Anal. Calcd. for $C_{16}H_{16}O$: C, 85.71; H, 7.14. Found: C, 85.62; H, 7.26.

Treatment of a carbon tetrachloride solution of III with bromine yielded the dibromo derivative, m.p. 96–97°.

Anal. Calcd. for $C_{16}H_{16}OBr_2$: C, 50.00; H, 4.17. Found: C, 50.28; H, 4.24.

Permanganate oxidation and ozonolysis of III yielded benzophenone, identified by its 2,4-dinitrophenylhydrazone and phenylhydrazone.

Distillation of III resulted in the formation of an appreciable amount of a viscous, nonvolatile residue, which was readily soluble in ether and gave a bright red color with concentrated sulfuric acid.

The reaction between allylmagnesium bromide and benzophenone yielded 1,1-diphenyl-3-butene-1-ol, b.p. 135–138° (0.5 mm.), n_D^{25} 1.5875, D_{25}^{25} 1.0756; infrared spectrum of liquid film on salt plate: 3500 and 1645 cm.$^{-1}$ Kharasch and Weinhouse reported the boiling point, 150–155° (3.0 mm.) and no other constants.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.71; H, 7.14. Found: C, 85.58; H, 7.35. This product yielded a dibromo derivative, m.p. 186–188°.

Anal. Calcd. for $C_{16}H_{16}OBr_2$: C, 50.00; H, 4.17. Found: C, 50.22; H, 4.32.

4,4-Diphenyl-3-butenyl acetate. The Grignard adduct was treated with 20.4 g. (0.2 mole) of acetic anhydride, and the mixture was allowed to stir for 2 hr. at the reflux temperature of the ethereal mixture. The cold mixture was then treated with 120.0 ml. of 1.7*M* hydrochloric acid. The ether layer, after being treated in the usual manner, yielded 14.5 g. (54.5%) of the unsaturated ester, b.p. 144–146° (0.8 mm.), n_D^{25} 1.5740, D_{25}^{25} 1.0960; infrared spectrum of liquid film on salt plate: 1735, 1600, and 1245 cm.$^{-1}$

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.20; H, 6.76. Found: C, 81.27; H, 6.82.

Saponification of this ester in ethanolic potassium hydroxide yielded the unsaturated carbinol (III), which was identified by its physical constants and its dibromo derivative, m.p. 96–97°. The odor of ethyl acetate was also very prevalent in the saponification mixture.

Method 2. A mixture of 10.0 g. (0.041 mole) of I and 4.2 g. (0.041 mole) of acetic anhydride in 15 ml. of glacial acetic acid was refluxed for 1 hr. The cold mixture was diluted with 100 ml. of water and extracted with 150 ml. of ether in two portions. The ether solution of the ester was treated with water, sodium bicarbonate, and saturated sodium chloride before drying it over anhydrous sodium sulfate. After removing the ether and a small amount of forerun, 1.5 g. of viscous liquid, b.p. 110–122° (0.6 mm.) was distilled. This substance solidified on standing, m.p. 64–68°. It did not depress the melting point of a pure sample of II (68–69°). Further distillation produced 6.3 g. (66.0%) of the unsaturated acetate, b.p. 140–143° (0.6 mm.), n_D^{25} 1.5738.

2,2-Diphenyltetrahydrofuran (II). Decomposition of the Grignard adduct with 32.0 ml. of 6.5*M* hydrochloric acid yielded a viscous liquid, which on cooling in an ice bath for 4 hr. deposited 10.7 g. of crystals, m.p. 64–68°. Recrystallization from light petroleum ether gave 9.8 g. of II, m.p. 68–69°. Distillation of the liquid which was filtered from the crude solid yielded 3.5 g. of product, b.p. 100–120° (0.5 mm.) which solidified, m.p. 66–68°, bringing the total yield to 13.3 g. (59.5%). Compound II gave a bright red color with concentrated sulfuric acid.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.71; H, 7.14. Found: C, 85.45; H, 7.19; infrared spectrum in CCl_4: 1076 cm.$^{-1}$; ultraviolet spectrum in 95% ethyl alcohol: 211, 227, 252, 258, and 264 mμ.

Compound II did not decolorize permanganate or add bromine.

Distillation of the residue remaining after removing product II yielded 3.4 g. (15.0%) of III.

Method 2. Compound I (5.0 g.) was heated in an oil bath at 130° for 2 hr. On cooling, 4.5 g. (97%) of crystals, m.p. 66–68° was obtained. This product did not depress the melting point of II.

Method 3. A mixture consisting of 1.0 g. of I, 15.0 ml. of dioxane, 30.0 ml. of water, and 10.0 ml. of sulfuric acid was allowed to stand at room temperature for 6 hr. and then was poured into 200 ml. of water. This yielded 0.84 g. (92%) of product, m.p. 67–69°. This product did not depress the melting point of compound II.

Mixture of 1,1-diphenylbutane-1,4-diol (I) *and 2,2-diphenyltetrahydrofuran* (II). Decomposition of the Grignard adduct with 60.0 ml. of 3.5*M* hydrochloric acid yielded 20.0–22.0 g. (80–90%) of crude material, m.p. 88–98 . This product has the same melting point as a synthetic mixture of I and II in a 70:30 weight ratio. The infrared absorption curves of the two mixtures are very similar, showing approximately the same amount of absorption at 1076, 3340, and 3500 cm.$^{-1}$ in particular.

Attempts to separate the two components of the mixture by four crystallizations from cyclohexane yielded a fraction, m.p. 61–75° (pure II, m.p. 68–69°) and another product, m.p. 99–106° (pure I, m.p. 108–109°).

Mixture of 1,1-diphenylbutane-1,4-diol (I), *2,2-diphenyltetrahydrofuran* (II), *and 1,1-diphenyl-1-butene-4-ol* (III). Decomposition of the Grignard adduct with 43.0 ml. of 5.0*M* hydrochloric acid gave a product, which on cooling for 4 hr. in an ice bath deposited 12.3 g. (51.0%) of crystals, m.p. 86–96°, which is the 70:30% mixture of I and II. The liquid which was obtained by filtration was distllled, yielding 3.5 g. (15.0%) of compound III.

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Polarographic Reduction of Some Aliphatic Ketones

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Aliphatic ketones are reduced at a dropping mercury electrode only at fairly negative potentials. Neiman and Markina[1] reported the half-wave potentials of acetone and methyl ethyl ketone as −2.20 and −2.25 v., respectively, in 0.025 *M* tetramethylammonium iodide solution. Von Stackelberg and Stracke[2] reported the reduction of acetone and cyclohexanone in 0.05*M* tetraethylammonium iodide–75% dioxane, with half-wave potentials of −2.45 v. and −2.46 v., respectively. The number of electrons involved in the electrode process has not been measured for such ketones. However, diffusion current values reported in the literature[2] suggest a one-electron electrode process. On the other hand, it is known that it is difficult to obtain bimolecular reduction products from aliphatic ketones other than acetone when the reduction is carried out either chemically or electrolytically.[3,4] Swann[4] has reported that electrolytic

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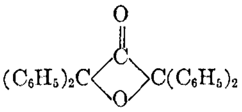
(1) M. B. Neiman and Z. V. Markina, *Zavodskaya Lab.*, **13**, 1177 (1947).

(2) M. von Stackelberg and W. Stracke, *Z. Elektrochem.*, **53**, 118 (1949).

(3) E. E. Royals, *Advanced Organic Chemistry*, Prentice-Hall, Inc., New York, 1954, p. 711.

reduction of acetone to pinacol can be effected in alkaline solution, but that the reaction is not general for aliphatic ketones. No pinacol was obtained, for example, upon electrolytic reduction of either methyl ethyl ketone or di-*n*-propyl ketone.

We have investigated the polarographic reduction of a series of aliphatic ketones and have isolated the products obtained in several instances when the electrolyses were carried out on a macro scale. The compounds studied were acetone, methyl cyclopropyl ketone, 1-phenylpropanone-2 (I), 1,3-diphenylpropanone-2 (II), 1,1,3-triphenylpropanone-2 (III), 1,1,3,3-tetraphenylpropanone-2 (IV), and the unusual molecule 2,2,4,4-tetraphenyl-3-oxetanone[5] (V). Macroelectrolyses were carried out with II, IV and V.



V

The results of the polarographic studies are summarized in Table I. It will be noted that the half-wave potentials obtained in ethanol are slightly more positive than those in dioxane, although the values are not widely different. This variation may arise from differences in liquid junction potentials in the two solvents. The values obtained for acetone and cyclohexanone are more negative than those reported by Neiman and Markina[1] and von Stackelberg and Stracke,[2] but are in more reasonable agreement with the values of the latter workers.

The half-wave potentials of the phenyl-substituted acetones become increasingly more positive as phenyl groups are substituted for hydrogen atoms in acetone. The oxetanone, V, has a half-wave potential of approximately -2.0 v., an unusually positive value for an aliphatic ketone. This compound also gives a larger diffusion current than the other ketones and there is a slight separation into two waves. Although the separation is not sharp, we have reported separate half-wave potentials in Table I.

Various attempts were made to determine by coulometric measurements the number of electrons involved in the electrode process. The experimental difficulties encountered when working at very negative potentials prevented conclusive evidence from being obtained. Best results were obtained with compound IV, but the volume correction for the blank was of the same order as the volume anticipated for reduction of the carbonyl group. A value of $n = 1.0$ was obtained for this compound but the data cannot be considered conclusive. Determinations were also run with the oxetanone, V, but the results were scattered, the values being nonintegral and considerably greater than two (see below). Evidence based on the polarographic diffusion currents indicate a one-electron electrode process for all compounds except V, but again data at such high potentials are inconclusive.

Controlled potential macroelectrolyses of II and IV gave the secondary alcohols, indicating, of course, an over-all two-electron process. From II essentially a quantitative yield of 1,1-diphenylpropanol-2 was obtained,[6] while the reduction of IV gave essentially, 1,1,3,3-tetraphenylpropanol-2 (VI) as the product. There was no evidence in either case of a bimolecular reduction product.

The macroelectrolysis of the oxetanone, V, apparently produced a mixture of products. As mentioned above, coulometric measurements of the number of electrons gave scattered, nonintegral values, considerably greater than two. Infrared analyses of the product and comparison with the spectra of pure samples of VI and of 2,2,4,4-tetraphenyl-3-oxetanol (VIII) indicated the presence of VII and another compound (or compounds) of structure similar to VI. The presence of the latter structure presumably resulted from opening of the oxetane ring. This ring has been found to open under the attack of chemical reducing agents,[7] yielding structures similar to VI. Such behavior would account for the scattered coulometric results.

TABLE I

HALF-WAVE POTENTIALS OF ALIPHATIC KETONES
(All $E_{1/2}$ Values Are Negative)

Compound	Dioxane[a] $E_{1/2}$	i_d/C	Ethanol[b] $E_{1/2}$	i_d/C
Acetone	2.61	2.0	2.53	3.2
Methyl cyclopropyl ketone	—	—	2.55	2.4
Cyclohexanone	2.54	2.2	—	—
I	2.45	2.5	2.34	3.0
II	2.22	2.4	2.10	2.6
III	2.16	2.3	—	—
IV	2.13	2.5	2.05	2.6
V	1.94	2.5	1.91	2.6
	2.05	2.5	2.08	1.7

EXPERIMENTAL

The polarographic data were obtained with a Leeds and Northrup Electro-chemograph Type E. Half-wave potentials were corrected for IR drop and for lag caused by galvanometer damping. The electrolysis cell was the usual H-type but in order to prevent the possibility of contamination of the cell solution by potassium ion a mercury-tetrabutylammonium chloride reference was used, the tetrabutylammonium chloride being at a concentration of $1M$. The agar plug was saturated with $1M$ tetrabutylammonium chloride. The potential of this reference cell was measured

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(4) S. Swann, Jr., in Weissberger's *Technique of Organic Chemistry*, Interscience Publishers, Inc., New York, 1956, Vol. II, p. 426.

(5) G. B. Hoey, D. O. Dean, and C. T. Lester, *J. Am. Chem. Soc.*, **77**, 391 (1955).

(6) Since the infrared spectra of pure 1,1-diphenylpropanol-2 and of the reduction product of II were identical, the highest order of impurity would be 5%.

(7) B. L. Murr, G. B. Hoey, and C. T. Lester, *J. Am. Chem. Soc.*, **77**, 4430 (1955).

against a saturated calomel electrode and all half-wave potentials were corrected to refer to the latter electrode.

The original runs were made with a solvent consisting of 75% dioxane–25% water, the supporting electrolyte being $0.05M$ tetrabutylammonium chloride. This was the solvent used by von Stackelberg and Stracke.[2] The dioxane was purified by the method of Hess and Frahm.[8] Later 80% ethanol–20% water was found to be a suitable solvent and was considerably more convenient than dioxane. A higher concentration of supporting electrolyte was used with the alcohol solutions, the cell solutions being $0.10M$ in both tetrabutylammonium chloride and tetrabutylammonium hydroxide. Blanks run with these solutions showed that appreciable decomposition of the supporting electrolyte did not occur below about −2.6 volts. The concentration of ketone in all cases was $0.001M$. A single capillary of Corning Marine barometer tubing was used. The value of $m^{2/3}t^{1/6}$ was 1.63 determined in 80% ethanol with an open circuit, and 1.45 at −2.40 v.

The macroelectrolyses were carried out using a potentiostat of the Lingane-Jones type.[9] A hydrogen-oxygen coulometer was used in the coulometric measurements. The cell, electrodes, and experimental procedures were essentially those recommended by Lingane.[10] In most cases identification of a product was carried out by comparison of its infrared spectrum to that of the authentic compounds.

The samples of III, IV, and V[5] were kindly furnished us by Dr. Charles T. Lester. The samples of polarographically pure tetrabutylammonium hydroxide and chloride were obtained from Southwestern Analytical Chemical Corp. All other organic reagents were Eastman white label products and were used without further purification.

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(8) K. Hess and H. Frahm, *Ber.*, **71**, 2627 (1938).

(9) J. J. Lingane and S. L. Jones, *Anal. Chem.*, **22**, 1169 (1950).

(10) J. J. Lingane, *Electroanalytical Chemistry*, 2nd Ed., Interscience Publishers, Inc., New York, 1958, p. 251.

Alkylation of Some Diacylhydrazines[1]

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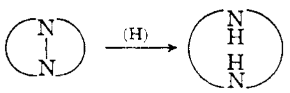
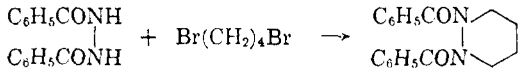
Received December 8, 1958

This report summarizes the preliminary work in a program aimed at the synthesis of bicyclic hydrazines (I) and conversion of the latter by hydrogenolysis to large ring diamines (II). The recent report[3] of the successful completion of a similar study has prompted us to terminate our own work in this area and to submit a brief account of experiments related to the syntheses of the precursors of the bicyclic hydrazines (I).



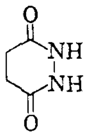
I II

Like Stetter and Spangenberger we were unable to effect the alkylation of 1,2-dibenzoylhydrazine with trimethylene bromide. We found, however, that 1,2-dibenzoylhydrazine and tetramethylene bromide in basic solution yield 1,2-dibenzoylhexahydropyridazine (III). The structure of III was established by its carbon, hydrogen analysis, its insolubility in basic solution, and its melting point.[4] Similar results have been obtained by using 1,2-diacetyl- and 1,2-diisobutyrylhydrazine.[3]

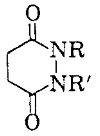


III

Alkylation of cyclic succinhydrazide (IV) by dimethyl sulfate in basic solution yielded 1,2-dimethylhexahydropyridazine-3,6-dione (Va), previously prepared by the hydrogenation of *N*,*N'*-dimethylmaleic hydrazide.[5] Alkylation of IV with ethyl iodide, however, yielded a product (Vb) bearing only one ethyl group. Assignment of structure Vb to the product is supported by the C, H analysis, the decreased melting point of the product relative to that of the starting material,[4] and the fact that the product could be extracted from acidic solution, but not from basic solution, in accord with the acidic properties of acylhydrazines containing the –CONH– group. Attempts to alkylate IV with tetramethylene bromide yielded a product, presumed to be VI. Although the product could not be purified sufficiently to yield satisfactory analytical results, the melting point (179–181°) agrees well with that (179–180°) reported[3] for VI, which was prepared from piperidazine and succinic anhydride. Extraction of the product from basic solution, and the decrease in the melting point relative to the starting material[4] is additional evidence in support of structure VI.

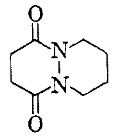


IV



V

a. $R = R' = CH_3$
b. $R = H; R' = C_2H_5$



VI

The cyclic succinhydrazide (IV) was prepared by catalytic hydrogenation of maleic hydrazide.[6] However, consistently successful reductions were obtained only if the latter compound was refluxed with a small quantity of Raney nickel before use.

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[1] Taken from the M.S. thesis of R. J. Landborg, State University of Iowa, August 1957.

[2] Present address: Union Carbide Research Institute, 32 Depot Plaza, White Plains, N. Y.

[3] H. Stetter and H. Spangenberger, *Ber.*, **91**, 1982 (1958).

[4] A decrease in m.p. usually accompanies substitution of an alkyl group for the peptide hydrogen of an acylhydrazine, R. L. Hinman and M. C. Flores, *J. Org. Chem.*, **24**, 660 (1959).

[5] K. Eichenberger, A. Staehelin, and J. Druey, *Helv. Chim. Acta*, **37**, 837 (1954).

[6] H. Feuer, G. B. Bachman, and E. H. White, *J. Am. Chem. Soc.*, **73**, 4716 (1951).