Synthesis and Reactions of (-)- and (+)-Carenones

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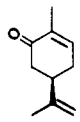
The (-)-carenes contain the same absolute stereochemistry as many cyclopropane-containing sesqui- and diterpenoids and would be valuable synthetic intermediates if they were readily available. We describe here a synthesis of (+)-car-3-en-2-one (3) from (-)-carvone hydrochloride by direct ring closure and a synthesis of (+)-car-2-en-4-one (11) via a sequence involving a Wharton rearrangement. With (+)-carvone hydrochloride as starting material, the previously unavailable (-)-carenones are obtained. Some conversions of these carenones into intermediates for the synthesis of higher terpenoids also are described.

The possibility of converting carvone derivatives into carenones has been recognized for many years. The first report[1] that carvone hydrobromide (**2a**) could be converted into car-3-en-2-one (**3**) by treatment with aqueous base was later corrected by Wallach,[2] who correctly identified eucarvone (**4**) as the product of this reaction. More modern investigations of this transformation were spurred primarily by theoretical considerations, questioning the stability of the carenones[3] and investigating the mechanism of the carenone–eucarvone rearrangement.[4]



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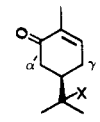
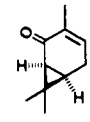


2a X=Br
b Cl
c F



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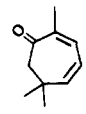

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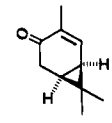

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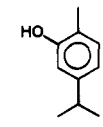

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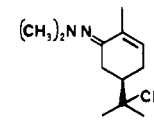
Our interest in this transformation was drawn by a need for quantities of chiral cyclopropanoids to be used in projected syntheses of tigliane and lathyrane diterpenoids. While many carene derivatives have been obtained from nonselective oxidations of carene with potassium permanganate,[5] chromium trioxide,[6] *tert*-butyl chromate,[7] and hydrogen peroxide,[8] these reactions yield complex mixtures and cannot serve as the starting point for any lengthy synthesis. Furthermore, commercially available carenes are uniformly of the wrong absolute stereochemistry to be of use in our project. However, because both carvone enantiomers are readily available, conversion of an appropriate carvone derivative into the carenones could initiate a straightforward route to the required cyclopropanoids.

Ring closure of carvone hydrochloride[9] (**2b**) can be envisioned at the γ-carbon of an extended enolate to afford car-2-en-4-one (**5**) or at the α'-carbon of the cross-conjugated enolate to afford car-3-en-2-one (**3**). Both ketones would be useful intermediates for the synthesis of a large group of sesqui- and diterpenoids. However, from the early work of van Tamelen, it appeared that the α'-product would be difficult to isolate. Despite initial formation of this product upon treatment of carvone hydrobromide with aqueous base, subsequent opening of the cyclopropyl ring gives eucarvone as the major product.[4] Furthermore, γ-alkylation of an extended enolate, a difficult transformation in all but the most favorable cases,[10] has not been reported on a carvone enolate.[11]

Our initial efforts to apply modern methods of enolate formation to carvone hydrochloride were largely disappointing, yielding complicated mixtures of starting material, eucarvone (**4**), carvacrol (**6**), and other components. However, treatment of carvone hydrochloride[9] with 1 equiv of sodium hydroxide in 25% aqueous dimethyl sulfoxide, conditions suggested to allow rapid equilibration of enolates,[12] was found to result in the desired α'-product in reasonable yield, contaminated only with eucarvone. Pure car-3-en-2-one was easily obtained by column chromatography. Obtaining the product of γ-alkylation was a more difficult task. Although this product (i.e., compound **5**) could occasionally be detected to the extent of a few percent in the reaction yielding compound **3**, we were unable to increase this yield to a useful value.

To favor ring closure to the γ-position, it appeared necessary to use a less reactive alkylating agent or to enhance the stability of the extended enolate. To explore the former approach, we prepared carvone hydrofluoride (**2c**),[13] but we were unable to bring about ring closure of its enolates. To explore the latter approach, we prepared carvone hydrochloride dimethylhydrazone (**7**). Corey has



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reported the α-alkylation of carvone dimethylhydrazone,[11] and indeed we obtained some evidence that anions derived

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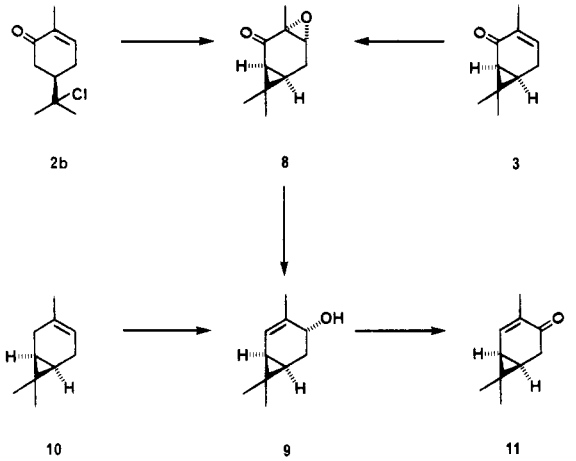
from carvone hydrochloride dimethylhydrazone were capable of undergoing ring closure. However, the question of which product was formed (α'- vs γ-alkylation) became a moot point when we discovered that the cyclopropyl ring did not survive standard conditions for the hydrolysis of the hydrazone.

Instead of pursuing other avenues that might result in ring closure of an extended enolate, we chose to investigate a slightly less direct route. Epoxidation of the carenone **3** with hydrogen peroxide and base affords an epoxide, presumed to be the trans isomer **8** because approach from the β-face of the molecule is hindered by the cyclopropyl ring. The same epoxide results directly from treatment



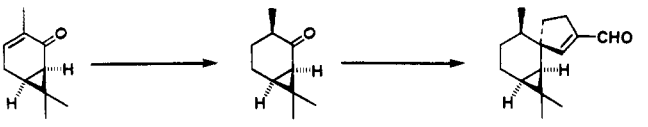
2b 8 3

10 9 11

of carvone hydrochloride with basic hydrogen peroxide.[5] After treatment of this epoxide with hydrazine hydrate, a rearranged allylic alcohol is obtained.[14] The structure of this alcohol was confirmed by an independent synthesis; it proved to be identical with one of the isomers obtained from the rose bengal sensitized photooxidation of (+)-3-carene (**10**).[15] Oxidation of this allylic alcohol **9** with pyridinium chlorochromate (PCC)[16] gives the desired ketone **11**. Although compound **11** is the enantiomer of the ketone resulting from direct γ ring- closure of (−)-carvone hydrochloride (i.e., compound **5**), synthesis of compound **5** by this slightly longer route merely requires starting with (+)-carvone rather than (−)-carvone. Thus both enantiomers of ketone **3** and the two enantiomeric carenones **5** and **11** can now be synthesized from (+)-or (−)-carvone.

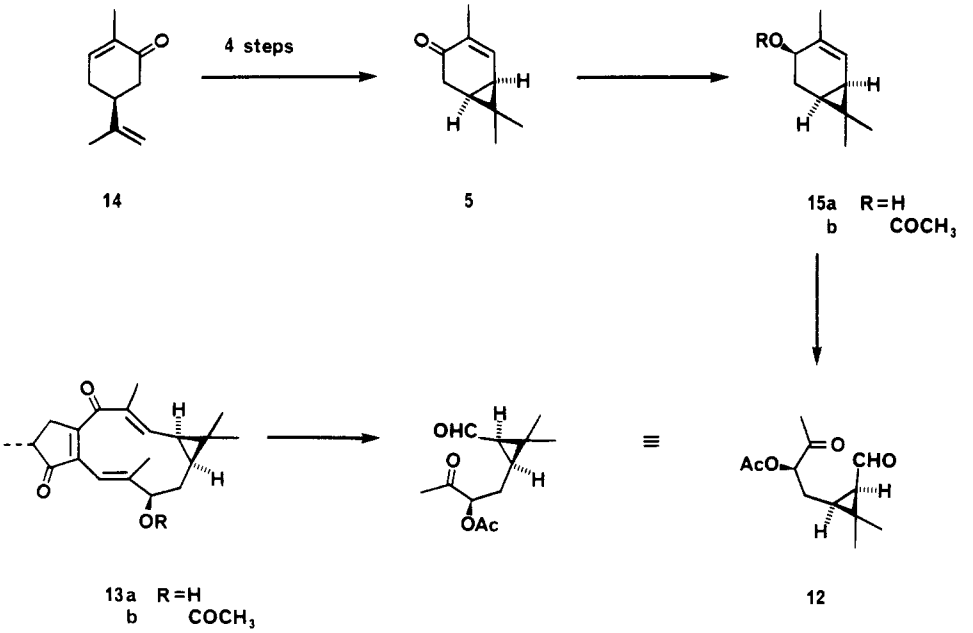
To demonstrate that chiral cyclopropanoids having the absolute stereochemistry of the lathyranoid diterpenes could be obtained by this approach, we undertook synthesis of the ketoaldehyde **12**. This compound has been identified as a degradation product of bertyadionol (**13a**)[17] and would be a useful synthetic intermediate for bertyadionol itself and other lathyranes as well. Starting with (+)-carvone (**14**), the carenone **5** was prepared via the four-step sequence described above (Scheme I). Reduction of this enone to the cis allylic alcohol **15a** was accomplished smoothly upon reaction with sodium borohydride in the presence of cerium chloride.[18] No evidence of conjugate reduction was detected, and only a few percent of the unwanted trans alcohol (which would be the enantiomer of compound **9**) was observed. After esterification with acetic anhydride/4-(dimethylamino)-pyridine,[19] ozonolysis of the allylic acetate gives the keto aldehyde **12**. This material was identical with that derived from the natural product.[17]

The carenone **16**, derived from (+)-carvone, is also a useful synthetic intermediate. For example, catalytic hydrogenation of compound **16** affords (+)-*cis*-caran-2-one (**17**), hydrogenation occurring from the less hindered face of the molecule. That this product is indeed the cis isomer



16 17 18

Scheme I



14 5 15a R=H
b COCH$_3$

13a R=H
b COCH$_3$ 12

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Table I. ^{13}C NMR Data for Carene Derivatives

C	3	8	9	11	15a	15b	17
C-1	33.6[a]	29.8[a]	22.8[a]	23.9[a]	22.6[a]	22.4[a]	33.9[a]
C-2	195.3	200.6	122.7	144.4	120.7	122.4	210.0
C-3	134.2	57.0	137.0	132.9	139.9	135.3	42.5
C-4	141.8	60.4	66.6	196.3	68.4	70.8	28.3
C-5	22.3	18.9	28.2	33.1	30.1	26.7	19.1
C-6	27.8[a]	20.5[a]	17.2[a]	23.2[a]	18.7[a]	18.5[a]	25.5[a]
C-7	20.9	22.7	22.4	24.7	24.7	24.9	23.4
C-8	15.3[b]	14.3[b]	14.8	13.2[b]	15.2	14.9	14.0[b]
C-9	25.6	27.6	27.6	27.4	27.4	27.3	29.7
C-10	13.6[b]	15.1[b]	20.8	15.8[b]	20.5	19.8	17.6[b]
CH_3CO						20.7	
CH_3CO						179.3	

[a,b] These assignments may be reversed.

was shown by its subsequent reaction with sodium ethoxide, which results in isomerization to *trans*-caran-2-one.[20] In a recent synthesis of (+)-vitrenal, Magari et al.[21] used racemic *cis*-caran-2-one, derived from piperitone, as a key intermediate. Use of the (+)-caranone in their sequence would afford the natural product (+)-vitrenal (18).

This investigation has shown that it is practical to use the absolute stereochemistry of the readily available carvones to derive various chiral cyclopropanoids via carene intermediates. Our results on the application of these chiral cyclopropanoids to problems in lathyranoid synthesis will be reported in due course.[22]

Experimental Section

Melting points were obtained on a Thomas-Hoover melting point apparatus and are uncorrected. The ^1H NMR spectra were recorded on a JEOL FX-90Q or a Brucker WM 360 spectrometer, using deuteriochloroform as the solvent. Chemical shifts are reported in the parts per million downfield from internal $(CH_3)_4Si$. The broad-band decoupled ^{13}C NMR spectra were obtained on a FX-90Q spectrometer, but most decoupled spectra were recorded on the Brucker instrument. The following parameters represent a typical set of experimental conditions: spectral width, 6000 Hz; acquisition time, 0.7 s; pulse width, 4.7 μs; data points, 8192. Chemical shifts are reported in parts per million downfield from $(CH_3)_4Si$, using deuteriochloroform as both the solvent and the internal standard (77.0). Low-resolution mass spectra were recorded with a Hewlett-Packard 5985B instrument; only selected ions are reported here. Electron-impact (EI) spectra were obtained at 70 eV; ion abundances are reported as percentages of the most abundant ion. Chemical-ionization spectra were obtained with methane as the reagent gas. High-resolution mass spectra were recorded on an AEI MS-902 instrument at Cornell University, Mass Spectrometry Laboratories. Microanalyses were performed by the Microanalysis Service, University of Iowa.

(+)-Car-3-en-2-one (3). A solution of sodium hydroxide (10.0 g, 0.25 mol) in 50% aqueous dimethyl sulfoxide was added dropwise to a stirred solution of (−)-carvone hydrochloride (48 g, 0.25 mol) in 20% aqueous Me_2SO at 0 °C. After 1 h the reaction was terminated by extracting with ether (3 × 150 mL), and the combined organic extracts were washed with water until the aqueous layer was neutral. The organic layer was then dried (Na_2SO_4) and concentrated in vacuo to afford 43 g of a mixture containing eucarvone (17%), unreacted starting material (40%), and the desired product 3 (42%) by GC. Purification by column chromatography (silica gel, 5% ethyl acetate in hexane) gave (+)-car-3-en-2-one (16.6 g, 67% yield based on unrecovered starting material). This material gave a ^1H NMR spectrum identical with that reported earlier;[5] $[\alpha]_D$ 153°; ^{13}C NMR, see Table I; EI GC–MS, 150 (M^+, 100), 135 (55), 109 (27), 108 (68), 107 (97), 91 (75), 79 (53), 77 (32), 67 (45).

(−)-Carvone Hydrofluoride (2c). A solution of (−)-carvone (1.5 g, 10 mmol) in THF (2.5 mL) was added over 10 min to an ice-cold solution of 70% HF–pyridine (10 mL). After 1.5 h, 20 mL of ice water was added, and the resulting mixture was extracted with methylene chloride (3 × 10 mL). After the combined organic extracts were dried (Na_2SO_4), concentration in vacuo gave (−)-carvone hydrofluoride (1.56 g, 92%) as a thin oil: $[\alpha]_D$ −90°; ^1H NMR δ 6.78 (1, br, H-2), 2.68–2.04 (5, m), 1.79 (3, s, H-7), 1.36 (6, d, J = 22 Hz, H-9,10); ^{13}C NMR δ 199.1 (C-6), 144.2 (C-2), 132.9 (C-1), 95.6 (d, J = 169 Hz, C-8), 44.4 (d, J = 23 Hz, C-4), 39.2 (d, J = 5.9 Hz, C-5), 26.8 (d, J = 4.4 Hz, C-3), 24.9 (d, J = 8.8 Hz, C-9(10)), 23.8 (d, J = 7.3 Hz, C-10(9)), 15.5 (C-7); EI GC–MS, 170 (M^+, 32), 150 (13), 127 (13), 109 (11), 108 (19), 107 (17), 95 (13), 82 (100), 81 (31), (calcd m/z 170.1107, found m/z 170.1100).

(−)-Carvone Hydrochloride Dimethylhydrazone (7). 1,1-Dimethylhydrazine (1.80 g, 30 mmol) and trifluoroacetic acid (114 mg, 1 mmol) were added to a stirred solution of (−)-carvone hydrochloride (3.73 g, 20 mmol) in anhydrous toluene (11 mL). With use of a Dean–Stark trap for azeotropic removal of water, the solution was heated at reflux for 1 h. After cooling to room temperature, the solution was diluted with water (20 mL) and extracted with ether. The combined ether extracts were dried (Na_2SO_4) and concentrated in vacuo to afford the dimethylhydrazone (4.48 g, 98%): ^1H NMR δ 6.08 (1, br s, H-2), 2.53 (6, $N(CH_3)_2$), 1.86 (s, 3, H-7), 1.60 (s, 6, H-9,10), 1.9–2.3 (m, 5); ^{13}C NMR δ 162.7 (C-6), 133.3 (C-1), 132.2 (C-2), 73.0 (C-8), 47.2 ($N(CH_3)_2$), 46.1 (C-4), 30.4 (C-9, 10), 27.8 (C-3), 27.3 (C-5), 18.0 (C-7); EI GC–MS, 228 (M^+, 17), 193 (2), 192 (2), 177 (1), 151 (100), 136 (1), 132 (5), 119 (3), 108 (27), 106 (14) (calcd m/z 228.1393, found m/z 228.1391.

(+)-α-3,4-Epoxycaran-2-one (8). A solution of sodium hydroxide (4 N, 10 mL) was added over 10 min to a solution of (−)-carvone hydrochloride (3.72 g, 20 mmol) and 30% hydrogen peroxide (7.5 mL, 73.5 mmol) in methanol (30 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and stir overnight, and then water (50 mL) was added and the mixture extracted with methylene chloride (3 × 30 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated in vacuo to afford epoxide 8 (2.83 g, 85%). This material gave a ^1H NMR spectrum identical with that reported earlier;[5] ^{13}C NMR, see Table I; EI GC–MS, 166 (M^+, 1), 151 (19), 137 (17), 123 (62), 122 (22), 109 (36), 95 (100), 82 (68); $[\alpha]_D$ +31.3°.

(+)-*trans*-Car-2-en-4-ol (9). Trimethylsilyl chloride (1.02 mL, 8 mmol) was added to a solution of epoxide 8 (665 mg, 4 mmol) and hydrazine hydrate (0.96 mL, 20 mmol) in anhydrous dimethylformamide (6 mL), and the resulting solution was stirred at room temperature for 7 h. The reaction mixture was then diluted with water and extracted with ether (3 × 10 mL), and the combined organic extracts were dried ($MgSO_4$). Evaporation of the ether gave a crude oil (577 mg, 95%), which could be used in the subsequent reactions. Kugelrohr distillation and further purification of the distillate by column chromatography gave 155 mg of pure alcohol 9. This compound gave a ^1H NMR spectrum identical with that previously reported;[5] ^{13}C NMR, see Table I; EI GC–MS 152 (M^+, 3), 137 (9), 134 (12), 119 (50), 110 (9), 109

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(100), 95 (21), 94 (15), 91 (43), 79 (16); $[\alpha]_D$ +189.7°.

(+)-Car-2-en-4-one (11). A solution of the alcohol **9** (88 mg, 0.58 mmol) in methylene chloride (2 mL) was added to a stirred suspension of PCC (230 mg, 1.07 mmol) and sodium acetate (17.5 mg, 0.21 mmol) in methylene chloride. After 3 h, workup in the usual manner[16] gave the desired ketone (74 mg, 85%). This compound gave a ^{1}H NMR spectrum identical with that previously reported;[5] ^{13}C NMR, see Table I; EI GC-MS 150 (M^+, 36), 135 (15), 122 (4), 109 (13), 107 (100), 108 (89), 91 (52), 79 (37), 67 (9).

(-)-*cis*-Car-2-en-4-ol (15a). Sodium borohydride (69 mg, 1.84 mmol) was added to a stirred solution of (-)-car-2-en-4-one (184 mg, 1.22 mmol; prepared via the sequence described above for the (+)-enantiomer) and $CeCl_3 \cdot 7H_2O$ (684 mg, 1.84 mmol) in 10 mL of MeOH. After 30 min, 10 mL of water was added, and the resulting solution was extracted with ether (3 × 10 mL). The combined ether extracts were dried ($MgSO_4$) and then concentrated in vacuo to afford essentially pure (-)-*cis*-car-2-en-4-ol (145 mg, 78%): $[\alpha]_D$ -169°; ^{1}H NMR δ 5.39 (1, br s, H-2), 3.86 (1, br t, J = 6 Hz, H-4), 1.76 (3, s, H-10), 1.06, 0.95 (3, 3, s, s, H-8, H-9); ^{13}C NMR, see Table I; EI GC-MS, 152 (M^+, 1), 137 (7), 134 (7), 119 (43), 110 (8), 109 (88), 95 (32), 94 (100), 91 (52), 79 (43). An analytical sample was obtained by column chromatography.

Anal. Calcd for $C_{12}H_{16}O$: C, 78.90; H, 10.59. Found: C, 79.63; H, 10.58.

(-)-*cis*-Car-2-en-4-yl Acetate (15b). 4-(Dimethylamino)-pyridine (59 mg, 0.48 mmol) and acetic anhydride (39.5 mg, 0.37 mmol) were added to a stirred solution of the alcohol **15a** (56 mg, 0.37 mmol) in 5 mL of methylene chloride, and the resulting solution was stirred overnight at room temperature. After addition of ether (5 mL), the solution was washed first with 2 N HCl and then with 0.5 M sodium bicarbonate and dried ($MgSO_4$). Evaporation of the solvent gave 66 mg (92%) of the desired acetate: $[\alpha]_D$ -69°; ^{1}H NMR δ 5.49 (1, s, H-2), 5.46 (1, br t, J = 8 Hz, H-4), 2.06 (3, s, CH_3CO), 1.64 (3, s, H-10), 1.07, 0.96 (3, 3, s, s, H-8 and H-9); ^{13}C NMR, see Table I; EI GC-MS 134 (18), 120 (10), 119 (100), 117 (5), 109 (8), 93 (12), 91 (23), 77 (7). An analytical sample was obtained by preparative layer chromatography.

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.01; H, 9.51.

Preparation of Keto Aldehyde 12. A solution of methylene chloride (3.6 mL) saturated with ozone at -78 °C was added to a solution of (-)-*cis*-car-2-en-4-yl acetate (12.3 mg, 0.6 mmol) in methylene chloride. After 20 min, dimethyl sulfide (10 μL, 0.13 mmol) was added, and the resulting solution was stirred overnight at room temperature. Evaporation of the volatile materials in vacuo gave compound **12** (12.5 mg, 88%). This material was identical (^{1}H NMR and TLC) with a sample prepared by degradation of bertyadionol;[17] EI GC-MS, 184 ($M^+ - C_2H_2O$, 4), 166 ($M^+ - CH_3CO_2H$, 5), 151 (15), 137 (24), 123 (28), 116 (25), 110 (89), 95 (81), 43 (100); CI GC-MS 227 ($M^+ + 1$, 2), 167 ($M^+ + 1 - CH_3CO_2H$, 100).

(+)-*cis*-Caran-2-one (17). A stirred solution of (-)-Car-3-en-2-one (10.8 g, 72 mmol) in ether (100 mL) was hydrogenated 0 °C and atmospheric pressure over 5% Pd/C. After 1600 mL of hydrogen was consumed, the mixture was filtered and the filtrate concentrated in vacuo to afford essentially pure ketone **17** (10.9 g, 98%). This compound gave a ^{1}H NMR spectrum identical with that reported for the (-)-enantiomer;[20] ^{13}C NMR, see Table I; EI GC-MS, 152 (M^+, 23), 137 (6), 124 (18), 110 (31), 109 (17), 95 (51), 82 (100), 81 (20), 67 (73); $[\alpha]_D$ +83.6.

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Registry No. 1, 6485-40-1; **2b**, 85710-71-0; **2c**, 88390-14-1; **3**, 22327-33-9; **5**, 88390-11-8; **8**, 22327-36-2; **9**, 4017-82-7; **11**, 6617-33-0; **12**, 41437-12-1; **15a**, 88390-12-9; **15b**, 88390-13-0; **16**, 53585-45-8; **17**, 16838-48-5; HF, 7664-39-3.

Synthesis and Ring-Opening Reactions in the 1,3′-Bicyclopropenyl Series

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Several 1,3′-bicyclopropenyl compounds were prepared by treating 1,3,3-trisubstituted cyclopropenes with methyllithium followed by reaction of the lithiate with cyclopropenylium perchlorate derivatives. Thermolysis of a sample of 3-methyl-1-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-2,3-diphenylcyclopropene at 120 °C produced a mixture of diphenylacetylene and (*E*)- and (*Z*)-2,3-diphenyl-2-hexen-4-yne. A reasonable mechanism to account for the formation of these products involves opening of the diphenyl-substituted cyclopropene ring followed by a subsequent fragmentation of the adjacent three-ring system and elimination of the acetylene moiety. In marked contrast to the thermal results, photolysis produced 4-methyl-1,3-diphenyl-2-(1-methyl-2-phenylethenyl)naphthalene. Further irradiation of this material gave a benzo[*c*]phenanthrene derivative by a nonoxidative photocyclization reaction. Formation of the styrylnaphthalene derivative involves addition of the initially generated vinyl carbene across the adjacent cyclopropenyl double bond to produce a spiro diradical. This transient species is converted to the final product via a cyclopropyl ring opening followed by a 1,7-sigmatropic hydrogen shift. Photolysis of bis(2,3-diphenylcycloprop-2-enyl)methane resulted in a novel intramolecular [2 + 2] cycloaddition followed by a facile cycloreversion of the initially produced quadricyclane to give tetraphenylbicyclo[2.2.1]heptadiene.

During the last decade there has been an increasing interest in small ring containing compounds. Some of these strained rings are of theoretical interest, and others are important in synthetic routes or as intermediates in reactions. Small-membered rings are also known to have a tremendous effect on reaction rates and reaction pathways when compared to larger ring containing compounds. Among the multitude of small-ring polycycles, cyclopropene represents one of the more intriguing systems. This molecule was first prepared some 60 years ago[1] but,

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(1) Demyanov, N. Y.; Doyarenko, M. N. *Bull. Acad. Sci. Russ.* **1922**, *16*, 297.

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