of *trans*-stilbene. Attempted hydrolysis of this adduct in a manner similar to that of the *trans*-stilbene adduct led to elimination of the elements of NOCl rather than hydrolysis.

4-Chloro-2-cyclopentenone.—A solution of 122 g (1.85 moles) of freshly distilled cyclopentadiene in 500 ml of carbon tetrachloride was cooled to −10° and nitrosyl chloride was added over a period of 3 hr. The temperature of the solution was not allowed to rise above 0° during the addition. The initially formed light green solution gradually turned to a dark brown during the course of the addition. Filtration of the slurry gave a light brown solid, which, when washed with cold methanol, gave 80 g (33%) of the white nitroso chloride dimer, mp 130–133°. An infrared spectrum identified the dimer and also showed no oxime to be present.

Anal. Calcd for $C_{10}H_{12}Cl_2N_2O_2$: C, 45.66; H, 4.56; Cl, 26.96: N, 10.65. Found: C, 45.97; H, 4.76; Cl, 26.87; N, 10.88.

The solid dimer was hydrolyzed by the general levulinic acid procedure at 50° for 3 hr. Work-up in the usual manner gave 24.4 g (34.5%) of the chloro ketone as a dark red oil which was difficult to distil without decomposition. An analysis of this oil by glpc at 100° (20% Carbowax 20M on Chromosorb P) showed only one chloro ketone product to be present. An analytical sample of this chloro ketone collected by gas–liquid partition chromatography showed carbonyl absorption at 1725 cm^{-1} and a shoulder at 1740 cm^{-1}. The nmr spectrum of this compound in CCl_4 showed absorption (relative to TMS as an internal standard) at δ 2.68 (complex multiplet for two protons at C-5), 5.14 (complex multiplet for proton at C-4), 6.22 (doublet with fine splitting for olefinic proton at C-2), and 7.62 (quartet for olefinic proton at C-3). Comparison of the infrared, ultraviolet, and nmr spectra of this compound with those of 4-bromo-2-cyclopentenone[8] served to identify it as 4-chloro-2-cyclopentenone.

***exo*-3-Chloronorcamphor and *exo*-3-Chlorodehydronorcamphor.**—These preparations were carried out using the procedure of Meinwald.[7]

Registry No.—Nitrosyl chloride, 2696-92-6; 2-chlorocyclopentanone, 694-28-0; 2-chlorocyclohexanone, 822-87-7; 2-chlorocycloheptanone, 766-66-5; 4-chloro-2-cyclopentenone, 14210-15-2.

Synthesis of Δ^3-Cyclopentenone and Δ^3-Cyclopentenol

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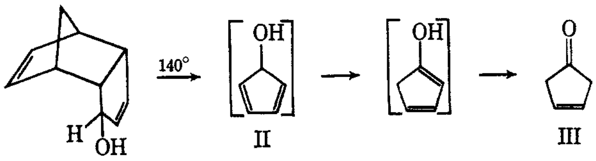
We wish to report the synthesis of Δ^3-cyclopentenone (III) and Δ^3-cyclopentenol (VI) by two independent routes, both giving isolated yields greater than 50%. Previous methods of synthesizing Δ^3-cyclopentenyl derivatives have given less satisfactory yields.[1–7]

Alder and Flock[1] have reported that the vapor phase pyrolysis of 1-dicyclopentadienol (I) produces a nearly quantitative yield of Δ^2-cyclopentenone, while the vapor phase pyrolysis of the alcohol in the presence of a catalytic amount of palladium on carbon produces a mixture of cyclopentenones, 20% of which is Δ^3-cyclopentenone. Rosenblum[8] has reported that the atmospheric pressure pyrolysis of 1-dicyclopentadienol gives a 31% yield of Δ^2-cyclopentenone along with unchanged alcohol.

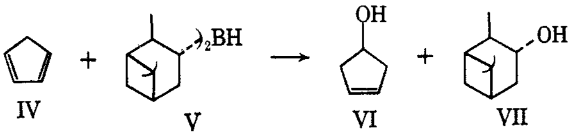
We have found that the atmospheric pressure pyrolysis of 1-dicyclopentadienol, using essentially the same conditions as those of Rosenblum, produces a 17% yield of Δ^2-cyclopentenone along with a 51% yield of Δ^3-cyclopentenone. Atmospheric pressure pyrolysis of the alcohol in the presence of a catalytic amount of palladium did not increase the yield of the Δ^3 ketone, but rather a 42% yield of Δ^2-cyclopentenone and a 17% yield of Δ^3-cyclopentenone were obtained.

All of these results are consistent with the view that the pyrolysis occurs *via* an initial reverse Diels–Alder reaction followed by isomerization of the 2,4-cyclopentadienol (II) to Δ^3-cyclopentenone which, depending upon the reaction conditions, is isomerized to a greater or lesser extent to the Δ^2 ketone.



I II III

Winstein and co-workers have reported that the monohydroboration of cyclopentadiene produces a 15^5–$30\%^{3,4}$ yield of 94% pure Δ^3-cyclopentenol. It has been demonstrated that the monohydroboration of cyclic dienes with alkyl-substituted boranes provides an increased yield of the corresponding unsaturated alcohol over that obtainable with borane itself.[9,10] Accordingly, we have monohydroborated cyclopentadiene with representative alkylboranes and have obtained Δ^3-cyclopentenol in greatly increased yields (Table I). Large-scale monohydroboration of cyclopentadiene with diisopinocampheylborane (V), obtained by the *in situ* hydroboration of α-pinene,[11,12] produces a 57% isolated yield of Δ^3-cyclopentenol which is greater than 99% pure by (glpc) analysis.



IV V VI VII

Consequently, the present procedures provide improved convenient synthetic routes to both Δ^3-cyclopentenone (III) and Δ^3-cyclopentenol (VI).

Experimental Section

1-Dicyclopentadienol (I) (mp 36–38°) was prepared in 56% yield by the selenium dioxide oxidation of dicyclopentadiene.[8]

Δ^3-Cyclopentenone (III).—Into a 200-ml three-necked flask, fitted with a nitrogen inlet and a Claisen head with a 6-in. side arm was placed 34.7 g (0.235 mole) of 1-dicyclopentadienol. The flask was heated over a free flame as a slow stream of dry nitrogen was passed through the alcohol. The distillate tempera-

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[3] S. Winstein, E. L. Allred, and J. Sonnenberg, *J. Am. Chem. Soc.*, **81**, 5883 (1959).

[4] E. L. Allred, J. Sonnenberg, and S. Winstein, *J. Org. Chem.*, **25**, 27 (1960).

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[6] P. D. Bartlett and M. R. Rice, *J. Org. Chem.*, **28**, 3351 (1963).

[7] F. Bennington and R. Morin, *ibid.*, **26**, 5210 (1961). These workers also reported that Dashkevich's synthesis could not be repeated.

[8] M. Rosenblum, *J. Am. Chem. Soc.*, **79**, 3179 (1957).

[9] G. Zweifel, K. Nagase, and H. C. Brown, *ibid.*, **84**, 183 (1962).

[10] G. Zweifel, K. Nagase, and H. C. Brown, *ibid.*, **84**, 190 (1962).

[11] G. Zweifel and H. C. Brown, *ibid.*, **86**, 393 (1964).

[12] H. C. Brown, N. R. Ayyangar, and G. Zweifel, *ibid.*, **86**, 397 (1964).

TABLE I

MONOHYDROBORATION OF CYCLOPENTADIENE PRODUCTS BY GLPC ANALYSIS

Reagent	Diene, mmoles	Borane, mmoles	% diol	% monool	Isomeric distribution of monool, % Δ^3-Cyclopentenol	Isomeric distribution of monool, % Δ^2-Cyclopentenol
Diborane[a]	20	3.33	26.5	34	97	3
Thexylborane[b]	20	5	27	49.2	98.9	1.1
Disiamylborane[c]	20	10	14	64.1	99.0	1.0
Diisopinocamphenylborane	20	10	7.5	83	100	0

[a] An unknown product (6.8% based on area) was noted with a retention time similar to the cyclopentenols. [b] 2,3-Dimethyl-2-butylborane. [c] Bis(3-methyl-2-butyl)borane.

ture was maintained at 140–150°. The products, collected in a flask cooled in a Dry Ice–acetone bath, were immediately fractionated to give 9.9 g (0.118 mole, 50.5% yield) of Δ^3-cyclopentenone (bp 28° at 17 mm, n^{20}D 1.4580), semicarbazone [mp 184–185° (lit.[1] bp 41° at 40 mm, n^{20}D 1.4536)], semicarbazone (mp 182°), and 3.4 g (0.041 mole, 17.2% yield) of Δ^2-cyclopentenone (bp 50° at 17 mm, n^{20}D 1.4813), 2,4-dinitrophenylhydrazone (mp 168–169° (lit.[1,8] bp 50° at 15 mm, n^{20}D 1.4810)), and 2,4-dinitrophenylhydrazone (mp 169–171°).

Pyrolysis of the alcohol as above, but with 0.5 mole% palladium on carbon added, produced a 17% yield of Δ^3-cyclopentenone and a 41.7% yield of Δ^2-cyclopentenone.

Reduction of the Δ^3-cyclopentenone with lithium aluminum hydride gave a 75% yield of Δ^3-cyclopentenol: bp 63.5–64° at 33 mm; n^{20}D 1.4698.

Monohydroboration of Cyclopentadiene with Alkylboranes.—The monohydroboration of cyclopentadiene with borane and alkylboranes was carried out using the procedure previously described[11,12] for the monohydroboration of 1,3-hexadiene. A solution of (borane) alkylborane in tetrahydrofuran was added to 20 mmoles (100% excess) of cyclopentadiene at 0°. After oxidation of the organoborane, the organic layer was isolated and the products were studied by capillary glpc on FFAP (free fatty acid phase). The isomeric distribution of cyclopentenols was determined by conversion of the alcohols to their acetates and analysis by capillary glpc on diethylene glycol succinate. The results are given in Table I. Because of its slower reactivity, the reaction of diisopinocampheylborane with cyclopentadiene was altered (see below).

Δ^3-Cyclopentenol (VI).—In a dry 1-l. flask, equipped with a magnetic stirrer, condenser, nitrogen inlet, and side arm, was placed 90 g (0.66 mole, 10% excess)[13] of dry α-pinene.[14] The flask, flushed with nitrogen, was immersed in an ice bath and 197 ml of a 1.52 M solution of borane (0.3 mole of BH_3) in tetrahydrofuran was added over a period of 15 min. The reagent was stirred for 2 hr at 0° and 39.6 g (0.6 mole, 100% excess) of freshly distilled cyclopentadiene (n^{20}D 1.4439) was added. The reaction mixture was slowly warmed to room temperature and stirred at room temperature for 17 hr. Excess hydride was decomposed by adding 10 ml of water and the organoborane was oxidized by adding 96 ml of 3 N sodium hydroxide, followed by dropwise addition of 96 ml of 30% hydrogen peroxide.

The aqueous layer was salted out with sodium chloride and the organic layer was removed. Cyclopentadiene and tetrahydrofuran were removed under vacuum. The mixture was then dissolved in 100 ml of ether and stirred for 30 min with 300 ml of a 1 M aqueous silver nitrate solution. The organic layer was removed and washed twice with aqueous silver nitrate. The aqueous layer was washed twice with ether. The aqueous layers were combined, an excess of sodium chloride was added to precipitate out silver chloride, and the alcohol was extracted with ether. After the ether layer was dried over magnesium sulfate, the ether was removed and the alcohol was distilled to give 14.4 g (0.172 mole, 57% yield) of Δ^3-cyclopentenol, bp 59–60° at 27 mm, n^{20}D 1.4698, and phenylurethan, mp 140–140.5° (lit.[4] bp 67–68° at 36 mm, n^{20}D 1.4673, mp 140.4–140.8°). The alcohol was shown to be contaminated by less than 1% of dicyclopentadiene by capillary glpc analysis on FFAP. Conversion of the alcohol to the acetate and capillary glpc analysis on diethylene glycol succinate showed the absence of Δ^2-cyclopentenol. The nmr and infrared spectra were identical with those of the Δ^3-cyclopentenol obtained from the lithium aluminum hydride reduction of Δ^3-cyclopentenone.

Registry No.—III, 14320-37-7; VI, 14320-38-8.

Base-Catalyzed Disproportionation of 2-Cyano-1,3-cyclohexadiene

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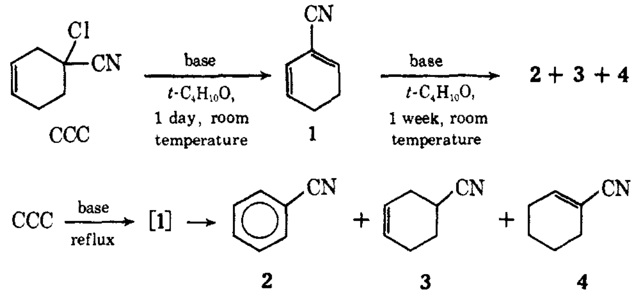
It was recently reported[1] that 1,3-cyclohexadiene treated with potassium *t*-butoxide in dimethyl sulfoxide (DMSO) underwent quantitative disproportionation to benzene and cyclohexene (55°, 24 hr). The kinetics exhibited a second-order dependence on cyclohexadiene concentration and it was postulated that the rate-determining step was hydride transfer from cyclohexadienyl anion to cyclohexadiene. In *t*-butyl alcohol, rather than DMSO, isomerization but not disproportionation occurred. More recently it was disclosed[2] that 1- and 2-bromo-1,3-cyclohexadiene treated with potassium *t*-butoxide in DMSO mostly underwent isomerization and disproportionation (which was not actually detected) was at best a very minor reaction.

In a related study conducted in these laboratories, it has been found that 2-cyano-1,3-cyclohexadiene when treated with sodium *t*-butoxide in refluxing *t*-butyl alcohol undergoes a very facile disproportionation to benzonitrile and a mixture of 1- and 4-cyanocyclohexene. The over-all course of the reactions involved is summarized in Scheme I. At room temperature, 4-chloro-4-cyanocyclohexene (hereinafter CCC) reacted smoothly with sodium *t*-butoxide in *t*-butyl alcohol to

SCHEME I



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[13] When stoichiometric amounts of α-pinene were used, lower yields of Δ^3-cyclopentenol were obtained. Even when a 10% excess of diborane was used, α-pinene was observed in the product, making extraction with silver nitrate necessary.

[14] α-Pinene was dried by distillation from lithium aluminum hydride.

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(2) A. T. Bottini and W. Schear, *J. Org. Chem.*, **30**, 3205 (1965).