1159, 1086, 1002, 998, 766, 745 cm$^{-1}$; nmr ($CDCl_3$–TMS) $\tau$ 2.3–3.3 (6 H, m), 3.48 (1 H, s), 6.10 (6 H, s), 6.23 (3 H, s); $\lambda_{max}^{EtOH-0.01\ N\ HCl}$ 228, 283, 312 m$\mu$ (log $\epsilon$ 4.29, 4.04, 4.08); $\lambda_{max}^{EtOH-0.01\ N\ NaOH}$ 255, 285 (sh), 360 m$\mu$ (log $\epsilon$ 4.04, 3.57, 4.44).

*Anal.* Calcd for $C_{16}H_{16}O_5$: C, 66.66; H, 5.59. Found: C, 66.84; H, 5.79.

Further elution of the column with benzene, chloroform, ethyl acetate, and mixtures of these solvents gave mixtures (2.9 g, 32%) which contained both VIII and IX and at least two other components (tlc) which were not identified. Three additional portions (10 g each) of VII were photolyzed and provided, after work-up, an additional 4.1 g (14%) of VIII, mp 107–108°.

**2,2′,3,3′-Tetrahydroxybenzophenone** (**X**).—A solution of VIII (4.0 g) in glacial acetic acid (60 ml) and 48% hydrobromic acid (40 ml) was refluxed for 5 hr. The solution was concentrated to *ca.* 50 ml, diluted with water (150 ml), and filtered. The filtrate was allowed to stand for 12 hr at room temperature, whereupon the precipitate was collected by filtration, washed with water, and dried to give fine yellow needles of X (2.65 g, 78%), mp 120–121°. Sublimation followed by recrystallization from water gave X with mp 121–122°: $\nu_{max}^{KBr}$ 3600–2700 (broad), 1626, 1475, 1449, 1332, 1279, 1442, 1190, 854, 752, 740 cm$^{-1}$; $\lambda_{max}^{EtOH-0.01\ N\ HCl}$ 223, 275, 350 m$\mu$ (log $\epsilon$ 4.30, 4.08, 3.56); $\lambda_{max}^{EtOH-0.01\ N\ NaOH}$ 240, 273 (sh), 308, 365 m$\mu$ (log $\epsilon$ 4.35, 4.04, 4.05, 3.38).

*Anal.* Calcd for $C_{13}H_{10}O_5$: C, 63.41; H, 4.09. Found: C, 63.03; H, 4.12.

**4,5-Dihydroxyxanthone** (**VIa**).—A mixture of X (1.5 g) and water (15 ml) was heated in a stainless steel bomb for 19 hr between 220–230°. The mixture was then cooled and the solid material was separated by filtration, washed with water, and dried. Sublimation afforded crystalline yellow VIa (0.91 g, 65%) which decomposed at 350°. Recrystallization from absolute alcohol furnished fine yellow needles: mp >350° (dec); $\nu_{max}^{KBr}$ 1600, 1468, 1374, 1350, 1255, 1170, 742 cm$^{-1}$; $\lambda_{max}^{EtOH-0.01\ N\ HC}$ 247, 300, 358 m$\mu$ (log $\epsilon$ 4.66, 3.82, 3.77); $\lambda_{max}^{EtOH-0.01\ N\ NaOH}$ 264, 316, 350, 410 m$\mu$ (log $\epsilon$ 4.62, 3.76, 3.63, 3.61); nmr (DMSO-$d_6$, TMS) $\tau$ 2.15–3.15 (m).

*Anal.* Calcd for $C_{13}H_8O_4$: C, 68.42; H, 3.53. Found: C, 68.01; H, 3.85.

**4,5-Dimethoxyxanthone** (**VIb**).—Methylation of 4,5-dihydroxyxanthone (VIa) (0.20 g) afforded 0.15 g (68%) of a crystalline white solid, mp 273–275° (subl). Sublimation followed by recrystallization furnished fine white needles of VIb (0.12 g): mp 273–274° (subl); $\nu_{max}^{KBr}$ 1660, 1490, 1441, 1360, 1339, 1282, 1230, 1078, 750 cm$^{-1}$; nmr ($CDCl_3$–TMS) $\tau$ 2.03–2.76 (6 H, m), 5.93 (6 H, s).

*Anal.* Calcd for $C_{15}H_{12}O_4$: C, 70.30; H, 4.72. Found: C, 70.14; H, 4.92.

**4,5-Diacetoxyxanthone** (**VIc**).—Acetylation of VIa (45 mg) afforded a white crystalline solid (58 mg, 94%), mp 263–268°. Sublimation furnished fine white needles of VIc: mp 270–272°; $\nu_{max}^{KBr}$ 1764, 1669, 1493, 1475, 1447, 1372, 1326, 1230, 1178, 753 cm$^{-1}$; nmr ($CDCl_3$–TMS) $\tau$ 1.80–2.78 (6 H, m), 7.59 (6 H, s).

*Anal.* Calcd for $C_{17}H_{12}O_6$: C, 65.38; H, 3.87. Found: C, 65.32; H, 4.04.

**Registry No.**—Ia, 35040-32-5; Ib, 35040-33-6; Ic, 35040-34-7; III, 35040-35-8; IV, 35040-36-9; V, 35040-37-0; VIa, 35040-38-1; VIb, 35040-39-2; VIc, 35040-40-5; VII, 35040-41-6; VIII, 35040-42-7; IX, 35042-49-0; X, 35042-50-3.

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# Semihydrogenation of 1-Phenyl-4-penten-2-yn-1-one and of 1-Phenyl-3-(cyclohexen-1-yl)-2-propynone[1]

ELLIOT N. MARVELL,* THOMAS GOSINK, PHILLIP CHURCHLEY, AND THOMAS H. LI

*Department of Chemistry, Oregon State University, Corvallis, Oregon 97331*

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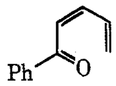
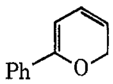
Semihydrogenation of 1-phenyl-4-penten-2-yn-1-one gave mainly 1-phenyl-2-penten-1-one. Addition of 1 mol of hydrogen to 1-phenyl-3-(cyclohexen-1-yl)-2-propynone (4) gave a mixture in which 6-phenyl-2,3-cyclohexa-2*H*-pyran and *cis*-2,3-cyclohexa-6-phenyl-3,4-dihydro-2*H*-pyran were identified by spectral methods and from which *cis*-2,3-cyclohexa-6-phenyltetrahydropyran and 3-cyclohexyl-1-phenyl-1-propanone could be isolated.

The synthesis of some cis dienones was a crucial part of a project aimed at elucidation of the electrocyclic equilibrium between $\alpha$-pyrans and cis dienones. Some early studies by Schinz and his students[2] have shown that semihydrogenation of some enynones gave mixtures which appeared to contain at least the $\alpha$-pyran valence isomer, and perhaps both the pyran and the cis dienone. We have investigated this semihydrogenation route to cis dienones with considerable care, and the results described here will show why we have become disenchanted with this beguilingly simple process.

Schinz[2c] indicated that partial reduction of dodec-5-en-3-yn-2-one gave mainly 2-hexyl-6-methyl-2*H*-pyran. To enhance the value of ultraviolet spectroscopy as an *a priori* device for distinguishing between cis dienone and $\alpha$-pyran forms, we decided to employ phenyl rather than methyl ketones. Ring closure would then be expected to lead to a large (*ca.* 40 nm) bathochromic shift.



**2**



**3**

**1-Phenyl-4-penten-2-yn-1-one** (**1**) was prepared by Jones oxidation of the corresponding alcohol,[3] and it was reduced over a variety of palladium catalysts under varying conditions. The product inevitably contained unreacted **1**, and, when its uv absorption was subtracted from that of the mixture, the difference spectrum had a $\lambda_{max}$ at 257 nm. 1-Phenyl-2-buten-1-one absorbs at 256 nm.[4] Thus the 257-nm band along with a band at 734 cm$^{-1}$ identified the main product as *cis*-1-phenyl-2-penten-1-one. Clearly a terminal vinyl group and the triple bond are reduced competitively.

$$\underset{\mathbf{1}}{PhCOC{\equiv}CCH{=}CH_2} \xrightarrow[Pd]{H_2} \mathbf{1} + \underset{cis}{PhCOCH{=}CHEt}$$

**1-Phenyl-3-(cyclohexen-1-yl)-2-propynone** (**4**) was selected as a second substrate to reduce the competition by the double bond. Semihydrogenation of **4** gives a

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[2] (a) V. Theus, W. Surber, L. Colombi, and H. Schinz, *Helv. Chim. Acta*, **37**, 239 (1955); (b) V. Theus and H. Schinz, *ibid.*, **39**, 1290 (1956); (c) W. Surber, V. Theus, L. Colombi, and H. Schinz, *ibid.*, **39**, 1299 (1956).

[3] Y. S. Zal'kind and A. I. Kulikov, *Zh. Obshch. Khim.*, **15**, 643 (1945).

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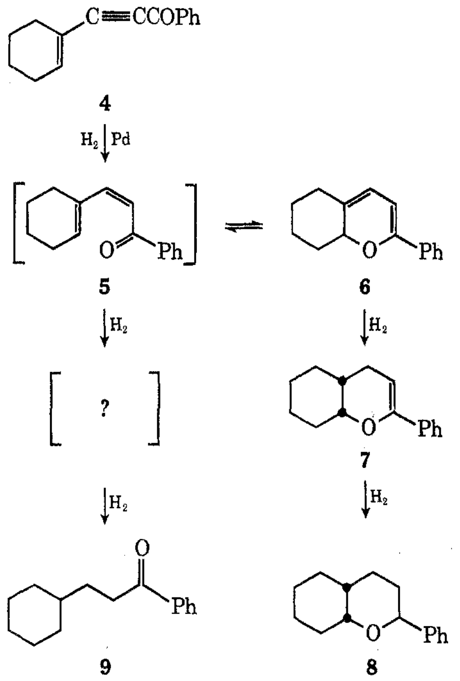
complex mixture. Persistent attempts to isolate either a pyran or a cis dienone were of little avail. Both fully saturated products **8** and **9** were isolated, but a combination of separative methods and spectral measurements provided strong support for the reaction series of Scheme I. No products of initial reduction of the cyclohexene bond or of a reduction level between **5** and **9** were uncovered.

SCHEME I



**Evidence for the Presence of 6.**—An unstable compound can be separated in impure form from the semihydrogenation mixture by column chromatography. This substance has $\lambda_{max}$ 338 nm ($\epsilon \sim 10{,}000$). Removal of the solvent gave a gummy residue having ir bands at 1660, 1600, 1575, 1500, 1083, 755, and 686 cm$^{-1}$. The nmr spectrum of the material was characterized by two bands at $\delta$ 5.49 (2 H) and 4.85 (1 H). While we were unable to isolate the pure compound because of its instability, we can assign the structure **6** to this substance. The most revealing piece of evidence is the uv band at 338 nm. This eliminates **5** from consideration since *trans*-3-(cyclohexen-1-yl)-1-phenyl-2-propen-1-one (**10**) has a $\lambda_{max}$ at 308 nm, while *trans*-chalcone and its cis isomer absorb at 299 and 290 nm, respectively.[5] Recently Dreux[6] has reported that 2,6-diphenyl-2,4-dimethyl-$\alpha$-pyran absorbs at 323 nm while 2,4,6-triphenyl-$\alpha$-pyran has a $\lambda_{max}$ at 340 nm.

The nmr and ir spectra add support to this assignment. If it is assumed that the phenyl region in the nmr corresponds to five protons, then the total proton count is 16. The olefinic protons in all known $\alpha$-pyrans except 2,2,4,6-tetraphenyl-$\alpha$-pyran lie between 4.5 and 5.7 ppm.[6,7] Generally the protons at $C_3$ and $C_4$ are separated by *ca.* 0.3 ppm and have $J \cong 6$ Hz, but apparently those in **6** coincidentally have the same chemical shift. In accord with this suspicion the singlet at $\delta$ 5.49 disappears almost completely if partial reduction is carried out with deuterium. Attempts to trap **6** by formation of a stable Diels–Alder adduct failed. Use of tetracyanoethylene, dimethyl acetylenedicarboxylate, or *N*-phenylmaleimide led in all cases to recovery of starting material.

**Evidence of the Presence of 7.**—The lack of clean selectivity for reduction of the triple bond of **4** leads to overhydrogenation products. Most interesting is the compound **7**, never isolated in pure form, which was identified by spectral means. Column chromatography of the semihydrogenation mixture gives a mixture whose main component has a doublet of doublets at $\delta$ 5.13 and a broad singlet at $\delta$ 4.09. Decoupling showed that the $\delta$ 5.13 peak is the X portion of a modified AMX pattern. The A proton appears as a doublet of doublets (broadened by further unresolved coupling) at $\delta$ 1.82, and the M proton as a doublet of quartets at $\delta$ 2.41. First-order analysis gives $J_{AX} \cong 6$, $J_{MX} \cong 3$, and $J_{AM} = 17$ Hz (probably a negative sign). In view of its magnitude[8] $J_{AM}$ must represent the geminal coupling constant for an allylic $CH_2$ group. The M proton is coupled to an additional proton with $J = 6.5$ Hz, while the A proton coupling is too small to be resolved. These data suggest that a $CHCH_2CH{=}C{<}$ group must be part of a ring system sufficiently rigid to fix the dihedral angle between the methine and the A proton close to 90°. The structure **7** fits this requirement, and inspection of models shows that only the cis ring juncture will permit the necessary dihedral angle. Further support for the cis ring juncture is provided by the hydrogenolysis experiment (see below).

**Isolation and Identification of 8 and 9.**—Both **8** and **9** can be separated from the semihydrogenation mixture by either vapor phase or column chromatography. However, they were isolated and identified from deliberate overhydrogenation experiments. If the normal semihydrogenation mixture was chromatographed to obtain a solution having $\lambda_{max}$ 338 nm, complete hydrogenation over either palladium or platinum oxide gave both **8** and **9**. **8** was identified by its nmr spectrum, which contains a doublet of doublets at $\delta$ 4.30 and a broad singlet at $\delta$ 3.70. Hydrogenolysis of **8** gave the known[9] *cis*-2-($\gamma$-phenylpropyl)cyclohexanol. **9** was identified by comparison with an authentic sample prepared by complete hydrogenation of **4** over platinum oxide. Its presence can be ascertained by the characteristic triplet at $\delta$ 2.84 for the $CH_2COPh$ protons.

**Conclusions.**—These results show that the selectivity of a palladium catalyst for the triple bond of an enynone with the acetylenic bond directly attached to the carbonyl group is discouragingly low. The reaction might be useful for preparation of either a cis dienone or the corresponding $\alpha$-pyran provided (a) the double bond provides no competition to the triple bond for primary hydrogen uptake and (b) the reduction products are stable enough to survive separation from the reaction mixture. Catalyst selectivity is much better for enynones if the triple bond is terminal in the conjugated

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system.[10-12] Success has also been achieved in cases where the triple bond, while not terminal in a conjugated system, was not adjacent to the carbonyl group.[13-15] During the course of this study we also found that the Diels–Alder route to cis dienones failed when **4** proved unreactive toward cyclopentadiene and 2,3-dimethyl-1,3-butadiene.

## Experimental Section

**1-Phenyl-4-penten-2-yn-1-ol.**—A cold ether solution of vinylacetylene (61 g, 1.18 mol) was added to a solution containing 0.8 mol of ethylmagnesium bromide under a nitrogen atmosphere. The solution was heated for 3 hr under reflux, and then 85 g (0.8 mol) of benzaldehyde was added. The reaction was stirred for 6 hr and the mixture was decomposed with saturated ammonium chloride. The ether solution was dried ($MgSO_4$) and the product was isolated as a yellow oil, bp 125° (5 mm), $n^{18}{}_{\rm D}$ 1.5730 [lit.[3] bp 125° (5 mm), $n^{17}{}_{\rm D}$ 1.5747]. The yield was 40 g (32%).

**1-Phenyl-4-penten-2-yn-1-one (1).**—A solution containing 2.18 g (0.22 mol) of chromium trioxide and 1.8 ml of concentrated sulfuric acid in 6.0 ml of water was added slowly to a cold solution of 5.0 g (0.032 mol) of 1-phenyl-4-penten-2-yn-1-ol in 10 ml of acetone. The product was extracted with ether and the extracts were dried ($MgSO_4$). After the ether had been removed the residue was chromatographed over 125 g of activity III alumina using petroleum ether (bp 30–60°) as eluent. A light yellow oil was isolated: yield 3.25 g; $\lambda_{\max}$ 270 nm ($\epsilon$ 5480); ir (neat) 2210, 1640, 1598, 1580, 1260 cm$^{-1}$. *Anal.* Calcd for $C_{11}H_8O$: C, 84,63; H, 5.13. Found: C, 84.43; H, 5.30.

A 2,4-dinitrophenylhydrazone was prepared according to the procedure of Shriner, Fuson, and Curtin,[16] mp 192–192.5°. *Anal.* Calcd for $C_{17}H_{12}N_4O_4$: C, 60.71; H, 3.57. Found: C, 60.91; H, 3.62.

**Semihydrogenation of 1.**—Solutions of **1** containing between 1.33 and 2.00 mmol of **1** were hydrogenated in the dark until between 0.9 and 1.2 molar equiv of hydrogen had been absorbed. About 20–30% of catalyst (by weight) compared with **1** was used. For most runs 5% palladium on calcium carbonate was employed either alone or with added zinc acetate or quinoline. Lindlar[17] catalyst gave no better results. Ethyl acetate, heptane, and methanol were used as solvents; no advantage was noted for any one of these. During the reaction ir bands at 2210, 1640, and 1260 cm$^{-1}$ diminished but did not disappear; bands at 1665, 1612, and 1225 cm$^{-1}$ appear. In the uv the $\lambda_{\max}$ at 270 nm diminishes and a new $\lambda_{\max}$ at 259 nm appears.

**1-Phenyl-3-(cyclohexen-1-yl)-2-propynone (4).**—Ethynylcyclohexene[18] (65.0 g, 0.61 mol) in ether was added to a solution containing 0.61 mol of ethylmagnesium bromide, and the reaction mixture was heated under reflux for 4 hr. This solution was cooled and 64.6 g (0.61 mol) of benzaldehyde in 100 ml of ether was added. After having been stirred for 6 hr, the solution was decomposed with saturated ammonium chloride. The crude 1-phenyl-3-(cyclohexen-1-yl)-2-propynol, mp 42°, was obtained by evaporation of the ether and was used in the next step.

This alcohol (41.0 g, 0.19 mol) was oxidized according to the procedure for preparation of **1**. The ketone **4** was isolated by chromatography over activity III alumina using petroleum ether as eluent. A light yellow oil was obtained: $n^{25}{}_{\rm D}$ 1.6040; uv max (EtOH) 304 nm ($\epsilon$ 10,800); ir (thin film) 1630, 1608, 1580, 1280 cm$^{-1}$; nmr ($CCl_4$) $\delta$ 8.0 and 7.36 (two m, 5 H), 6.43 (m, 1 H), 2.25 (m, 4 H), and 1.69 (m, 4 H). It was isolated in 84% yield. *Anal.* Calcd for $C_{15}H_{14}O$: C, 85.71; H, 6.66. Found: C, 85.64; H, 6.69.

A 2,4-dinitrophenylhydrazone prepared by the procedure of Shriner, Fuson, and Curtin[16] melted at 213–214°. *Anal.* Calcd for $C_{21}H_{18}N_4O_4$: C, 64.62; H, 4.61. Found: C, 64.47; H, 4.83.

**Semihydrogenation of 4.**—A series of runs under varied conditions using the infrared spectrum of the crude product as an analytical measure suggested that the outcome was influenced only in small measure whether palladium on calcium carbonate or Lindlar catalyst was used, whether ethyl acetate or cyclohexane was the solvent, and whether quinoline was present or absent. The following procedure was then adopted.

The catalyst, 5% palladium on calcium carbonate (200 mg), was prehydrogenated under cyclohexane. A solution of 400 mg of *freshly chromatographed* **4** in cyclohexane was added *via* a serum cap and hydrogenation was allowed to proceed at 1 atm hydrogen pressure until 1 molar equiv had been added. The catalyst was removed by filtration and the solvent by evaporation. The crude product was treated as described below.

**Identification of 2,3-Cyclohexa-6-phenyl-2*H*-pyran (6).**—The crude product from semihydrogenation of **4** was chromatographed on 25 times its weight of Mallinckrodt 100 mesh silicic acid using hexane as an eluent. Overreduced products eluted first followed by an unstable yellow oil: uv max (cyclohexane) 338 nm ($\epsilon$ $\sim$10,000); ir (thin film) 1660, 1600, 1575, 1373, 1265, 1083 cm$^{-1}$; nmr ($CCl_4$) $\delta$ 7.48 and 7.19 (two m), 5.51 (s), 4.86 (m), and 2.3–1.2 (broad m) with relative areas of 5:1.8:0.8:8.8. The oil was unstable and could not be isolated in a pure state. *Anal.* Calcd for $C_{15}H_{16}O$: C, 84.95; H, 7.59. Found: C, 84.10; H, 7.62; C, 83.84; H, 7.61.

**Attempted Formation of Diels–Alder Adducts of 6.**—A solution containing 0.125 g of the semihydrogenation product of **4** and 0.080 g of dimethyl acetylenedicarboxylate in 10 ml of benzene was heated at reflux under nitrogen for 10 hr. Examination of the reaction mixture by vpc on a 20% Apiezon on Chromosorb W column at 162° before and after heating showed that no reaction had occurred. The same mixture was heated in xylene with an equivalent result.

A mixture of 170 mg of *N*-phenylmaleimide and 210 mg of the semihydrogenation product of **4** was heated under reflux for 16 hr. Examination *via* vpc on a 20% SE-30 on 45/60 mesh Chromosorb W column at 188° showed that no reaction took place.

**Identification of *cis*-2,3-Cyclohexa-6-phenyl-3,4-dihydropyran (7).**—If the mixture from semihydrogenation of **4** (450 mg of **4** and 1.26 molar equiv of hydrogen added) was chromatographed over silicic acid as described above except that 10% benzene in petroleum ether was used as the eluent, a fraction having uv max (EtOH) 218, 227, 239, 263, and 336 nm was isolated, nmr ($CCl_4$) $\delta$ 7.5 and 7.19 (2 m), 5.46 (s), 5.13 (d of d), 4.09 (broad s), 2.84 (t, $J$ = 6.5 Hz), and 2.5–1.0 (complex m). Irradiation of the $\delta$ 5.13 band collapsed two quartets at $\delta$ 2.51 and 2.34 to a pair of doublets and a pair of doublets at $\delta$ 1.90 and 1.73 to a pair of singlets. Irradiation of the $\delta$ 4.09 band causes a change in a part of the complex multiplet near $\delta$ 2.08, and conversely irradiation in this region sharpens the broad singlet at $\delta$ 4.09 quite effectively. Interpretation is given in the discussion section of this paper.

Direct vpc separation of the semihydrogenation mixture on a 5 ft × 0.25 in. 20% SE-30 on Chromosorb W column at 182° gave four peaks, the second of which was mainly **7**, nmr ($CCl_4$) $\delta$ 5.13 and 4.09, mol wt 214 (mass spectrum).

***cis*-2,3-Cyclohexa-6-phenyltetrahydropyran (8). A. From Hydrogenation of 6.**—After 1.14 molar equiv of hydrogen had been added to 110 mg of **4** as described earlier, the product mixture was divided into two halves. To the first half 0.20 g of platinum oxide catalyst was added, and the mixture was hydrogenated until absorption ceased. The catalyst was removed by filtration and the solvent by evaporation. Vpc analysis on the SE-30 column at 188° gave three peaks. The first to elute was a liquid, nmr ($CCl_4$) $\delta$ 7.20 (s, 5 H), 4.31 (m, 1 H), 3.68 (broad s, 1 H), 2.0–1.0 (m, 13 H).

The second half of the semihydrogenation mixture was chromatographed over silicic acid as described for identification of **6**. The main material isolated was hydrogenated over platinum oxide until saturated. This material was chromatographed over activity II–III alumina using a gradient elution with pentane containing increasing amounts of benzene. The early fractions (20%) contained an oil, ir (thin film) 1095, 1060, 988, 950, 750, 696 cm$^{-1}$, nmr ($CCl_4$) as above. *Anal.* Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.00; H, 9.12.

**B. From Semihydrogenation of 4.**—A sample (400 mg) of **4** was hydrogenated (1.01 molar equiv) as described above. The

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[15] R. Ahmad and B. C. L. Weedon, *ibid.*, 3299 (1953).

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product was separated by vpc on the SE-30 column, and the first peak had spectral properties which identified it as **8**.

**3-Cyclohexyl-1-phenylpropan-1-one** (**9**). **A. From 4.**—A mixture of 2.66 g of platinum oxide and 39.0 g (0.18 mol) of **4** was hydrogenated at 20 psig initial hydrogen pressure in a Parr shaker. Chromatography of the crude product over activity III alumina gave a white solid: mp 43°; ir ($CCl_4$) 1676, 1593, 736, 690 $cm^{-1}$; nmr ($CCl_4$) $\delta$ 7.3 (m, 5 H), 2.84 (t, $J = 6.7$ Hz, 2 H), and 1.9–1.0 (broad m, 14 H); 80% yield. *Anal.* Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.54; H, 9.15.

**B. From Hydrogenation of 6.**—The product described under part A of the preparation of **8** above was separated by vpc into three fractions. The third fraction (last to elute) was identified spectrally as **9**.

**C. From Semihydrogenation of 4.**—The semihydrogenation product described in part B of the preparation of **8** was separated by vpc. The last material to elute was identified spectrally as **9**.

*trans*-**3-(Cyclohexen-1-yl)-1-phenyl-2-propen-1-ol.**—A solution of 5.0 g (0.03 mol) of **4** in 100 ml of ether was added to a suspension of 0.82 g (0.024 mol) of lithium aluminum hydride in ether. The mixture was stirred for 5 hr at room temperature and for 30 min at reflux. The mixture was carefully treated with saturated ammonium chloride, and the ether layer was separated and dried ($MgSO_4$). After the ether layer had been concentrated to *ca.* 100 ml, an equal volume of petroleum ether was added and a white solid was precipitated: mp 64–65; ir ($CCl_4$) 3160, 1630, 1185, 1088, 960, 755, 600 $cm^{-1}$; nmr ($CCl_4$) $\delta$ 6.99 (s, 5 H), 5.88 and 5.40 (modified AB, $J_{AB} = 15$ Hz, 2 H), *ca.* 5.48 (?, 1 H), 4.79 (m, 1 H), 3.31 (OH), 1.78 (m, 4 H), and 1.49 (m, 4 H); yield 3.09 g. *Anal.* Calcd for $C_{15}H_{18}O$: C, 84.61; H, 8.46. Found: C, 84.30; H, 8.46.

*trans*-**3-(Cyclohexen-1-yl)-1-phenyl-2-propen-1-one** (**10**). **From the Alcohol.**—The above alcohol was oxidized as described for the preparation of **4**. The crude reaction product was chromatographed an activity II alumina with 5% benzene in petroleum ether. The main fraction, a yellow oil, was recrystallized from petroleum ether to give a white solid: mp 68.5–69.5°; uv max (EtOH) 307.5 nm ($\epsilon$ 23,900); ir ($CCl_4$) $\delta$ 7.88 and 7.46 (two m, 5 H), 7.27 and 6.76 (AB, $J = 16.0$ Hz), 6.18 (m, 1 H), 2.22 (broad s, 4 H), 1.69 (broad s, 4 H). *Anal.* Calcd for $C_{15}H_{16}O$: C, 84.95; H, 7.59. Found: C, 85.05; H, 7.77.

*cis*-**2-(3-Phenylpropyl)cyclohexanol.**—A sample (100 mg) of **8** was hydrogenated at atmospheric pressure over 25 mg of palladium on charcoal in 5 ml of glacial acetic acid. The product, a colorless oil, was heated with 125 mg of 2,4-dinitrobenzoyl chloride for several minutes and the crystalline product was recrystallized from 95% ethanol, mp 101–102° (lit.[9] mp 101–102°).

**Attempted Preparation of Diels–Alder Adducts of 4.**—A solution of 131 mg of **4** and 100 mg of 2,3-dimethylbutadiene in 20 ml of benzene was heated under reflux for 12 hr. Vpc analysis showed that no reaction had occurred. The solution was then heated for 4 days at 105° in a sealed tube. Analysis again showed no reaction.

A solution of 600 mg of **4** and 600 mg of cyclopentadiene in 3 ml of xylene was heated in a sealed tube at 145° for 12 hr. Again no reaction occurred.

**Registry No.**—**1**, 16278-55-0; **1** DNP, 21961-16-0; **4**, 16616-44-7; **4** DNP, 35030-87-6; **6**, 35030-88-7; **8**, 35030-89-8; **9**, 28861-24-7; **10**, 35030-91-2; *trans*-3-(cyclohexen-1-yl)-1-phenyl-2-propen-1-ol, 35030-92-3.

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# Rates of Electrocyclic Reactions. Conversion of α-Pyrans to Cis Dienones[1]

ELLIOT N. MARVELL,* THOMAS CHADWICK, GERALD CAPLE, THOMAS GOSINK, AND GERALD ZIMMER

*Department of Chemistry, Oregon State University, Corvallis, Oregon 97331*

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The equilibrium constant, $K_{18} = 0.094$, for the interconversion of 1-oxa-2,5,5,8a-tetramethyl-5,6,7,8-tetrahydronaphthalene (**3**) and *cis*-$\beta$-ionone (**2**) was measured at several temperatures, $\Delta H° = 5.5$ kcal/mol and $\Delta S° = 14$ eu. Both the rate of conversion of **3** to **2** ($k_1$) and the reverse rate ($k_{-1}$) were measured directly by nmr at several temperatures. At 18° $k_{-1}$ equals $1.39 \times 10^{-3}$ $sec^{-1}$ and $k_1$ is $1.31 \times 10^{-4}$ $sec^{-1}$ with $\Delta H^{\ddagger} \cong 19$ kcal/mol for the reverse reaction. An indirect method of determining the rate ($k_1$) of ring-opening of an $\alpha$-pyran *via* rapid selective reduction of the cis dienone was developed. Tested on **3** this method gave $k_1$ as $3.2 \times 10^{-5}$ $sec^{-1}$ at 15°. At 14.6° the rate of the retroelectrocyclic reaction of 2,2,4,6-tetramethyl-$\alpha$-pyran is $1.6 \times 10^{-4}$ $sec^{-1}$, while the rate for 2,4-dimethyl-2,6-diphenyl-$\alpha$-pyran is $5.35 \times 10^{-4}$ $sec^{-1}$. In all cases it was established that reduction occurred solely at the carbonyl group.

The number of simple unstrained molecules with five or fewer carbons which have proved synthetically inaccessible must be vanishingly small; so $\alpha$-pyran, a member of this select group, merits some attention. Preparation of a simple $\alpha$-pyran was first reported[2] in 1917, but the report and the pyran proved equally short-lived, since von Auwers[3] showed that the compound was 2-vinyl-2,5-dihydrofuran and not methyl-$\alpha$-pyran. Interestingly, the first authentic relatively simple $\alpha$-pyran was inadvertently brought to light in 1957.[4] Recently Dreux[5] has notably lengthened the list of known $\alpha$-pyrans, but $\alpha$-pyran itself still has eluded all pursuers.[6]

Failure of our early attempts to prepare some $\alpha$-pyrans[7] was quite reasonably attributable to the often postulated[8] rapid and reversible equilibrium between the $\alpha$-pyran and cis dienones. Though the evidence leading to the postulation of this equilibrium is persua-

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