and the *tert*-butyl alcohol was removed on a rotary evaporator at 40 °C. The concentrated aqueous solution was extracted with peroxide-free ether to obtain neutral fragments and then acidified and extracted continuously with ether for 14 h to isolate the acidic products.

The neutral fraction was shown by GC analysis to contain only one component. A few milligrams of this was purified by preparative GC and identified as 6-methyl-2,5-heptanedione from the following spectral data: NMR (100 MHz, CCl_4, Fourier transform) 1.08 (d, 6), 2.11 (s, 3), 2.58 (5) [lit.[15] 1.05 (d, 6), 2.06 (s, 3), 2.54 (5)]; mass spectrum (11 eV) *m/e* 142 (0.5, M^+), 99 (100), 71 (7), 43 (5); chemical ionization MS, 183 $(M + 43)^+$, 171 $(M + 29)^+$, 143 $(M + 1)^+$ (base peak), 125 $[(M + 1) - 18]^+$, 99 $(M - 43)^+$, 71 $(M - 71)^+$.

The sole significant acidic product was identified as levulinic acid by the GC retention times of the acid and its methyl ester (from diazomethane treatment) on columns A and B, respectively, in comparison to authentic reference samples.

Ozonolysis of Cembrene-C. Ozone was bubbled through a solution of 1 mg of cembrene-C in 2 mL of ethyl acetate at −70 °C for 6 min, at which time the solution remained blue. Part of the ozonolysis mixture was treated with *o*-phenylenediamine according to the procedure of Moore and Brown[12] to convert any glyoxal to quinoxaline. The latter was identified in the final reaction mixture by GC analysis on columns A and C (peak enhancement using an authentic sample).

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Registry No.—**1**, 31570-39-5; **2**, 64363-64-0; 6-methyl-2,5-heptanedione, 13901-85-4.

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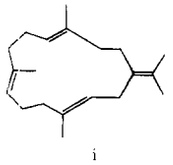

i

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Controlled-Potential Reduction of Cyclopropyl Ketones

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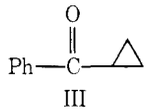
There are many instances of cyclopropyl systems reacting in a manner similar to double bonds. For example, addition reactions to cyclopropanes resulting in ring opening to 1,3-disubstitution products have been found with iodine,[1] bromine,[2] hydrogen bromide,[2,3a,b] hydrogen,[3b] and malonic ester anion.[4] Cyclopropyl rings have been used as double bond equivalents in Friedel–Crafts alkylations[5] and in Diels–Alder reactions.[6] Spectral studies have shown that cyclopropyl rings can affect absorption maxima in the ultraviolet region in much the way as does a double bond.[7]

We wished to see if this analogy could be realized in the electrochemical reduction of cyclopropyl ketones as compared to α,β-unsaturated ketones. Although there have been polarographic studies[8] of such systems there are no reported controlled potential reductions *with product isolation*. The polarography carried out revealed that the half-wave reduction potentials for cyclopropyl ketones is in between that of saturated ketones and α,β-unsaturated ketones, thus indicating a possible interaction of the cyclopropyl ring with the carbonyl group.

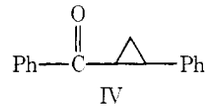
The reduction of α,β-unsaturated ketones follows the scheme shown in Scheme I. Which of the pathways obtains depends on the structure of the ketone and the potential at which the reduction is carried out. In some cases it is only possible to effect 2-e additions.

A similar scheme for cyclopropyl ketones would be Scheme II. Products B′, C′, and E′ could reflect interactions between the initially formed 1-e addition product and the cyclopropyl ring, I ↔ II, and would indicate an analogy to the olefinic system. The behavior of radicals of type I produced by chemical means has been studied by Neckers et al.[9]

Two ketones were subjected to polarography and controlled potential reduction, phenyl cyclopropyl ketone, III, and *trans*-1-benzoyl-2-phenylcyclopropane, IV.

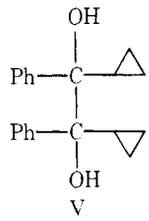


III

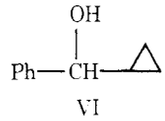


IV

From the controlled-potential reduction of ketone III, an 80% material balance was obtained which consisted of 40% starting ketone, III, 43% dimeric glycol, V, and 17% of the 2-e reduction product, cyclopropylphenylcarbinol, VI. These products provide no evidence for the interaction I ↔ II nor the analogy of this system with the double bond counterpart.



V



VI

The ketone IV on controlled-potential reduction provided (90% recovery) a mixture of the starting material, 25%, and γ-phenylbutyrophenone, VII. This result can be explained in terms of the increased importance of the type of interaction shown above, I ↔ II, when a phenyl is present to stabilize radical character as in IIa.

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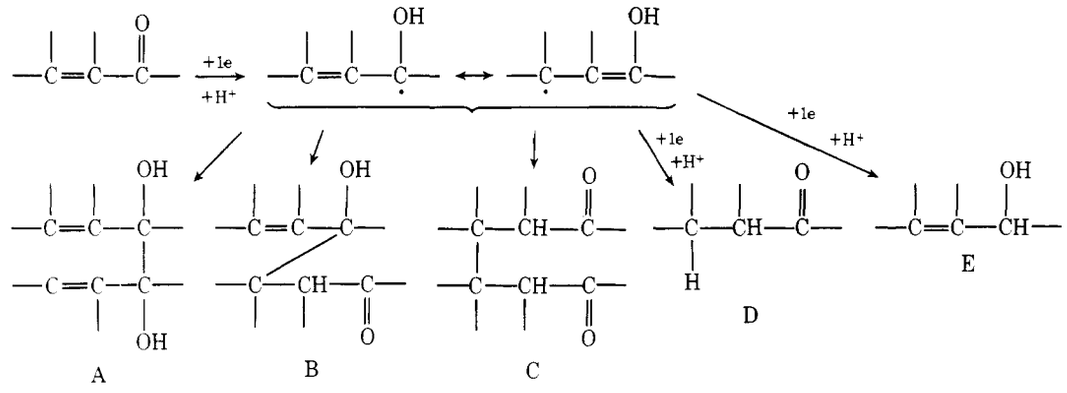
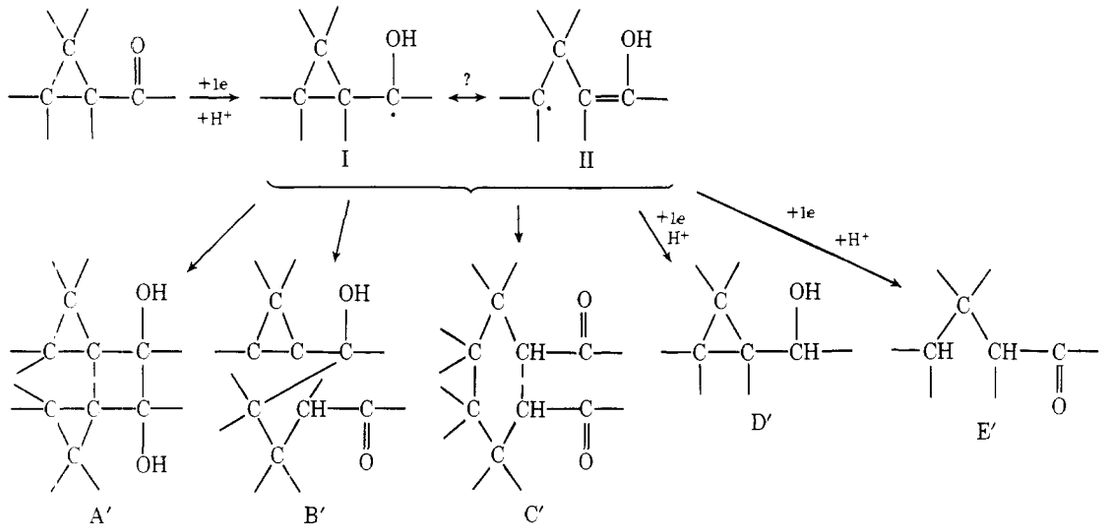
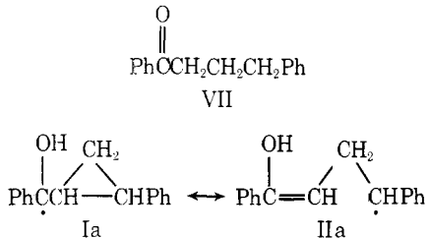
Scheme I



Scheme II





Experimental Section

Melting points are not corrected. NMR spectra were recorded on the Varian Model EM-360 using $CDCl_3$ as solvent and tetramethylsilane as an internal standard. IR spectra were taken on the Perkin-Elmer Model 257 spectrometer in spectral grade $CHCl_3$ as solvent. Gas chromatographic analysis was done on the Hewlett Packard Model 5712A. UV spectra were run on a Cary 14 recording spectrophotometer. The pH of solutions were measured with a Corning Digital 110 pH meter. Polarographic runs and controlled potential electrolyses were done on a Princeton Applied Research Model 170 Electrochemistry system (dropping mercury electrode and a saturated calomel electrode, SCE, for the polarography).

Preparation of Buffer. Na_2HPO_4 (14.196 g, 0.10 mol) was dissolved in 200 mL of distilled water. Enough water was then added to make 500 mL of 0.20 M Na_2HPO_4 solution. To this solution was added, with stirring, enough solid citric acid to bring the pH to approximately 3. Distilled water was added to increase the volume to 950 mL and then the pH was brought to exactly 3 with 1 M citric acid solution. Finally, the total volume was brought to 1 L.

Polarography of Ketones III and IV. The polarography was carried out in a 20-mL H-type polarographic cell. Solutions were purged with N_2 for 15 min before polarograms were run. The half-wave potential ($E_{1/2}$) for III (2.82×10^{-3} M in 1:1 EtOH/buffer) was -1.32 V vs. SCE for the addition of the first electron and -1.40 V for the addition of the second electron. For ketone IV (4.33×10^{-4} M in 3:2 EtOH/buffer) one wave with $E_{1/2} = -1.0$ V was observed.

Controlled-Potential Electrolysis of Ketones III and IV. The electrolysis cell was a convential three-electrode system, namely, mercury (instrument grade) pool working electrode (cathode), a saturated calomel reference electrode, and a Ag|AgCl auxiliary electrode (anode) which was separated from the solution by a fritted glass disk. Both reductions were carried out under N_2 atmosphere and with the mercury pool being stirred rapidly by a magnetic stirrer. Prior to each electrolysis the system was purged with N_2 for 30 min until a steady current for the system was reached.

Ketone III. EtOH/buffer (1:1, 220 mL) was placed in the electrolysis cell and purged with N_2 and the reduction potential was set at -1.38 V. After a steady background current was obtained 1.46 g (0.01 mol) of cyclopropyl phenyl ketone (III) in 30 mL of EtOH was added. The current returned to background level after 5 h. The pH of the solution was adjusted to 8 with saturated $NaHCO_3$ solution and the resulting solution was then extracted four times with 100-mL portions of $CHCl_3$. The $CHCl_3$ extracts were combined, dried over anhydrous $MgSO_4$, filtered, and concentrated to a cloudy oil.

Ketone IV. EtOH/buffer (3:2, 200 mL) was placed in the electrolysis cell and purged with N_2 and the reduction potential was set at -1.20 V and a steady background current obtained. *trans*-1-Benzoyl-2-phenylcyclopropane (IV) (2.15 g, 9.69×10^{-3} mol) in 50 mL of EtOH was added. After 21 h the current returned to background level. The solution was distilled under reduced pressure on a rotary evaporator to remove the ethanol. The pH of the aqueous solution which remained was brought to 8 by the addition of saturated $NaHCO_3$ solution and the solution was extracted five times with 100-mL portions of $CHCl_3$. The organic extracts were combined, dried over anhydrous $MgSO_4$, filtered, and concentrated to a cloudy, viscous oil (2 g, 90% recovery).

Product Isolation and Identification

Products of Electrolysis of Ketone III. The cloudy oil

obtained from work-up of the reduction of cyclopropyl phenyl ketone (III) was chromatographed on 85 g of Silicar CC-7, eluting with 10% ether in hexane. Three peaks totaling 1.0427 g were obtained. The first peak, 418 mg (40.09%), was the starting ketone III. The second peak, 447.6 mg (42.93%), was identified as the dimeric glycol (V). The final peak, 177.1 mg (16.98%), was determined by NMR analysis to be the 2-e reduction product, cyclopropylphenylcarbinol (VI).

Peak 2. Glycol: NMR δ 0.43 (m, 8 H), 1.55 (m, 2 H), 2.20 (s, 1 H, exchangeable with D_2O), 2.40 (s, 1 H, exchangeable with D_2O), 7.14 (m, 10 H); IR 1440 (w) 3580 (m); mp 115–120 °C. Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.63; H, 7.48. Found: C, 81.56; H, 7.52. This material is a mixture of *dl* and meso diols.

Peak 3. Cyclopropylphenylcarbinol: NMR δ 0.48 (m, 4 H), 1.22 (m, 1 H), 2.04 (s, 1 H, exchangeable with D_2O), 3.98 (d, 1 H, J = 8 Hz), 7.22 (m, 5 H).

Products of Electrolysis of Ketone IV. Thin-layer chromatography and GC analysis showed the viscous oil isolated from the reduction of 1-benzoyl-2-phenylcyclopropane (IV) contained only two products. One of the products had the same retention times as the starting material, and the NMR of the mixture indicated the presence of the ketone (IV). Area calculations of the GC trace showed the starting material comprised 24.8% of the mixture. The viscous oil was recrystallized from hexane to give a white crystalline substance that still contained some of the starting ketone. The crystals were chromatographed twice on Silicar CC-7, eluting with 15% ether in hexane. The only pure product isolated from the column, other than starting material, proved to be the 2-e reduction product, γ-phenylbutyrophenone, VII. Several fractions contained mixtures (by NMR and GC) of IV and VII. Evidence for the structure of VII is given below.

γ-Phenylbutyrophenone (VII): NMR δ 2.10 (m, 2 H), 2.82 (m, 4 H), 7.05–7.98 (m, 10 H); IR 1450 (m), 1580 (m), 1600 (m), 1680 (s), 2940 (m), 3000–3090 (m); UV λ_{max} 228 nm, ϵ 15 068 (1.46×10^{-5} M in hexane); mass spectrum, molecular ion peak at 224, intense peaks at 120 and 105, base peak at 77. Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.52; H, 7.20; mp 51–52 (lit.[10] mp 56–57 °C).

Registry No.—III, 3481-02-5; IV, 1145-92-2; V, 60079-97-2; VI, 1007-03-0; VII, 5407-91-0.

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