at 0 °C and was then poured over ice containing 2 N hydrochloric acid (4 equiv). The product was then extracted into ether. The ether solution was dried and evaporated under vacuum, and the product was distilled.

3,3,5,5-Tetramethylcyclohexanone (18). By the above procedure compound **18** was formed in 76% yield from 16 g (0.1 mol) of chloride **7a** and in 80% yield from 20 g (0.1 mol) of bromide **8b**. Compound **18** was purified by distillation, bp 82–83 °C (9 mm), n^{20}D 1.4521 [lit.[29] bp 59–61 °C (5.5 mm), n^{20}D 1.4520].

2-Ethyl-3,3-dimethylcyclohexanone (19). By the above procedure compound **19** was formed in 62% yield from 4 g (0.026 mol) of chloride **13** and was purified by distillation, bp 86 °C (6 mm), n^{25}D 1.4556.

Anal. Calcd for $C_{10}H_{18}O$: C, 77.92; H, 11.69. Found: C, 78.17; H, 11.87.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research and also to the University Research Council, University of North Carolina, for partial support.

Registry No.—**7a,** 17530-69-7; **7b,** 13271-49-3; **8,** 17520-15-9; **10,** 35173-23-0; **11,** 22592-18-3; **13,** 61426-12-8; **14,** 57237-89-5; **15,** 34019-86-8; **16,** 57238-62-7; **17,** 60018-04-4; **18,** 14376-79-5; **19,** 61426-13-9.

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Selective Reductive Cleavage of the Propargyl Oxygen Bond of Acetylenic Epoxides. A General Synthesis of 2-Ethynylcycloalkanones

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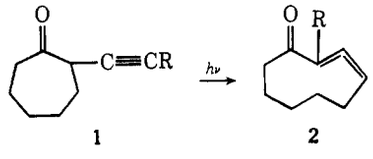
Received October 14, 1976

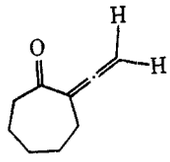
The reduction of the acetylenic epoxides **9** with lithium in liquid ammonia leads to the selective cleavage of the propargyl oxygen bond and produces a mixture of *cis*- and *trans*-2-ethynylcycloalkanols. The 2-ethynylcycloalkanols can be oxidized to 2-ethynylcycloalkanones which are useful substrates for photochemical ring expansions.

2-Alkynylcycloalkanones, e.g., **1,** on photolysis undergo a novel two-atom ring expansion to produce the interesting cyclic allenones **2.**[1,2] Although the cyclopentyl, cyclohexyl, and cycloheptyl analogues of **1** are readily prepared by reaction of acetylide anion or a substituted acetylide anion with the corresponding cycloalkene oxide and careful oxidation of the resulting alcohol,[1,2] this method fails with higher homologues because of the inertness of the cycloalkene oxides to carbon nucleophiles. Consequently, we sought a general method for the preparation of 2-ethynylcycloalkanones which would be applicable to a variety of ring sizes and which would use the readily available cyclic ketones as starting materials. Fur-



1 2

thermore, because 2-alkynylcycloalkanones such as 1 undergo a facile acid- or base-catalyzed isomerization to the conjugated allenones **3**, we preferred to generate them as needed by oxidation of the corresponding alcohols **4**.



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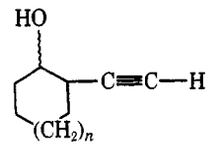

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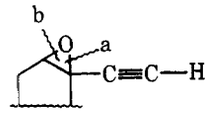
In considering potential routes to the required 2-ethynylcycloalkanols **4** we considered the possibility that an acetylenic epoxide **5**, potentially readily available from the corresponding

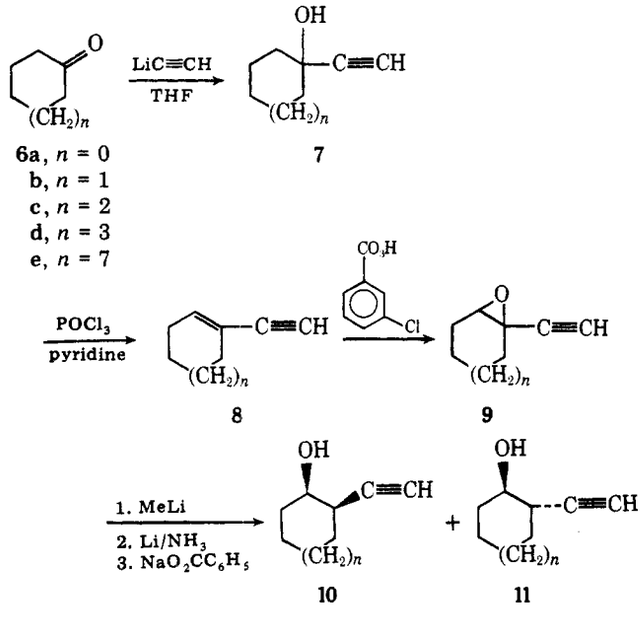


5

cycloalkanone, might undergo selective reductive cleavage of bond a when treated with an alkali metal in liquid ammonia. Although such reductive openings of epoxides are well known,[3] two problems were anticipated in the case of **5**. First, the reductive opening of unsymmetrical epoxides usually proceeds to give the more substituted alcohol (cleavage of bond b), and secondly, acetylenes themselves are readily reduced under similar conditions. However, we felt that the acetylene functional group might provide sufficient activation of the propargyl C–O bond that the reductive cleavage might proceed in the desired direction and this would overcome the first of the anticipated problems. It also seemed likely that the second problem could be overcome by prior formation of the acetylide anion, a standard method used to prevent reduction of acetylenes when other functional groups are reduced by alkali metals in liquid ammonia.[4]

The required acetylenic epoxides **5** were readily prepared by the general route shown in Scheme I. This route to the

Scheme I



acetylenic epoxides utilized standard methods and the overall yields were very good except in the case in which $n = 0$, where the high volatility of some of the intermediates led to loss of material.

Initial studies of the reduction of the epoxy acetylenes **9** were conducted with the cyclohexyl analogue **9b** because one of the expected reduction products, *trans*-2-ethynylcyclohexanol (**11b**), is a known compound. Treatment of **9b** with lithium in liquid ammonia produced a mixture of alcohols in good yield which contained the desired *cis*- and *trans*-2-ethynylcyclohexanols. The NMR spectrum of the product, however, indicated that overreduction had occurred and ~15% olefinic alcohols had been produced as well.

Table I. Reduction of Epoxy Acetylenes (9 → 10 + 11)

Epoxy acetylene (9) n	Yield, %[a]	Cis/trans
0	63	1:3
1	92	7:3
2	81	4:6
3	90	
7	85	

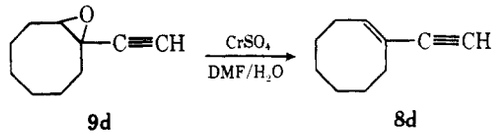
[a] Yields are isolated yields of purified materials.

It was found that the overreduction could readily be prevented by converting the terminal acetylene to its anion prior to reduction. The optimum procedure involved the cautious addition of 1 equiv of methyllithium in ether to a solution of the acetylenic epoxide in liquid ammonia–ether prior to reduction. With this procedure **9b** was smoothly reduced with no overreduction, and a 7:3 mixture of *cis*- and *trans*-2-ethynylcyclohexanols was obtained in 92% distilled yield. Sodium benzoate was used to destroy excess lithium in these reductions because of indications in the literature that ammonium chloride will protonate anions more rapidly than it destroys excess lithium.

Table I summarizes the purified yields of alcohols obtained by this procedure. In each case a mixture of *cis*- and *trans*-acetylenic alcohols was obtained as indicated in Scheme I and Table I. The fact that a mixture is obtained presents no difficulty in our work because oxidation of either isomer produces the same acetylenic ketone.

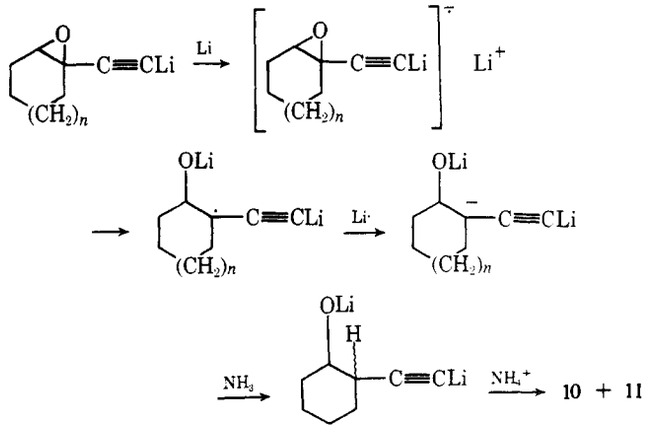
When the reduction was carried out on the cyclododecyl system **9e** a 6% yield of ethylidenecyclododecane was obtained in addition to an 85% yield of a mixture of *cis*- and *trans*-2-ethynylcyclododecanols. This product presumably arises by deoxygenation of the epoxide[3a] to the enyne and subsequent reduction.

We also examined the use of chromium(II) sulfate[5] as a reagent for the reduction of the epoxy acetylenes. However, the reduction of epoxy acetylene **9d** gave only the enyne **8d**.

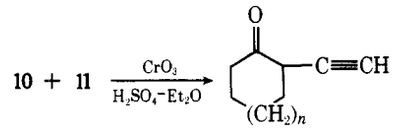


9d **8d**

A possible mechanism for these reductions is shown below.



The mixtures of alcohols obtained were oxidized to the sensitive 2-ethynylcycloalkanones (**12**) by a modification of Brown's procedure.



12

Although we have examined only five systems for this selective reductive opening of acetylenic epoxides, it should provide a general route to cyclic and acyclic β-hydroxy acetylenes which cannot be prepared by direct opening of an epoxide with acetylide anion.

Experimental Section

All boiling points are uncorrected. Melting points were determined in Pyrex capillary tubes using a Mel-Temp apparatus and are uncorrected. Infrared spectra were obtained on Beckman IR-8 or Acculab 3 spectrometers. Nuclear magnetic resonance spectra were obtained on Varian Associates Models A-60, A-60A, EM-360, T-60, and HA-100 instruments. Mass spectra were obtained on a MAT CH-5 mass spectrometer at 70 eV. Exact molecular weights were obtained by peak matching on the parent ion in the mass spectrum. Gas chromatographic analyses were conducted on an F & M Model 700 and a Bendix Model 2300 gas chromatographs. Elemental analyses were performed by the analytical service of the Department of Medicinal Chemistry, University of Kansas, Lawrence, Kans. Ultraviolet spectra were recorded on a Beckman DB spectrometer using isooctane as a solvent.

1-Ethynylcycloalkanols (7). 1-Ethynylcyclopentanol (**7a**) and 1-ethynylcyclohexanol (**7b**) were purchased from Aldrich Chemical Co.

1-Ethynylcyclododecanol (7e). In a three-necked, round-bottom flask equipped with a serum cap, a gas inlet tube, and stopper was placed 250 mL of dry tetrahydrofuran. The vessel was purged with nitrogen and cooled in a dry ice–acetone bath, and acetylene (purified by passing through concentrated sulfuric acid and solid potassium hydroxide) was introduced into the flask (ca. 2–3 mL/min) for 30 min. A solution of 60 mL of 2.0 M *n*-butyllithium in hexane (0.12 mol) was added via a syringe over a 30-min period. The stopper was replaced with an addition funnel and a solution of 18.2 g (0.10 mol) of cyclododecanone in 30 mL of tetrahydrofuran was added to the lithium acetylide solution over a 5-min period. The reaction mixture was stirred for 20 min at −78 °C and allowed to warm to room temperature (ca. 1 h) and 30 mL of water was added. The layers were separated, the water layer extracted with ether, and the organic layers dried ($MgSO_4$) and concentrated under vacuum to afford the crude product which was recrystallized from hexane to give 17.85 g (86%) of white crystals: mp 95.5–96 °C (lit.[6] mp 98–98.5 °C); IR (CCl_4) 3610, 3470, 3310, 2940, 2860, 1465, 1440, 1345, 1160, 1060, and 1000 cm^{-1}; NMR (CCl_4) δ 2.34 (s, 1 H) and 1.20–1.90 (m, 23 H); mass spectrum *m/e* (rel abundance) 208 (M^+, 0.3), 55 (100).

Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.73; H, 11.85.

1-Ethynylcyclooctanol (7d). Using the procedure described for the preparation of **7e,** 12.60 g (0.10 mol) of cyclooctanone gave 15.10 g of a clear liquid which was recrystallized from pentane to afford 12.80 g (84%) of white needles: mp 44–44.5 °C (lit.[7] mp 47 °C); IR (CCl_4) 3600, 3470, 3310, 2920, 2860, 2700, 2110, 1465, 1445, 1325, 1260, 1140, 1060, 1000, and 980 cm^{-1}; NMR δ 3.15 (br s, 1 H), 2.33 (s, 1 H), and 1.20–2.10 ppm (m, 14 H).

1-Ethynylcycloheptanol (7c). To 25 g (0.25 mol) of lithium acetylide–ethylenediamine complex suspended in 200 mL of tetrahydrofuran which had been saturated with acetylene gas for 20 min at 0 °C was slowly added 22.4 g (0.20 mol) of cycloheptanone in 20 mL of tetrahydrofuran. The reaction mixture was maintained at 0 °C for 36 h and quenched with water and 10% hydrochloric acid. The mixture was extracted with ether, and the ether extracts washed with 10% hydrochloric acid and brine, dried ($MgSO_4$), and concentrated to give 28.20 g of a yellow liquid. Distillation gave 21.10 g (76%) of a clear liquid: bp 56–60 °C (0.65 Torr) [lit.[8] bp 80–81 °C (10 Torr)]; IR (CCl_4) 3600, 3470, 3300, 2950, 2860, 2700, 2110, 1460, 1445, 1330, 1205, and 1030 cm^{-1}; NMR (CCl_4) δ 3.30 (m, 1 H), 2.36 (s, 1 H), and 1.30–2.10 (m, 12 H).

General Procedure for the Preparation of 1-Ethynylcycloalkenes (8). 1-Ethynylcyclooctene (8d). To a cold (0 °C) solution of 19.30 g (0.13 mol) of 1-ethynylcyclooctanol in 70 mL of pyridine maintained under nitrogen was added, with stirring, 20 mL (0.20 mol) of phosphorus oxychloride over a 30-min period. The reaction mixture was allowed to warm to room temperature, stirred for 15 h, and then heated to 70 °C for 0.75 h. After cooling 200 g of ice was added, the layers were separated, and the aqueous layer was extracted with ether. The combined ether extracts were washed with 10% hydrochloric acid, water, and saturated aqueous sodium bicarbonate solution, dried ($MgSO_4$), and concentrated to give 13.81 g of a yellow liquid. Kugelrohr distillation gave 13.23 g (78%) of a colorless liquid: bp 92–93 °C (23 Torr); IR (CCl_4) 3310, 3030, 2950, 2875, 2690, 2100, 1630, 1470, and 1445 cm^{-1}; NMR (CCl_4) δ 6.14 (t, 1 H, J = 8 Hz), 2.63 (s, 1 H), 2.00–2.60 (m, 5 H), and 1.50 (br s, 7 H); mass spectrum *m/e* (rel intensity) 134 (M^+, 29), 91 (100).

Anal. Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.59; H, 10.71.

1-Ethynylcyclopentene (8a). Using the procedure described for the preparation of **8d,** 11.16 g (0.10 mol) of 1-ethynylcyclopentanol was dehydrated with 15 mL (0.15 mol) of phosphorus oxychloride in 80 mL of pyridine. The crude product was distilled to give 5.17 g (56%) of a colorless liquid: bp 60–62 °C (100 Torr) (lit.[9] bp 144 °C); IR (CCl_4) 3310, 3060, 2960, 2860, 2110, 1450, and 960 cm^{-1}; NMR (CCl_4) δ 6.02 (m, 1 H), 2.81 (s, 1 H), and 1.60–2.70 (m, 6 H).

1-Ethynylcyclohexene (8b). Using the procedure described for the preparation of **8d,** 32.00 g (0.25 mol) of 1-ethynylcyclohexanol was dehydrated with 40 mL (0.40 mol) of phosphorus oxychloride in 200 mL of pyridine. The crude product was distilled to give 21.74 g (82%) of a colorless liquid: bp 71–72 °C (60 Torr) [lit.[8] bp 60 °C (30 Torr)]; IR (CCl_4) 3300, 3030, 2940, 2860, 2840, 2100, 1630, 1440, and 930 cm^{-1}; NMR (CCl_4) δ 6.10 (m, 1 H), 2.65 (s, 1 H), 1.85–2.28 (m, 4 H), and 1.40–1.85 (m, 4 H).

1-Ethynylcycloheptene (8c). Using the procedure described for the preparation of **8d,** 8.41 g (0.061 mol) of 1-ethynylcycloheptanol was dehydrated with 10 mL (0.10 mol) of phosphorus oxychloride in 30 mL of pyridine. Distillation of the crude product gave 4.91 g (67%) of a colorless liquid: bp 50–52 °C (1.00 Torr) [lit.[8] bp 65 °C (10 Torr)]; IR (CCl_4) 3310, 3030, 2930, 2860, 2100, 1630, 1455, 1445, and 863 cm^{-1}; NMR (CCl_4) δ 6.25 (t, 1 H, J = 6 Hz), 2.64 (s, 1 H), 2.00–2.45 (m, 4 H), and 1.35–1.90 (m, 6 H).

***cis*- and *trans*-1-Ethynylcyclododecene (8e).** Using the procedure described above for the preparation of **8d,** 20.8 g (0.10 mol) of 1-ethynylcyclododecanol was dehydrated with 15 mL (0.15 mol) of phosphorus oxychloride in 70 mL of pyridine. The crude product was distilled in a Kugelrohr apparatus to afford 13.04 g (79%) of a colorless liquid which was a 1:1 mixture of isomers by VPC[10] analysis: bp 61–62 °C (0.08 Torr); IR (CCl_4) 3310, 3020, 2960, 2860, 2100, 1460, and 1445 cm^{-1}; NMR (CCl_4) δ 5.80 (t, 1 H, J = 8 Hz), 2.94 (s, ~0.5 H), 2.54 (s, ~0.5 H), 2.00–2.40 (m, 4 H), and 1.10–1.80 (m, 16 H); mass spectrum *m/e* (rel intensity) 190 (M^+, 15), 79 (100).

Anal. Calcd for $C_{14}H_{22}$: C, 88.35; H, 11.65. Found: C, 88.54; H, 11.78.

General Procedure for the Preparation of Acetylenic Epoxides 9. 1-Ethynyl-9-oxabicyclo[6.1.0]nonane (9d). To a solution of 12.59 g (0.094 mol) of **8d** in 30 mL of methylene chloride at 0 °C was added over a 30-min period a solution of 19.1 g (0.094 mol) of 85% *m*-chloroperbenzoic acid in 150 mL of methylene chloride. The reaction mixture was stirred at 0 °C for 0.25 h and at room temperature for 1.2 h. Sodium sulfite solution (10%) was added until the reaction mixture gave a negative test to starch–iodide paper. Aqueous sodium bicarbonate solution was carefully added, the layers separated, and the organic layer washed with saturated aqueous sodium bicarbonate and water, dried (Na_2SO_4), and concentrated under vacuum to give 13.88 g of a yellow liquid which was distilled in a Kugelrohr apparatus to give 12.24 g (87%) of a colorless liquid: bp 37 °C (0.08 Torr); IR (CCl_4) 3300, 2940, 2870, 2680, 1465, 1445, 1250, and 940 cm^{-1}; NMR (CCl_4) δ 2.91 (dd, 1 H, J = 11, 4.5 Hz), 2.19 (s, 1 H), 1.95–2.20 (m, 2 H), and 1.10–1.80 (m, 10 H); mass spectrum *m/e* (rel intensity) 150 (M^+, 27), 79 (100).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 80.06; H, 9.47.

1-Ethynyl-6-oxabicyclo[3.1.0]hexane (9a). Using the procedure described for the preparation of **9d,** 4.04 g (0.044 mol) of 1-ethynylcyclopentene and a slight excess of 85% *m*-chloroperbenzoic acid gave, upon distillation, 3.01 g (58%) of a colorless liquid: bp 60–62 °C (30 Torr); IR (CCl_4) 3300, 3020, 2950, 2920, 2850, 1440, 1400, 1300, 935, and 855 cm^{-1}; NMR (CCl_4) δ 3.48 (s, 1 H), 2.30 (s, 1 H), and 1.20–2.30 ppm (m, 6 H); mass spectrum *m/e* (rel intensity) 108 (M^+, 59), 79 (100).

Anal. Calcd for C_7H_8O: C, 77.75; H, 7.46. Found: C, 77.70; H, 7.44.

1-Ethynyl-7-oxabicyclo[4.1.0]heptane (9b). Using the procedure described for the preparation of **9d,** 15.9 g (0.15 mol) of 1-ethynylcyclohexene and a slight excess of 85% *m*-chloroperbenzoic acid gave, after distillation, 14.91 g (81%) of a colorless liquid: bp 70–72 °C (15 Torr); IR (CCl_4) 3300, 2910, 2870, 2690, and 1440 cm^{-1}; NMR (CCl_4) δ 3.22 (t, 1 H, J = 4.5 Hz), 2.23 (s, 1 H), 2.00 (m, 4 H), and 1.40 (m, 4 H); mass spectrum *m/e* (rel intensity) 122 (M^+, 11), 78 (100).

Anal. Calcd for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.62; H, 8.43.

1-Ethynyl-8-oxabicyclo[5.1.0]octane (9c). Using the procedure described for the preparation of **9d,** 9.00 g (0.075 mol) of 1-ethynylcycloheptene and a slight excess of 85% *m*-chloroperbenzoic acid gave after distillation 8.21 g (80%) of a colorless liquid: bp 42–44 °C (0.6 Torr); IR (CCl_4) 3300, 3020, 2930, 2860, 2100, and 1235 cm^{-1}; NMR (CCl_4) δ 3.14 (br t, 1 H, J = 5 Hz), 2.17 (s, 1 H), and 1.00–2.30 ppm (m, 10 H); mass spectrum *m/e* (rel intensity) 136 (M^+, 24), 91 (100).

Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.46; H, 9.10.

***cis*- and *trans*-1-Ethynyl-13-oxabicyclo[10.1.0]tridecane (9e).** Using the procedure described for the preparation of **9d,** 12.92 g (0.068 mol) of a mixture of *cis*- and *trans*-**8e** and a slight excess of 85% *m*-chloroperbenzoic acid gave, after Kugelrohr distillation (92–94 °C, 0.10 Torr), 10.87 g (78%) of a colorless liquid containing both geometrical isomers in approximately equal amounts (as determined by NMR analysis): IR (CCl_4) 3310, 2940, 2870, 1470, 1450, and 1120 cm^{-1}; NMR (CCl_4) δ 2.90 (m, 1 H), 2.30 (s, ~0.5 H), 2.15 (s, ~0.5 H), and 1.00–2.00 ppm (m, 20 H); mass spectrum *m/e* (rel intensity) 206 (M^+, 36), 82 (100).

Anal. Calcd for $C_{14}H_{22}O$: C, 81.46; H, 10.75. Found: C, 81.25; H, 10.93.

General Procedure for the Reduction of the Acetylenic Epoxides 9. *cis*- and *trans*-2-Ethynylcyclohexanol (10b and 11b). To 30 mL of dry ammonia under argon in a three-necked flask equipped with a serum cap, a mechanical stirrer with a glass stirring blade, and a dry ice condenser topped with an argon inlet were added a few crystals of triphenylmethane and 1.92 g (15.7 mmol) of **9b** in 5 mL of ether. Methyllithium in ether (1.8 M) was added via a syringe (*Caution*: extremely vigorous reaction!) until a red triphenylmethane end point was achieved. Small pieces of lithium wire were then added until the blue color persisted, enough sodium benzoate[15] was added to dissipate the blue color, and 5.3 g (0.1 mol) of ammonium chloride was added. The ammonia was allowed to evaporate, the residue taken up in ether and water, the layers separated, and the ether layer washed with saturated aqueous sodium bicarbonate, dried (Na_2SO_4), and concentrated under vacuum to give 1.91 g (98%) of a yellow liquid. Vacuum transfer (25–45 °C, 0.02 Torr) gave 1.78 g (92%) of a colorless liquid which VPC analysis[11,12] indicated was a 7:3 mixture of **10b** and **11b:** IR (CCl_4) 3580, 3300, 2940, 2870, 2120, 1455, 1405, and 1080 cm^{-1}; NMR (CCl_4) δ 3.50 (m, ~2.5 H), 2.75 (m, ~0.5 H), 2.10 (d, 1 H, J = 2 Hz), and 1.00–2.00 ppm (m, 8 H).

***cis*- and *trans*-2-Ethynylcyclopentanol (10a and 11a).** Using the procedure described for the reduction of **9b,** 1.26 g (11.7 mmol) of **9a** was reduced to give 1.09 g (85%) of a yellow liquid. The crude product was shown to consist of a 1:3 mixture of the cis and trans alcohols by VPC[12,13] analysis. The crude product was chromatographed on 60 g of activity grade II Woelm silica gel, eluting with hexane–ether mixtures. The total amount of **10a** and **11a** obtained was 0.68 g (63%). Some fractions contained either pure cis or trans alcohol. *cis*-2-Ethynylcyclopentanol (**10**), which eluted first, was a colorless liquid: IR (CCl_4) 3560, 3300, 2960, 2900, 2870, 2110, 1465, 1445, 1370, 1340, 1255, 1200, 1095, and 1025 cm^{-1}; NMR (CCl_4) δ 4.10 (m, 1 H), 2.55 (m, 1 H), 2.11 (d, 1 H, J = 2 Hz), and 1.50–2.10 (m, 7 H). *trans*-2-Ethynylcyclopentanol (**11a**) was a colorless liquid: IR (CCl_4) 3600, 3490, 3310, 2960, 2880, 2120, 1470, 1450, 1205, 1090, and 1025 cm^{-1}; NMR (CCl_4) δ 4.08 (m, 2 H), 2.02 (d, 1 H, J = 2.5 Hz), and 1.40–1.80 (m, 6 H).

***cis*- and *trans*-2-Ethynylcycloheptanol (10c and 11c).** Using the procedure described above for the reduction of **9b,** 0.98 g (7.2 mmol) of **9c** was reduced to give, after vacuum transfer into a dry ice trap (60–75 °C, 0.1 Torr), 0.81 g (82%) of a colorless liquid which was a 6:4 mixture of cis and trans isomers as determined by VPC analysis:[12,14] IR (CCl_4) 3670, 3300, 2930, 2860, 2690, 2120, 1460, 1450, 1400, 1260, and 1050 cm^{-1}; NMR (CCl_4) δ 3.70 (m, 1 H), 3.25 (br s, 1 H), 2.85 (m, ~0.5 H), 2.50 (m, ~0.5 H), 2.14 (d, ~0.5 H), 2.12 (d, ~0.5 H), and 1.20–2.00 ppm (m, 10 H).

***cis*- and *trans*-2-Ethynylcyclooctanol (10d and 11d).** Using the procedure described above for the reduction of **9b,** 4.50 g (0.03 mmol) of **9d** was reduced to give, after vacuum transfer into a dry ice trap (60–75 °C, 1.0 Torr), 4.08 g (90%) of a colorless liquid which was shown to be a 6:4 mixture of cis and trans isomers (isomers unassigned) by VPC[10] analysis: IR (CCl_4) 3580, 3300, 2960, 2860, 2120, 1470, 1050, and 1030 cm^{-1}; NMR (CCl_4) δ 3.75 (m, 1 H), 3.10 (m, ~1 H), 2.80 (m, ~0.5 H), 2.50 (m, ~0.5 H), 2.06 (d, ~0.5 H), 2.04 (d, ~0.5 H), and 1.20–2.10 ppm (m, 12 H); mass spectrum *m/e* (rel intensity) 152 (M^+, 7), 54 (100).

Anal. Calcd for $C_{10}H_{16}O$: C, 81.46; H, 10.75. Found: C, 81.25; H, 10.93.

***cis*- and *trans*-2-Ethynylcyclododecanol (10e and 11e).** This reduction was carried out using the procedure described above for **9b,** except that a 1:2 mixture of ether–ammonia (120 mL total) was used as the solvent. Reduction of 2.952 g (0.013 mol) of **9e** gave 2.952 g (95%) of a colorless liquid. Chromatography of this crude mixture on 150 g of activity grade I Woelm silica gel and eluting with hexane and increasing amounts of ether gave three compounds. The first, 0.17 g (6%) of a colorless liquid eluted with 100% hexane, was identified as ethylidenecyclododecane: IR (CCl_4) 2940, 2850, 1470, and 1440 cm^{-1}; NMR (CCl_4) δ 5.22 (q, 1 H, J = 7 Hz), 2.00 (m, 4 H), 1.56 (d, 3 H, J = 7 Hz), and 1.30–1.70 ppm (m, 18 H); irradiation of the quartet at δ 5.22 collapsed the doublet at δ 1.56 to a singlet; mass spectrum *m/e* (rel intensity) 194 (M^+, 14), 56 (100).

Anal. Calcd for $C_{14}H_{26}$: C, 86.51; H, 13.49. Found: C, 86.54; H, 13.35.

Further elution gave 2.50 g (85%) of a 6:4 mixture of the *cis*- and *trans*-2-ethynylcyclododecanol **10** and **11e** (isomers unassigned). Fractions containing both pure isomers were obtained. The minor and more polar isomer was a liquid. The major and less polar isomer was a solid (mp 69–69.5 °C). The mixture gave the following spectral data: IR (CCl_4) 3580, 3310, 2940, 2870, 2120, 1470, 1445, and 1110 cm^{-1}; NMR (CCl_4) δ 3.75 (m, 1 H), 2.60 (m, 1 H), 2.00 (d, ~0.4 H, J = 2 Hz), 1.95 (d, ~0.6 H, J = 2 Hz), and 1.20–1.80 ppm (m, 20 H). An analytical sample of the less polar isomer was prepared by sublimation at 60–80 °C (0.03 Torr): mp 69–69.5 °C; mass spectrum *m/e* (rel abundance) 208 (M^+, 1), 54 (100).

Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.76; H, 11.61.

General Procedure for the Oxidation of *cis*- and *trans*-2-Ethynylcycloalkanols (10 and 11).[16] 2-Ethynylcyclododecanone (12e). To a cold (−5 to −10 °C) solution of 1.03 g (5.0 mmol) of **10e** and **11e** in 10 mL of ether in a 25-mL, three-necked flask equipped with a drying tube, a thermometer, and a serum cap was added, over a 5-min period, 5.5 mL (2.2 equiv) of *cold* 0.67 M sodium dichromate in sulfuric acid. The reaction mixture was stirred for 1.5 h at −5 to −10 °C, the layers separated, and the ether washed once with aqueous saturated sodium bicarbonate and several times with brine, dried (Na_2SO_4), and concentrated under vacuum to give 0.94 g (92%) of a colorless liquid: IR (CCl_4) 3310, 2940, 2870, 2120, 1715, 1465, and 1440 cm^{-1}; NMR (CCl_4) δ 3.10–3.30 (m, 1 H), 2.60 (m, 2 H), 2.14 (d, 1 H, J = 2 Hz), and 1.00–2.00 (m, 18 H); UV (isooctane) λ_{max} 276 nm (ϵ 99); mass spectrum *m/e* (rel intensity) 206 (M^+, 10), 79 (100).

Exact molecular weight. Calcd for $C_{14}H_{22}O$: 206.167. Found: 206.167.

2-Ethynylcyclooctanone (12d). Procedure A. Using the procedure described above for the preparation of **12e,** 0.46 g (3.0 mmol) of **10d** and **11d** was oxidized to give 0.23 g (81%) of a light yellow oil which contained some allenone and alcohol by IR analysis, but otherwise gave the same spectral data as that recorded for the compound prepared by procedure B.

2-Ethynylcyclooctanone (12d). Procedure B. To 2.1 mL (2.1 equiv) of 0.67 M sodium dichromate in sulfuric acid and 10 mL of ether at −10 °C was added dropwise a solution of 0.31 g (2.0 mmol) of **10d** and **11d** in 10 mL of ether over a 5-min period. The solution was maintained at −5 to −10 °C for 1.25 h, and the ether layer decanted, washed once with saturated aqueous sodium bicarbonate and several times with brine, dried (Na_2SO_4), and concentrated to give 0.27 g (88%) of a colorless liquid: IR (CCl_4) 3300, 2930, 2860, 2690, 2120, 2100, 1715, 1450, and 1250 cm^{-1}; NMR (CCl_4) δ 3.25 (dt, 1 H, J = 2.5, 7 Hz), 2.20 (d, 1 H, J = 2.5 Hz), and 1.00–3.00 (m, 12 H); UV (isooctane) λ_{max} 276 nm (ϵ 81); mass spectrum *m/e* (rel intensity) 150 (M^+, 55), 94 (100).

Exact molecular weight. Calcd for $C_{10}H_{14}O$: 150.104. Found: 150.104.

Acknowledgments. We are indebted to the National Science Foundation (Grant MPS 73-08764) and the General Research Fund of the University of Kansas for partial support of this work.

Registry No.—**7a,** 17356-19-3; **7b,** 78-27-3; **7c,** 2809-78-1; **7d,** 55373-76-7; **7e,** 14519-31-4; **8a,** 1610-13-5; **8b,** 931-49-7; **8c,** 2809-83-8; **8d,** 61967-54-2; *cis*-**8e,** 61967-55-3; *trans*-**8e,** 61967-56-4; **9a,**

34329-47-0; **9b**, 932-03-6; **9c**, 61967-57-5; **9d**, 61967-59-7; *cis*-**9e**, 61967-58-6; *trans*-**9e**, 62014-82-8; **10a**, 61967-60-0; **10b**, 61967-61-1; **10c**, 61967-62-2; **10d**, 61967-63-3; **10e**, 61967-64-4; **11a**, 61967-50-8; **11b**, 55506-28-0; **11c**, 25127-83-7; **11d**, 61967-51-9; **11e**, 62057-82-3; **12d**, 61967-52-0; **12e**, 61967-53-1; acetylene, 74-86-2; cyclododecanone, 830-13-7; cyclooctanone, 502-49-8; cycloheptanone, 502-42-1; ethylidenecyclododecane, 56888-86-9.

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(10) A 6 ft × 0.25 in. column packed with 10% Dow 710 silicone oil on 60/80 mesh Chromosorb W was employed for this analysis.
(11) A 6 ft × 0.25 in. column packed with 15% Carbowax 20M/NaOH on 60/80 mesh Chromosorb W was employed for this analysis.
(12) The trans isomer was identified by coinjection with an authentic sample.
(13) A 6 ft × 0.25 in. column packed with 15% SF-96 silicone oil on 60/80 mesh Chromosorb W was employed for this analysis.
(14) A 6 ft × 0.25 in. column packed with 15% Carbowax 20M on 60/80 mesh Chromosorb W was employed for this analysis.
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Chlorocarbonylbis(triphenylphosphine)iridium-Catalyzed Isomerization, Isoaromatization, and Disproportionation of Some Cycloalkanones Having Exocyclic Double Bonds

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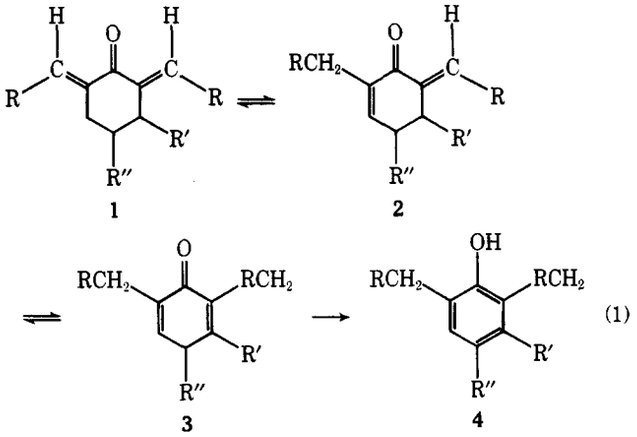
Received August 10, 1976

Chlorocarbonylbis(triphenylphosphine)iridium has been shown to be an efficient catalyst at 250 °C for isoaromatization of 2,6-diarylidenecyclohexanones. A stepwise migration of the exocyclic double bonds takes place followed by thermal tautomerization of the cyclohexa-2,5-dienone system. 2-Arylidene-1-tetralones undergo similar transformations to the corresponding naphthols. 2,7-Dibenzylidenecycloheptanone, which cannot form an aromatic system without loss of H_2, exhibits only *E–Z* isomerization. 3,7-Dibenzylidenecycloheptane-1,2-dione is partly converted into 3,7-dibenzyltropolone, and partly disproportionates to dibenzylcycloheptanedione and to polymer precursor. Unsaturated cyclopentanones react to give disproportionation products along with double bond migration into the five-membered ring.

2-Benzylphenols and naphthols have been known for many years to possess specific bacteriostatic and fungistatic activities.[1] They are, however, of little practical value since most of their present syntheses are inefficient and low yielding processes. Direct benzylation of phenols give, in general, mixtures of isomers.[2] Isomerization of benzylidenecyclohexanones[3-7] by acids (PPA, HOAc–HBr) is often accompanied by skeletal rearrangements[8] and ring expansion,[9] whereas heterogeneous transition metal catalysts (Ni, Pd/C, PtO_2)[10] frequently cause oxygen extrusion[11] or, in alcoholic media, result in transfer hydrogenation of the carbon–carbon double bonds.[12]

In a preliminary communication[13] we reported that isoaromatization of 2,6-dibenzylidenecyclohexanones to 2,6-dibenzylphenols can be accomplished in excellent yields by the versatile iridium catalyst, $IrCl(CO)(PPh_3)_2$. We have now extended this study to include further arylidenecyclohexanones, as well as some derivatives of α-tetralone, cyclopentanone, cycloheptanone, and cycloheptanedione.

Isomerization of Diarylidenecyclohexanones. As described in the Experimental Section, (*E,E*)-2,6-dibenzylidenecyclohexanone (**1**, R = C_6H_5; R′ = R″ = H) is converted to 2,6-dibenzylphenol (**4**, R = C_6H_5; R′ = R″ = H) simply by heating the ketone and the catalyst (a high boiling solvent may be used) for 1.5–2 h at 230–250 °C. The reaction is stepwise (vide infra) as shown in eq 1.



(1)

The catalysis proceeds equally well (though at different rates) when the phenyl moieties in **1**, R = C_6H_5; R′ = R″ = H, are exchanged by substituted aryl groups, provided the substituents neither coordinate irreversibly to the catalyst (as does NO_2) nor extend serious steric effects (e.g., ortho substituents).

A summary of some representative experiments using $IrCl(CO)(PPh_3)_2$ as catalyst is given in Table I.

The application of some other typical catalysts, viz., $RhCl_3 \cdot 3H_2O$, $RhCl(PPh_3)_3$, and $RuCl_2(PPh_3)_3$, gives less satisfactory results.

The stepwise nature of reaction 1 follows directly from its kinetic curves (Figure 1).[14] While the equilibration of **1** and **2** and of **2** and **3** is assisted by the iridium catalyst, the tau-