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Thermal Rearrangement of 3-Methylenespiro[5.6]dodeca-1,4,9-triene and Spiro[5.6]dodeca-1,4,9-trien-3-one

Diane F. Murray,* Mary W. Baum, and Maitland Jones, Jr.*

Department of Chemistry, Princeton University, Princeton, New Jersey 08544

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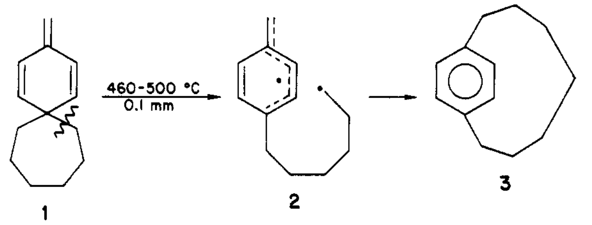
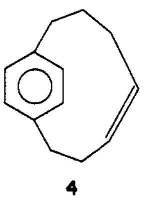
Introduction of a double bond into the seven-membered ring of 3-methylenespiro[5.6]dodeca-1,4-diene (1) or spiro[5.6]dodeca-1,4-dien-3-one (16) alters the thermal behavior of both compounds. Pyrolysis of 3-methylenespiro[5.6]dodeca-1,4,9-triene (5) affords the isomeric hydrocarbon *cis,cis*-2,5-dimethylene-7-vinylbicyclo[4.3.0]non-3-ene (11). Pyrolysis of the related ketone spiro[5.6]dodeca-1,4,9-trien-3-one (6) gives a mixture of *cis,cis*-5-methylene-9-vinylbicyclo[4.3.0]-3-nonen-2-one (21), *cis,cis*-5-methylene-7-vinylbicyclo[4.3.0]-3-nonen-2-one (22), and *trans,trans*-2,4,5a,6,8a,8b-hexahydroacenaphthylen-5(1*H*)-one (23). Mechanistic rationales for these reactions are presented.

Among the most convenient routes to small [*n*]paracyclophanes is the method of van Straten, de Wolf, and Bickelhaupt which involves the pyrolysis of spirotrienes.[1] For example, flow pyrolysis of 3-methylenespiro[5.6]dodeca-1,4-diene (1) at 460–500 °C provides [7]paracyclophane (3) in 10–15% yield.[1] The proposed mechanism for this reaction involves the formation and recombination of diradical 2.[1] In an attempt to prepare the unknown [7]paracyclophan-4-ene (4),[2] we investigated the thermal behavior of 3-methylenespiro[5.6]dodeca-1,4,9-triene (5). However, incorporation of a double bond into the seven-membered ring of 1 dramatically alters its thermal behavior. We also have found that the thermal reactivity of the related ketone, spiro[5.6]dodeca-1,4,9-trien-3-one (6), differs significantly from that reported for the simple dienone, spiro[5.6]dodeca-1,4-dien-3-one.

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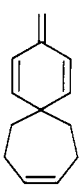
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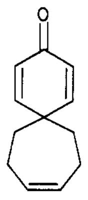
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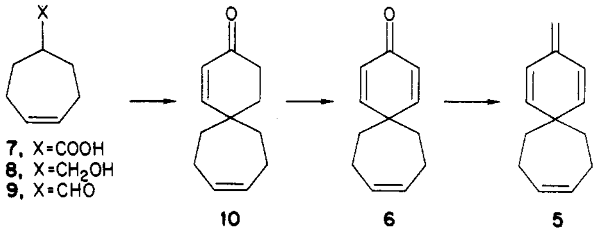
Results and Discussion

Tetraene 5 and trienone 6 were prepared from 4-cycloheptenecarboxylic acid[4] (7). Reduction of 7 with lithium aluminum hydride, followed by oxidation of the resulting alcohol 8[5] with pyridinium chlorochromate, gave 4-cycloheptenecarboxaldehyde[4b] (9). Aldehyde 9 was converted to trienone 6 via the spiroannelation method of Kane and Jones.[6] Accordingly, the piperidine enamine of 9 was



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[1] van Straten, J. W.; de Wolf, W. H.; Bickelhaupt, F. *Rec. Trav. Chim. Pays-Bas* **1977**, *96*, 88.

[2] The smallest known [n]paracyclophane incorporating a carbon-carbon double bond in the bridge is [8]paracyclophan-5-ene.[3]

[3] (a) Cram, D. J.; Knox, G. R. *J. Am. Chem. Soc.* **1961**, *83*, 2204–2205. (b) Cram, D. J.; Montgomery, C. S.; Knox, G. R. *Ibid.* **1966**, *88*, 515–525. (c) Tsuji, T.; Nishida, S. *J. Chem. Soc., Chem. Commun.* **1972**, 284–285. (d) Tsuji, T.; Nishida, S. *Chem. Lett.* **1973**, 1335–1338. (e) Tsuji, T.; Nishida, S. *J. Am. Chem. Soc.* **1973**, *95*, 7519–7520. (f) Tsuji, T.; Shibata, T.; Hienuki, T.; Nishida, S. *Ibid.* **1978**, *100*, 1806–1814. (g) Cope, A. C.; Pawson, B. A. *J. Am. Chem. Soc.* **1968**, *90*, 636–639.

[4] (a) Stork, G.; Landesman, H. K. *J. Am. Chem. Soc.* **1956**, *78*, 5129–5130. (b) Schwarz, M.; Besold, A.; Nelson, E. R. *J. Org. Chem.* **1965**, *30*, 2425–2428.

[5] Marshall, J. A.; Partridge, J. J. *J. Org. Chem.* **1968**, *33*, 4090–4097.

[6] Kane, V. V.; Jones, M., Jr. *Org. Synth.* **1981**, *61*, 129–133.

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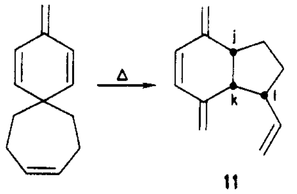
prepared and was treated sequentially with methyl vinyl ketone, acetic acid, and sodium hydroxide to afford spiro[5.6]dodeca-1,9-dien-3-one (**10**). Oxidation of **10** with 2 equiv of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone provided **6**. Treatment of **6** with methylenetriphenylphosphorane in diethyl ether gave **5**.

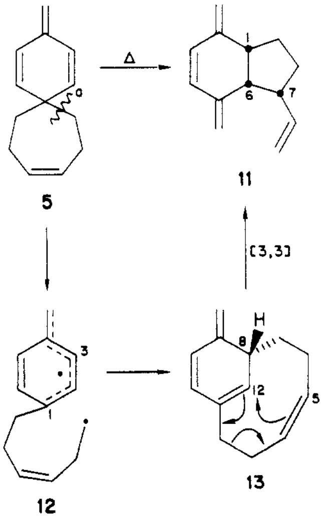
Flash-vacuum pyrolysis of tetraene **5** at 440 °C afforded, in addition to starting material, a single volatile product which was identified as *cis,cis*-2,5-dimethylene-7-vinylbicyclo[4.3.0]non-3-ene (**11**). The structure of **11** was deduced from its spectral data (see Experimental Section). In the 250-MHz ^1H NMR spectrum of **11**, the methine proton H_k appears as a triplet as a result of $J_{jk} = J_{kl} = 8.2$ Hz. In cyclopentane rings, vicinal coupling constants of 8 Hz for cis protons and 0–3 Hz for trans protons are predicted by the Karplus equation and are the typically observed values.[7] It follows that H_k is cis to both H_j and H_l.



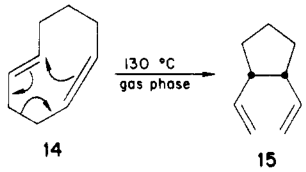
5 **11**

The pyrolysis of **5** was repeated under a variety of conditions. The effective temperature range for the pyrolysis was limited by the occurrence of almost no reaction at 400 °C and exclusive polymerization at 500 °C. The presence of Pyrex beads in the thermolysis tube and/or a slow stream of argon gas affected only the per cent conversion of the starting material. The isolated yield of **11** was only ca. 10% because of the tedious gas chromatographic separation of **5** and **11**.

The formation of **11** from **5** can be accounted for by the initial cleavage of bond "a" in **5** to produce diradical **12**.

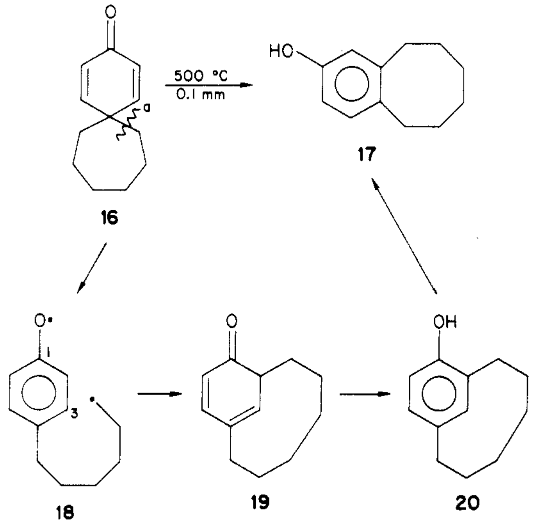


Recombination of the diradical at C-3 would give **13**. The *cis,trans*-1,5-cyclononadiene substructure within **13** is arranged ideally for a concerted [3.3]sigmatropic (Cope) rearrangement to give **11**. Examination of molecular models shows that formation of the bond between C-5 and C-12 in **13** must occur trans to the hydrogen at C-8 and so must lead to a cis ring fusion in **11**. The relative configuration at C-7 in **11** is determined by the conformation (chair or boat) through which the Cope rearrangement proceeds. The observed cis relationship between the hydrogens at C-6 and C-7 in **11** is consistent with a chair transition state for the [3,3] sigmatropic shift. A precedent for **13** → **11** has been reported. Thermolysis of *cis,trans*-1,5-cyclononadiene (**14**) at 130 °C gives *cis*-1,2-divinylcyclopentane (**15**) by a [3,3] sigmatropic rearrangement which occurs via a chair transition state.[8]



It was surprising to find that diradical **12** followed a different pathway from the corresponding diradical **2**. The potential radical recombination of **12** at its terminal methylene position may fail because of the shorter effective length of the alkenyl side chain in **12** compared to the corresponding saturated side chain in **2**. Alternatively, recombination of **12** at the terminal methylene may occur reversibly, whereas recombination of **12** at C-3 leads to **11** via tetraene **13**.

In view of the contrasting thermal rearrangement pathways followed by tetraene **5** and triene **1**, it was of interest to investigate the thermal behavior of trienone **6**. It is known that pyrolysis of dienone **16**, in which the seven-membered ring is saturated, affords 8-hydroxybenzocyclooctene (**17**) in 80% yield.[9] The first step in this pyrolysis is believed to be generation of diradical **18** by cleavage of bond "a" in **16**.[9] The unpaired electron density of phenoxy radicals is largely associated with the ring carbons ortho and para to the oxygen atom,[10] and diradical **18** apparently recombines at C-2 to give dienone **19**. Subsequent tautomerization of **19** would give [6]metacyclophan-9-ol (**20**). Under the reaction conditions, **20** apparently isomerizes to the thermodynamically more stable ortho isomer **17**.[9]



In striking contrast to **16** → **17**, pyrolysis of trienone **6** gave a mixture of *cis,cis*-5-methylene-9-vinylbicyclo[4.3.0]-3-nonen-2-one (**21**), *cis,cis*-5-methylene-7-vinyl-

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[7] Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectrometric Identification of Organic Compounds"; Wiley: New York, 1981; 4th ed., pp 209–210.

[8] Vogel, E.; Grimme, W.; Dinné, E. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 739–740.

[9] van Straten, J. W.; Ph.D. Thesis, Vrije Universiteit, Amsterdam, The Netherlands, 1978. For an updated view from the Amsterdam group, see: Jenneskens, L. W., De Wolf, W. H.; Bickelhaupt, F. *Tetrahedron* **1985**, *41*, 3779–3784.

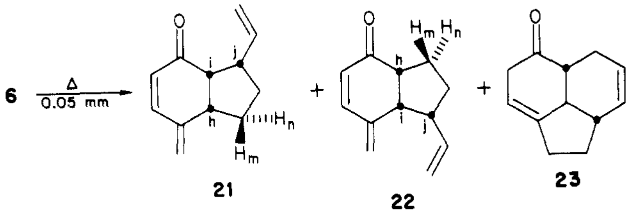
[10] Stone, T. J.; Waters, W. A. *J. Chem. Soc.* **1964**, 213–218.

Table I. Pyrolysis of Trienone 6

temp, °C	total isolated % yield of crude volatile products[a]	% composition[b] 6	21	22	23
445	100	100			
500	79	72	24	4	
550	66	8	30	38	24
600	24		15	34	51

[a] Includes 0–35% unidentified low molecular weight fragments as indicated by GLC analysis. [b] Relative ratios determined by GLC analysis.

bicyclo[4.3.0]-3-nonen-2-one (**22**), and *trans,trans*-2,4,5a,6,8a,8b-hexahydroacenaphthylen-5(1*H*)-one (**23**).



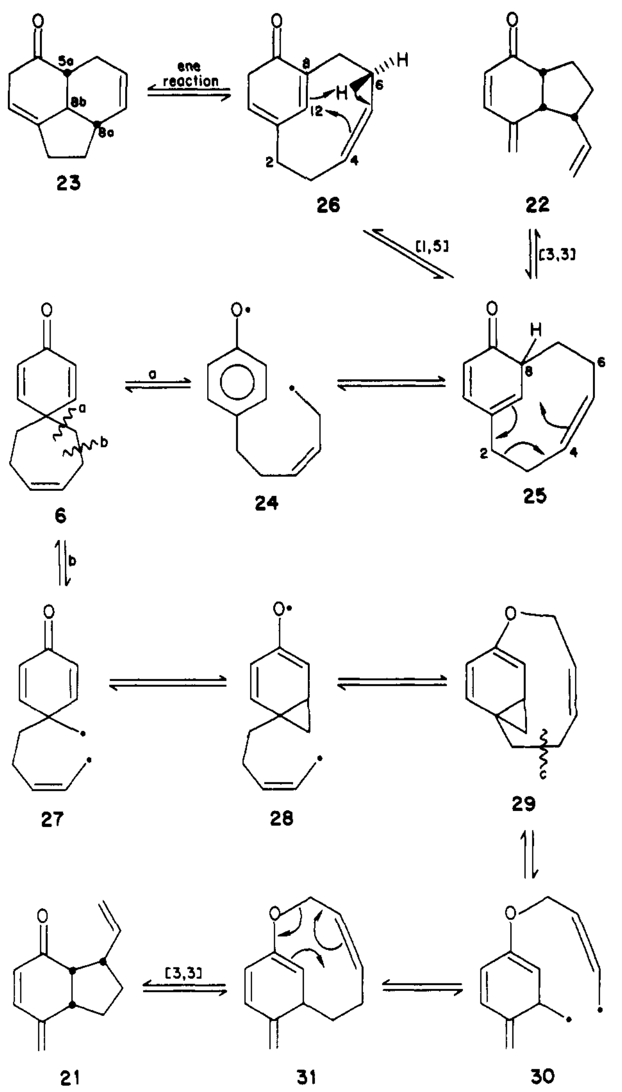
Furthermore, the product composition was found to be temperature dependent (Table I). As the temperature of the reaction was increased, more of the starting ketone was consumed. However, this was accompanied by extensive polymerization. In each case, actual yields of GC isolated products were only 2–6%. The presence or absence of Pyrex beads in the thermolysis tube did not alter the outcome of the pyrolysis.

The structure assignments of ketones **21**–**23** were made based on their spectral characteristics (see Experimental Section). Both **21** and **22** exhibit carbonyl absorptions at 1672 cm^{-1} in their infrared spectra, indicative of an α,β-unsaturated ketone in a six-membered ring. The ^1H and ^{13}C NMR spectra of **21** and **22** are consistent with the assigned structures. The cis,cis stereochemistry of **21** and **22** follows from the multiplicities and coupling constants observed for the aliphatic methine protons in the 250-MHz ^1H NMR spectra of these compounds. In each case, H_i appears as a triplet (or pseudo triplet) as a result of being coupled equally (or nearly equally) to H_h and H_j with $J_{hi} \approx J_{ij}$ = 8–11 Hz. In addition, H_h is split into a triplet of doublets. This pattern arises from equal coupling of H_h to H_i and H_m with $J_{hi} = J_{hm}$ = 8–9 Hz to give a triplet, which is split into doublets by H_n with J_{hn} = 3 Hz.

In contrast to ketones **21** and **22**, the infrared spectrum of **23** contains a carbonyl absorption at 1720 cm^{-1}, which is indicative of a saturated ketone. The ^1H NMR spectrum of **23** is the most complex of all these products. Complete analysis of this spectrum required the addition of a shift reagent (see Experimental Section). The trans,trans stereochemistry of **23** was established by two nuclear Overhauser effect (NOE) experiments involving the three aliphatic methine protons (see Experimental Section).

Formation of ketones **21**–**23** from pyrolysis of trienone **6** can be accounted for by the mechanisms outlined in Scheme I. Initial cleavage of bond "a", followed by recombination of the resulting diradical **24** would give the intermediate trienone **25**, analogous to the formation of **19** from **16**. Unlike **19**, **25** does not tautomerize to a phenol. Apparently, two competing rearrangements of **25** occur faster than aromatization. The *cis,trans*-1,5-cyclononadiene portion of **25** undergoes a [3,3] sigmatropic rearrangement to provide product **22**. As previously discussed for **13** → **11**, the cis,cis stereochemistry of **22** is a consequence of this concerted reaction. Alternatively, a [1,5] sigmatropic shift of the hydrogen at C-8 in **25** would give the trienone intermediate **26**. Trienone **26** also contains a *cis,trans*-1,5-cyclononadiene moiety. However, examination of molecular models shows that the double bonds of the cyclononadiene in **26** cannot attain the proper orientation for a [3,3] sigmatropic shift. In contrast, the geometry of **26** is favorable for an intramolecular ene reaction. This proceeds by transfer of a hydrogen from C-6 to C-8 in **26** with concomitant bond formation between C-4 and C-12 to afford the tricyclic dienone **23**. The trans ring fusion between C-5a and C-8b in **23** is dictated by the stereoselectivity of the ene reaction whereby the new C–C and C–H bonds are formed cis to each other.[11] Furthermore, in a concerted ene reaction the axis of the allylic C–H bond must be alligned parallel to the p orbitals of the adjacent double bond.[11] It is apparent from molecular models that this type of arrangement in **26** would result in a trans configuration of the hydrogen at C-8a relative to the hydrogen at C-8b in **23**.

Scheme I



A likely precursor to product **21** is enol ether **31**. A [3,3] sigmatropic shift involving oxygen (a Claisen rearrangement) of **31** would afford **21**. The cis,cis stereochemistry of **21** is consistent with a chair transition state for this reaction. Formation of **31** from trienone **6** can be accounted for by initial cleavage of bond "b" in **6**. This would generate intermediate **27** which contains an allylic radical

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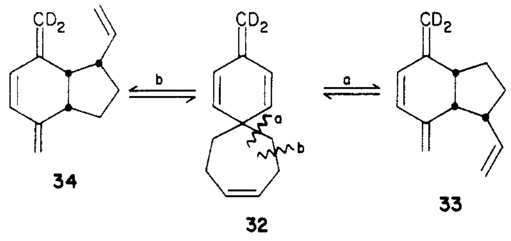
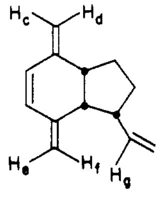
[11] For reviews see: (a) Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 556–577. (b) Oppolzer, W.; Snieckus, V. *Ibid.* **1978**, *17*, 476–486.

and a homoallylic radical. Delocalization of the homoallylic radical into the enone can occur through the norcaradiene intermediate **28**.[12] In **28** the alkenyl chain is bent out of the plane of the six-membered ring at the quaternary cyclopropyl carbon. Therefore, the allylic radical should easily be able to recombine with the alkoxy radical to give bridged intermediate **29**. Subsequent scission of bond "c" in **29**, followed by rearrangement of the resulting cyclopropylcarbinyl radical to the corresponding homoallylic radical, would produce diradical **30**. Recombination of the radicals in **30** would provide enol ether **31**.

Isolation of trienones **21** and **22** in the pyrolysis of ketone **6** raises the question of whether the pyrolysis of the corresponding tetraene **5** is proceeding by an exclusive or competitive scission of bond "a" and/or "b" in **5**. These alternatives can be distinguished by deuterium labeling of the terminal methylene in **5** (olefin **32**). Cleavage at bond "a" in **32** would lead to olefin **33**. Cleavage at bond "b" would give the isomeric product **34**.



In order to interpret the result of the labeling experiment, it was necessary to assign at least one of the four terminal methylene protons, H_c–H_f, in the ^1H NMR spectrum of **11**. Among these protons, only H_f is close to the vinyl substituent at C-7 in **11**. Therefore, only H_f can show an NOE when H_g is irradiated and in this way the signal for H_f could be assigned.



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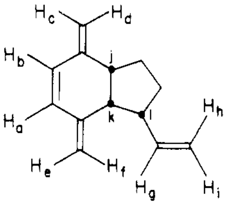
The labeled tetraene **32** was synthesized from trienone **6** and dideuteriomethylenetriphenylphosphorane. Tetraene **32** was pyrolyzed at 450 °C and 0.05 mm and gave only **33**. Consequently, **11** must be formed from **5** by exclusive cleavage of bond "a" in **5**.

In summary, trienone **6** exhibits more varied thermal reactivity than the corresponding tetraene **5**. It is possible that this is simply a consequence of the higher temperature that is required for pyrolysis of the ketone. Unfortunately, tetraene **5** gives exclusively polymeric products above 490 °C.

Experimental Section

Melting points were obtained using a Thomas-Hoover melting point apparatus and are uncorrected. Proton magnetic resonance spectra were recorded on a Perkin-Elmer R-32 90-MHz spectrometer, a JEOL FX90Q 90-MHz spectrometer, or a Bruker WM 250-MHz spectrometer. Carbon magnetic resonance spectra were obtained with the Brucker instrument at 62.9 MHz. Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer. Electron-impact mass spectra were obtained with a Du Pont 21-492B mass spectrometer at an ionization potential of 70 eV. GC/MS analyses were carried out on a Hewlett-Packard 5992B gas chromatograph/mass spectrometer. Gas chromatography was performed on a Varian Aerograph Model A-90-P chromatograph (thermal conductivity detector) with helium as the carrier gas. High-performance liquid chromatography (HPLC) was carried out with a Perkin-Elmer 254-0310 Series 2/2 liquid chromatograph equipped with a 50-Hz dual pump module and a Perkin-Elmer LC-75 spectrophotometric UV detector. Relative product ratios determined by GC analyses are proportional to peak areas and are uncorrected for differences in detector response. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, GA.

The following lettering and numbering schemes are used for the assignment of ^1H and ^{13}C NMR signals, respectively.



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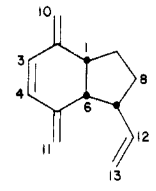

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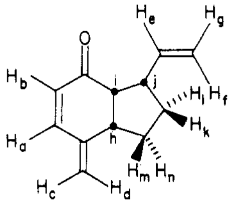

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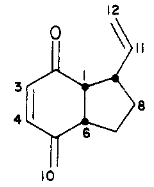

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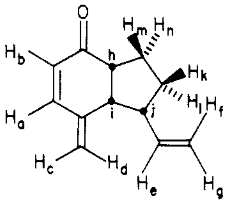

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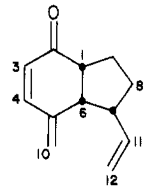

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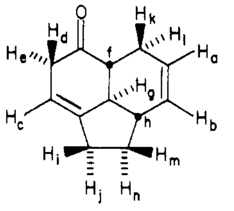

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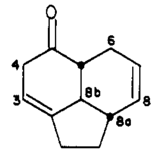

23

The ^1H NMR assignments are based on the observed multiplicities and coupling constants of the signals. In addition, for compounds **11**, **21**, **22**, and **23**, the assignments were derived from appropriate decoupling and/or nuclear Overhauser effect (NOE) experiments.

4-Cycloheptenecarboxylic Acid[4] **(7).** Argon was passed through a stirred solution of cyclopentanone (150 g, 1.78 mol), pyrrolidine (177 g, 2.49 mol), and *p*-toluenesulfonic acid (0.75 g, 3.9 mmol) in benzene (720 mL) for 30 min. The reaction flask was then equipped with a Dean-Stark water separator, and the reaction mixture was refluxed under argon for 4 h. At that time, the theoretical amount of water (32 mL) had distilled. The benzene and excess pyrrolidine present were distilled under argon. Distillation (60 °C, 2.0 mm) of the residue gave 1-*N*-pyrrolidylcyclopentene[13] (**35**) (187 g, 77% yield) as a very air-sensitive colorless liquid: IR ν (neat) 3070, 2900, 1632, 1490, 1460, 1450, 1440, 1385, 1355, 1330, 1315, 1295, 1270, 1160, 1040, 960, 950 cm^{-1}.

Freshly distilled acrolein (76.4 g, 1.36 mol) was added dropwise over 1 h to a stirred solution of **35** (187 g, 1.36 mol) in anhydrous diethyl ether (380 mL) that was maintained at 0 °C under argon.

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(12) For one example of the addition of a homoallylic carbon free radical to an adjacent enone to give a (cyclopropylcarbinyl)phenoxy radical see: Barton, D. H. R.; Beaton, J. M. *J. Am. Chem. Soc.* **1961**, *83*, 4083–4089.

(13) Kuehne, M. E. *J. Am. Chem. Soc.* **1959**, *81*, 5400–5405.

The resulting yellow solution was allowed to warm slowly to room temperature and was stirred at room temperature for 18 h. Evaporation of the solvent at reduced pressure provided a viscous yellow oil. Distillation (130 °C, 1.0 mm) of this material gave 2-*N*-pyrrolidylbicyclo[3.2.1]octan-8-one[4] (**36**) (136 g, 52% yield) as a light yellow liquid: ^{1}H NMR δ (CCl$_4$) 1.1–3.2 (complex m); IR ν (neat) 2960, 2875, 2780, 1750, 1475, 1455, 1370, 1355, 1340, 1315, 1245, 1200, 1185, 1145, 1115, 1075, 1065, 1015, 1000 cm^{-1}.

Methyl iodide (120 g, 0.845 mol) was added dropwise over 45 min to a mechanically stirred solution of **36** (136 g, 0.704 mol) in methanol (635 mL) under argon at room temperature. After the addition was complete, the reaction mixture was refluxed for 45 min and allowed to stand at room temperature overnight. The methanol and excess methyl iodide were evaporated at reduced pressure and 40% aqueous potassium hydroxide (145 mL) was added to the black viscous residue. The resulting solution was refluxed for 5 h, cooled, and diluted with water (45 mL). The aqueous solution was washed with ether (200 mL), cooled to 0 °C, and then acidified with concentrated hydrochloric acid (110 mL). The acidified mixture was extracted with ether (1 × 140 mL and 5 × 85 mL), and the combined ether extracts were dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure afforded an oily brown solid which was recrystallized from pentane to give **7** (61.5 g, 62% yield) as a light yellow solid: mp 68–70 °C, lit.[4a] mp 65–67 °C; ^{1}H NMR δ (CCl$_4$) 12.09 (s, 1 H, COOH), 5.93–5.55 (m, 2 H, CH=CH), 2.8–1.2 (complex m, 9 H); IR ν (CCl$_4$) 3030, 2940, 1705, 1530, 1445, 1420, 1315, 1295, 1235, 1180, 1120, 1055, 940 cm^{-1}.

5-(Hydroxymethyl)cycloheptene[5] (8). A solution of **7** (30.7 g, 219 mmol) in anhydrous ether (1.2 L) was added to a mechanically stirred suspension of lithium aluminum hydride (16.6 g, 438 mmol) in anhydrous ether (500 mL) at a sufficient rate to reach and maintain reflux. After the addition was complete, the mixture was refluxed for 3 h under argon and then cooled to 0 °C. The cold reaction mixture was stirred vigorously and quenched by the dropwise addition of water (17 mL), 15% aqueous sodium chloride (17 mL), and water (70 mL). The resulting mixture was filtered, and the filter cake was extracted two times by refluxing in ether (300 mL) for 1 h. The filtrate and ether extracts were combined, washed with 7% aqueous sodium hydroxide (175 mL) and water (2 × 175 mL), and dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure provided **8** (27.6 g, 100% yield) as a light yellow liquid: ^{1}H NMR δ (CCl$_4$) 5.99–5.65 (m, 2 H, CH=CH), 3.71–3.19 (m, 3 H, CH$_2$OH), 2.55–1.97 (m, 4 H, C*H*$_2$CH=CH), 1.97–1.42 (m, 3 H), 1.42–0.86 (m, 2 H); IR ν (CCl$_4$) 3650, 3340, 3025, 2910, 2850, 1660, 1445, 1380, 1255, 1070, 1045, 1010, 940, 905 cm^{-1}.

4-Cycloheptenecarboxaldehyde[4b] (9). A solution of **8** (27.9 g, 221 mmol) in dry methylene chloride (50 mL) was added in one portion to a stirred suspension of pyridinium chlorochromate (76.1 g, 353 mmol) in dry methylene chloride (445 mL) that was maintained at room temperature under argon. The orange pyridinium chlorochromate was immediately reduced to a gummy black solid. After the reaction mixture was stirred at room temperature for 3 h, anhydrous ether (445 mL) was added and the supernatant liquid was decanted from the black gum. The insoluble residue was washed with anhydrous ether (4 × 100 mL), and the combined organic solutions were passed through a short pad of florisil. Evaporation of the solvent at reduced pressure afforded a green oil which was distilled (74 °C, 10 mm) to give **9** (16.9 g, 62% yield) as a colorless liquid: ^{1}H NMR δ (CCl$_4$) 9.62 (s, 1 H, CHO), 5.96–5.60 (m, 2 H, CH=CH), 2.72–1.20 (complex m, 9 H); IR ν (CCl$_4$) 3025, 2930, 2845, 2810, 2710, 1731, 1445, 1370, 1255, 1070, 910 cm^{-1}.

Spiro[5.6]dodeca-1,9-dien-3-one (10). Following the spiroannelation procedure of Kane and Jones,[6] **9** (33.8 g, 273 mmol) was treated with piperidine (32.5 g, 382 mmol) in toluene (370 mL). The resulting orange oil was Kugelrohr distilled (60 °C, 0.1 mm) to provide 5-(*N*-piperidylmethylene)cycloheptene (**37**) (46.6 g, 89% yield) as a light yellow liquid: ^{1}H NMR δ (CCl$_4$) 5.93–5.62 (m, 2 H, CH=CH), 5.29 (s, 1 H, C=CHN), 2.51 (t, *J* = 4.5 Hz, 4 H, CH$_2$N), 2.40–2.03 (m, 8 H), 1.78–1.25 (m, 6 H); IR ν (CCl$_4$) 3025, 2940, 2855, 2790, 1655, 1445, 1375, 1305, 1275, 1250, 1220, 1185, 1170, 1155, 1130, 1115, 1038, 862 cm^{-1}.

Enamine **37** (46.6 g, 244 mmol) was immediately treated sequentially with (1) methyl vinyl ketone (18.8 g, 268 mmol) in dry ethanol (1.5 L), (2) a solution of sodium acetate (43.6 g) in glacial acetic acid (74 mL) and water (134 mL), and (3) 20% aqueous sodium hydroxide (200 mL). Distillation (90–95 °C, 0.5 mm) of the crude oil provided **10** (31.5 g, 73% yield) as a light yellow liquid. An analytically pure sample of **10** was obtained by GLC (10 ft × 0.25 in. 10% FFAP column, 180 °C): ^{1}H NMR δ (CDCl$_3$) 6.87 (d, *J* = 10.3 Hz, 1 H, COCH=C*H*), 5.88 (d, *J* = 10.3 Hz, 1 H, COC*H*=CH), 5.70 (t, *J* = 3.0 Hz, 2 H, CH=CH), 2.44 (t, *J* = 6.9 Hz, 2 H, COCH$_2$), 2.34–2.07 (m, 4 H, C*H*$_2$CH=CH), 1.93 (t, *J* = 6.9 Hz, 2 H, COCH$_2$C*H*$_2$), 1.83–1.58 (m, 4 H, C*H*$_2$CH$_2$CH=CH); ^{13}C NMR δ (CDCl$_3$) 199.6 (CO), 158.1 (C-1), 130.9 (C-9 and C-10), 126.7 (C-2), 38.2 (C-6), 36.1 (C-8 and C-11), 33.9 (C-4), 32.3 (C-5), 24.0 (C-7 and C-12); IR ν (CCl$_4$) 3025, 2930, 2845, 1684, 1455, 1435, 1418, 1385, 1232, 1214, 1159, 1098, 940 cm^{-1}.

Anal. Calcd for C$_{12}$H$_{16}$O: C, 81.77; H, 9.15. Found: C, 81.70; H, 9.16.

Spiro[5.6]dodeca-1,4,9-trien-3-one (6). Powdered 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (79.9 g, 352 mmol) was added to a stirred solution of **10** (31.0 g, 176 mmol) in dry dioxane (600 mL) under argon. The reaction mixture was refluxed with stirring for 24 h, cooled, and filtered. The filtered solid was washed with several portions of dioxane. The filtrate and washings were combined and the solvent was removed by evaporation at reduced pressure to give a viscous brown oil. This residue was dissolved in ether (1 L) and the ether solution was washed with 15% aqueous sodium hydroxide (4 × 500 mL). The combined aqueous washes were then extracted with ether (3 × 500 mL). The ether layers were combined, washed with saturated aqueous sodium chloride (4 × 500 mL), and dried over anhydrous magnesium sulfate. Evaporation of the ether at reduced pressure gave a brown oil which was Kugelrohr distilled (100–110 °C, 0.1 mm) to provide **6** (18.9 g, 62% yield) as a colorless liquid. An analytically pure sample of **6** was obtained by GLC (10 ft × 0.25 in. 10% FFAP column, 190 °C): ^{1}H NMR δ (CDCl$_3$) 7.07 (d, *J* = 10.2 Hz, 2 H, COCH=C*H*), 6.21 (d, *J* = 10.2 Hz, 2 H, COC*H*=CH), 5.72 (t, *J* = 2.9 Hz, 2 H, CH=CH), 2.38–2.17 (m, 4 H, C*H*$_2$CH=CH), 1.81–1.66 (m, 4 H, C*H*$_2$CH$_2$CH=CH); ^{13}C NMR δ (CDCl$_3$) 185.8 (CO), 155.0 (C-1 and C-5), 130.8 (C-9 and C-10), 127.5 (C-2 and C-4), 43.2 (C-6), 36.0 (C-8 and C-11), 24.4 (C-7 and C-12); IR ν (CCl$_4$) 3025, 2930, 2850, 1667, 1631, 1450, 1398, 1255, 1170, 1086, 875, 845 cm^{-1}.

Anal. Calcd for C$_{12}$H$_{14}$O: C, 82.72; H, 8.10. Found: C, 82.57; H, 8.13.

3-Methylenespiro[5.6]dodeca-1,4,9-triene (5). A solution of *n*-butyllithium in hexane (10.5 mL, 21.7 mmol) was added dropwise to a stirred suspension of methyltriphenylphosphonium bromide (8.84 g, 24.8 mmol, dried at 100 °C and 1 mm for 10–20 h immediately before use) in anhydrous ether (330 mL) that was maintained at room temperature under argon. The resulting yellow solution, which contained a small amount of solid excess methyltriphenylphosphonium bromide, was stirred at room temperature for 3 h. A solution of **6** (2.70 g, 15.5 mmol) in dry ether (110 mL) was then added dropwise to the reaction mixture. After addition of the ketone was complete, the reaction mixture was heated at reflux for 20 h. The mixture was then filtered and the residue washed with ether (300 mL). The combined ethereal filtrates were washed with water (2 × 150 mL) and dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure afforded a yellow oil. Kugelrohr distillation (70 °C, 0.05 mm) of this material gave **5** (2.60 g, 97% yield) as a light yellow liquid. Final purification by GLC (10 ft × 0.25 in. 10% FFAP column, 125 °C) provided **5** as a colorless oil: ^{1}H NMR δ (CDCl$_3$) 6.15 (d, *J* = 10.1 Hz, 2 H, C*H*=CHC=CH$_2$ or CHC*H*C=CH$_2$), 5.94 (d, *J* = 10.1 Hz, 2 H, C*H*=CHC=CH$_2$ or CH=C*H*C=CH$_2$), 5.70 (t, *J* = 2.9 Hz, 2 H, CH=CH), 4.80 (s, 2 H, C=CH$_2$), 2.25–2.12 (m, 4 H, C*H*$_2$CH=CH), 1.71–1.56 (m, 4 H, C*H*$_2$CH$_2$CH=CH); ^{13}C NMR δ (CDCl$_3$) 138.0 (C-3), 137.3 (C-1 and C-5 or C-2 and C-4), 131.2 (C-9 and C-10), 125.0 (C-1 and C-5 or C-2 and C-4), 111.3 (exocyclic methylene C), 41.1 (C-6), 39.0 (C-8 and C-11), 23.7 (C-7 and C-12); IR ν (CCl$_4$) 3095, 3025, 2925, 2845, 1757, 1660, 1587, 1450, 1435, 910, 874 cm^{-1}.

Anal. Calcd for C$_{13}$H$_{16}$: C, 90.64; H, 9.36. Found: C, 90.54; H, 9.36.

General Procedure for Flash-Vacuum Pyrolysis. A horizontal quartz tube (25 × 2.5 cm with a thermocouple insert) was wrapped with Chromel wire (0.4 mm diameter) and asbestos tape. The ends of the wire were connected to a Variac for controlling the temperature. The quartz tube, empty or packed with 3-mm Pyrex beads, was connected via 18/9 ball-and-socket joints to a 10-mL round-bottomed flask at one end and a U-shaped trap at the opposite end. The U trap led to a second trap which was connected to a vacuum pump. The pyrolysis tube was heated to the desired temperature and allowed to equilibrate for 1 h. The starting compound (300–600 mg) then was added to the 10-mL flask, the system was evacuated to 0.05–0.07 mm, and the traps were cooled to –196 °C. The starting material was distilled slowly into the pyrolysis furnace by heating the 10-mL flask in a Kugelrohr oven. The crude products collected in the first trap and were analyzed by GC–MS, GLC, and ^{13}C NMR. The products were separated and purified by GLC or HPLC.

General Procedure for Flow Pyrolysis. Flow pyrolysis was carried out in the apparatus described above for flash-vacuum pyrolysis. However, the 10-mL round-bottomed flask was replaced with a 5-mL bulb which had a hose connection opposite the 18/9 socket joint. A source of dry argon[14] that could be controlled by a needle valve was attached to the bulb. The quartz tube was heated to the pyrolysis temperature, the 5-mL bulb containing the starting material was cooled to –78 °C, and the system was evacuated to 0.07 mm. At this point, argon was bled into the system until the pressure reached 0.80 mm. Once the gas flow was adjusted, the receiver traps were cooled to –78 °C, and the starting material was warmed in an oil bath until it slowly distilled. The crude products were collected in the first trap and were analyzed by GC–MS.

Pyrolysis of 5. Pyrolysis of **5** was carried out by the general procedures described above. The crude product consisted of a white polymeric film and a colorless oil. The oil was found by GC–MS (3 ft × 0.25 in. 2% OV-101 column, 92 °C), GLC (10 ft × 0.25 in. 10% FFAP column, 125 °C), and ^{13}C NMR analysis to contain **5** and **11**. As the temperature of the pyrolysis was increased from 400 to 490 °C, the relative ratio of **5**:**11** varied from 97:3 to 53:47. Purification of the crude oil by GLC (above conditions) gave *cis,cis*-2,5-dimethylene-7-vinylbicyclo[4.3.0]nona-3-ene (**11**) as a colorless oil: ^{1}H NMR δ (CDCl$_3$) 6.11 (s, 2 H, H_a and H_b), 5.60–5.41 (m, 1 H, H_g), 5.03 (d, J = 1.6 Hz, 1 H, H_e), 5.01 (d, J = 1.6 Hz, 1 H, H_c or H_d), 4.96 (d, J = 1.6 Hz, 1 H, H_c or H_d), 4.88 (d, J = 1.6 Hz, 1 H, H_f), 4.78 (ddd, J_{gh} = 16.9 Hz, J_{hi} = 2.3 Hz, J_{hl} = 1.0 Hz, 1 H, H_h), 4.74 (ddd, J_{gi} = 10.0 Hz, J_{hi} = 2.3 Hz, J_{il} = 0.6 Hz, 1 H, H_i), 2.92 (t, J_{jk} = J_{kl} = 8.2 Hz, 1 H, H_k), 2.95–2.78 (m, 1 H, H_j), 2.78–2.63 (m, 1 H, H_l), 2.17–1.78 (m, 3 H, cyclopentyl CH$_2$), 1.68–1.50 (m, 1 H, cyclopentyl CH$_2$); ^{13}C NMR δ (CDCl$_3$) 145.6 (C-2), 143.0 (C-5), 140.9 (C-12), 130.6 and 130.3 (C-3 and C-4), 114.1 and 113.5 (C-11 and C-13), 111.5 (C-10), 49.7, 47.9, and 40.5 (C-1, C-6, and C-7), 30.7 and 30.2 (C-8 and C-9); IR ν (CCl$_4$) 3080, 3030, 2950, 2870, 1675, 1635, 1420, 1340, 1190, 990, 910, 880 cm^{-1}. Exact mass calcd for $C_{13}H_{16}$: 172.125. Found: 172.125.

Pyrolysis of 6. Trienone **6** was pyrolyzed according to the general procedure for flash-vacuum pyrolysis described above. The crude product consisted of a brown polymer and an oil. Analysis of the crude oil by GC–MS (3 ft × 0.25 in. 2% OV-101 column, 110 °C), GLC (6 ft × 0.25 in. 20% SE-30 column, 145 °C), and ^{13}C NMR spectroscopy indicated the presence of starting material and three isomeric $C_{12}H_{14}O$ products. The relative ratios of these four components as a function of temperature are summarized in Table I. Purification of the crude oil by GLC (above conditions) and HPLC (25 cm × 16 mm SI 100 silica column, 1:1 methylene chloride/hexane) gave *cis,cis*-5-methylene-9-vinylbicyclo[4.3.0]-3-nonen-2-one (**21**), *cis,cis*-5-methylene-7-vinylbicyclo[4.3.0]-3-nonen-2-one (**22**), and *trans,trans*-2,4,5a,6,8a,8b-hexahydroacenaphthylen-5(1*H*)-one (**23**) as colorless oils.

Data for 21: ^{1}H NMR δ (CDCl$_3$) 6.96 (d, J = 9.9 Hz, 1 H, H_a), 5.91 (d, J = 9.9 Hz, 1 H, H_b), 5.45 (d, J_{cd} = 1.4 Hz, 1 H, H_c or H_d), 5.45–5.29 (m, 1 H, H_e), 5.34 (d, J_{cd} = 1.4 Hz, 1 H, H_c or H_d), 4.86 (ddd, J_{ef} = 16.8 Hz, J_{fg} = 1.9 Hz, J_{fj} = 1.1 Hz, 1 H, H_f),[15] 4.80 (ddd, J_{eg} = 10.0 Hz, J_{fg} = 1.9 Hz, J_{gj} = 0.9 Hz, 1 H, H_g),[15] 3.23 (t, J_{hi} = J_{ij} = 9.0 Hz, 1 H, H_i), 2.84–2.67 (m, 2 H, H_j, containing H_h t of d at δ 2.78, J_{hi} = J_{hm} = 9.0 Hz, J_{hn} = 3.0 Hz),[16] 2.48–2.30 (m, 1 H, H_n), 2.06–1.85 (m, 1 H, H_m), 1.85–1.70 (m, 1 H, H_k), 1.70–1.57 (m, 1 H, H_l); ^{13}C NMR δ (CDCl$_3$) 200.5 (CO), 147.0 (C-4), 141.4 (C-5), 137.7 (C-11), 127.7 (C-3), 121.6 (C-10), 115.0 (C-12), 50.0, 48.1 and 47.2 (C-1, C-6, and C-9), 29.5 and 25.9 (C-7 and C-8); IR ν (CCl$_4$) 3085, 3030, 2960, 2915, 2895, 1672, 1585, 1450, 1425, 1390, 1335, 1315, 1220, 1125, 995, 918, 907 cm^{-1}. Exact mass calcd for $C_{12}H_{14}O$: 174.104. Found: 174.101.

Data for 22: ^{1}H NMR δ (CDCl$_3$) 6.96 (d, J = 9.9 Hz, 1 H, H_a), 5.91 (d, J = 9.9 Hz, 1 H, H_b), 5.72–5.55 (m, 1 H, H_e), 5.36 (s, 1 H, H_c), 5.20 (s, 1 H, H_d), 4.99 (ddd, J_{eg} = 10.2 Hz, J_{fg} = 1.9 Hz, J_{gj} = 0.6 Hz, 1 H, H_g), 4.87 (ddd, J_{ef} = 17.0 Hz, J_{fg} = 1.9 Hz, J_{fj} = 0.9 Hz, 1 H, H_f), 2.86 (t of d, J_{hi} = J_{hm} = 8.0 Hz, J_{hn} = 2.9 Hz, 1 H, H_h), 2.62 (d of d (pseudo t)), J_{ij} = 11.0 Hz, J_{hi} = 8.0 Hz, 1 H, H_i), 2.46–2.28 (m, 1 H, H_n), 2.28–2.10 (m, 1 H, H_j), 2.02–1.76 (m, 2 H, H_m and H_k), 1.58–1.39 (m, 1 H, H_l); ^{13}C NMR δ (CDCl$_3$) 200.4 (CO), 145.8 (C-4), 140.9 (C-5), 140.6 (C-11), 126.3 (C-3), 121.4 (C-10), 115.7 (C-12), 50.6, 49.6, 49.4 (C-1, C-6, and C-7), 30.3 and 26.0 (C-8 and C-9); IR ν (CCl$_4$) 3095, 3030, 2960, 2900, 2875, 1672, 1585, 1435, 1425, 1390, 1335, 1315, 1220, 1125, 993, 920, 908 cm^{-1}. Exact mass calcd for $C_{12}H_{14}O$: 174.104. Found: 174.102.

Further evidence for the structures of **21** and **22** was obtained by the addition of 0.24 equiv of the shift reagent tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium [Eu(fod)$_3$] to the ^{1}H NMR samples of **21** and **22**. (Higher concentrations of shift reagent could not be used due to severe line broadening.) Since the europium presumably coordinates preferentially with the carbonyl substituent in these compounds,[17] the largest changes in chemical shifts ($\Delta\delta$) are expected for the protons closest to the carbonyls. The most significant changes were observed for the olefinic protons. Consistent with the assigned structures, protons a–d in **21** and **22** are shifted almost identically, with H_b exhibiting the greatest change ($\Delta\delta$ = 0.54 and 0.57 for **21** and **22**, respectively). In contrast, the olefinic protons e–g of trienone **21** are shifted more ($\Delta\delta$ = 0.27, 0.12, and 0.08 for H_e, H_f, and H_g, respectively) than those of the isomeric ketone **22** ($\Delta\delta$ = 0.10, 0.07, and 0.06 for H_e, H_f, and H_g, respectively), reflecting the proximity of the vinyl substituent to the carbonyl in **21**.

Data for 23: ^{1}H NMR δ (expanded convolution difference spectrum in CDCl$_3$) 5.65 (dddd, J_{ab} = 10.3 Hz, J_{ak} = 4.7 Hz, J_{al} = 2.4 Hz, J_{ah} = 2.4 Hz, 1 H, H_a), 5.61–5.47 (m, 2 H, H_b and H_c), 2.95 (dddd, J_{de} = 22.8 Hz, J_{cd} = 6.6 Hz, J_{dg} = 2.1 Hz, J_{dj} = 2.1 Hz, 1 H, H_d), 2.97–2.87 (br m, 1 H, H_g, coincident with the right half of the signal for H_d), 2.79 (dddd, J_{de} = 22.8 Hz, J_{ce} = 6.0 H_z, J_{eg} = 3.0 Hz, J_{ej} = 2.8 Hz, 1 H, H_e), 2.80–2.70 (br m, 1 H, H_h, coincident with the right half of the signal for H_e), 2.70 (ddd, J_{fg} = 10.5 Hz, J_{fl} = 7.2 Hz, J_{fk} = 4.8 Hz, 1 H, H_f), 2.38–2.15 (m, 2 H, H_i and H_j), 2.15–1.77 (m, 3 H, H_k, H_l, and H_n), 1.77–1.62 (m, 1 H, H_m); ^{1}H NMR δ (expanded convolution difference spectrum in 50:50 CDCl$_3$/C$_6$D$_6$, resolution of H_n and H_m) 1.44 (dtd, J_{mn} = 12.6 Hz, J_{hm} = J_{im} = 5.1 Hz, J_{jm} = 1.2 Hz, 1 H, H_m), 1.62 (dtd, J_{mn} = 12.6 Hz, J_{hn} = J_{in} = 10.2 Hz, J_{jn} = 7.0 Hz, 1 H, H_n); ^{1}H NMR δ (expanded convolution difference spectrum in C$_6$D$_6$) 5.42 (dddd, 1 H, H_a), 5.29 (br d, J_{ab} = 10.3 Hz, 1 H, H_b), 5.20–5.14 (m, 1 H, H_c), 2.67–2.56 (m, 3 H, H_d, H_e, and H_f), 2.54–2.42 (m, 1 H, H_g), 2.42–2.29 (m, 1 H, H_h), 2.12–2.01 (m, 2 H, H_i and H_j), 1.85–1.73 (m, 2 H, H_k and H_l), 1.63–1.45 (m, 1 H, H_n), 1.43–1.30 (m, 1 H, H_m); ^{13}C NMR δ (CDCl$_3$) 213.5 (CO), 143.4 (C-2a), 130.0, 124.8, 113.3 (C-3, C-7, and C-8), 44.7 (C-5a), 41.9 (C-8a or C-8b), 37.6 (C-4), 37.2 (C-8a or C-8b), 31.4 (C-2 or C-6), 27.7 (C-2 or C-6), 21.7 (C-1); IR ν (CCl$_4$) 3025, 2935, 2895, 2870, 2855, 1720, 1460, 1435, 1400, 1300, 1280, 1210, 1162, 1000, 910 cm^{-1}. Exact mass calcd for $C_{12}H_{14}O$: 174.104. Found: 174.103.

The assignments of the signals in the ^{1}H NMR of **23** are supported by the changes in chemical shifts ($\Delta\delta$) which occured upon

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[14] Argon was bubbled through a trap maintained at –78 °C to remove traces of water.

[15] The right and left halves of the resonances for H_f and H_g, respectively, are coincident.

[16] Only two thirds of the triplet of doublets for H_h is apparent in this multiplet. Separation of the signal for H_h was achieved by adding 0.12 equiv of the shift reagent tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium [Eu(fod)$_3$] to the NMR sample of **21**.

[17] (a) Pavia, D. L.; Lampman, G. M.; Kriz, G. S., Jr. "Introduction to Spectroscopy"; W. B. Saunders: Philadelphia, 1979; pp 162–163. (b) Reference 7, pp 212–214.

addition of 0.15 equiv of Eu(fod)$_3$ to the NMR sample of **23** in C_6D_6: $\Delta\delta$ 0.07 (H_a), 0.05 (H_b), 0.12 (H_c), 0.46 (H_d, H_e, and H_f), 0.19 (H_g), 0.07 (H_h), 0.06 (H_i and H_j), 0.23 (H_k and H_l), 0.05 (H_m), 0.05 (H_n). These data provided a clear assignment of the resonances due to H_g and H_h. Since H_g is closer to the carbonyl than H_h, the multiplet between δ 2.54 and 2.29 that exhibited the larger shift was assigned to H_g.

The trans,trans stereochemistry assigned to dienone **23** follows from two complementary NOE experiments. In the ^{1}H NMR spectrum of **23** in C_6D_6 with 0.15 equiv Eu(fod)$_3$ present, the signal for H_f overlaps with the signals for H_d and H_e. However, the signals for H_f, H_g, and H_h are well separated from each other. Since neither H_d or H_e will show an NOE when H_g or H_h is saturated, any enhancement of the H_d–H_e–H_f multiplet under these conditions can be attributed to H_f. Irradiation of H_g has no effect on this multiplet. However, saturation of H_h produces an approximately 50% increase in the intensity of the H_d–H_e–H_f signal. It follows that H_f is trans to H_g and cis to H_h.

3-(Dideuteriomethylene)spiro[5.6]dodeca-1,4,9-triene (32). A solution of **6** (800 mg, 4.59 mmol) in anhydrous ether (35 mL) was treated with a solution of *n*-butyllithium (6.43 mmol) and (trideuteriomethyl)triphenylphosphonium bromide (2.64 g, 7.34 mmol) in ether (100 mL) according to the procedure employed for the preparation of **5** from **6**. Kugelrohr distillation (70 °C, 0.05 mm) of the crude product provided **32** (669 mg, 84% yield) as a colorless liquid. The ^{1}H and ^{13}C NMR spectra of the distilled product were identical with those of the undeuterated olefin **5** with the following exceptions: ^{1}H NMR δ ($CDCl_3$) 4.80 ($C{=}CH_2$, absent); ^{13}C NMR δ ($CDCl_3$) 111.3 (exocyclic methylene C, absent).

Pyrolysis of 32. Pyrolysis of **32** was carried out at 450 °C according to the general procedure described above for flash-vacuum pyrolysis. Purification of the crude oil by GLC (10 ft × 0.25 in. 10% FFAP column, 135 °C) gave **32** and *cis,cis*-2-(dideuteriomethylene-5-methylene-7-vinylbicyclo[4.3.0]non-3-ene (**33**) as a colorless oil. The ^{1}H and ^{13}C NMR spectra of the GLC isolated product **33** were identical with those of the undeuterated hydrocarbon **11** with the following exceptions: ^{1}H NMR δ ($CDCl_3$) 5.01 and 4.96 (H_c and H_d, absent); ^{13}C NMR δ ($CDCl_3$) 111.5 (C-10, absent).

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Registry No. **5**, 99018-47-0; **6**, 99018-48-1; **7**, 1614-73-9; **8**, 17328-87-9; **9**, 2401-88-9; **10**, 99018-49-2; **11**, 99018-50-5; **21**, 99018-51-6; **22**, 99018-52-7; **23**, 99018-53-8; **32**, 99018-54-9; **33**, 99018-55-0; **35**, 7148-07-4; **36**, 5473-11-0; **37**, 99018-56-1; (trideuteriomethyl)triphenylphosphonium bromide, 1787-44-6; cyclopentanone, 120-92-3; pyrrolidine, 123-75-1; piperidine, 110-89-4; methyl vinyl ketone, 78-94-4; 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, 84-58-2; methyltriphenylphosphonium bromide, 1779-49-3; acrolein, 107-02-8.

The Nature of Cationic Intermediates Derived from α-Thiophosphoryl and α-Thiocarbonyl Mesylates. Neighboring Thiophosphoryl and Thiocarbonyl Participation

Xavier Creary* and M. E. Mehrsheikh-Mohammadi

Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556

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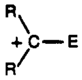
A series of mesylate derivatives of α-hydroxy thiophosphonates, RCH(OMs)PS(OEt)$_2$ (**8**), have been prepared. These mesylates can react by k_c processes under solvolytic conditions if cation stabilizing groups such as *p*-anisyl or *p*-thioanisyl groups are present. However, under conditions of appropriate electron demand, mesylates **8** can react by k_Δ processes involving thiophosphoryl participation. The cyclic intermediate ions capture acetic acid at phosphorus and lead ultimately to α-thio acetate derivatives of phosphonates. This overall transformation converts the P=S function to the P=O group. Rates of acetolyses of **8** can exceed those of the *O*-phosphoryl analogues by large factors when k_Δ processes are involved (as expected for anchimerically assisted processes). Mesylate derivatives of α-hydroxy thio esters, $R_2C(OMs)CSOCH_3$ (**9**), can also react by k_Δ processes as shown by enhanced rates relative to simple ester analogues. The substrate (*R*)-(−)-PhCH(OMs)CSOCH$_3$ (**38**) gives an acetolysis product that is largely retained, while **9** (R = Me) gave a large fraction of a rearranged product. These data all argue in favor of neighboring thiocarbonyl participation in **8**, giving cyclized intermediate cations. The behavior of mesylates **8** and **9** can therefore be quite different from that of the corresponding *O*-phosphoryl and carbonyl analogues. Neighboring group participation in **8** and **9** accounts for the differences. The contrasting behavior of **8** and **9** also argues *against* neighboring phosphoryl or carbonyl participation in solvolyses of mesylate derivatives of α-hydroxy phosphonates or α-keto mesylates.

Our studies[1] and those of others[2–5] have firmly established the existence of carbocations of general type **1** where the group E is formally electron withdrawing relative to hydrogen. Such intermediates **1** can be generated under



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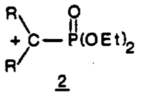

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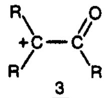

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[1] For examples of cation 1 where E = PO(OEt)$_2$, see: (a) Creary, X.; Geiger, C. C.; Hilton, K. *J. Am. Chem. Soc.* **1983**, *105*, 2851–2858. (b) Creary, X.; Underiner, T. L. *J. Org. Chem.* **1985**, *50*, 2165–2170. For a discussion of the chemistry of cation 1, where E = COR, and leading references, see: (c) Creary, X. *Acc. Chem. Res.* **1985**, *18*, 3–8. (d) Creary, X. *J. Am. Chem. Soc.* **1984**, *106*, 5568–5577. (e) Creary, X.; Geiger, C. C. *Ibid.* **1982**, *104*, 4151–4162.

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