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Notes

Reductive Decyanation of β,γ-Epoxy Nitriles. A New Synthesis of β-Isopropylidene Alcohols

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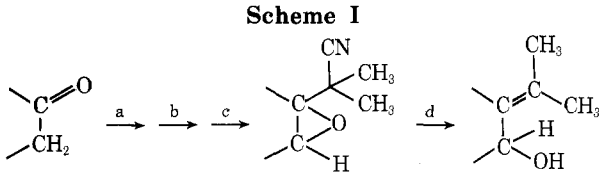
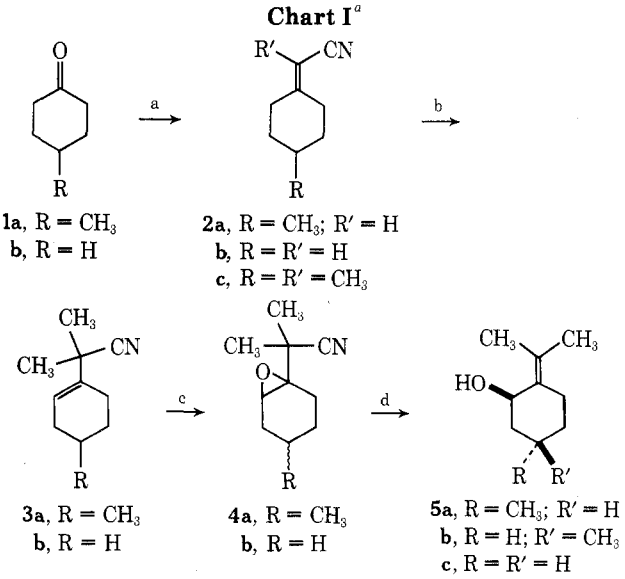
In the course of studies aimed at the synthesis of natural sesquiterpenoids we discovered that β,γ-epoxy nitriles underwent reductive decyanation–elimination to allylic alcohols upon treatment with sodium in liquid ammonia.[1] The epoxy nitriles could be prepared quite easily from ketones by a sequence involving (a) condensation with diethyl sodiocyanomethylphosphate, (b) geminal alkylation with methyl iodide, and (c) epoxidation with *m*-chloroperoxybenzoic acid (Scheme I). Since this initial discovery we have examined a number of additional substrates to ascertain the generality of the sequence and to optimize the reaction conditions. We have also carried out some preliminary studies of the oxidation of the allylic alcohol products. These results are reported herein.

Scheme I



Condensation of 4-methylcyclohexanone (**1a**) with diethyl sodiocyanomethylphosphonate afforded the nitrile **2a.** Alkylation of this nitrile in tetrahydrofuran using excess lithium diisopropylamide as the base and excess methyl iodide gave only the monomethylated conjugated nitrile **2c.** Presumably addition of the amide to the conjugated double bond effectively competes with proton abstraction, as is found for conjugated esters.[2] Schlessinger found that a 1:1 complex of lithium diisopropylamide and hexamethylphosphoric triamide (HMPA) showed a strong preference for proton abstraction in such cases.[2] Following his procedure we obtained an 80:20 mixture of di- and monomethylated product. However, with a 3:1 ratio of HMPA to base, dimethylation proceeded smoothly to give nitrile **3a.** Epoxidation of unsaturated nitrile **3a** afforded the epoxy nitrile **4a** as an apparent mixture of stereoisomers. Reduction–elimination of this mixture with sodium in liquid ammonia gave a roughly 2:1 mixture of alcohols **5a** and **5b,** *trans*- and *cis*-pulegol, in nearly 90% yield (Chart I).

Chart I[a]

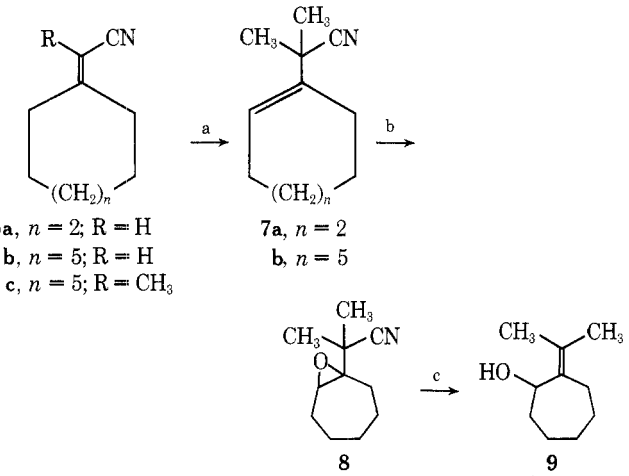


[a] a, $NaCH(CN)PO(OEt)_2$; b, $(i\text{-}Pr)_2NLi$, CH_3I, HMPA; c, $m\text{-}ClC_6H_4CO_3H$; d, Na, NH_3.

Application of the above scheme to cyclohexanone (**1b**) afforded 2-isopropylidenecyclohexanol (**5c**) in 46% overall yield. Similarly, cycloheptanone was converted to 2-isopro-

pylidenecycloheptanol (**9**) in 44% overall yield (Chart II). Work on the cyclodecanone series had to be abandoned because conditions could not be found for effecting complete methylation of the cyclodecylidenenitrile **6b**. Our best attempt afforded a 3:1 mixture of dialkylated (**7b**) and monoalkylated (**6c**) products.

Chart II [a]



6a, $n = 2$; R = H
b, $n = 5$; R = H
c, $n = 5$; R = CH_3

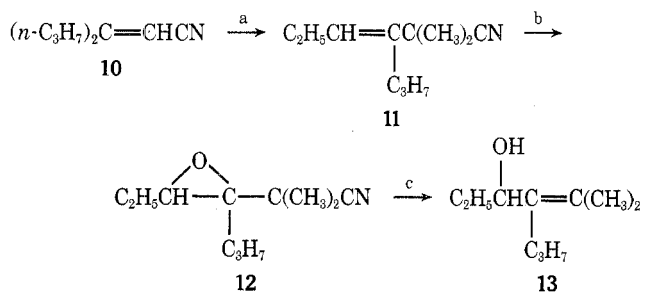
7a, $n = 2$
b, $n = 5$

8 **9**

[a] a, $(i\text{-Pr})_2NLi$, CH_3I, HMPA; b, $m\text{-}ClC_6H_4CO_3H$; c, Na, NH_3.

An acyclic example of the β-alkylidene alcohol synthesis is shown in Chart III. In this case all reactions proceeded smoothly and the alcohol **13** could be prepared in 55% overall yield starting with 4-heptanone. No attempt was made to ascertain the stereochemistry of unsaturated nitrile **11**.

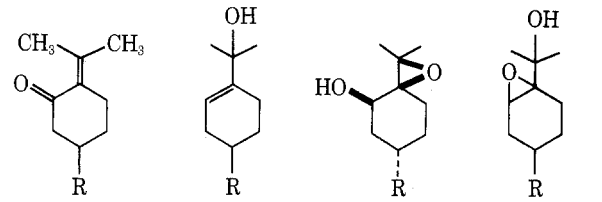
Chart III [a]



10 **11** **12** **13**

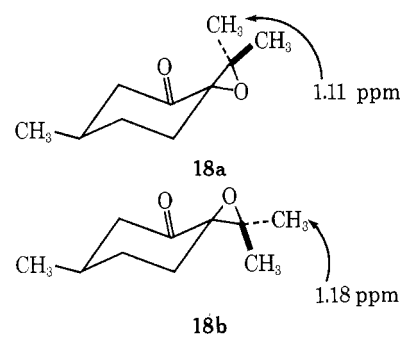
[a] a, $(i\text{-Pr})_2NLi$, CH_3I, HMPA; b, $m\text{-}ClC_6H_4CO_3H$; c, Na, NH_3.

We next examined the oxidation of these allylic alcohols to the isopropylidene ketones. This structural feature is found in a variety of cyclic and acyclic terpenes.[3,4] Attempts to oxidize the methyl isopropylidenecyclohexanol mixture **5a** and **5b** with various chromic acid reagents, including the chromium trioxide–pyridine complex,[5] led to extensive allylic rearrangement. Manganese dioxide showed greater promise, although the results varied considerably with the age of the oxidant. With a fresh batch of MnO_2 in cyclohexane we observed a rapid initial buildup of (±)-pulegone (**14a**) followed by a slow production of material with considerably longer gas chromatographic retention time. One of these products could be assigned the epoxy alcohol structure **16a** on the basis of spectral and gas chromatographic comparison with a sample prepared via epoxidation of the alcohol mixture **5a** and **5b** with *m*-chloroperoxybenzoic acid. Since *cis*-pulegol, obtained by reduction of (+)-pulegone with lithium aluminum hydride,[6] could be oxidized to pulegone in over 80% yield with MnO_2, the anomalous oxidation product **16a** must arise from the *trans*-pulegol (**5a**) present in the mixture. This presumption was further strengthened by the observation that epoxidation of *cis*-pulegol (**5b**) with *m*-chloroperoxybenzoic acid led to rearranged epoxy alcohol **17a** whereas the 2:1 mixture **5a,b** gave mainly the unrearranged epoxide **16a**.



14a, R = CH_3 **15a**, R = CH_3 **16a**, R = CH_3 **17a**, R = CH_3
b, R = H **b**, R = H **b**, R = H **b**, R = H

Further confirmation of structure **16a** for the epoxy alcohol obtained from either MnO_2 or *m*-chloroperoxybenzoic acid oxidation of *trans*-pulegol was secured through oxidation of **16a** with Collin's reagent to the known epoxy ketone **18a**.[7] Epoxidation of natural (+)-pulegone with alkaline hydrogen peroxide afforded the previously reported mixture of this epoxy ketone and the stereoisomer **18b**.[7] Additional support for these stereochemical assignments[7] was derived from the observed chemical shift of the epoxide methyl substituent syn to the ketone carbonyl. Models show that in the cis isomer **18a** this methyl grouping should fall within the shielding cone of the carbonyl grouping whereas the same methyl substituent should be deshielded by the carbonyl grouping in the trans isomer **18b**.[7]



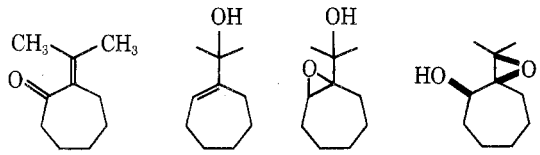
18a **18b**

The MnO_2 oxidation picture was further complicated by the finding that in benzene an older batch of the oxidant gave a mixture of pulegone (**14a**)[8] and the isomerized alcohol **15a** as the major products.[9] Only small amounts of longer retention time materials were produced under these circumstances. Again, a portion of the starting material (**5b**) underwent rapid oxidation to (±)-pulegone; the remainder (**5a**) slowly isomerized. The newer batch of MnO_2 oxidant yielded (±)-pulegone (**14a**) and epoxy alcohol **16a** but no allylic isomer **15a** in benzene. Evidently this remarkable olefin epoxidation reaction depends upon the exact nature of the MnO_2, which is possibly a function of its age. The allylic alcohol grouping no doubt also plays a part in the reaction, since a sample of 9-octalin was recovered unchanged after stirring with MnO_2 in benzene for several days.

Oxidation of 2-isopropylidenecyclohexanol (**5c**) with MnO_2 afforded only a trace of the ketone **14b**. The major product was rearranged alcohol **15b** or the epoxy alcohol **16b** depending upon the batch of MnO_2. Direct epoxidation of alcohol **14b** with *m*-chloroperoxybenzoic acid gave a mixture of isomeric epoxy alcohols **16b** and **17b**.

Oxidation of 2-isopropylidenecycloheptanol (**9**) with MnO_2 afforded the ketone **19** in over 20% yield and either rearranged alcohol **20** or an epoxy alcohol (possibly **21**) depending upon the batch of MnO_2. Direct epoxidation with *m*-chloroperoxybenzoic acid afforded authentic epoxy alco-

hol **22**, whose spectral properties differed from those of the MnO_2-derived material.



19 **20** **21** **22**

Experimental Section[10]

4-Methylcyclohexylideneacetonitrile (2a). The method of Wadsworth and Emmons[11] was employed. To 1.72 g (41.0 mmol) of ether-washed, 57% NaH in mineral oil under an argon atmosphere was added 100 ml of dry 1,2-dimethoxyethane (DME). Diethyl cyanomethylphosphonate (7.26 g, 41.0 mmol) in 20 ml of dry DME was added dropwise with cooling and stirring. After the evolution of hydrogen had ceased, 4.14 g (37.0 mmol) of 4-methylcyclohexanone was added and the reaction mixture was allowed to come to room temperature and to stir overnight. The mixture was poured into 200 ml of water and the product was isolated with ether, affording 3.99 g (80%) of the nitrile **2a:** bp 58–59° (0.5 mm); λ_{max} (film) 4.52, 6.13 μ; δ_{TMS} ($CDCl_3$) 0.92 (d, CH_3, J = 6 Hz), 1.03–3.13 (m, 9 H), 5.09 ppm (s, vinyl H).

Anal. Calcd for $C_9H_{13}N$: C, 79.95; H, 9.69; N, 10.36. Found: C, 79.82; H, 9.94; N, 10.35.

Cyclohexylideneacetonitrile (2b). By the above procedure, 4.12 g of cyclohexanone gave 4.23 g (82%) of nitrile **2b:** bp 88–89° (6 mm); λ_{max} (film) 4.52, 6.12 μ; δ_{TMS} ($CDCl_3$) 1.47–1.88 (s, broad, 6 H), 2.07–2.66 (m, 4 H, allylic CH_2's), 5.05 ppm (m, vinyl H); reported bp 98–100° (12 mm).[12]

Cycloheptylideneacetonitrile (6a). By the above procedure 3.62 g of cycloheptanone gave 3.56 g (81.5%) of nitrile **6a:** BP 94–95° (0.5 mm); λ_{max} (film) 4.52, 6.19 μ; δ_{TMS} ($CDCl_3$) 1.35–2.03 (s, broad, 8 H), 2.24–2.86 (m, 4 H, allylic CH_2's), 5.20 ppm (m, vinyl H).

Anal. Calcd for $C_9H_{13}N$: C, 79.95; H, 9.69; N, 10.36. Found: C, 79.76; H, 9.76; N, 10.32.

Cyclodecylideneacetonitrile (6b). By the above procedure 3.0 g of cyclodecanone gave 2.64 g (78%) of nitrile **6b:** bp 118–120° (0.5 mm); λ_{max} (film) 4.48, 6.14 μ; δ_{TMS} (CCl_4) 1.41–2.01 (m, 14 H), 2.01–2.71 (m, 4 H, allylic CH_2's), 5.20 ppm (s, vinyl H).

Anal. Calcd for $C_{12}H_{19}N$: C, 81.29; H, 10.80; N, 7.90. Found: C, 81.44; H, 11.01; N, 7.68.

3-Propyl-2-hexenenitrile (10). By the above procedure 4.21 g (37.0 mmol) of 4-heptanone gave 3.73 g (74%) of the nitrile **10:** bp 74–75° (0.5 mm); λ_{max} (film) 4.52, 6.15 μ; δ_{TMS} ($CDCl_3$) 0.75–1.05 (m, 6 H, CH_3's), 1.15–1.86 (m, 4 H, homoallylic CH_2's), 1.93–2.54 (m, 4 H, allylic CH_2's), 5.08 ppm (s, vinyl H).

Anal. Calcd for $C_9H_{15}N$: C, 78.78; H, 11.02; N, 10.21. Found: C, 78.96; H, 11.09; N, 10.25.

2-Methyl-2-(4-methyl-1-cyclohexenyl)propanenitrile (3a). The procedure of Herrmann, Kieczykowski, and Schlessinger[2] was modified. To a mixture of 21.3 ml (152 mmol) of diisopropylamine in 120 ml of dry tetrahydrofuran (THF), at 0° under an argon atmosphere, was added, via a syringe, 69.0 ml of 2.2 M butyllithium. After stirring for 15 min at 0° the mixture was cooled to −78° and 82 ml (456 mmol) of dry hexamethylphosphoric triamide (HMPA) was added. After 30 min at −78°, 5.14 g (38 mmol) of 4-methylcyclohexylideneacetonitrile (**2a**) was added in 20 ml of dry THF. After stirring for 15 min at −78° the mixture was quenched with excess methyl iodide (11.4 ml, 114 mmol) and allowed to slowly come to room temperature (1–2 hr). The mixture was poured into 150 ml of water and the product was isolated by extraction with ether. The combined ether extracts were washed with saturated ammonium chloride and with copious amounts of water. After drying and removal of the solvent, 4.67 g (76%) of the alkylated nitrile **3a** was obtained: bp 70–75° (0.5 mm); λ_{max} (film) 4.50, 7.25, 7.35 μ; δ_{TMS} (CCl_4) 0.94 (d, CH_3, J = 6 Hz), 1.41 (s, 6 H, *gem*-dimethyl), 5.84 ppm (m, vinyl H).

Anal. Calcd for $C_{11}H_{17}N$: C, 80.93; H, 10.50; N, 8.58. Found: C, 80.92; H, 10.66; N, 8.52.

When the alkylation was performed as described above but with 27 ml (152 mmol) of HMPA an 80:20 mixture of nitriles **3a** and **2c** was obtained as evidenced by spectral and gas chromatographic analysis.

2-Methyl-2-(1-cyclohexenyl)propanenitrile (3b). By the procedure described above, 4.44 g of cyclohexylidenenitrile (**2b**) gave 5.23 g (79%) of alkylated nitrile **3b:** bp 67–68° (0.5 mm); λ_{max} (film) 4.49, 7.25, 7.35 μ; δ_{TMS} (CCl_4) 1.42 (s, 6 H, *gem*-dimethyl), 1.52–1.78 (m, 4 H), 1.88–2.20 (m, 4 H, allylic CH_2's), 5.86 ppm (m, vinyl H).

Anal. Calcd for $C_{10}H_{15}N$: C, 80.48; H, 10.13; N, 9.39. Found: C, 80.30; H, 10.29; N, 9.34.

2-Methyl-2-(1-cycloheptenyl)propanenitrile (7a). By the procedure described above, 2.70 g of cycloheptylideneacetonitrile (**6a**) gave 2.82 g (86.5%) of nitrile **7a:** bp 78–80° (0.5 mm); λ_{max} (film) 4.55, 7.20, 7.30 μ; δ_{TMS} (CCl_4) 1.42 (s, 6 H, *gem*-dimethyl), 1.96–2.39 (m, 4 H, allylic CH_2's), 6.02 ppm (t, vinyl H).

Anal. Calcd for $C_{11}H_{17}N$: C, 80.93; H, 10.50; N, 8.58. Found: C, 80.71; H, 10.58; N, 8.45.

3-Propyl-2,2-dimethyl-3-hexenenitrile (11). By the procedure described above, 2.75 g (20 mmol) of 3-propyl-2-hexenenitrile (**10**) gave 2.92 g (89%) of the alkylated nitrile **11:** bp 48–49° (0.5 mm); λ_{max} (film) 4.49, 7.20, 7.31 μ; δ_{TMS} (CCl_4) 1.52 (s, 6 H, *gem*-dimethyl), 1.83–2.60 (m, 4 H, allylic CH_2's), 5.35 ppm (t, J = 8 Hz, vinyl H).

Anal. Calcd for $C_{11}H_{19}N$: C, 79.94; H, 11.59; N, 8.47. Found: C, 79.76; H, 11.79; N, 8.50.

2-Isopropylidene-5-methylcyclohexanol (5a,b). A solution of 4.0 g (24.6 mmol) of the cyclohexenylpropanenitrile (**3a**) and 8.5 g (49.2 mmol) of *m*-chloroperoxybenzoic acid (97%) in 100 ml of dichloromethane was stirred at room temperature overnight. The reaction mixture was poured into 25 ml of 10% sodium sulfite solution and the organic layer was separated, washed with water, and dried. The solvent was removed to give 4.3 g (98%) of epoxy nitrile **4a:** λ_{max} (film) 4.45, 7.20, 7.40 μ; δ_{TMS} (CCl_4) 0.88 (d, CH_3, J = 6 Hz), 1.29 and 1.32 (s, 6 H, *gem*-dimethyl), 3.13–3.30 ppm (m, 1 H).

The reduction procedure of Arapakos, Scott, and Hubert[13] was followed. To a solution of 3.8 g (167 mmol) of sodium in 250 ml of liquid ammonia was added 4.0 g (22.3 mmol) of the epoxy nitrile **4a** in 6 ml of dry ether. After 20 min excess ammonium chloride was added to discharge the blue color, the ammonia was evaporated, and the residue was dissolved in 200 ml of water. Extraction with ether afforded 3.0 g (87%) of the alcohol **5a,b:** bp 90–91° (0.5 mm); λ_{max} (film) 3.05, 6.00 μ; δ_{TMS} (CCl_4) 0.85 and 1.10 (d, J = 6 Hz, CH_3's in trans and cis isomers **5a** and **5b**), 1.66–1.80 (m, vinyl CH_3's), 4.48–4.84 ppm (m, carbinyl H's).

Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.73; H, 11.92.

2-Isopropylidenecyclohexanol (5c). Using the procedure described above, 4.12 g of cyclohexenyl nitrile **3b** gave 4.44 g of epoxy nitrile **4b:** λ_{max} (film) 4.50, 7.20, 7.30 μ; δ_{TMS} (CCl_4) 1.29 and 1.32 (s, 6 H, *gem*-dimethyl), 3.22 ppm (m, 1 H).

Reduction of the epoxy nitrile as described above gave the allylic alcohol **5c** in 84– yield. Purification was effected by sublimation (60°, 0.5 mm): mp 54–56°; λ_{max} (KBr) 3.15, 6.02 μ; δ_{TMS} (CCl_4) 1.64 and 1.71 (s, 6 H, CH_3's), 2.62 (s, 1 H, OH), 4.74 ppm (m, 1 H, carbinyl H).

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.84; H, 11.72.

2-Isopropylidenecycloheptanol (9). Using the procedure described above, 1.49 g of the cycloheptenyl nitrile **7a** gave 1.48 g (90%) of the epoxy nitrile **8:** δ_{TMS} (CCl_4) 1.30 (s, CH_3's), 3.07–3.24 ppm (m, 1 H).

Reduction of the epoxy nitrile afforded the allylic alcohol **9** in 70% yield: bp 100° (bath temperature) (5 mm); λ_{max} (film) 3.00, 6.00 μ; δ_{TMS} (CCl_4) 1.68 and 1.74 (s, 6 H, CH_3's), 4.40–4.74 ppm (m, carbinyl H).

Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.89; H, 12.00.

4-Isopropylidene-3-hexenol (13). Using the above procedure, 2.23 g of 3-propyl-2,2-dimethyl-3-hexenylnitrile (**11**) gave 2.17 g (89%) of the epoxy nitrile **12:** λ_{max} (film) 4.50, 7.22, 7.37 μ; δ_{TMS} (CCl_4) 1.40 and 1.46 (s, 6 H, *gem*-dimethyl), 3.20 ppm (t, J = 6 Hz, 1 H).

Reduction of the epoxy nitrile **12** as described above gave the allylic alcohol **13** in 75% yield: bp 75–80° (bath temperature) (16 mm); λ_{max} (film) 2.92, 6.13 μ; δ_{TMS} (CCl_4) 1.66 (s, 6 H), 4.41 ppm (t, J = 6 Hz, carbinyl H).

Anal. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.66; H, 13.16.

Oxidation of 2-Isopropylidene-5-methylcyclohexanol (5a,b). A. With Manganese Dioxide. A solution of 1.82 g (11.7 mmol) of 2-isopropylidene-5-methylcyclohexanol (**5a,b**) in 400 ml of cyclohexane was treated with four 20-g portions of powdered manganese dioxide over a 24-hr period until only a trace of starting alcohol could be detected in the gas chromatogram of an aliquot.

The mixture was filtered, the filter cake was washed with 400 ml of cyclohexane, and the filtrate was concentrated and distilled, giving 0.54 g (30%) of (±)-pulegone (**14a**), bp 85° (bath temperature) (0.4 mm), whose spectral properties and GC retention times matched those of an authentic sample of natural pulegone.[7]

The expended manganese dioxide was thoroughly extracted with ether in a Soxhlet extractor to give 0.72 g of epoxy alcohol **16a,** bp 90° (bath temperature) (0.4 mm). Redistillation (60°, 0.2 mm) gave a sample which crystallized upon standing. Recrystallization from hexane at 0° yielded colorless, cubic crystals, mp 43–44°.

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.57; H, 10.66. Found: C, 70.43; H, 10.87.

When the above oxidation was performed in benzene with an older batch of MnO_2, gas chromatographic analysis showed a mixture of (±)-pulegone (35%), allylic alcohol **15a** (40%), and long retention time material (25%).

B. With *m*-Chloroperoxybenzoic Acid. To a solution of 0.68 g (4.4 mmol) of isomeric pulegols **5a** and **5b** in 50 ml of methylene chloride was added 1.04 g (6.65 mmol) of solid *m*-chloroperoxybenzoic acid. The mixture was stirred overnight, diluted with ether, and washed with sodium sulfite and sodium bicarbonate. Drying and removal of solvent under reduced pressure gave 0.75 g (100%) of an oily mixture of epoxy alcohols **16a** and **17a:** λ_{max} (film) 2.93, 6.89, 7.27, 9.63 μ; δ_{TMS} (CCl_4) 3.65 (m, carbinyl H of **16a**), 3.25 (m, carbinyl H of **17a**), 1.32 (s, *gem*-CH_3's of **16a**), 1.16 (s, *gem*-CH_3's of **17a**) 0.90 ppm (d, J = 6 Hz, CH_3 of **16a** and **17a**). Integration of the NMR spectrum indicated a 3:1 mixture of **16a** and **17a.**

Epoxidation of Allylic Alcohol 15a. The above procedure was applied to 0.93 g (6.0 mmol) of allylic alcohol **15a** to give 0.95 g (92%) of epoxy alcohol **17a** upon distillation (50°, 0.04 mm): λ_{max} (film) 2.93, 6.89, 7.45, 8.65, 10.46, 11.80 μ; δ_{TMS} (CCl_4) 3.25 (m, carbinyl H), 1.15 (s, *gem*-CH_3's), 0.90 ppm (d, J = 6 Hz, ring CH_3).

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.57; H, 10.66. Found: C, 70.30; H, 10.83.

Epoxidation of Pulegone. To a stirred solution of 6.08 g (40.0 mmol) of (+)-pulegone (**14a**), 40 ml of methanol, and 11.5 ml of 30% hydrogen peroxide at 15° was added 3.3 ml of 6 *N* aqueous sodium hydroxide. After 3 hr water was added and the mixture was extracted with ether to give 6.04 g (90%) of epoxy ketones **18a** and **18b:** bp 65° (bath temperature) (0.2 mm); λ_{max} (film) 5.78, 6.85, 7.29 μ; δ_{TMS} (CCl_4) 1.36 (s, anti CH_3 of **18a** and **18b**), 1.18 (s, syn CH_3 of **18b**), 1.11 (s, syn CH_3 of **18a**), 1.08 ppm (d, J = 6 Hz, ring CH_3 of **18a** and **18b**).[7]

Oxidation of Epoxy Alcohol 16a. Collin's reagent was prepared from 1.20 g (12.0 mmol) of chromic anhydride and 1.86 ml (24.0 mmol) of pyridine.[5] To the stirred mixture was added 0.34 g (2.0 mmol) of epoxy alcohol **16a** (from MnO_2 oxidation of alcohol **5a,b**) in 5 ml of methylene chloride. After 15 min, the mixture was extracted with ether, washed with 5% NaOH, 5% HCl, $NaHCO_3$, and brine, and dried over magnesium sulfate to give 0.30 g of solid ketone **18a.** Crystallization from pentane afforded 0.15 g (45%) of needles: mp 77–78°; λ_{max} (film) 5.78, 6.85, 7.29 μ; δ_{TMS} (CCl_4) 1.36 (s, anti CH_3), 1.11 (s, syn CH_3), 1.08 ppm (d, J = 6 Hz, ring CH_3). An additional recrystallization from pentane gave the analytical sample, mp 78.5–79.5°.

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.41; H, 9.59. Found: C, 71.67; H, 9.72.

The identical material, mp 78–79°, was obtained upon oxidation, as described above, of epoxy alcohol **16a** obtained from alcohol **5a,b** via *m*-chloroperoxybenzoic acid epoxidation.

Oxidation of 2-Isopropylidenecyclohexanol (5c). A. With Manganese Dioxide. A solution of 1.06 g (7.6 mmol) of 2-isopropylidenecyclohexanol (**5c**) in 250 ml of cyclohexane was stirred with 20 g of activated manganese dioxide at room temperature for 5 hr, at which time an additional 20 g of MnO_2 was added. Stirring was continued for 13 hr, the solid was filtered and washed with cyclohexane, and the filtrate was concentrated under reduced pressure. The residue was purified by thick layer chromatography on silica gel (20% ether–benzene development) and distillation (60°, 0.2 mm) to give 0.043 g (4%) of 2-isopropylidenecyclohexanone (**14b**):[4] λ_{max} (film) 5.92, 6.21 μ; δ_{TMS} (CCl_4) 1.90, 1.73 ppm (vinyl CH_3's).

Extraction of the solid manganese dioxide with ether afforded 0.44 g of epoxy alcohol **16b:** bp 80° (bath temperature) (0.2 mm); λ_{max} (film) 2.97, 10.03, 11.62 μ; δ_{TMS} (CCl_4) 3.60 (m, carbinyl H), 2.72 (s, OH), 1.27 ppm (s, *gem*-CH_3's).

Anal. Calcd for $C_9H_{16}O_2$: C, 69.20; H, 10.33. Found: C, 68.94; H, 10.55.

B. With *m*-Chloroperoxybenzoic Acid. According to the procedure outlined above for alcohol **5a,b,** 0.29 g (2.1 mmol) of 2-isopropylidenecyclohexanol (**5c**) afforded 0.32 g of epoxy alcohols **16b** and **17b:** λ_{max} (film) 2.95, 10.03, 11.60 μ; δ_{TMS} (CCl_4) 3.60 (m, carbinyl H of **16b**), 3.21 (m, carbinyl H of **17b**), 1.27 (s, *gem*-CH_3's of **16b**), 1.16, 1.10 ppm (*gem*-CH_3's of **17b**).

Oxidation of 2-Isopropylidenecycloheptanol (9). A. With Manganese Dioxide. The procedure described for alcohol **5a,b** was applied to 0.93 g (6.0 mmol) of 2-isopropylidenecycloheptanol (**9**) affording 0.19 g (21%) of ketone **19:** bp 80° (bath temperature) (0.2 mm); λ_{max} (film) 5.93, 6.24 μ; δ_{TMS} (CCl_4) 1.79, 1.74 ppm (s, vinyl CH_3's).

Extraction of the solid MnO_2 with ether yielded 0.15 g of oil containing ketone **19** plus alcoholic material whose NMR spectrum was compatible with a rearranged epoxy alcohol structure **21:** λ_{max} (film) 2.97, 5.93, 6.24 μ; δ_{TMS} (CCl_4) 3.21 (t, carbinyl H), 1.17, 1.10 ppm (*gem*-CH_3's).

B. With *m*-Chloroperoxybenzoic Acid. The procedure described for alcohol **5a,b** was applied to 0.60 g (3.9 mmol) of 2-isopropylidenecycloheptanol (**9**), affording 0.63 g (95%) of epoxy alcohol **22:** bp 80° (bath temperature) (0.2 mm); λ_{max} (film) 2.90 μ; δ_{TMS} (CCl_4) 3.61 (m, carbinyl H), 2.80 (s, OH), 1.31 ppm (s, *gem*-CH_3's).

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.57; H, 10.66. Found: C, 70.71; H, 10.93.

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Registry No.—**1a,** 589-92-4; **1b,** 108-94-1; **2a,** 54353-77-4; **2b,** 4435-18-1; **2c,** 54353-78-5; **3a,** 54353-79-6; **3b,** 54353-80-9; *cis*-**4a,** 54353-81-0; *trans*-**4a,** 54382-84-2; **4b,** 54353-82-1; **5a,** 18649-91-7; **5b,** 29910-20-1; **5c,** 54353-83-2; **6a,** 22734-05-0; **6b,** 54353-84-3; **7a,** 54353-85-4; **8,** 54353-86-5; **9,** 54353-87-6; **10,** 54353-88-7; **11,** 54353-89-8; **12,** 54353-90-1; **13,** 54353-91-2; (±)-**14a,** 3285-04-9; (+)-**14a,** 89-82-7; **14b,** 13747-73-4; **15a,** 25910-97-8; **16a,** 54382-85-3; **16b,** 54353-92-3; **17a,** 54382-86-4; **17b,** 54353-93-4; **18a,** 7599-91-9; **18b,** 13902-36-8; **19,** 23438-72-4; **21,** 54353-94-5; **22,** 54353-95-6; cycloheptanone, 502-42-1; diethyl cyanomethylphosphonate, 2537-48-6; cyclodecanone, 1502-06-3; 4-heptanone, 123-19-3; hexamethylphosphoric triamide, 49778-01-0; manganese dioxide, 1313-13-9; *m*-chloroperoxybenzoic acid, 937-14-4.

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of polystyrene. Nuclear magnetic resonance spectra were recorded with a Varian T-60 spectrometer. Signals are reported as the chemical shift downfield from tetramethylsilane (TMS) in parts per million (ppm) of the applied field. The multiplicity of the peak is abbreviated: singlet, s; doublet, d; triplet, t; quartet, q; and multiplet, m. Coupling constants are reported in hertz. Melting points were determined on a calibrated Thomas capillary melting point apparatus. Melting points are not corrected.

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Iodonium Ylides. Reactions of Phenyldimedonyliodone with Diphenylketene and Phenyl Isocyanate

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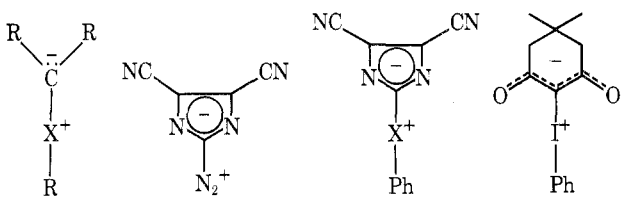
While the chemistry of phosphorous, nitrogen, and sulfur ylides has been studied extensively,[1] little is known of the halogen ylides. Halonium ylides of general structure **1** have been proposed when various carbenes are generated in the presence of alkyl and aryl halides,[2] but their high reactivity has largely precluded their isolation and study. We know of only one report concerning the formation of stable halonium ylides by carbene trapping. Sheppard and Webster[3] found that the thermal decomposition of 3,5-dicyanodiazoimidazole (**2**) in chlorobenzene, bromobenzene, or iodobenzene gave the corresponding chloronium, bromonium, and iodonium ylides **3a, 3b,** and **3c.** Some iodonium ylides have also been prepared by a different method which involves the treatment of various β-diketones and β-keto esters with aryliodoso compounds.[4,5] For example, phenyldimedonyliodone (**4**),[6,7] one of the most stable iodonium yl-

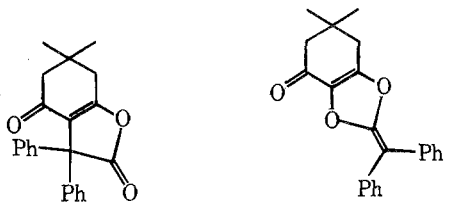


1 **2** **3a**, X = Cl; **b**, X = Br; **c**, X = I **4**

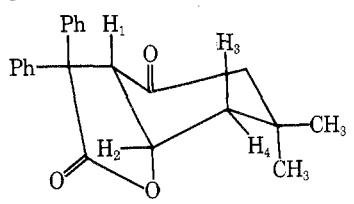
ides, has been synthesized in high yield by condensation of iodosobenzene with dimedone in the presence of acetic anhydride.[5] However, chemical studies on **4** have been limited to its reactivity toward highly electrophilic agents and to its proclivity for nucleophilic cleavage and thermal decomposition and rearrangement.[6,8] We were, therefore, prompted to initiate a systematic study of **4** in order to *begin* to elaborate the chemical properties of halonium ylides. In this note, we describe reactions of **4** with two representative electrophilic heterocumulenes.

When phenyldimedonyliodone (**4**) was allowed to react with diphenylketene in dichloromethane at room temperature, lactone **5** and ketene acetal **6** were *isolated* in yields of 32 and 44% by column chromatography on Florasil. Iodobenzene is also formed in this reaction, and, in a control study, the yield of iodobenzene was determined by GLC analysis to be 99%. The structures of **5** and **6** were initially deduced from spectral (ir, NMR, uv, mass) and analytical (C, H) data.

The mass spectra of both compounds show the expected molecular ion peaks at *m/e* 332. However, while the parent ion peak in the spectrum of **5** is also the base peak, the base peak in the spectrum of **6** is at *m/e* 166 and must be that of a fragment ion derived from scission of the exocyclic carbon–carbon double bond. The ^{1}H NMR spectra of **5** and **6**



5 **6**



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are similar in that each exhibits a six-hydrogen singlet, a pair of two-hydrogen singlets, and a ten-hydrogen phenyl resonance. Their uv spectra are also similar, but the absorption maximum (α,β-unsaturated ketone) in the spectrum of **6** is red shifted by 11 mμ relative to that of **5**. The ir spectrum of **5** exhibits carbonyl bands at 5.50 (lactone) and 5.99 μ (ketone) while the ir spectrum of **6** shows a carbonyl band at 6.01 μ (ketone) and exocyclic double-bond absorption at 5.78 μ. Finally, the melting point of **6** is 60° higher than that of **5**, presumably because of its greater molecular symmetry.

The structure assigned to **5** was confirmed by its catalytic hydrogenation in 54% yield to the saturated lactone **7**, which was in turn characterized by its elemental composition (C, H) and spectra (ir, NMR, uv, mass). In particular, the ir spectrum of **7** exhibits a carbonyl band at 5.72 μ as expected for a saturated γ-lactone while the uv spectrum shows only benzenoid absorption at 259 mμ (ε 633). The ^{1}H NMR spectrum of **7** exhibits *two* methyl singlets at δ 0.87 and 0.81, a ten-line multiplet at δ 5.0 (H-2, $J_{2,3} \simeq 11$, $J_{2,1} \simeq 8.5$, $J_{2,4} \simeq 6.5$ Hz), a doublet at δ 4.42 (H-1, $J_{1,2} \simeq 8.5$ Hz), and complex multiplets for the phenyl and methylene hydrogens. The doublet resonance for H-1 at δ 4.42 may seem anomalously downfield for a proton in that environment. However, inspection of Dreiding models indicates very clearly that H-1 lies in the deshielding region of one of the benzene rings.

The structure assigned to **6** was confirmed by oxidative cleavage of the exocyclic carbon–carbon double bond. When **6** was allowed to react with ozone and treated subsequently with basic hydrogen peroxide, benzophenone was isolated in 66% yield and characterized as its 2,4-dinitrophenylhydrazone. The ketene acetal proved remarkably resistant to hydrolysis. Even when **6** was warmed to dissolution in concentrated sulfuric acid and poured into water, it was recovered unreacted in 86% yield. The inertness of **6** toward hydrolytic cleavage may reflect the aromaticity of its conjugate acid **8**.

The production of iodobenzene, lactone **5**, and acetal **6** is a consequence of *formal* 1,3-addition of the dimedonyl unit in **4** to either the carbon–carbon or carbon–oxygen double bond of diphenylketene. There are not sufficient data to allow commitment to any one of several possible mechanisms for this reaction, but we would like to discuss specifically the mechanism shown in Scheme I. It seems reason-