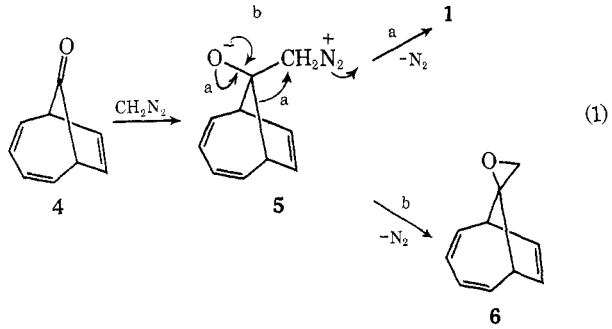
Bicyclo[4.2.2]deca-2,4,9-trien-7-one (**1**, 50–85%) and spiro[bicyclo[4.2.1]nona-2,4,7-trien-9,2'-oxirane] (**6**, 15–50%) result from reaction of bicyclo[4.2.1]nona-2,4,7-trien-9-one (**1**) and diazomethane. Bicyclo[4.2.2]deca-2,4,9-trien-7-one tosylhydrazone (**7**) is converted by methyllithium to bicyclo[4.2.2]deca-2,4,7,9-tetraene (**8**, 78%), *cis*-9,10-dihydronaphthalene (**9**, <1%), and naphthalene (5%). 7-Acetoxy- (**10**) and 7-pyrrolidinobicyclo[4.2.2]deca-2,4,7,9-tetraenes (**11**) are formed in excellent yields from acid-catalyzed reactions of **1** with isopropenyl acetate and pyrrolidine, respectively. Bases convert **1** to bicyclo[4.2.2]deca-2,4,9-trien-7-one enolate (**2**); **2** reacts with deuterium oxide to give *anti*-8-deuteriobicyclo[4.2.2]deca-2,4,9-trien-7-one (**13**), which is then converted to 8,8-dideuteriobicyclo[4.2.2]deca-2,4,9-trien-7-one (**15**) upon much longer exposure to the basic deuterating medium. Enolate **2** reacts with acetyl chloride to yield **10** (85%) and with trimethylsilyl chloride to form 7-trimethylsiloxybicyclo[4.2.2]deca-2,4,7,9-tetraene (**12**, 72%). Methylation of **2** in hexamethylphosphoramide or dimethylformamide at 0° produces 7-methoxybicyclo[4.2.2]deca-2,4,7,9-tetraene (**16**, 92%); in glyme **16** (43%) and 8,8-dimethylbicyclo[4.2.2]deca-2,4,9-trien-7-one (**18**, 26%) are formed. Enolate **2** rearranges slowly to the β-tetralone anion and probably the anion of *cis*-9,10-dihydro-2-naphthol; secondary methylation products are 2-methoxy-3,4-dihydronaphthalene (**22**) and 2-methoxynaphthalene (**23**). Thermolysis of **16** gives naphthalene (66%) and **23** (33%). Enolate **2** reacts with isoamyl nitrite to produce bicyclo[4.2.2]deca-2,4,9-triene-7,8-dione monooxime (**32**, 63%) and with methyl formate to yield 8-formylbicyclo[4.2.2]deca-2,4,9-trien-7-one (**35**, 95%). Oxime **32** is converted to bicyclo[4.2.2]deca-2,4,9-triene-7,8-dionequinoxaline (**33**) by *o*-phenylenediamine; **35** and hydrazine give 3,4-diazatricyclo[5.4.2.$0^{2,6}$]trideca-2,5,8,10,12-pentaene (**36**). 8-Diazobicyclo[4.2.2]deca-2,4,9-trien-7-one (**37**, 55%) forms from **35**, tosyl azide, and triethylamine. Diazo ketone **37** photolyzes in dioxane–water to bicyclo[4.2.1]nona-2,4,7-triene-*syn*-9-carboxylic acid (**39**, 61%). Decomposition of **37** by acetic acid and by hydrogen chloride occurs with rearrangement to *exo*- and *endo*-2-acetoxybicyclo[5.2.1]deca-3,5,8-trien-10-ones (**43** and **44**), and *exo*-2-chlorobicyclo[5.2.1]deca-3,5,8-trien-10-one (**54**, 94%), respectively. Chloride **54** reacts with silver acetate yielding **43** (53%); hydrogenolysis of **54** produces bicyclo[5.2.1]decan-10-one (**56**, 61%). Hydrogenation of **43** gives *exo*-2-acetoxybicyclo[5.2.1]decan-10-one (**50**, 73%) which upon saponification and oxidation results in bicyclo[5.2.1]deca-2,10-dione (**52**, ~100%). Acetate **43** and chloride **54** rearrange to *endo*-6-(*cis*-2'-acetoxyvinyl)-*cis*-bicyclo[3.3.0]octa-3,7-dien-2-one (**58**, 93%) and *endo*-6-(*cis*-2'-chlorovinyl)-*cis*-bicyclo[3.3.0]octa-3,7-dien-2-one (**60**, 100%), respectively. Lead tetraacetate oxidizes **1** to *anti*-8-acetoxybicyclo[4.2.2]deca-2,4,9-trien-7-one (**64**, 100%). Attempted Wolff–Kishner reductions of bicyclo[4.2.2]deca-2,4,9-trien-7-one hydrazone (**66**) or the semicarbazone produce 2,3-diazatricyclo[6.3.1.$0^{4,11}$]dodeca-1,5,9-triene (**70**, 47–54%). 3-Methyl-2,3-diazatricyclo[6.3.1.$0^{4,11}$]dodeca-1,5,9-triene (**73**, 75%) is formed from **1** and methylhydrazine. Photolysis of **1** leads to tricyclo[3.3.2.$0^{2,8}$]deca-3,6-dien-9(10)-one (**78**, 68%), which reverts to **1** upon treatment with acid.

The properties and interconversions of C_{10} bicyclopolyunsaturated systems are subjects of intense interest.[2] We now describe the chemistry of bicyclo[4.2.2]deca-2,4,9-trien-7-one (**1**) and its derivatives, and the 8-ketobicyclo[4.2.2]deca-2,4,9-trien-7-yl carbanion (**2**) and carbonium ion (**3**).



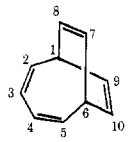
1 **2** **3**

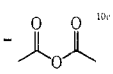
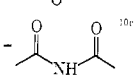
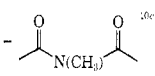
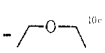
Ketone **1** (50–85%) along with spiro[bicyclo[4.2.1]nona-2,4,7-trien-9,2'-oxirane] (**6**, 15–50%) are obtained from reactions of bicyclo[4.2.1]nona-2,4,7-trien-9-one (**4**)[3a–c] with diazomethane and lithium chloride[3d] in methanol–chloroform–ether at 0°. Ketone **1** and epoxide **6** are presumably formed by nucleophilic approach of diazomethane



4 **5** **6** (1)

Table I
^{1}H NMR For Substituted Bicyclo[4.2.2]deca-2,4,7,9-tetraenes

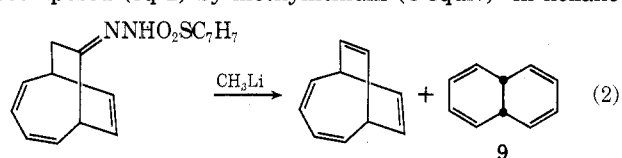


Substituent	^{1}H NMR, δ						
	$H_{2,5}$	$H_{3,4}$	H_7	H_8	$H_{9,10}$	$H_{1,6}$	H_s[a]
7-H (8)[b]	6.12	5.74		5.50	5.50	3.15	5.50
7-OAc (10)[b]	6.10	5.69		5.35	5.49	3.23	2.03
7-$OSi(CH_3)_3$ (12)	6.15	5.75		4.78	5.50	3.18	0.11
7-OCH_3 (16)[b]	6.10	5.65		4.50	5.48	3.20	3.40
7-$N(CH_2)_4$ (11)	6.15	5.80		4.15	5.55	3.40	3.00, 185
7-CH_3[11c]	6.4–5.7	6.4–5.7		5.28	5.5	3.07	1.74
7-Br[11b]	5.9	5.9		5.4	5.9	3.4, 3.1	
7-CO_2CH_3[11b]	5.8	5.8		6.7	5.8	3.8, 3.3	3.67
7,8-$(CO_2CH_3)_2$[10a]	6.18	5.86			5.67	3.70	
3,4- 	7.55		5.78	5.78	5.78	3.55–3.8	
3,4- 	6.50		4.75	4.75	4.75	2.3–2.7	
3,4- 	7.39		5.79	5.79	5.79	3.5–3.7	
3,4- 	6.10		5.69	5.69	5.69	3.1–3.3	

[a] Proton resonance of the substituent at C-7. [b] Proton assignments were based on double-irradiation experiments.

from the less hindered anti side of **4**, forming the zwitterionic intermediate **5**, which collapses to products (eq 1). Ketone **1** was obtained preparatively from the reaction mixture by (1) formation and separation of its semicarbazone and regeneration of **1** in pyruvic acid under argon at 25°, or, more advantageously, by (2) formation of the Girard's reagent T adduct and hydrolysis of the water-soluble intermediate. The structure of **1** was proven by its hydrogenation to bicyclo[4.2.2.]decan-7 one, which was prepared independently by ring expansion of bicyclo[4.2.1]nonan-9-one with diazomethane.[3b]

Ketone **1** is converted readily to bicyclo[4.2.2]deca-2,4,9-trien-7-one tosylhydrazone (**7**). Tosylhydrazone **7** is decomposed (eq 2) by methyllithium (4 equiv)[4] in hexane

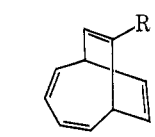


(2)

7 8 9

at 25° to bicyclo[4.2.2]deca-2,4,7,9-tetraene (**8**, 78%); *cis*-9,10-dihydronaphthalene (**9**, <1%), and naphthalene (5%) are also produced. This preparation of **8** is a more advantageous and rapid route than those previously reported.[2] Tetraenes **8** and **9** were identified by comparison to authentic samples.[5]

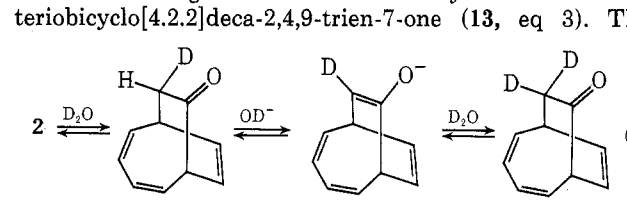
Ketone **1** provides a useful entry to 7-substituted bicyclo[4.2.2]deca-2,4,7,9-tetraenes via acid-catalyzed processes. Isopropenyl acetate reacts with **1** as accelerated by *p*-toluenesulfonic acid to give 7-acetoxybicyclo[4.2.2]deca-2,4,7,9-tetraene (**10**). Supportive data for the structure assigned as **10** include its ^{1}H NMR properties (Table I); double irradiation of the bridgehead multiplet at δ 3.23 causes simplification of the absorbances at δ 6.10, 5.49 (to s), and 5.35 (to s). The structure of **10** is confirmed by its acid-catalyzed hydrolysis to **1** (~100%).



10, R = $OCCH_3$
11, R = N
12, R = $OSi(CH_3)_3$

Acid-catalyzed condensation of **1** with pyrrolidine yields 7-pyrrolidinobicyclo[4.2.2]deca-2,4,7,9-tetraene (**11**), an extremely hygroscopic enamine. The structure of **11** is revealed by its ^{1}H NMR absorptions (Table I) and by its hydrolysis to **1** (100%).

Various bases convert **1** to its enolate ion (**2**). Enolate **2** undergoes facile monodeuteration. Thus treatment of **1** at 25–30° in carbon tetrachloride for 12 hr with deuterium oxide containing sodium deuteroxide yields *anti*-8-deuteriobicyclo[4.2.2]deca-2,4,9-trien-7-one (**13**, eq 3). The



(3)

13 14 15

stereochemical assignment of **13** is based upon deuteration from the less hindered anti side of **2**. Steric factors allow rapid monodeuteration as compared to slow dideuteration of **1**. Proton removal from **13** and thus deuteration of **13** via **14** to **15** are hindered processes. However, at relatively long exposure times (12 days) and using higher concentrations of sodium deuterioxide, **13** undergoes effective dideuteration to 8,8-dideuteriobicyclo[4.2.2]deca-2,4,9-trien-7-one

Table II
Product Distribution from Reaction of Bicyclo[4.2.2]deca-2,4,9-trien-7-one (1) with Potassium *tert*-Butoxide and Methyl Fluorosulfonate in Polar Solvents

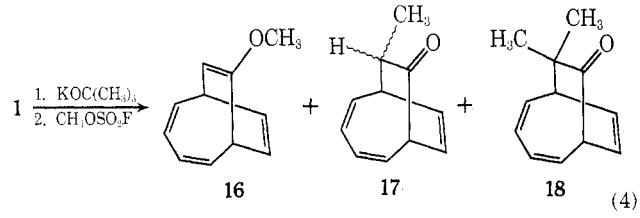
Potassium *tert*-butoxide, contact time,[a] 0-10°	Solvent	Product percentage 16	1	18	22	23
4 min[b]	Hexamethylphosphoramide	92.2	2.5	3.0	0.6	1.5
4 min	Dimethylformamide	93.0	3.1	2.8	0.2	0.9
14 min	Hexamethylphosphoramide	91.0	0.8	5.5	1.2	1.0
30 min	Dimethylformamide	82.0	7.1	1.0	5.5	2.6
12 hr	Dimethylformamide	72.0	1.0	1.0	7.4	16.0
24.5 hr	Dimethylformamide	60.0	3.5	1.5	10.0	12.0

[a] Typical reaction used 3 equiv of potassium *tert*-butoxide. [b] Average of seven reactions; see Table III.

(**15**). Dideuterio ketone **15** is prepared much more advantageously under more forcing conditions involving reaction of **2** with excess potassium *tert*-butoxide (≫2 equiv) in hexamethylphosphoramide, quenching with deuterium oxide, and neutralization with boron trifluoride etherate.

Enolization of **1** in basic media to **2** also allows synthesis of 7-substituted bicyclo[4.2.2]deca-2,4,7,9-tetraenes. Thus reaction of **1** with potassium *tert*-butoxide (2 equiv) in glyme (5 min) at 25° and then acetyl chloride gives acetoxytetraene **10** in 83% yield, recovered **1** (8%), and unidentified products (9%). 7-Trimethylsiloxybicyclo[4.2.2]deca-2,4,7,9-tetraene (**12**, 72%) is obtained upon addition of trimethylsilyl chloride to **1** and potassium *tert*-butoxide in glyme. Silyl ether **12** is very sensitive to atmospheric moisture and its structure is assigned from its ir and ^{1}H NMR absorptions (Table I) and its hydrolysis to **1** (~100%).

A study has been made of methylation of **2**. Reaction of **1** with excess potassium *tert*-butoxide (~3 equiv) in glyme for 4 min at 25° and then rapid addition of methyl fluorosulfonate (3 equiv) gives the following products (eq 4) in the indicated yields: 7-methoxybicyclo[4.2.2]deca-2,4,7,9-tetraene (**16**, 43%), recovered **1** (9.5%), 8-methylbicyclo-[4.2.2]deca-2,4,9-trien-7-one (**17**, ~1%),[6a] and 8,8-dimethylbicyclo[4.2.2]deca-2,4,9-trien-7-one (**18**, 26%)[6b] along with unidentified components (~20%) of higher retention times. All products were separated by preparative GLC.[7]

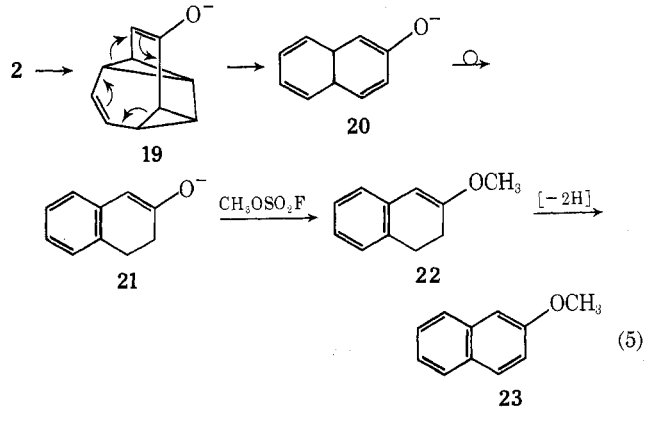


16 **17** **18** (4)

Purified methoxytetraene **16** is homogeneous upon GLC analysis; it does not rearrange or decompose during GLC treatment. The structure of **16** is partly assigned on the basis of its ^{1}H NMR absorptions (Table I) along with double-irradiation experiments; decoupling of bridgehead proton (C-1, -6) absorptions at δ 3.20 simplifies the resonances at δ 6.10, 5.48 (to s), and 4.50 (to s). The structure and the homogeneity of **16** are confirmed by hydrolysis of the sample to **1** (100%).

Methyl ketone **17** is difficult to separate from **1** and its presence in **1** is established by mass spectral analysis (*m/e* 160). Dimethyl ketone **18** exhibits carbonyl (1700 cm^{-1}) and *gem*-dimethyl (1380 and 1370 cm^{-1}) ir absorptions along with ^{1}H NMR and mass spectral properties consistent with the structural assignment.

Polar solvents enhance the efficiency of O-methylation of **2** to **16**. Thus when **1** is treated with potassium *tert*-butoxide (3 equiv) in hexamethylphosphoramide at 0–5° for 4 min followed by excess methyl fluorosulfonate (Table II), methoxytetraene **16** is formed in 92.2% average yield along with recovered **1** (2.5%), methyl ketone **17** (trace), dimethyl ketone **18** (3.0%), 2-methoxy-3,4-dihydronaphthalene[8] (**22**, 0.6%), and 2-methoxynaphthalene[8] (**23**, 1.5%). Similar results are obtained when methylation of **1** is effected in dimethylformamide at 0–5° (Table II). Methoxydihydronaphthalene (**22**) presumably results upon conversion of **1** to **19**, rearrangement to **20**, and then isomerization and methylation (eq 5, or/and methylation and isomerization). Oxidation, after rearrangement of **19**, in combination with methylation and isomerization accounts for formation of **23**.



(5)

After it had been communicated by us[1b] that **1** (a) undergoes efficient base-catalyzed deuterium exchange to **13** and **15**, (b) reacts with potassium *tert*-butoxide (3 equiv) in hexamethylphosphoramide at 5° for 4 min and then excess methyl fluorosulfonate to give **16** as isolated in 93–95% yield, and (c) is converted by potassium *tert*-butoxide (3 equiv, 3 min) in glyme at 20° and then acetyl chloride to **10** in 83% yield (>90% efficiency), Goldstein and Klein[9] reported that reaction of **1** with potassium *tert*-butoxide in dimethyl sulfoxide or dimethylformamide at 0–10° and then dimethyl sulfate gives **16** seriously contaminated with **22** as derived by rapid isomerization of **2** to **20** and its subsequent methylation. These authors state[9] that (1) methylation of **1** was effected under "closely similar conditions" to those communicated by us; (2) no evidence was provided concerning the homogeneity or the proof of structure of the **16** in our prior report;[1b] (3) if **1** is exposed to potassium *tert*-butoxide at 0–10° for as long as 20 min and then dimethyl sulfate is added, only **22** is obtained (and thus, presumably, during the basic treatment, **2** is isomerized completely to **20**), and (4) their most efficient preparative procedure for methylation of **1** gives **22** in only 40% efficiency even "under conditions of deliberately incomplete deprotonation of **1**".

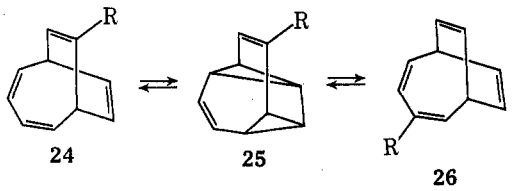
We should like to emphasize presently that **16** is pro-

Table III
Product Distribution from Reaction of Bicyclo[4.2.2]deca-2,4,9-trien-7-one (1) with Potassium *tert*-Butoxide and Methyl Fluorosulfonate in Hexamethylphosphoramide

	Product percentage				
Trial	16	1	18	22	23
1	95.0	4.0	1.0		
2	92.0	5.0	1.5		1.5
3	91.0	3.0	2.9		3.1
4	90.0	1.5	6.1	1.7	1.0
5	93.0	1.0	3.0	1.0	2.0
6	92.0	1.0	5.1	0.7	1.2
7	93.0	2.3	1.8	1.1	1.8
Average	92.2	2.5	3.0	0.6	1.5

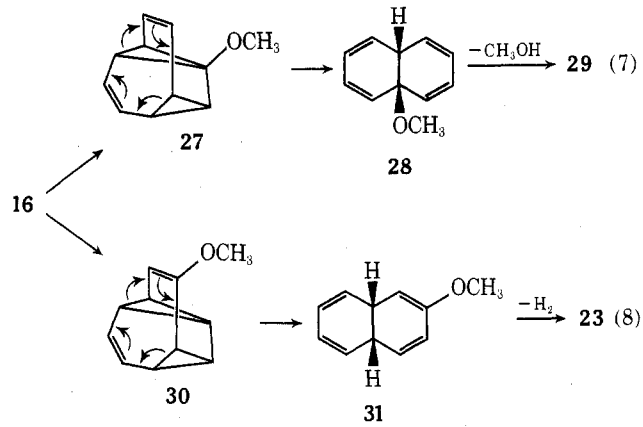
duced in 93–95% yield from **2** as previously communicated.[1b] The data from which the previous report was made are summarized in Table III. The yields quoted previously[1b] and as now repeated are accurate and satisfactorily reproducible (also see Experimental Section). Secondly, in our publication[1b] it was pointed out explicitly that the structure and the homogeneity of **16** are established from its analysis, ir and ^{1}H NMR spectra, and origins and in particular from its hydrolysis to **1** in "essentially quantitative yield". It is indeed unfortunate that our report has been misrepresented. Thirdly, enolate **2**, though generated essentially quantitatively, rearranges slowly. When the methylations with methyl fluorosulfonate are run after increased contact times of **1** with potassium *tert*-butoxide, there is a decrease in the yield of methoxytetraene **16** and a concomitant increase in the by-products obtained (Table II). After contact of **2** with potassium *tert*-butoxide for 24.5 hr at 0° and then methylation, the major product is still tetraene **16** (60%) but now significant amounts of methyl ether **22** (10%) and methoxynaphthalene **23** (12%) are formed. During our study of the methylation of enolate **1**, **22** and **23** were never formed as major reaction products. Further, enolate **1**, as generated using a twofold excess of potassium *tert*-butoxide in dimethylformamide at 0° for 0.5 hr, gives ketone **1** (92%) upon quenching with water; no β-tetralone is obtained under conditions where >2% could be detected. Under the conditions of the preparative experiments presently described, rapid rearrangement of **2** to **20** is not observed.

A subject of particular interest in the present research is that the 7-substituted tetraenes **10**, **11**, **12**, and **16** (represented as **24**), as prepared initially or upon gas chromatography at elevated temperatures, might isomerize (rapidly) to 3-substituted bicyclo[4.2.2]decatetraenes (**26**) via internal addition (internal Diels–Alder reaction) to **25** and opening (retro Diels–Alder reaction) as do analogous tetraenes[10] (eq 6). Tetraenes **10**, **11**, **12**, and **16** upon preparation (as previously described) and **10**, **12**, and **16** after gas chromatography at temperatures up to 200° hydrolyze quantitatively to **1**, and thus, under the indicated conditions, they do not rearrange to their corresponding 3-substituted bicyclo[4.2.2]decatetraenes (eq 6).[11]

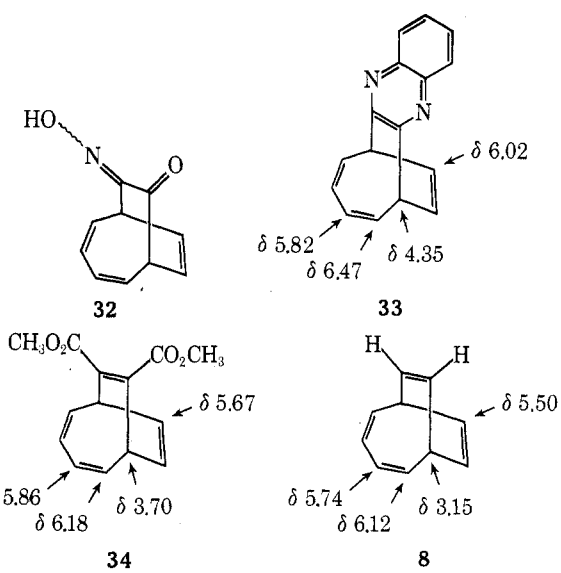


24 25 26 (6)

Methoxytetraene **16** displays expected thermal behavior, however, after extended exposure to elevated temperatures. Thus when **16** is heated for 0.5 hr at 200° in hexamethylphosphoramide, naphthalene (**29**, 17%) and 2-methoxynaphthalene (**23**, 10%) are obtained along with unrearranged **16** (73%). Heating **16** neat in a sealed evacuated tube for 21 hr at 200° gives methanol, **29** (59%), **23** (30%), and recovered **16** (11%). Thermolysis of **16** probably occurs via allowed internal Diels–Alder reactions (**27** and **30**, eq 7 and 8) and subsequent disallowed openings to *cis*-9,10-dihydronaphthalene derivatives (**28** and **31**) which then aromatize. The sequence in eq 7 is favored over that in eq 8 by about 2:1; the reasons for this difference are not clear.



Base-catalyzed enolization of **1** provides for further functionalization at C-8. Reaction of potassium *tert*-butoxide and isoamyl nitrite[12] with **1** in *tert*-butyl alcohol gives bicyclo[4.2.2]deca-2,4,9-triene-7,8-dione monoxime (**32**, 63%), which is converted by *o*-phenylenediamine in acetic acid to bicyclo[4.2.2]deca-2,4,9-triene-7,8-dionequinoxaline (**33**).

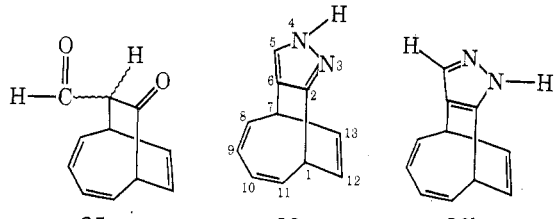


Quinoxaline **33** is identified by its ir and mass spectral properties, proper combustion analysis, and ^{1}H NMR absorptions typical of bicyclo[4.2.2]deca-2,4,7,9-tetraenyl systems.

Comparison of the ^{1}H NMR absorptions of quinoxaline **33**, 7,8-dicarbomethoxybicyclo[4.2.2]deca-2,4,7,9-tetraene (**34**), and bicyclo[4.2.2]deca-2,4,7,9-tetraene (**8**) reveals a large effect of the quinoxaline moiety. As expected from their similarities in symmetry, **33**, **34**, and **8** display identical line shape patterns in the ^{1}H NMR of the vinylic region. Diester **34**, a relatively electron-deficient tetraene, shows sizable downfield ^{1}H NMR shifts for protons at C-1, -6, -2, -5, -9, and -10 (Table I) relative to parent **8** ($\Delta\delta$ 0.55, 0.06, and 0.17, respectively). Quinoxaline **33** reveals even greater

downfield shifts for such protons ($\Delta\delta$ 1.20, 0.35, and 0.52, respectively). These shifts probably stem from inductive effects, since they fall off with distance from the substituent; neither **33** nor **34** shows any noticeable ^{1}H NMR shifts for their protons at C-3 and -4.

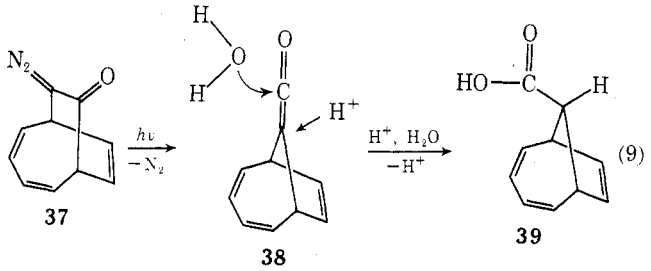
Ketone **1** is also functionalized at C-8 by base-catalyzed condensation with excess methyl formate and sodium methoxide (4 equiv) in ether to give 8-formylbicyclo[4.2.2]deca-2,4,9-trien-7-one (**35**), mp 56–57°, in 95% yield. Formyl ketone **35** is characterized by spectral means and by reaction with hydrazine[13] to form 3,4-diazatricyclo[5.4.2.0^{2,6}]trideca-2,5,8,10,12-pentaene (**36a,b**). The



35 **36a** **36b**

product, a pyrazole derivative, probably exists as a mixture of tautomers **36a** and **36b.**

Formyl ketone **35** is converted by tosyl azide and triethylamine[14] to 8-diazobicyclo[4.2.2]deca-2,4,9-trien-7-one (**37,** 55%). Diazo ketone **37** is a yellow solid exhibiting intense ir absorptions for a diazo group (2150 cm^{-1}) and carbonyl group stretching (1650 cm^{-1}), a mass spectral ion at *m/e* 144 (P − N_2), and ^{1}H NMR absorptions typical for trienyl systems. Photolysis of **37** in dioxane–water results in ring contraction (**38**) and hydration to give bicyclo[4.2.1]nona-2,4,7-triene-*syn*-9-carboxylic acid (**39,** 61%, eq 9). The syn carboxylic acid (**39**) is identical (ir, melting



37 **38** **39** (9)

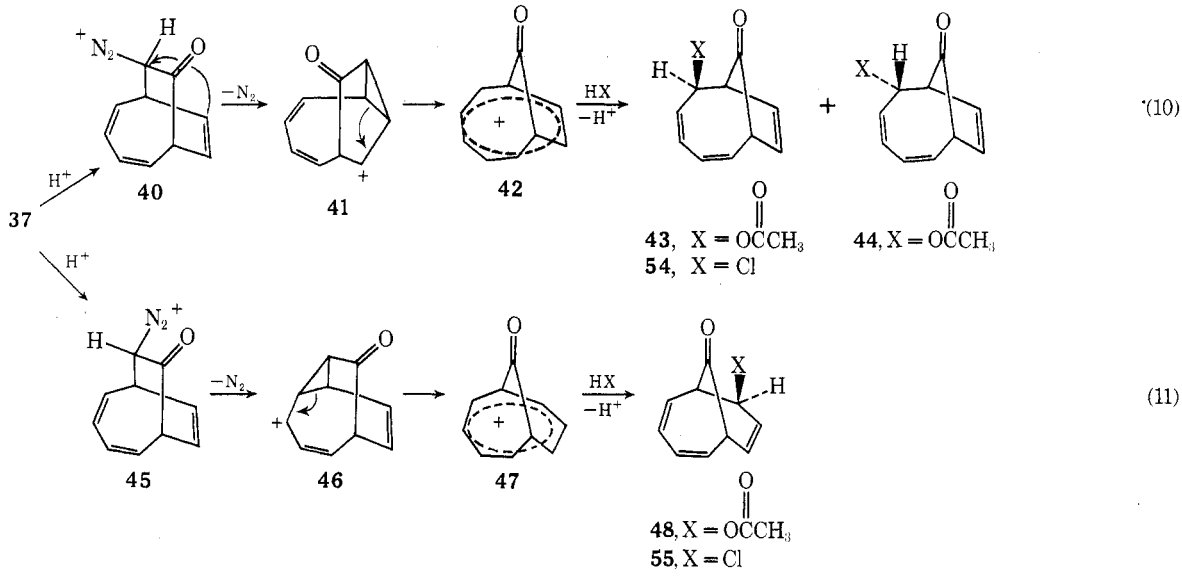
point, and ^{1}H NMR) with that prepared by chromic acid oxidation of bicyclo[4.2.1]nona-2,4,7-triene-*syn*-9-carboxaldehyde[15] and is shown to be homogeneous by reaction with diazomethane to give methyl bicyclo[4.2.1]nona-2,4,7-triene-*syn*-9-carboxylate (93%). The mechanistic aspect of interest in the conversion of **37** to **39** (eq 9) is that ketene **38** hydrates by a process in which a proton is delivered to C-9 from the anti direction.

Protic decomposition of **37** results in profound structural rearrangement, presumably via a cationic process involving isomeric derivatives of **3.** Thus **37** reacts with glacial acetic acid at 25° to yield a mixture of *exo-* and *endo*-2-acetoxybicyclo[5.2.1]deca-3,5,8-trien-10-one (**43** and **44,** eq 10). Precision rectification effects removal of the minor endo acetate **44** from **43.** The ^{1}H NMR of the reaction products (**43** and **44**) reveals immediately that they are not 8-acetoxybicyclo[4.2.2]deca-2,4,9-trien-7-ones [*anti*-8-acetoxybicyclo[4.2.2]deca-2,4,9-trien-7-one (**64**) has been independently prepared in this research and will be discussed later].

Acid-catalyzed decomposition of **37** with rearrangement might be expected to occur by one of the following sequences (eq 10 and 11) to give products of different bicyclic structural types. One sequence (eq 10) involves proton delivery to **37** from the less hindered anti side, loss of nitrogen with back-side interaction of the monoene (C-9, -10) bridge to **41** with collapse to bishomotropylium ion **42,** and exchange with acetic acid to produce exo,endo acetoxy ketones **43** and **44** as major and minor products, respectively. An alternative sequence (eq 11, as analogous to electrophilic additions to bicyclo[4.2.2]deca-2,4,7,9-tetraenes[16]) could arise from migration of the diene bridge to C-8 of **37,** reorganization of **46** to bishomotropylium ion **47,** and conversion to *exo-* and *endo*-7-acetoxybicyclo[4.3.1]deca-2,4,8-trien-10-one (**48** and **49**) by reaction with acetic acid.

As part of the evidence that acetoxy ketone **43** forms instead of **48** as the major product of acetolysis of **37,** the acetate was hydrogenated (eq 12) in ethanol with palladium on carbon as catalyst to *exo*-2-acetoxybicyclo[5.2.1]decan-2-one (**50,** 73%). Saponification of **50** by sodium hydroxide in methanol gave *exo*-2-hydroxybicyclo[5.2.1]decan-2-one (**51**), which is oxidized quantitatively by chromium trioxide in acetone to bicyclo[5.2.1]decane-2,10-dione (**52,** eq 12). Diketone **52** is dissimilar in ^{1}H NMR, ir, and physical properties to bicyclo[4.3.1]decane-7,10-dione (**53,** the product expected from **48** by hydrogenation, saponification, and then oxidation with chromium trioxide) as prepared previously via reaction of 1-morpholinocycloheptene and acryloyl chloride.[17]

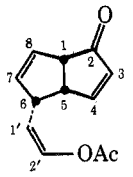
To obtain additional information concerning the acid-catalyzed decomposition process of **37** and as possible further corroboration that **43** is the major product of its reac-



40 **41** **42** **43**, X = OCCH$_3$; **54**, X = Cl **44**, X = OCCH$_3$ (10)

45 **46** **47** **48**, X = OCCH$_3$; **55**, X = Cl (11)

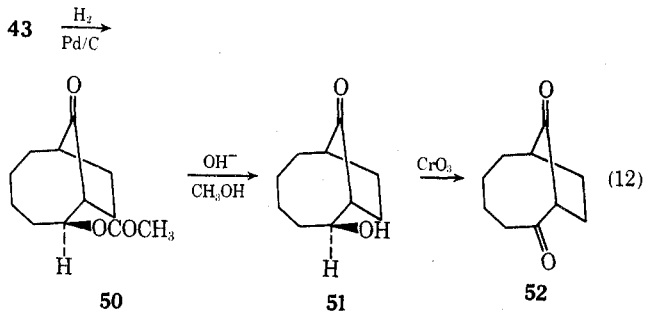
Table IV
Double Irradiation of 58[a,b]



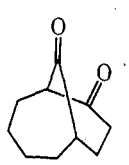
58

	^{1}H NMR, δ								
	7.50	7.14	6.08	5.80	5.50 H at C	4.69	4.14	3.80	3.46
Irradiation of H at C	-4	-2'	-3	-7	-8	-1'	-6	-5	-1
-4		−	+	−	−	−	−	+	−
-2'	−		−	−	−	+	+	−	−
-3	+	−		−	−	−	−	+	−
-7	−	−	−		+	−	+	−	+
-8	−	−	−	+		−	+	−	+
-1'	−	+	−	−	−		+	−	−
-6	−	+	−	+	+	+		+	+
-5	+	−	+	−	−	−	+		+
-1	−	−	−	+	+	−	+	+	

[a] −, no effect; +, pattern simplification upon double irradiation. [b] Shift of $CH_3C(=O)O-$ at δ 2.10.



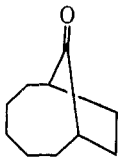
50 51 52



53

tion with acetic acid, a study was made of the behavior of **37** with hydrogen chloride. Diazo ketone **37** is decomposed rapidly in hydrogen chloride to *exo*-2-chlorobicyclo-[5.2.1]deca-3,5,8-trien-10-one (**54**) in 94% yield. The structure and stereochemistry assigned to **54** are based on its spectral properties, transformations, and by extension of the mechanistic principles used to account for the formation of **43** from **37**.

For proof of its bicyclic ring system, **54** was hydrogenolyzed in ethanol over palladium on carbon to bicyclo-[5.2.1]decan-10-one (**56**, 61%). The product exhibits car-

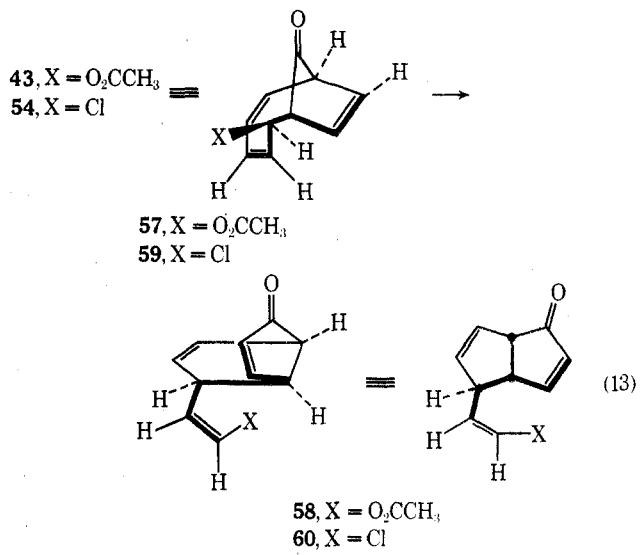


56

bonyl absorption at 1730 cm^{-1} (lit. 1731 cm^{-1})[18a] and its structure was conclusively established by its conversion to bicyclo[5.2.1]decan-10-one 2,4-dinitrophenylhydrazone, which melts at 175–176° (lit.[18a] 176–177.5°) and shows no melting point depression upon admixture with an authentic sample.[18b,c]

It is also pertinent that chloro ketone **54** reacts with silver acetate in acetic acid to give acetoxy ketones **43** and **44** in 53% conversion. The spectral properties (ir, ^{1}H NMR, and GLC) of the product show that the ratio of **43** and **44** from the silver acetate reaction is essentially the same as that from decomposition of diazo ketone **37** by acetic acid. It is thus apparent that the cationic intermediates (**42**) in reactions of **54** with silver acetate–acetic acid and of **37** with acetic acid are essentially identical.

Attempts to purify acetoxy ketone **43** and chloro ketone **54** by preparative GLC lead to Cope rearrangements. Thus **43** rearranges to *endo*-6-(*cis*-2'-acetoxyvinyl)-*cis*-bicyclo[3.3.0]octa-3,7-dien-2-one (**58**, 93%) at a column temperature of 225° (eq 13) and **54** isomerizes to *endo*-6-(*cis*-2'-chlorovinyl)-*cis*-bicyclo[3.3.0]octa-3,7-dien-2-one (**60**, 100%) at column temperatures above 160° (eq 13). The re-



43, X = O_2CCH_3
54, X = Cl

57, X = O_2CCH_3
59, X = Cl

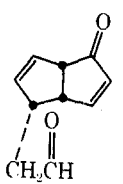
58, X = O_2CCH_3
60, X = Cl

(13)

active conformations **57** and **59** (eq 13) for Cope rearrangements of **43** and **54** thus lead, in keeping with mechanism requirements, to products (**58** and **60**) containing the more stable cis ring junctures and cis stereochemistry for the exocyclic olefinic moieties.

The structure of **58** is assigned in part on the basis of infrared absorptions for ester carbonyl (1760 cm^{-1}) and α,β-unsaturated carbonyl (1695 cm^{-1}), by complete analysis of its ^{1}H NMR spectrum, and by double-irradiation experiments (Table IV). Comparison of the ^{1}H NMR of **58** to that of bicyclo[3.3.0]oct-3-en-2-one (**61**)[19] supports the assignment that **58** contains the bicyclo[3.3.0] system. Assignment of the cis stereochemistry of the C-1'–C-2' olefin of **58** is supported by the ^{1}H NMR coupling constant (J = 6 Hz) for the proton absorption of δ 7.14 and 4.69. The J value is well within accepted values for cis olefinic protons[20] (J = 6–12 Hz) and is too small for trans olefinic protons (J = 12–18 Hz).

The structure of **58** is further elucidated upon its hydrolysis by aqueous trifluoroacetic acid to *endo*-6-(1'-oxoethyl)-*cis*-bicyclo[3.3.0]octa-3,7-dien-2-one (**62**) in 75% yield. The structure of **62** is consistent with its exact mass measure-

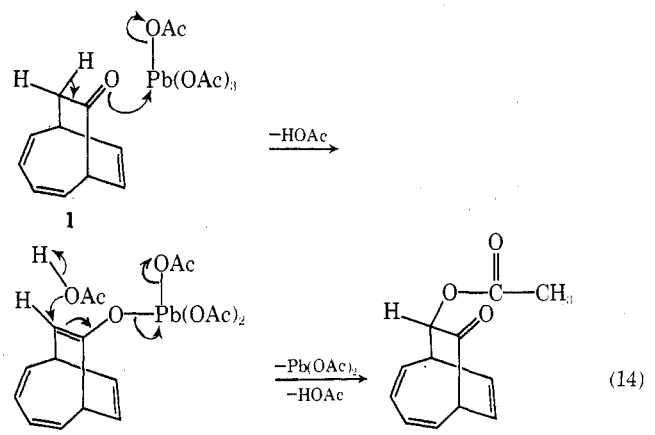


62

ment (*m/e* 162), infrared absorptions at 1715 and 1700 cm^{-1} for aldehyde and α,β-unsaturated ketone stretching, and ^1H NMR absorptions with coupling constants and shifts of C-3 and C-4 protons similar to those of **61**.

Chloro ketone **60** is assigned from its infrared carbonyl stretching absorption at 1700 cm^{-1}, mass spectrum (*m/e* 180), and ^1H NMR absorptions similar to those of **58, 62,** and **67**. Partial double-irradiation experiments are also consistent with the assigned structure of **60**.

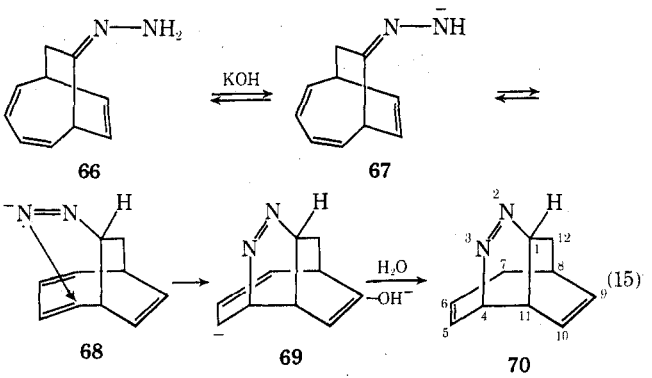
Ketone **1** has also been functionalized in its C-8 position by oxidation with lead tetraacetate (1 equiv) in refluxing acetic acid to give *anti*-8-acetoxybicyclo[4.2.2]deca-2,4,9-trien-7-one (**64**, 100%, eq 14). The stereochemistry of **64** is



(14)

tentatively assigned on the basis of probable reaction mechanisms involving carbonyl oxygen coordination with lead tetraacetate to produce enol lead(IV) complex **63** and acetic acid (eq 14); attack of **63** by acetic acid and/or acetate ion from the less hindered side (anti to the diene bridge) or/and collapse of **63** via a cyclic process occurring favorably from the anti direction will give **64**. Acetoxy ketone **64** shows no evidence of thermal rearrangement.

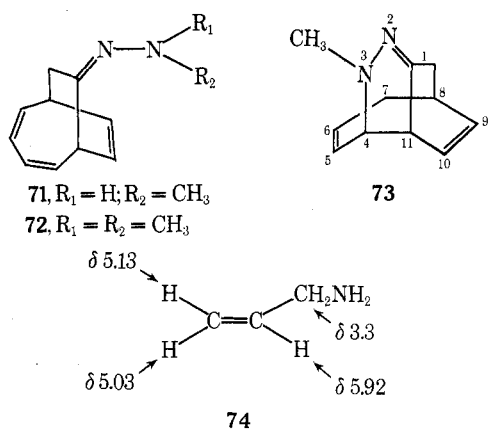
Attempts to reduce **1** by Wolff–Kishner sequences fail to produce bicyclo[4.2.2]deca-2,4,7-triene (**65**), a hydrocarbon of interest in these laboratories. Rather ketone **1** reacts with hydrazine and potassium hydroxide in ethylene glycol at 170–200° to give 2,3-diazatricyclo[6.3.1.$0^{4,11}$]dodeca-2,5,9-triene (**70**, 47%). Similarly **70** is formed (48–54%) from (1) bicyclo[4.2.2]deca-2,4,9-trien-7-one semicarbazone and potassium hydroxide at 200°, and (2) bicyclo[4.2.2]deca-2,4,9-trien-7-one hydrazone (**66**)[21] and potassium *tert*-butoxide in dimethyl sulfoxide at 25–30°. Pyrazoline **70** may be produced from **66** via a sequence as in eq 15.



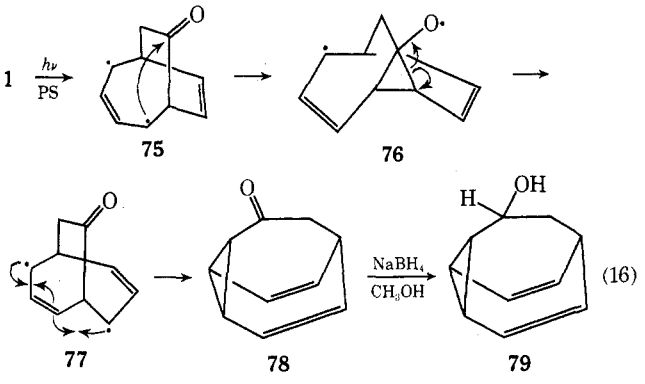
(15)

Pyrazoline **70** displays ir azo absorption at 1650 cm^{-1}; its uv spectrum shows end absorption (λ_{max} 220 nm, ϵ_{max} 3700) and that consistent with a pyrazoline (λ_{max} 333 nm, ϵ_{max} 330).[22] Its ^1H NMR reveals resonances consistent with the assigned structure. The structure of **70** is delineated by ^1H NMR double irradiation and europium shift reagent effects. Double irradiation at δ 2.80 (H at C-7) simplifies only the absorption at δ 6.03 (H at C-9, -10); decoupling the triplet at δ 4.84 (H at C-1) simplifies the septuplet at δ 1.73 (H at C-12). Assignments of the protons at C-1, -4, and -11 are based on the magnitude of the shifts caused by europium complexation; protons closest to the azo group complexed by europium should have the largest shift. The olefinic protons on C-9 and -10 and the exo proton on C-12 are the farthest removed from the azo linkage and show the least effect in their chemical shifts.

To learn more about its hydrazones, **1** was converted by methylhydrazine and 1,1-dimethylhydrazine to bicyclo[4.2.2]deca-2,4,9-trien-7-one methylhydrazone (**71**, 100%) and bicyclo[4.2.2]deca-2,4,9-trien-7-one dimethylhydrazone (**72**, 75%), respectively. Reaction of **71** and potassium hydroxide at 200° or of **1**, methylhydrazine, and potassium hydroxide in ethylene glycol at 200° yields 3-methyl-2,3-diazatricyclo[6.3.1.$0^{4,11}$]dodeca-1,5,9-triene (**73**, 75%). Dimethylhydrazone **72** is not changed by potassium hydroxide at these elevated temperatures. Heterocycle **73** exhibits proper ir and mass spectra (*m/e* 174) and appropriate ^1H NMR absorptions. The ^1H NMR assignments of **73** are consistent with those of **74**.

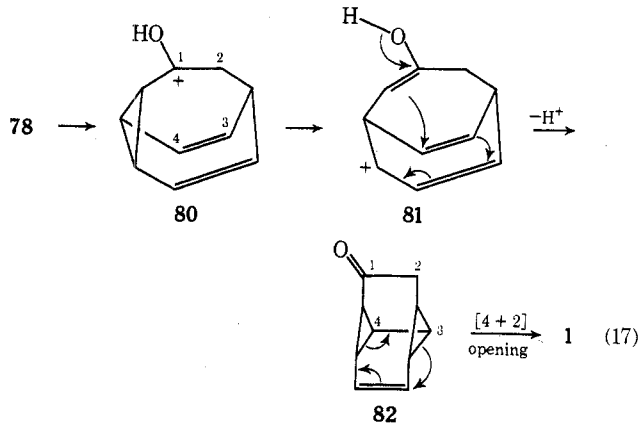


Ketone **1** responds photochemically; irradiation of **1** in acetone through Vycor yields tricyclo[3.3.2.$0^{2,8}$]deca-3,6-dien-9(10)-one (**78**, 68%), along with **1** (10%) and an unidentified isomer.[23] Photoisomerization of **1** using Michler's ketone as sensitizer and Pyrex optics also produces **78** (44%). Ketone **78** is identical with an authentic sample[24] and it is reduced by sodium borohydride to tricyclo[3.3.2.$0^{2,8}$]deca-3,6-dien-9-ol (**79**, 88%), a fluctional molecule. Photosensitized conversion of **1** to **78** is rationalizable by a diradical sequence as in eq 16.



(16)

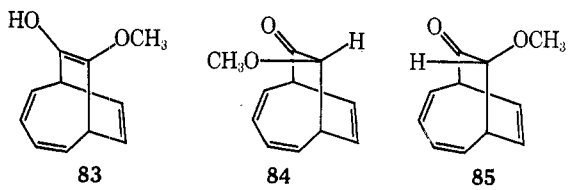
Ketone **78** reacts with dilute trifluoroacetic acid to produce **1** quantitatively. Further, **78** is converted by *p*-tosylhydrazide in ethanol containing hydrochloric acid to tosylhydrazone **7**. A possible sequence for acid-catalyzed



(17)

rearrangement of 78 to 1 is indicated in eq 17. A related cationic rearrangement of bullvalene to bicyclo[4.2.2]deca-2,4,7,9-tetraene (8) is known.[11b]

Refluxing acetoxy ketone 64 in methanol containing *p*-toluenesulfonic acid as catalyst quantitatively produces *syn*- and *anti*-8-methoxybicyclo[4.2.2]deca-2,4,9-trien-7-one (84 and 85, respectively) as a 93:7 mixture. The gross structures of 84 and 85 are assignable on the basis of their spectral properties. The conversion of 64 to 84 and 85 may arise via 7-hydroxy-8-methoxybicyclo[4.2.2]deca-2,4,7,9-tetraene (83, as generated by any of a number of sequences). Tautomerization of enol 83 by proton transfer from the less hindered anti side yields 84 as the major product; reaction from the syn side gives 85.



Investigations of the synthesis and chemistry of *syn*- and *anti*-8-hydroxybicyclo[4.2.2]deca-2,4,9-trien-7-ones as well as bicyclo[4.2.2]deca-2,4,9-triene-7,8-dione are presently under way in these laboratories. Further, synthesis of triene 65 and determination of the properties of the bicyclo[4.2.2]deca-2,4,9-trien-7-yl radical, carbanion, carbonium ion, and carbene, respectively, are being studied.

Experimental Section

General. Elemental analyses were performed by Chemalytics, Inc., Tempe, Ariz. and Microanalysis, Inc., Wilmington, Del. Melting points (uncorrected) were determined using a Thomas-Hoover capillary melting point apparatus. Infrared spectra were obtained on Perkin-Elmer Model 137 or 457 recording spectrophotometers. Proton magnetic resonance spectra were determined on Varian Associates NMR spectrophotometers, Models A-60, A-60A, and HA-100. Unless noted otherwise, all spectra were measured in chloroform-*d* or carbon tetrachloride solutions using tetramethylsilane as an internal standard. Ultraviolet spectra were determined using a Cary Model 14 recording spectrophotometer. Mass spectra were obtained using an AEI Model MS9 spectrometer. GLC analyses and separations were performed on an Aerograph instrument, Model A-90-C. GLC column A was prepared from 20% SE-30 on Chromosorb W (0.25 in. × 12 ft); column B consisted of 15% Carbowax 20M on Chromosorb W (0.25 in. × 10 ft); and column C was made of 12% Apiezon J on Chromosorb P (0.125 in. × 10 ft). In the Experimental Section, compounds are always listed in their order of elution.

Bicyclo[4.2.1]nona-2,4,7-trien-9-one (4). Ketone 4 was prepared by the method of Antkowiak[3a,b] in 49–65% yield from cyclooctatetraene in 99+% purity (GLC, column A).

Reaction of Bicyclo[4.2.1]nona-2,4,7-trien-9-one (4) and Diazomethane. Ketone 4 was treated with diazomethane as previously reported[3b] to produce bicyclo[4.2.2]deca-2,4,9-trien-7-one (1) and spiro[bicyclo[4.2.1]nona-2,4,7-trien-9,2′-oxirane] (6). Separation, analysis, and isolation of the products by GLC (column A) gave epoxide 6 (15–50%) and ketone 1 (85–50%).

The spectral properties of 6 follow: ir (neat) 980 (m), 860 (s), and 745 cm^{-1} (s); exact mass, calcd, 146.0732; found, 146.0734.

Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.89. Found: C, 81.99; H, 6.88.

Ketone 1 has the following properties: ir (neat) 1710 cm^{-1} (s); uv λ_{max} (EtOH) 202, 258, 265, and 300 nm (ϵ_{max} 4250, 3070, 2920, and 373); exact mass, calcd, 146.0732; found, 146.0734.

Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.89. Found: C, 82.20; H, 6.83.

Bicyclo[4.2.2]deca-2,4,9-trien-7-one Semicarbazone. The crude mixture from ring expansion of 4 containing ketone 1 (85%) and epoxide 6 (15%, 3.15 g, 0.0185 mol) was dissolved in ethanol (250 ml)–water (20 ml) and semicarbazide hydrochloride (5 g) and sodium acetate (7.5 g) were added. The mixture was warmed for 1 hr at 75°, concentrated under reduced pressure to half volume, and cooled in ice. The crude semicarbazone (3.29 g, 88% based on 1) was filtered and air dried. Bicyclo[4.2.2]deca-2,4,9-trien-7-one semicarbazone was obtained as white crystals, mp 199.5–200.5°, from 50% aqueous ethanol: exact mass, calcd, 203.1059; found, 203.1061.

Anal. Calcd for $C_{11}H_{13}N_3O$: C, 65.00; H, 6.45. Found: C, 64.68; H, 6.43.

Preparative Isolation of Bicyclo[4.2.2]deca-2,4,9-trien-7-one (1). The previously reported[3b] separation of ketone 1 from the ring-expansion mixture via the Girard's reagent T adduct was used extensively for isolation of ketone 1.

Alternatively, if ketone 1 is stored as its semicarbazone, regeneration may be effected as follows. Semicarbazone (3.00 g, 0.015 mol) was dissolved in pyruvic acid (16 g) and stirred for 30 hr under argon. The mixture was diluted with water, neutralized with aqueous sodium bicarbonate, and extracted with ether. The ether layer was washed with brine, dried, and concentrated under reduced pressure. Pure 1 was obtained by distillation, bp 83–86° (0.2 mm) (0.50 g, 23%). (The efficiency of recovery of 1 by this method is expected to be much greater in larger scale experiments.)

Reaction of Bicyclo[4.2.2]deca-2,4,9-trien-7-one Tosylhydrazone (7)[3b] with Methyllithium.[4] A suspension of tosylhydrazone 7 (0.200 g, 0.00064 mol) in hexane (5 ml) was flushed with argon at 0°. Methyllithium (2.0 ml, 1.45 *M*, 2.9 mmol) was added slowly, the system was warmed to 25°, and the mixture was stirred for 3 hr. After addition of water and separation, the water layer was extracted with ether. The combined organic layers were washed with brine, dried, and concentrated. The residue (72 mg, 84%) consisted of five components (GLC analysis, column A); the three major components (98% of the mixture) were *cis*-9,10-dihydronaphthalene (9, 1%), bicyclo[4.2.2]deca-2,4,7,9-tetraene (8, 94%), and naphthalene (5%). Preparative GLC (column A) provided pure samples of 9, 8, and naphthalene; the retention times and spectral properties of each product matched those of authentic samples. The ^1H NMR of 8 is in Table I.

7-Acetoxybicyclo[4.2.2]deca-2,4,7,9-tetraene (10). Ketone 1 (0.50 g, 0.0034 mol), isopropenyl acetate (15 ml), and a trace of *p*-toluenesulfonic acid were refluxed for 60 hr. Potassium carbonate was added, the solvent was removed under reduced pressure, and the residue was distilled, bp 78–79° (0.05 mm). The distillate (0.55 g, 86%) gave only one GLC peak (column A). Preparative GLC yielded pure 10: ir (neat) 1760 (s) and 1210 cm^{-1} (s); ^1H NMR, see Table I.

Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.62; H, 6.35.

Hydrolysis of 7-Acetoxybicyclo[4.2.2]deca-2,4,7,9-tetraene (10). Hydrochloric acid (3 *N*, 0.25 ml) was added to acetoxytetraene 10 (0.20 g, 0.0011 mol) in hexamethylphosphoramide (3 ml) and stirred overnight at 25°. The mixture was poured into water and the resultant suspension was extracted with ether. After standard work-up of the organic layer, the resultant oil (0.16 g) was a 19:1 mixture of ketone 1 and acetate 10 by GLC (column A) and ^1H NMR analysis.

7-Pyrrolidinobicyclo[4.2.2]deca-2,4,7,9-tetraene (11). A mixture of 1 (0.16 g, 0.0011 mol) and pyrrolidine (0.16 g, 0.0022 mol) in benzene (10 ml) containing several grains of *p*-toluenesulfonic acid was refluxed for 12 hr making use of a Dean-Stark water separator. The red-brown solution, after concentration in vacuo, produced a dark brown residue (0.22 g). After storage under reduced pressure for several hours, the highly water sensitive product was transferred in carbon tetrachloride to a NMR tube under argon. ^1H NMR analysis showed that 11 (ca. 90%) had formed; 1 and benzene were slight impurities; ^1H NMR, see Table I. The sensitivity of 11

precluded ir or combustion analysis; upon standing in carbon tetrachloride for 1 day, complete hydrolysis of 11 to 1 and pyrrolidine had occurred; exact mass, calcd, 199.1361; found, 199.1359.

Hydrolysis of 7-Pyrrolidinobicyclo[4.2.2]deca-2,4,7,9-tetraene (11). Enamine 11 in carbon tetrachloride containing 1% Me_4Si was swirled with hydrochloric acid (3 *N*, 3 drops) for 15 min at 25°. The aqueous layer was removed and the organic layer was dried over anhydrous potassium carbonate. The solution, on analysis by ^1H NMR and GLC (column A), contained ketone 1 exclusively.

Reaction of Bicyclo[4.2.2]deca-2,4,9-trien-7-one (1) with Potassium *tert*-Butoxide and Acetyl Chloride in Glyme. Potassium *tert*-butoxide (0.22 g, 0.002 mol) was added all at once to ketone 1 (0.10 g, 0.0007 mol) in dry glyme (5 ml) at 25°, and the resulting brown slurry was stirred rapidly for 4–5 min. Acetyl chloride (0.16 ml, 0.002 mol) was added and the mixture was stirred for 5 min. After addition of potassium carbonate (0.2 g) the solvent was aspirated, and the residue was dissolved in ether (15 ml), filtered, and concentrated. GLC analysis (column A) of the oily residue (0.12 g) revealed a three-component mixture: unidentified impurity (9%), 1 (8%), and 7-acetoxybicyclo[4.2.2]deca-2,4,7,9-tetraene (10, 83%). Preparative GLC provided pure 1 and 10.

7-Trimethylsiloxybicyclo[4.2.2]deca-2,4,7,9-tetraene (12). Ketone 1 (0.292 g, 0.002 mol) was dissolved in dried glyme (15 ml) and potassium *tert*-butoxide (0.9 g, 0.008 mol) was added. After the solution was stirred for 3 min, trimethylsilyl chloride (1.1 g, 0.010 mol) was added and the mixture was stirred for 5 min. The solution was concentrated and the residue was distilled to provide a pale yellow oil (0.33 g, 76%), bp 65–67° (0.05 mm). GLC analysis (column A) showed the distillate to be a mixture of 12 (overall yield 72%) and 1 (7%). Silyl ether 12 has the following properties: ir (neat) 1660 (m), 1200 (s), 940 (s), and 840 cm^{-1} (s); ^1H NMR, see Table I; exact mass, calcd, 218.1127; found, 218.1123. Ether 12 hydrolyzes on standing for only a few hours in the atmosphere.

Base-Catalyzed Mono- and Dideuteration of Bicyclo[4.2.2]deca-2,4,9-trien-7-one (1). Deuterium oxide (3 drops) containing sodium hydride (57% suspension in mineral oil, 5 grains) was added to 1 (50 mg) in carbon tetrachloride (0.5 ml) containing 1% TMS. The reaction was run in a NMR tube continually tumbled at 25°; reaction progress was monitored by examining the absorption at δ 2.55 for peak and integration disappearance. After 12 hr, half of the organic phase was removed, dried (potassium carbonate), and concentrated to *anti*-8-deuteriobicyclo[4.2.2]deca-2,4,9-trien-7-one (13, 25 mg): ^1H NMR δ 5.9 (m, 6 H, H at C-2, -3, -4, -5, -9, -10), 3.5 (m, 1 H, H at C-6), 3.0 (m, 1 H, H at C-1), and 2.55 (m, 1 H, H at C-8); exact mass, calcd, 147.0794; found, 147.0791.

The remaining organic layer was tumbled continually (an additional 8.5 days) at 25° until the methylene absorption disappeared. The aqueous layer was removed. The organic layer was worked up as above to yield 8,8-dideuteriobicyclo[4.2.2]deca-2,4,9-trien-7-one (15, 25 mg): ^1H NMR δ 5.9 (m, 6 H, H at C-2, -3, -4, -5, -9, -10), 3.5 (m, 1 H, H at C-6), and 3.0 (m, 1 H, H at C-1); exact mass, calcd, 148.0857; found, 148.0854.

Reaction of Bicyclo[4.2.2]deca-2,4,9-trien-7-one (1) with Potassium *tert*-Butoxide and Deuterium Oxide. Ketone 1 (1.0 g, 0.00685 mol) was added to potassium *tert*-butoxide (2.50 g, 0.022 mol) in dry hexamethylphosphoramide (50 ml) at 0–5° and stirred for 4 min. Deuterium oxide (5 ml) was added and stirring was continued for 4 min. Boron trifluoride etherate was then slowly added until the mixture was slightly acidic. After water had been added the mixture was extracted with ether. Standard work-up with subsequent distillation yielded 8,8-dideuteriobicyclo-[4.2.2]deca-2,4,9-trien-7-one (15, 0.75 g, 75%), bp 72–76° (0.1 mm).

Reaction of Bicyclo[4.2.2]deca-2,4,9-trien-7-one (1) with Potassium *tert*-Butoxide and Water in Dimethylformamide. Ketone 1 (0.15 g, 0.001 mol) containing naphthalene (0.13 g, 0.001 mol) as an internal standard was dissolved in dry dimethylformamide (5 ml) and added to potassium *tert*-butoxide (0.22 g, 0.002 mol) in dimethylformamide (5 ml) at 0°. The mixture was stirred for 0.5 hr, poured into water, neutralized with 3 *N* hydrochloric acid, and extracted with ether. Standard work-up and concentration gave 0.25 g (92%) of a residue containing 1 and naphthalene (GLC analysis, column A). NMR analysis of the product showed the ratio of naphthalene to 1 to be 1.0:0.92.

Reaction of Bicyclo[4.2.2]deca-2,4,9-trien-7-one (1) with Potassium *tert*-Butoxide and Methyl Fluorosulfonate in Glyme. Ketone 1 (0.10 g, 0.00069 mol) was dissolved in dry glyme (5 ml) and potassium *tert*-butoxide (0.25 g, 0.0022 mol) was added at 25°. After the solution was stirred for 4 min, methyl fluorosulfonate (0.25 g, 0.0022 mol) was added all at once and the mixture was stirred for an additional 1 min. The solvent was removed under reduced pressure and the residue was dissolved in chloroform and analyzed by GLC (column A).

The product mixture contained 7-methoxybicyclo[4.2.2]deca-2,4,7,9-tetraene (16, 43%), 1 (9.5%), 8-methylbicyclo[4.2.2]deca-2,4,9-trien-7-one (17, trace), and 8,8-dimethylbicyclo[4.2.2]deca-2,4,9-trien-7-one (18, 26%), as well as several very minor unidentified components of longer retention times.

Pure dimethyl ketone 18 was obtained by preparative GLC. 18 is unstable upon storage in air: ^1H NMR δ 5.9 (m, 6 H, H at C-2, -3, -4, -5, -9, -10), 3.5 (m, 1 H, H at C-6), 2.6 (m, 1 H, H at C-1), and 1.2 (d, 6 H, methyl C-H); exact mass, calcd, 174.1044; found, 174.1041.

Mass spectral analysis of ketone 1 as collected by GLC from the reaction mixture indicated the presence of methyl ketone 17, *m/e* 160. The amount of 17 present was estimated by comparing the mass spectral peaks of 1 and 17.

Reaction of Bicyclo[4.2.2]deca-2,4,9-trien-7-one (1) with Potassium *tert*-Butoxide and Methyl Fluorosulfonate in Hexamethylphosphoramide. Ketone 1 (0.50 g, 0.0034 mol) was added to potassium *tert*-butoxide (1.25 g, 0.011 mol) in dried hexamethylphosphoramide (30 ml) at 0–5° under argon and the solution was stirred for 4 min. Methyl fluorosulfonate (1.2 ml, 1.85 g, 0.016 mol) was added all at once and stirring of the mixture was continued for 4 min. The reaction mixture was quenched with aqueous sodium bicarbonate and the aqueous layer was washed with ether. Standard work-up and concentration yielded a yellow oil (0.54 g, 99%) which contained five components by GLC analysis (columns A and C). The major product was 7-methoxybicyclo-[4.2.2]deca-2,4,9-trien-7-one (16) in the percentage shown in Tables II and III. Similar results were obtained using dimethylformamide as solvent (see Table II).

Methoxytetraene 16 was collected by preparative GLC: ir (neat) 1670 (m), 1620 (w), 1210 (s), and 830 cm^{-1} (s); ^1H NMR, see Table I; exact mass, calcd, 160.0888; found, 160.0886.

Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.29; H, 7.74.

Reactions were run varying the contact time of 1 with potassium *tert*-butoxide before quenching with methyl fluorosulfonate; the product distribution for base times of 14 min, 30 min, 8 hr, and 24.5 hr are summarized in Table II.

Reaction of β-Tetralone with Potassium *tert*-Butoxide and Dimethyl Sulfate in Dimethylformamide. β-Tetralone (0.58 g, 0.004 mol) in dry dimethylformamide (10 ml) was treated with potassium *tert*-butoxide (0.55 g, 0.005 mol) in dimethylformamide (5 ml) for 15 min at 0° and then dimethyl sulfate (0.58 g, 0.005 mol) was added. The mixture was stirred for 10 min and poured into aqueous sodium bicarbonate. Product work-up in the usual manner and distillation of the residue produced a clear liquid (0.44 g), bp 144° (11 mm). GLC analysis (column A) showed the product to contain β-tetralone (5.0%), 22 (94%, overall yield 65%), and an unidentified component (1%) of mass *m/e* 172 representing a dimethylation product.

Pure 22 was collected by preparative GLC: ir (neat) 1640 cm^{-1} (m); ^1H NMR δ 6.9 (m, 4 H, aromatic C–H), 5.5 (s, 1 H, H at C-1), 3.68 (s, 3 H, methyl C–H), 2.9 (m, 2 H, H at C-4), and 2.40 (m, 2 H, H at C-3); exact mass, calcd, 160.0888; found, 160.0890.

Hydrolysis of 7-Methoxybicyclo[4.2.2]deca-2,4,7,9-tetraene (16). Methoxytetraene 16 (0.07 g, 0.00043 mol) was dissolved in chloroform-*d* (0.5 ml) containing 1% Me_4Si and naphthalene (ca. 0.11 g) as internal standards. Initial NMR analysis showed an aromatic:olefinic proton ratio of 1.0:0.82. The solution was treated with hydrochloric acid (3 *N*, 0.25 ml) and mixed for 1 hr at 25°. The aqueous layer was removed and the organic layer was dried over anhydrous potassium carbonate. The product was found to be exclusively naphthalene and ketone 1 by ^1H NMR and GLC (column A) methods; ^1H NMR analysis showed the aromatic:olefinic proton ratio to be 1.0:0.83, indicating essentially quantitative formation of 1.

Thermal Rearrangement of 7-Methoxybicyclo[4.2.2]deca-2,4,7,9-tetraene (16). Method A. 7-Methoxybicyclo[4.2.2]deca-2,4-,7,9-tetraene (16, 0.25 g, 0.0014 mol) in dry hexamethylphosphoramide (3 ml) was heated for 0.5 hr at 200°. After cooling to 25°, the mixture was poured into aqueous sodium bicarbonate and extracted with ether. The ethereal extracts were worked up in the usual way and concentrated to a mixture (0.24 g) (GLC, column A) containing three components corresponding in retention times to naphthalene (29, 18%), 7-methoxytetraene (16, 72%), and 2-methoxynaphthalene (23, 10%).

Method B. 7-Methoxybicyclo[4.2.2]deca-2,4,7,9-tetraene (**16**, 0.15 g, 0.0009 mol) was placed in a tube, evacuated to 0.05 mm, and sealed at 25°. Ether **16** was then heated to 200° for 21 hr, the tube was opened, and the product was analyzed by GLC (column A) and preparative GLC followed by ^{1}H NMR and ir spectral methods. The mixture consisted of three major and one minor products: methanol, naphthalene (**29**, 59%), 7-methoxytetraene (**16**, 11%), and 2-methoxynaphthalene (**23**, 30%).

2-Methoxynaphthalene (23). 2-Naphthol (3.4 g, 0.0237 mol) was dissolved in hexamethylphosphoramide (20 ml) and sodium hydride (1.05 g, 57% suspension, 0.025 mol) was added at 25° all at once. The mixture was stirred for 0.25 hr and methyl iodide (1.55 ml, 0.025 mol) was added. After 5 min the mixture was worked up and concentrated. Crystallization of the residue from ethanol yielded **23** (3.32 g, 89%): mp 70–71.5° (reported mp 72°);[25] ir (KBr) 1480 (m), 1030 (m), 840 (m), 820 (m), and 745 cm^{-1} (m); ^{1}H NMR δ 7.75–6.9 (m, 7 H, H at C-1, -3, -4, -5, -6, -7, -8) and 3.75 (s, 3 H, methyl C–H).

Bicyclo[4.2.2]deca-2,4,9-triene-7,8-dione Monooxime (32). Ketone 1 (1.02 g, 0.007 mol) and potassium *tert*-butoxide (7.5 g, 0.07 mol) were stirred in *tert*-butyl alcohol (75 ml) for 0.75 hr under argon. Isoamyl nitrite (3.0 ml) was added and stirring was continued for 1 hr; isoamyl nitrite (2.5 ml) was again added and the mixture was stirred for 0.5 hr. The solution was poured into ether–ice water and the aqueous layer was extracted with ether. The aqueous layer was acidified with acetic acid and reextracted with ether. The latter ethereal layers were worked up in the usual manner and concentrated in vacuo. Solution of the crude product (0.75 g, 63%) in methylene chloride and recrystallization from 1:2 methylene chloride–cyclohexane produced **32**, a yellow powder: mp 178–178.5°; ir (KBr) 3300 (s), 1710 (s), and 1690 cm^{-1} (s); ^{1}H NMR δ 5.9 (m, 6 H, H at C-2, -3, -4, -5, -9, -10), 4.3 (dd, 1 H, H at C-6), and 3.7 (m, 1 H, H at C-1); exact mass, calcd, 175.0633; found, 175.0636.

Anal. Calcd for $C_{10}H_9NO_2$: C, 68.56; H, 5.18. Found: C, 68.30; H, 5.30.

Bicyclo[4.2.2]deca-2,4,9-triene-7,8-dionequinoxaline (33). Oximino ketone **32** (0.5 g, 0.0029 mol) and *o*-phenylenediamine (0.31 g, 0.0029 mol) were refluxed in ethanol (10 ml)–acetic acid (10 ml) for 1 hr. The mixture was cooled and poured into water; the product was filtered and air dried (0.30 g, 46%). Recrystallization from methanol produced **33**: mp 194.5–195°; ir (KBr pellet) 1500 (m), 950 (s), 760 (s), and 730 cm^{-1} (s); ^{1}H NMR δ 8.02 and 7.67 (two m, 4 H, H on aromatic nucleus), 6.47 (m, 2 H, H at C-2, -5), 6.02 (m, 2 H, H at C-9, -10), 5.82 (m, 2 H, H at C-3, -4), and 4.35 (m, 2 H, H at C-1, -6). Proton assignments for **33** are based on double irradiation; irradiation of the multiplet at δ 4.35 (H at C-1, -6) causes simplification of the multiplet at δ 6.47 and collapse of the absorption at δ 6.02 to a singlet; exact mass, calcd, 232.1000; found, 252.1004.

Anal. Calcd for $C_{16}H_{12}N_2$: C, 82.73; H, 5.21; N, 12.06. Found: C, 82.48; H, 5.19; N, 12.10.

8-Formylbicyclo[4.2.2]deca-2,4,9-trien-7-one (35). Ketone **1** (0.88 g, 0.006 mol) was added to freshly prepared sodium methoxide (1.30 g, 0.024 mol) in dry ether (100 ml). After introduction of methyl formate (1.45 g, 0.024 mol), the mixture was stirred for 22 hr. Cold hydrochloric acid (3 *N*, 50 ml) was added and the mixture was extracted with ether. The combined ethereal washes were worked up; concentration of the solution yielded a brown oil (1.00 g, 95%) which precipitated from pentane as a tan solid. Pure **35** was prepared by elution through a silica gel column (25% ether–75% cyclohexane solvent) and crystallization from pentane at −78°: mp 56–57°; ir (KBr pellet) 1660 (s), 1580 (s), and 1120 cm^{-1} (m); ^{1}H NMR δ 8.1 (s, 1 H, aldehydic C–H), 5.9 (m, 7 H, H at C-2, -3, -4, -5, -8, -9, -10), and 3.5 (m, 2 H, H at C-1, -6); exact mass, calcd, 174.0681; found, 174.0683.

Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 75.55; H, 5.75.

3,4-Diazatricyclo[5.4.2.0^{2,6}]trideca-2,5,8,10,12-pentaene (36). Formyl ketone **35** (0.52 g, 0.003 mol) was dissolved in ethanol (1 ml). Anhydrous hydrazine (0.13 g, 0.004 mol) in ethanol (3 ml) was added (precipitation occurred immediately) and the stirred mixture was refluxed for 18 hr. The dark solution was cooled, poured into water, and extracted with ether. The dark oil (0.52 g) obtained from concentration of the organic phase, on elution through a silica gel column (ethyl acetate solvent), yielded a difficultly crystallizable oil (0.44 g, 86%). Pure **36** was prepared by crystallization from benzene–cyclohexane: mp 106–107°; ir (KBr) 3250 cm^{-1} (s); ^{1}H NMR δ 9.25 (br s, 1 H, N–H, shift is concentration dependent, disappears upon addition of D_2O), 7.15 (s, 1 H, H at C-5), 5.9 (m, 6 H, H at C-8, -9, -10, -11, -12, -13), and 4.0 (m, 2 H, H at C-1, -7); exact mass, calcd, 170.0844; found, 170.0847.

Anal. Calcd for $C_{11}H_{10}N_2$: C, 77.62; H, 5.92. Found: C, 77.35; H, 6.09.

7-Diazobicyclo[4.2.2]deca-2,4,9-trien-8-one (37). Formyl ketone **35** (1.0 g, 0.0575 mol) was dissolved in methylene chloride (30 ml) and triethylamine (1.22 g, 0.12 mol) and tosyl azide (1.1 g, 0.0575 mol) were added at 25°. The mixture was stirred for 4 hr. Potassium hydroxide (5 g) in water (60 ml) was added and the mixture was then stirred for 15 min. After layer separation and extraction of the aqueous portion with methylene chloride, the combined organic phases were washed with water and dried over anhydrous potassium carbonate. Concentration yielded a dark brown oil (0.92 g) which contained **37** and tosyl azide as indicated by micro TLC analysis on silica gel G with 1:1 ether–hexane solvent. Separation on a silica gel column (1:3 ether–cyclohexane) yielded **37** as a bright yellow liquid which crystallized at −20° and remained solid upon rewarming (0.52 g, 55%): mass spectrum (P − N_2) *m/e* 144; ^{1}H NMR δ 5.9 (m, 6 H, H at C-2, -3, -4, -5, -9, -10) and 3.65 (m, 2 H, H at C-1, -6).

Photolysis of 7-Diazobicyclo[4.2.2]deca-2,4,9-trien-8-one (37) in Water–Dioxane. Diazo ketone **37** (0.75 g, 0.0044 mol) was dissolved in *p*-dioxane (50 ml) and water (25 ml) and the solution was degassed with argon for 0.5 hr. The solution was then irradiated with a 450-W medium-pressure Hanovia lamp in all-quartz equipment for 6 hr. Upon completion of the experiment, **37** was absent as evidenced by the lack of evolution of nitrogen upon addition of a drop of concentrated hydrochloric acid to an aliquot of the reaction mixture. The solution was concentrated and then the residue was triturated with aqueous potassium carbonate and extracted with ether. The aqueous layer was acidified with hydrochloric acid and extracted with ether. After standard work-up and concentration of the organic phase, a single product (0.43 g, 61%) as evidenced by micro TLC analysis (1:1 ether–petroleum ether solvent) was obtained.

The product was filtered through silica gel and recrystallized from ether–petroleum ether at −78° to provide pure bicyclo[4.2.1]nona-2,4,7-triene-*syn*-9-carboxylic acid (**39**), mp 173–174.5° (lit.[15] mp 173–174°), as white crystals: ir (KBr) 3150 (br, s), 1730 (s), and 1680 cm^{-1} (s); ^{1}H NMR δ 11.2 (s, 1 H, –COOH, shift is concentration dependent), 6.1 (m, 4 H, H at C-2, -3, -4, -5), 5.25 (d, 2 H, H at C-7, -8), and 3.3 (m, 3 H, H at C-1, -6, -9); exact mass, calcd, 162.0681; found, 162.0683.

Methyl Bicyclo[4.2.1]nona-2,4,7-triene-*syn*-9-carboxylate. Crude acid **39** (0.35 g, 0.0022 mol) from the preceding photolysis was dissolved in ether (50 ml), treated with diazomethane (0.3 *M*, 30 ml, excess) at 25°, and stirred for 0.5 hr. Formic acid was added to destroy excess diazomethane. The ether layer was extracted with aqueous sodium bicarbonate and saturated brine, dried, and concentrated to a yellow oil (0.41 g) which was ca. 99% pure by GLC analysis (column A). Distillation afforded methyl bicyclo[4.2.1]nona-2,4,7-triene-*syn*-9-carboxylate as a white solid: bp 66.5° (0.05 mm); mp 27–29° (0.37 g, 93%); ir (neat) 1720 (s), 1220 (s), and 1205 cm^{-1} (s); ^{1}H NMR δ 5.9 (m, 4 H, H at C-2, -3, -4, -5), 5.15 (d, 2 H, H at C-7, -8), 3.5 (s, methyl C–H) superimposed on 3.3 (m, H at C-1, -6, -9, total 6 H); exact mass, calcd, 176.0837; found, 176.0840.

Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 75.19; H, 6.90.

***exo*-2-Acetoxybicyclo[5.2.1]deca-3,5,8-trien-10-one (43).** Diazo ketone **37** (0.88 g, 0.0051 mol) was dissolved in acetic acid (12 ml) and stirred at 25° for 4 hr. The mixture was concentrated and distilled to give **43** (0.87 g, 84%): bp 102–103° (0.1 mm); ir (neat) 1760 (s), 1740 (s), 1370 (m), and 1230 cm^{-1} (s); ^{1}H NMR δ 5.9 (m, 6 H, H at C-3, -4, -5, -6, -8, -9), 5.00 (t, 1 H, H at C-2), 3.24 (m, 1 H, H at C-7), 3.05 (dd, 1 H, H at C-1), and 2.11 (s, 3 H, methyl C–H). Double irradiation at δ 3.05 simplifies the triplet at δ 5.00; irradiation of the triplet causes simplification of the absorption at δ 3.05. This decoupling indicates that the proton bound to carbon substituted by acetoxyl is adjacent to a bridgehead proton. Additional properties of **43** follow: uv λ_{max} (EtOH) 200, 225, and 285 nm (ϵ_{max} 6080, 4000, and 600); exact mass, calcd, 204.0786; found, 204.0788.

Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.60; H, 5.88. Found: C, 70.80; H, 5.83.

Attempts to purify **43** by GLC (column A, injector 250°, column 225°) produced *endo*-6-(*cis*-2′-acetoxyvinyl)-*cis*-bicyclo[3.3.0]-octa-3,7-dien-2-one (**58**) as the major product (93%) as a pale yellow solid, mp 69–71°. Rearrangement of **43** was temperature dependent. Only 70% of the rearranged product was formed at

150° (injector 200°) while 85% conversion was observed at 180° (injector 230°): ir (KBr) 1760 (s), 1695 (s), 1220 (s), and 1040 cm^{-1} (s); ^1H NMR coupling constants δ 7.50 (dd, J = 6, 3 Hz), 7.14 (dd, J = 6, 1 Hz), 6.08 (dd, J = 6, 1.5 Hz), 4.69 (dd, J = 10, 6 Hz), and 4.14 (t, J = 10 Hz); uv λ_{max} (ether) 208 nm (ϵ_{max} 31,500); exact mass, calcd, 204.0786; found, 204.0788.

Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.60; H, 5.88. Found: C, 70.68; H, 5.90.

***endo*-6-(1′-Oxoethyl)-*cis*-bicyclo[3.3.0]octa-3,7-dien-2-one (62).** Acetoxy ketone **58** (53.1 mg, 0.00026 mol) in chloroform-*d* (0.5 ml) was treated with water (3 drops) containing trifluoroacetic anhydride (1 drop) for 6 days with continuous swirling; the reaction was monitored by ^1H NMR. The aqueous layer was removed; the organic layer was dried (K_2CO_3) and concentrated to a clear oil (39.0 mg) which contained two major components by GLC analysis (column A). The products, **62** (80%, overall yield 75%) and **58** (15%), were collected by preparative GLC.

Keto aldehyde **62** was purified with large loss to yield 8 mg of pure compound: ^1H NMR δ 9.80 (s, 1 H, H at C-1′), 7.32 (dd, J = 6, 2.5 Hz, 1 H, H at C-4), 6.02 (dd, J = 6.2 Hz, 1 H, H at C-3), 5.6 (m, 2 H, H at C-7, -8), 3.55 (m, 3 H, H at C-1, -5, -6), and 2.6 (br d, 2 H, H at C-2′); exact mass, calcd, 162.0681; found, 162.0683.

Catalytic Hydrogenation of *exo*-2-Acetoxybicyclo[5.2.1]deca-3,5,8-trien-10-one (43). Ketone **43** (1.06 g, 0.0052 mol) was dissolved in absolute ethanol (100 ml), 10% palladium on carbon (0.1 g) was added, and the mixture was placed in a Parr apparatus (50 lb) for 6 hr. After the mixture had been filtered and concentrated, the residue was taken up in ether and concentrated (1.07 g). The material was eluted through silica gel, first with ether–cyclohexane (1:3) and then with ether, to a clear liquid (0.80 g, 73%) which crystallized. *exo*-2-Acetoxybicyclo[5.2.1]decan-10-one (**50**) was collected by preparative GLC (column A) as a white solid: mp 47–49°; ir (KBr) 1730 (s), 1370 (m), 1240 (s), and 1230 cm^{-1} (s); ^1H NMR δ 2.05 (s, acetoxy methyl C–H) superimposed on 1.85 (m, aliphatic C–H); exact mass, calcd, 210.1256, found, 210.1260.

Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.55; H, 8.63. Found: C, 68.28; H, 8.57.

Reaction of *exo*-2-Acetoxybicyclo[5.2.1]decan-10-one (50) with Sodium Hydroxide in Methanol–Water. Acetoxy ketone **50** (0.70 g, 0.0033 mol) was dissolved in hot methanol (10 ml) and sodium hydroxide (1 pellet, ca. 0.004 mol) dissolved in water (1 ml) was added. The mixture was stirred at 25° for 1 day and poured into water. The aqueous layer was extracted with ether. The ether extract was processed in the usual manner to yield an oil (0.52 g) which was greater than 99% pure (GLC, column A). The material was eluted through silica gel (gradient elution 20% ether–cyclohexane, 50% ether–cyclohexane, ether) to produce an oil which crystallized from pentane at −78° to white *exo*-2-hydroxybicyclo[5.2.1]decan-10-one (**51**): mp 47–48.5° (0.27 g, 50%); ir (KBr) 3450 (s) and 1730 cm^{-1} (s); exact mass, calcd, 168.1150; found, 168.1153.

Bicyclo[5.2.1]decane-2,10-dione (52). Hydroxy ketone **51** (0.20 g, 0.0012 mol) was dissolved in acetone (10 ml). Chromium trioxide in 25% sulfuric acid (2.6 *M*, 1 ml, 0.0026 mol) was added dropwise and the mixture was stirred for 0.5 hr. Methanol (0.15 ml) and then water were added, and the mixture was extracted with ether. The aqueous layer was acidified and extracted with ether; the aqueous layer was then made alkaline and reextracted with ether. The ether extracts were processed and concentrated to a liquid (0.21 g, 100%) which contained one component based on GLC analysis (column A). The material was purified by preparative GLC to yield **52** as a clear liquid: ir (neat) 1730 (s) and 1700 cm^{-1} (s); exact mass, calcd, 166.0994; found, 166.0996. The product was dissimilar in all respects to bicyclo[4.3.1]decane-7,10-dione (**53**) prepared from 1-morpholinocycloheptene and acryloyl chloride.

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.13; H, 8.53.

***exo*-2-Chlorobicyclo[5.2.1]deca-3,5,8-trien-10-one (54).** Diazo ketone **37** (0.69 g, 0.004 mol) was dissolved in dry ether (10 ml) and hydrogen chloride was bubbled through the solution for 15 min. The mixture was kept for 15 min, then diluted with ether and extracted with water, aqueous sodium bicarbonate, and saturated brine. The organic layer was dried and concentrated to **54**, a yellow liquid (0.68 g, 94%). The compound was extremely labile. Its purification was unsuccessful: ir (neat) 1740 cm^{-1} (s); ^1H NMR δ 5.9 (m, 7 H, H at C-2, -3, -4, -5, -6, -8, -9) and 3.2 (m, 2 H, H at C-1, -7); exact mass, calcd, 180.0342; found, 180.0344.

Attempts to distil or preparatively GLC **54** led to quantitative rearrangement to *endo*-6-(2′-*cis*-chlorovinyl)-*cis*-bicyclo[3.3.0]octa-3,7-dien-2-one (**60**) as a yellow liquid: ir (neat) 1700 cm^{-1} (s); ^1H NMR δ 7.5 (dd, 1 H, H at C-4), 5.9 (m, 5 H, H at C-3, -7, -8, -1′, -2′), 2.75 (m, 2 H, H at C-5, -6), and 2.5 (m, 1 H, H at C-1); uv λ_{max} (ether) 208 nm (ϵ_{max} 31.3 × 10^3); exact mass, calcd, 180.0342; found, 180.0342.

Anal. Calcd for $C_{10}H_9ClO$: C, 66.49; H, 5.02, Found: C, 66.14; H, 4.87.

Bicyclo[5.2.1]decan-10-one (56). Chloro ketone **54** (0.48 g, 0.0027 mol) in absolute ethanol containing 10% palladium on carbon (0.06 g) was placed in a Parr apparatus (hydrogen pressure 50 lb) for 6 hr. The mixture was filtered and the residue was washed with ether. The filtrate was concentrated and the residue was taken up in ether and processed to a yellow oil (0.40 g). Micro TLC analysis (1:9 ethyl acetate–petroleum ether) of the oil showed two components, R_f values of 0.8 and 0.5.

The crude product was eluted through a silica gel column (5% ethyl acetate–petroleum ether solvent); the first material off the column (0.28 g) was a mixture of a saturated and unsaturated ketone by GLC (column A), ir, and mass spectral measurements (*m/e* 150, 152).

The ketones were dissolved in absolute ethanol (35 ml) containing 10% palladium on carbon (0.05 g) and rehydrogenated at atmospheric pressure. Hydrogen uptake ceased after 2 hr and the product was worked up as before to an oil (0.25 g, 61%) which was greater than 98% pure by GLC analysis. Pure **56** was collected by preparative GLC and has spectral properties identical with those previously reported:[13a] mass spectrum *m/e* 152; ^1H NMR δ 2.1 (s) superimposed on 1.9 (m); exact mass, calcd, 152.1201; found, 152.1204. The ir differed from that reported for bicyclo[4.3.1]decan-10-one (Sadtler No. 28389).

Bicyclo[5.2.1]decan-10-one 2,4-Dinitrophenylhydrazone. Ketone **56** (0.076 g, 0.0005 mol) was treated with 2,4-dinitrophenylhydrazone (0.2 g) in concentrated sulfuric acid (2 ml), water (3 ml), and methanol (5 ml) to yield a crude derivative (0.14 g, 82%). Bicyclo[5.2.1]decan-10-one dinitrophenylhydrazone recrystallized from ethanol as bright orange plates, mp 175–176° (lit.[18a] mp 176–177.5°), *m/e* 332. Admixture with an authentic sample[18b] showed no melting point depression. Both samples possess identical ir spectral properties: ir (KBr) 3300 (w), 3100 (w), 1610 (s), and 1330 cm^{-1} (s); exact mass, calcd, 332.1484; found, 332.1488.

***exo*-2-Acetoxybicyclo[5.2.1]deca-3,5,8-trien-10-one (43).** Chloro ketone **54** (0.24 g, 0.0013 mol) was dissolved in acetic acid (5 ml) containing silver acetate (0.43 g, 0.0026 mol) in a flask wrapped with aluminum foil. The mixture was stirred at 25° for 3 days, diluted with ether (40 ml), and filtered. The light tan precipitate was washed with ether. The combined filtrate was worked up and concentrated. Evaporative distillation (0.075 mm) of the yellow liquid (0.19 g) provided a liquid (0.16 g) containing 10% **54** by GLC analysis. The major component of the mixture (80%) was **43** (overall yield 47%) identical with previously prepared **43** which also rearranges to **58** upon preparative GLC as previously described.

Attempted Wolff–Kishner Reduction of Bicyclo[4.2.2]deca-2,4,9-trien-7-one (1). Ketone **1** (0.25 g, 0.0017 mol), potassium hydroxide (0.75 g), and hydrazine hydrate (1.5 ml) were refluxed in ethylene glycol (4 ml) for 2 hr. The mixture was cooled, poured into water, and extracted with pentane. The pentane solution was concentrated to an off-white solid (0.13 g) which contained two highly volatile materials (5%) of short retention time and a material (95%) of long retention time by GLC analysis (column A).

2,3-Diazatricyclo[6.3.1.$0^{4,11}$]dodeca-2,5,9-triene (**70**, overall yield 47%) was collected as a white solid by preparative GLC, mp 170–172°. A fresh SE-30 GLC column was necessary for consistent GLC results: ir (mull) 1650 (w), 1560 (w), and 940 cm^{-1} (m); ^1H NMR δ 6.03 (m, 2 H, H at C-9, -10), 5.53 (m, 2 H, H at C-4, -5), 5.03 (m, 1 H, H at C-6), 4.84 (t, 1 H, H at C-1), 2.80 (m, 2 H, H at C-7, -8), 2.40 (m, 1 H, H at C-11), 2.40 (m, 1 H, H at C-11), 2.20 (dt, 1 H, H at C-12), and 1.73 (septet, 1 H, H at C-12); exact mass, calcd, 160.1000; found, 160.1003.

Anal. Calcd for $C_{10}H_{12}N_2$: C, 74.97; H, 7.55; N, 17.48. Found: C, 74.79; H, 7.72; N, 17.57.

Bicyclo[4.2.2]deca-2,4,9-trien-7-one Hydrazone (66). Ketone **1** (0.22 g, 0.0015 mol) and hydrazine hydrate (10 ml) were warmed for 2 hr at 75°. The mixture was extracted with chloroform. The chloroform layers were filtered through potassium carbonate and concentrated to give **66** as a yellow oil (0.23 g, 96%): ir (neat) 3330 (m), 3200 (m), and 1650 cm^{-1} (m); ^1H NMR δ 5.8 (m, 6 H, H at C-2, -3, -4, -5, -9, -10), 4.75 (broad s, 2 H, NH, disappears with D_2O), 3.5 (m, 1 H, H at C-6), 2.9 (m, 1 H, H at C-1), and 2.4 (m, 2 H, H at C-8); exact mass, calcd, 160.1000; found, 160.1003.

Attempted Wolff–Kishner Reduction of Bicyclo[4.2.2]deca-2,4,9-trien-7-one Hydrazone (66). Potassium *tert*-butoxide (0.15

g, 0.0014 mol) was dissolved in dry dimethyl sulfoxide (1.5 ml). Hydrazone **66** (0.15 g, 0.0009 mol) dissolved in dry dimethyl sulfoxide (3.0 ml) was added in 5 min. After stirring for 2 hr, the mixture was quenched with pentane and water. The aqueous layer was then washed with ether and the combined organic layer was concentrated to a tan solid (0.08 g) which was 92% pyrazoline **70** by GLC analysis (overall yield 50%). Two volatile products (combined yield 8%) were not identified.

2,3-Diazatricyclo[6.3.1.0^{4,11}]dodeca-2,5,9-triene (70). Bicyclo[4.2.2]deca-2,4,9-trien-7-one semicarbazone (1.54 g, 0.0076 mol) and potassium hydroxide (3.5 g) were refluxed in ethylene glycol (20 ml) for 2.5 hr. The mixture was cooled and worked up as before to yield a tan solid (0.68 g) which was 94% **70** by GLC analysis (column A) (overall yield 54%). Two volatile minor components were not identified.

Bicyclo[4.2.2]deca-2,4,9-trien-7-one Methylhydrazone (71). Ketone 1 (0.12 g, 0.0008 mol) was warmed to 75° with methylhydrazine (5 ml) for 18 hr. Water was added and the mixture was extracted with chloroform. The organic layer was dried through potassium carbonate and concentrated to **71** (0.14 g, 100%): ir (neat) 3350 (m), 1620 (m), and 1100 cm^{-1} (s); ^{1}H NMR δ 5.75 (m, 6 H, H at C-2, -3, -4, -5, -9, -10), 3.9 (m, 1 H, NH, disappears with D_2O), 3.35 (quintet, 1 H, H at C-6), 2.8 (d imposed on m, 4 H, H at C-1, methyl CH), and 2.4 (m, 2 H, H at C-8); exact mass, calcd, 174.1157; found, 174.1159.

3-Methyl-2,3-diazatricyclo[6.3.1.0^{4,11}]dodeca-1,5,9-triene (73). Ketone 1 (0.28 g, 0.0019 mol), potassium hydroxide (0.75 g), and methylhydrazine (1.5 ml) were refluxed in ethylene glycol (4 ml) for 2.5 hr. The reaction mixture was worked up as before to yield a yellow oil (0.24 g, 74%) which was homogeneous by GLC analysis (column A).

Pure **73** was collected by preparative GLC. A fresh SE-30 column was necessary for consistent GLC results: ir (neat) 1640 (w), 1610 (w), 1600 (w), and 1420 cm^{-1} (m); ^{1}H NMR δ 6.00 (m, 2 H, H at C-9, -10), 5.80 (m, 1 H, H at C-5), 5.36 (m, 1 H, H at C-5), 3.82 (m, 1 H, H at C-4), 3.49 (m, 2 H, H at C-8, -11), 2.75 (s, 3 H, methyl C-H), 2.48 (dd, 1 H, H at C-12), 2.1 (m, 2 H, H at C-7, -12), and 1.64 (dd, 1 H, H at C-7); exact mass, calcd, 174.1157; found, 174.1159.

Anal. Calcd for $C_{11}H_{14}N_2$: C, 75.82; H, 8.10; N, 17.08. Found: C, 75.68; H, 8.01; N, 16.77.

Bicyclo[4.2.2]deca-2,4,9-trien-7-one Dimethylhydrazone (72). Ketone 1 (0.10 g, 0.00063 mol) and dimazine (5 ml) were refluxed for 36 hr. The mixture was diluted with water and extracted with methylene chloride. The organic layer was concentrated to **72**, a yellow oil (0.09 g, 75%): ir (neat) 1610 cm^{-1} (m); ^{1}H NMR δ 5.7 (m, 6 H, H at C-2, -3, -4, -5, -9, -10), 3.4 (m, 1 H, H at C-6), 2.7 (m, 3 H, H at C-1, -8), and 2.3 (d, 6 H, methyl CH); exact mass, calcd, 188.1313; found, 188.1315.

Irradiation of Bicyclo[4.2.2]deca-2,4,9-trien-7-one (1) in Acetone. Ketone 1 (0.50 g, 0.0034 mol) in acetone (150 ml) was degassed with argon for 0.5 hr and irradiated with a 450-W Hanovia medium-pressure lamp through a Vycor filter for 9 hr in an all-quartz apparatus fitted with a reflux condenser and a stirrer. The solvent was removed under reduced pressure. The residue (0.6 g) was loaded on a silica gel column (90 g), gradient eluted with 5% ethyl acetate–petroleum ether (500 ml) and 35% ethyl acetate–petroleum ether (1 l.), and collected in 12-ml fractions.

Fractions 28–35 contained ketone 1 (0.05 g, 10%). Fractions 38–41 contained a clear oil, isomeric with the starting ketone, and homogeneous by GLC (column A) (0.06 g, 12%) of unidentified structure: exact mass, calcd, 146.0732; found, 146.0734.

Upon concentrating cuts 43–50, tricyclo[3.3.2.0^{2,8}]deca-3,6-dien-9(10)-one (**78**) remained as a clear oil (0.34 g, 68%) homogeneous by GLC analysis. Pure **78** was obtained by preparative GLC, mp 40–41° (lit.[25] mp 36–37°), and is identical with an authentic sample: ir (neat) 1665 cm^{-1} (s); ir (CCl_4) 1685 cm^{-1} (lit. 1685 cm^{-1}); ^{1}H NMR δ 5.8 (m, 4 H, H at C-3, -4, -6, -7) and 2.5 [m, 6 H, H at C-1, -2, -5, -8, -10 (-9)]; uv λ_{max} (heptane) 200, 290, 300, 312, and 322 nm (ϵ_{max} 7400, 130, 105, 85, and 61); exact mass, calcd, 146.0732; found, 146.0734. The NMR of **74** is temperature dependent as reported.

Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.89. Found: C, 81.93; H, 7.19.

Irradiation of Bicyclo[4.2.2]deca-2,4,9-trien-7-one (1) in Ether. Ketone 1 (0.50 g, 0.0034 mol) in anhydrous ether (100 ml) was purged with argon for 0.5 hr and irradiated with a 450-W Hanovia medium-pressure lamp for 9 hr with Pyrex optics. Concentration under reduced pressure yielded a yellow oil (0.50 g, 100%) which contained (GLC, column A) ketone 1 (25%), unidentified isomer (27%), and tricyclo[3.3.2.0^{2,8}]deca-3,6-dien-9(10)-one (**78**, 48%).

Irradiation of Bicyclo[4.2.2]deca-2,4,9-trien-7-one (1) with Michler's Ketone as Sensitizer. Ketone 1 (0.25 g, 0.0017 mol) and Michler's ketone (0.50 g) in benzene (100 ml) were degassed with argon for 0.5 hr and irradiated with a 450-W Hanovia medium-pressure lamp through Pyrex optics for 2.5 hr. The solution was filtered, concentrated, and eluted through a silica gel column with ether. The residue was sublimed at 50–60° (0.1 mm) to yield **78** as a white solid (0.11 g, 44%).

Reaction of Barbaralone with Diazomethane.[24] Barbaralone was prepared[3a,b] in 64% yield from bicyclo[4.2.1]nona-2,4,7-trien-9-one by Michler's ketone sensitized irradiation: mp 49–51°; ^{1}H NMR δ 5.7 (complex t, 2 H, H at C-3, -7), 4.3 (complex t, 4 H, H at C-2, -4, -6, -8), and 2.7 (t, 2 H, H at C-1, -5).

Alcoholic ethereal diazomethane (125 ml, 0.33 *M*, 0.041 mol) was added at −5° to barbaralone (0.81 g, 0.0061 mol) in methanol (15 ml). After 28.5 hr, solvent and excess diazomethane were removed under reduced pressure to yield a yellow oil (0.91 g, 100%) consisting of 9-aldehydotricyclo[3.3.1.0^{2,8}]nona-3,6-diene (54%) and tricyclo[3.3.2.0^{2,8}]deca-3,6-dien-9(10)-one (**78**, 46%). The aldehyde and ketone **78** were purified by preparative GLC (column A); 9-aldehydotricyclo[3.3.1.0^{2,8}]nona-3,6-diene exhibits ^{1}H NMR absorptions at δ 9.5 (d, 1 H, aldehydic CH), 5.7 (t, 2 H, H at C-3, -7), 4.1 (m, 4 H, H at C-2, -4, -6, -8), 2.8 (m, 2 H, H at C-1, -5), and 2.0 (m, 1 H, H at C-9). Ketone **78** is identical with that previously prepared.

Reaction of Tricyclo[3.3.2.0^{2,8}]deca-3,6-dien-9-one (78) with Tosyl Hydrazide. Ketone **78** (0.20 g, 0.00135 mol), tosyl hydrazide (0.25 g, 0.00135 mol), and concentrated hydrochloric acid (1 drop) in absolute ethanol (6 ml) were stored for 2 hr at 25° and 10 hr at −5°. The mixture was concentrated to ca. 2 ml under reduced pressure and stored at −25° and the resulting precipitate was filtered (0.28 g, 68%). The white crystalline product is identical with **7** previously prepared, mp 155–157°. The residue after filtration also is exclusively **7** (by ^{1}H NMR analysis).

Reaction of Tricyclo[3.3.2.0^{2,8}]deca-3,6-dien-9-one (78) with Dilute Trifluoroacetic Acid. Ketone **78** (ca. 25 mg) in chloroform-*d* (0.5 ml) was treated with water (3 drops) and trifluoroacetic anhydride (1 drop) and swirled overnight at 25°. After the aqueous layer had been separated, the organic layer was removed, dried over anhydrous potassium carbonate, and filtered. ^{1}H NMR and GLC analysis of the resultant solution revealed the exclusive presence of **1**.

Tricyclo[3.3.2.0^{2,8}]deca-3,6-dien-9-ol (79). Ketone **78** (0.16 g, 0.0011 mol) was dissolved in methanol (5 ml) and cooled to 0°. Sodium borohydride (0.20 g, excess) in water (2 ml) and sodium hydroxide (2 *N*, 0.4 ml) was added to the ketone solution. The mixture was stored at 0° for 15 hr. After vacuum evaporation of the methanol, the residue was taken up in ether, worked up in the usual fashion, and concentrated to an oil (0.14 g, 88%) which contained only one component (GLC, column A).

Alcohol **79** was collected by preparative GLC: ir (neat) 3350 (s), 1645 (w), and 1620 cm^{-1} (w); ^{1}H NMR δ 5.8 (m, 2 H, H at C-3, -7), 5.1 (br t, 2 H, H at C-4, -6), 3.8 (m, 1 H, H at C-9), 2.3 (br m, 6 H, H at C-1, -2, -5, -8, -10), and 2.0 (s, 1 H, hydroxylic OH, shift is concentration dependent, disappears upon addition of D_2O); uv λ_{max} (ethanol) 198 and 225 nm (ϵ_{max} 12,100 and 3670); exact mass, calcd, 148.0888; found, 148.0891.

Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 81.14; H, 8.39.

The infrared data previously reported[24] match the observed spectrum of **79**. The ^{1}H NMR of **79** is temperature dependent.

***anti*-8-Acetoxybicyclo[4.2.2]deca-2,4,9-trien-7-one (64).** Ketone 1 (0.50 g, 0.0034 mol) and lead tetraacetate (1.5 g, 0.0034 mol) were refluxed in acetic acid (20 ml) for 5 hr. The mixture was poured into water and extracted with ether and methylene chloride, and the combined organic extracts were treated in the usual manner and concentrated. Upon storage at −20°, the crude product crystallized (0.70 g, 100%); GLC analysis (column A) showed the material to be 99% pure. Distillation afforded **64**, pale yellow crystals: bp 94–96° (0.04 mm); mp 81–82°; ir (KBr pellet) 1740 (s) and 1220 cm^{-1} (s); ^{1}H NMR δ 5.9 (m, 6 H, H at C-2, -3, -4, -5, -9, -10), 5.35 (m, 1 H, H at C-8), 3.6 (m, 2 H, H at C-1, -6), and 2.0 (s, 3 H, methyl CH); exact mass, calcd, 204.0786; found, 204.0783.

Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.60; H, 5.88. Found: C, 70.71; H, 5.67.

Acid-Catalyzed Reaction of *anti*-8-Acetoxybicyclo[4.2.2]deca-2,4,9-trien-7-one (64) with Methanol. Ketone **64** (0.20 g, 0.0001 mol) in methanol (10 ml) containing 25 grains of *p*-toluenesulfonic acid was refluxed for 7 hr. The mixture was worked

up as usual and concentrated to a yellow oil (0.18 g, 100%) which was a 93:7 mixture of syn and anti isomers (column A). *syn*-8-Methoxybicyclo[4.2.2]deca-2,4,9-trien-7-one (**84**) was obtained by preparative GLC: ir (neat) 1720 cm^{-1}; ^1H NMR δ 5.8 (m, 6 H, H at C-2, -3, -4, -5, -9, -10), 4.05 (dd, 1 H, H at C-8), 3.7 (m, 2 H, H at C-1, -6), and 3.35 (s, 3 H, methoxy CH); exact mass, calcd, 176.0837; found, 176.0835.

Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 75.15; H, 6.89.

Registry No.—**1,** 36628-97-4; **1** semicarbazone, 54549-46-1; **4,** 34733-74-9; **6,** 36628-98-5; **7,** 36629-01-3; **8,** 15677-13-1; **10,** 36629-05-7; **11,** 36629-06-8; **12,** 36629-04-6; **13,** 54594-41-1; **15,** 36629-00-2; **16,** 36629-02-4; **18,** 36661-61-7; **22,** 40815-23-4; **23,** 93-04-9; **32,** 54549-47-2; **33,** 54549-48-3; **35,** 54549-49-4; **36,** 54549-50-7; **37,** 54549-51-8; **39,** 54549-59-6; **39** Me ester, 54549-60-9; **43,** 54549-61-0; **50,** 54549-62-1; **51,** 54549-63-2; **52,** 54549-52-9; **54,** 54549-64-3; **56,** 4696-15-5; **56** 2,4-DNP, 54549-53-0; **58,** 54549-65-4; **60,** 54549-66-5; **62,** 54549-67-6; **64,** 54549-68-7; **66,** 54549-54-1; **70,** 54618-47-2; **71,** 54657-23-7; **72,** 54549-55-2; **73,** 54549-56-3; **78,** 15719-09-2; **79,** 54549-57-4; **84,** 54549-69-8; **84** 2,4-DNP, 54549-70-1; diazomethane, 334-88-3; semicarbazide hydrochloride, 563-41-0; isopropenyl acetate, 108-22-5; pyrrolidine, 123-75-1; potassium *tert*-butoxide, 865-47-4; acetyl chloride, 75-36-5; trimethylsilyl chloride, 75-77-4; deuterium oxide, 7789-20-0; methyl fluorosulfonate, 421-20-5; β-tetralone, 530-93-8; dimethyl sulfate, 77-78-1; 2-naphthol, 135-19-3; isoamyl nitrite, 110-46-3; *o*-phenylenediamine, 95-54-5; methyl formate, 107-31-3; tosyl azide, 938-10-3; methylhydrazine, 60-34-4; dimazine, 57-14-7; barbaralone, 6006-24-2; 9-aldehydotricyclo[3.3.1.$0^{2,8}$]nona-3,6-diene, 54549-58-5; tosyl hydrazide, 1576-35-8; trifluoroacetic acid, 76-05-1; methanol, 67-56-1.

References and Notes

(1) (a) Abstracted from the Ph.D. Dissertation of J. B. Press, The Ohio State University, Columbus, Ohio, 1973. (b) This research has also been described in part by J. B. Press and H. Shechter, *Tetrahedron Lett.*, 2677 (1972).

(2) This work has been reviewed by (a) T. L. Burkoth and E. E. van Tamelen, "Nonbenzenoid Aromatics", Vol. 1, J. R. Snyder, Ed., Academic Press, New York, N.Y., 1969, Chapter 3; (b) L. T. Scott and M. Jones, Jr., *Chem. Rev.*, **72,** 181 (1972).

(3) (a) T. A. Antkowiak, Ph.D. Dissertation, The Ohio State University, Columbus, Ohio, 1968; (b) T. A. Antkowiak, D. C. Sanders, G. B. Trimitsis, J. B. Press, and H. Shechter, *J. Am. Chem. Soc.*, **94,** 5366 (1972); (c) see also L. A. Paquette, R. H. Meisinger, and R. E. Wingard, *Ibid.*, **94,** 2155 (1972); E. Vedejs, R. A. Gabel, and P. D. Weeks, *Ibid.*, **94,** 5842 (1972); (d) a modification of the method of M. Stoll and W. Scherrer, *Helv. Chim. Acta*, **23,** 941 (1940).

(4) An extension of the methods of R. Shapiro and M. Heath, *J. Am. Chem. Soc.*, **89,** 5734 (1967), and G. Kaufman, F. Cook, H. Shechter, J. Bayless, and L. Friedman, *Ibid.*, **89,** 5736 (1967).

(5) We should like to acknowledge the gift by Dr. M. J. Broadhurst.

(6) (a) The stereochemistry of **17** is not known. (b) 7-Methoxy-8-methylbicyclo[4.2.2]deca-2,4,7,9-tetraene, a product possibly expected from dimethylation of **2,** has not been found.

(7) Treatment of **1** with less potassium *tert*-butoxide (~1.25 equiv) in glyme at 25° and subsequent quenching with methyl fluorosulfonate results in enhanced recovery of **1,** lower conversion to **16,** and no **18.**

(8) These products were identified by comparison with authentic samples.

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(11) (a) Comparison of the ^1H NMR of **10, 11, 12,** and **16** and that for previously reported tetraenes (Table I) indicates that there are strong electronic effects by the 7 substituent on the proton resonance at C-8. With respect to unsubstituted tetraene **8** with C-8 proton absorption at δ 5.5, electron-withdrawing groups at C-7 cause significant shifts downfield whereas electron donors produce large upfield shifts. Thus the 7-bromo[11b] and 7-acetyl derivatives[11b] show resonance for their C-8 protons at δ 5.9 and 6.7, respectively, whereas the 7-acetoxy (**10**), 7-methyl,[11c] 7-trimethylsiloxy (**12**), 7-methoxy (**16**), and 7-pyrrolidino (**11**) derivatives display absorptions at δ 5.35, 5.28, 4.78, 4.50, and 4.15, respectively. (b) H. P. Löffler and G. Schröder, *Angew. Chem., Int. Ed. Engl.*, **7,** 736 (1968). (c) G. Schröder, U. Prange, and J. F. M. Oth, *Chem. Ber.*, **105,** 1854 (1972).

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(23) The minor product may be tricyclo[5.3.0.$0^{2,10}$]deca-3,5-dien-8-one. The properties and the possible structure of this product are discussed in ref 1a.

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