

## Electroorganic Preparations

## XXXI. Reduction of Acetylacetone in Hydrochloric Acid

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Acetylacetone (I) (pentanedione-2,4) has been reduced electrolytically in 0.5 N hydrochloric acid; the major products were 3-hydroxy-3-methylbutanone-2 (IIa), 3-methylbutanone-2 (IIb), *trans*-4,5-dimethyloct-4-ene-2,7-dione (III), and 3-acetyl-4-hydroxy-1,2,4-trimethylcyclopent-1-ene (IVa). The formation of these products can be explained by a primary inter- and intramolecular pinacolization.

Acetylacetone (I) and other  $\beta$ -diketones have previously been reduced electrolytically,<sup>1-4</sup> and by other means,<sup>5-9</sup> and several compounds, such as hydrocarbons, alcohols, pinacols, carbo- and heterocyclic compounds, have been described as products. Although some of the reports which have been made before NMR-measurements became available must be treated with a certain caution, it is apparent that the product distribution is very much dependent on the experimental conditions.

The present study is concerned with the electrolytic reduction of acetylacetone in 0.5 N hydrochloric acid; of the four major products isolated under these conditions, only IIb<sup>7</sup> has previously been obtained by reduction of I, and none of the other products reported in the literature have been found as major products.

## RESULTS AND DISCUSSION

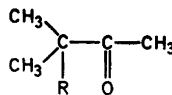
The reduction potential of acetylacetone in 0.5 N hydrochloric acid is close to the decomposition potential of the medium; some hydrogen evolution takes place during the reduction of I, and the amount of electricity consumed by acetylacetone has thus not been measured exactly; the measurements indicate, however, that  $n$  is between 1 and 2.

Reductions were performed in batches ranging from 5 to 50 g; the concentration of hydrogen ions was kept constant by addition of concentrated hydrochloric acid during the electrolysis. By VPC of the reaction mixture,

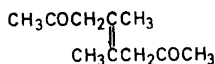
no acetic acid and only traces of acetone or 2-propanol were detected. The catholyte was extracted with methylene chloride, the more volatile parts of the extract fractionally distilled, and the residue chromatographed on silica; the following four major products were obtained in the yields indicated: 3-hydroxy-3-methyl-2-butanone (IIa) (33 %), 3-methyl-2-butanone (IIb) (7 %), *trans*-4,5-dimethyl-4-octene-1,7-dione (III) (15 %), and 3-acetyl-4-hydroxy-1,2,4-trimethyl-1-cyclopentene (IVa) (5 %). No other major products have been detected by VPC, TLC, or NMR, but a small yield (0.1 %) of 1,1,2,2-tetra-acetythane (V) and traces of several other products have been isolated.



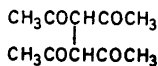
I



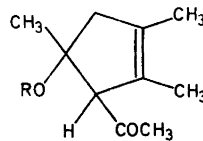
II a R = OH  
b R = H



III

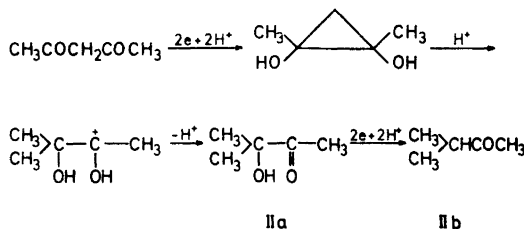


V



IV a R = H  
b R = CH<sub>3</sub>CO

*3-Hydroxy-3-methyl-2-butanone (IIa)*. The major reduction product was identified as IIa from its b.p., IR-, and NMR-spectra, and corroborated by its refractive index. Another fraction was similarly identified as IIb. IIa and IIb may be formed in the following way:



The first step is a reductive formation of an internal pinacol (VI); such compounds have previously been suggested as intermediates in abnormal Clemmensen reductions;<sup>6,7</sup> recently *cis* and *trans* cyclopropanediol derivatives have been isolated from electrolysis of  $\beta$ -dicarbonyl compounds in tetrahydrofuran.<sup>3</sup> Attack by a proton on the cyclopropane ring of VI produces the protonated form of IIa which like other  $\alpha$ -hydroxy ketones may be reduced further to IIb. The alternative pathway involving a pinacol rearrangement to 3-methyl-3-butanone (VII) seems less likely as attempts to add water to VII under the experimental conditions were not met with success.

*trans-4,5-Dimethyl-4-octene-2,7-dione (III)*. The structure of this compound was proved by its NMR-spectrum, which contained only three singlets ( $\delta = 1.67$ ,  $\sum H = 3$ ;  $\delta = 2.07$ ,  $\sum H = 3$ ;  $\delta = 3.12$ ,  $\sum H = 2$ ), the IR-spectrum, and elementary analysis. The configuration around the double bond was indicated by the Overhauser effect produced on irradiation of the methylene singlet at  $\delta = 3.12$ ; an increase (about 20 %) of the intensity of the signal at  $\delta = 1.67$  compared to that at  $\delta = 2.07$  proved the spatial proximity of the methylene group and the methyl group resonating at  $\delta = 1.67$ , and thus that the configuration is E.

*3-Acetyl-4-hydroxy-1,2,4-trimethyl-1-cyclopentene (IVa)*. The fourth major product has been suggested to have the structure IVa on the basis of the following data. The empirical formula, obtained from the mass spectrum, was  $C_{10}H_{16}O_2$ ; the IR-spectrum which had absorption bands at  $3450\text{ cm}^{-1}(\text{m})$  and  $1695\text{ cm}^{-1}(\text{s})$  showed that one oxygen atom was in a hydroxyl group and the other one in a carbonyl group. The presence of the former was substantiated by acetylation with acetic anhydride to a monoacetyl derivative (IVb). No oxygen atoms are thus available for ring formation which excludes pyran and furan derivatives.

The NMR-spectrum (in  $\text{CS}_2$ ) contained the following signals:  $\delta = 1.32$  (singlet),  $\sum H = 3$ ;  $\delta = 1.44 - 1.58$  (closely spaced multiplet),  $\sum H = 3$ ;  $\delta = 1.58 - 1.70$  (closely spaced multiplet),  $\sum H = 3$ ;  $\delta = 2.00$  (singlet),  $\sum H = 3$ ;  $\delta = 2.20 - 2.52$  (unresolved multiplet),  $\sum H = 2$ ;  $\delta = 2.90 - 3.15$  (broad signal  $\sim 14\text{ Hz}$ ),  $\sum H = 2$ .

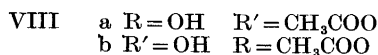
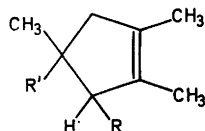
The signal at  $\delta = 1.32$  is caused by a methyl group  $\beta$  to a hydroxyl group and at a tertiary carbon atom, and that at  $\delta = 2.00$  by a methyl group adjacent to a carbonyl group. The two multiplets at about  $\delta = 1.50$  and  $\delta = 1.64$  have been interpreted as two methyl signals, broadened by homoallylic couplings. As one of the signals (at  $\delta \sim 1.50$ ) is slightly broader (10.5 Hz compared to 9 Hz) than the other, one of the methyl groups couples to more protons than the other methyl group; one of them is supposed to couple to a methylene group, and the other one to a methine group.

The protons of the methylene group give a broad unresolved multiplet at  $\delta = 2.20 - 2.52$ , whereas the methine proton and that in the hydroxyl group coincide at  $\delta = 2.90 - 3.15$ .

The NMR-spectrum of the acetylated compound (IVb) was quite similar to that of IVa, except for the signal from the added acetoxy group and the absence of the hydroxyl proton.

The mass spectrum showed, among other features, the degradation pattern of a benzene nucleus; 1,2-dimethylcyclopenta-1,3-dienes have been found to

produce benzene derivatives on electron impact.<sup>10</sup> This and the abovementioned data show that the compound must have the structure (VIII); a 1,2-dimethylcyclopenta-1,3-diene may be formed from VIII by loss of water.



A non-cyclic compound can be excluded from the absence of ethylenic protons and a six-membered carboxylic or a heterocyclic ring from the formula. As the methyl group ( $\delta = 1.32$ ) is at a tertiary carbon, only two possibilities remain, VIIIa and b.

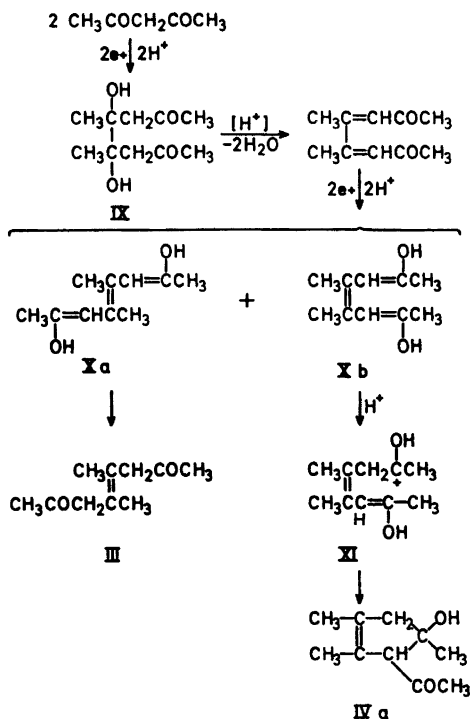
The choice can be made on the basis of the NMR-signal of the methine proton. If R=OH (VIIIa), the methine proton would, besides being allylic, be bonded to a hydroxyl-bearing carbon, and the signal would be expected at  $\delta > 4$ , whereas an allylic proton neighbour to a carbonyl group (R=CH<sub>3</sub>CO, VIIIb=IVa) would be expected to resonate about  $\delta = 3$ , which is in accordance with the observed spectrum. The methyl signal at  $\delta = 1.32$  is also in accordance with the hydroxyl group being at C-4.

The stereochemical structure of the compound has not been proved; three pieces of evidence, however, point to a *trans*-relationship of the methyl group at C-4, and the acetyl group at C-3. The acetylated compound (IVb) has a considerable thermal stability (unaffected by heating for 20 h at 110°C) which points to the absence of an easy *cis*-elimination. The carbonyl frequency of the methyl ketone shifts from  $\nu = 1695 \text{ cm}^{-1}$  in IVa to  $1715 \text{ cm}^{-1}$  in the acetylated compound; this may reflect the presence of some hydrogen bonding in IVa (and thus a *cis*-relationship between the hydroxyl and the carbonyl group) which is absent in IVb. Further, the reaction scheme suggested below would on steric grounds seem to favour the *trans*-relationship indicated above; according to the Z-E convention, IVa is thus suggested to be Z.

The primarily formed compound IX is similar to that isolated from reduction of dimedone in various alcohols or DMF;<sup>4</sup> the loss of water produces a conjugated diketone which would be easier reducible than I. A 1,8-reduction produces a mixture of Xa and Xb; Xa forms on tautomerization III, which as a non-conjugated ketone is difficult to reduce further.

Under acid catalysis, a cyclization of XI by internal condensation takes place; on steric grounds a transition state in which the methyl group and the acetyl group would be as far apart as possible would be favoured, and this would lead to a *trans*-arrangement of the two groups in the product.

Besides the compounds IIa, IIb, III, and IVa, a small amount of 1,1,2,2-tetraacetyethane (0.1 %) (V) was isolated; this is an oxidation product and is probably formed through a mercury compound. Several other compounds have also been isolated in small yields (< 2 %), but they have not been characterized yet. In more strongly acid solution, organo-mercury compounds become more important products; some of these compounds survive purifica-



tion on a column, but decompose rapidly when not in solution. The structure of these compounds is studied at present.

Compounds IIa, III, and IVa require two electrons per molecule acetylacetone, whereas IIb consumes four. Application of these data to polarographic conditions is difficult for two reasons; the chemical steps interposed between the electron transfer reactions in the bimolecular process might be slow, so the reduction at the DME may occur as a one-electron reaction; furthermore, the relative importance of the intra- and intermolecular pinacolization may change with concentration.

From this investigation it might be concluded that the reduction products of acetylacetone in 0.5 N hydrochloric acid can be explained by assuming that primarily a mixture of inter- and intramolecular pinacols are formed and the isolated products are obtained from these by further reaction and/or reduction.

#### EXPERIMENTAL

*Apparatus.* For the electrochemical reductions, a fully transistorized potentiostat (Tage Juul Electronics, Copenhagen) capable of delivering 3 A at 100 V was used.

The NMR-spectra were recorded on a Varian Associates A-60 or HA-100 spectrometer; tetramethylsilane (TMS) was used as internal standard. The IR-spectra were recorded on a Beckman IR-18 spectrophotometer or on a Perkin-Elmer Infraord; for the

UV-spectra a Bausch and Lomb Spectronic 505 was used, and for the mass spectra a Hitachi-Perkin-Elmer RMU-6D.

*Reduction of acetylacetone (I)*. 10 ml (9.8 g) of acetylacetone were reduced at  $-1.25$  V (SCE) in a deaerated, pre-reduced 0.5 N hydrochloric acid. During the reduction, pH was kept constant by addition of hydrochloric acid. The reduction consumed between 1 and 2 F/mol. The reduction completed, the reaction mixture was extracted four times with methylene chloride which was then dried (magnesium sulphate) and removed by distillation. The extracted products were fractionated by distillation, yielding 0.6 g IIb and 3.2 g IIa. The residue (from the distillation) was separated on a column of silica with methylene chloride and ether as eluent, starting with methylene chloride, and gradually increasing the ether content to 10 %. Isolated were traces of IIa, I, IIb, and V, before the two major fractions III (1.2 g) and IVa (0.4 g). Traces of three compounds, the constitution of which has not been established yet, were isolated in the later fractions. The products were characterized as follows.

*3-Methylbutanone-2 (IIb)*, b.p.  $93^{\circ}\text{C}$  ( $92^{\circ}_{738}$ ),<sup>11</sup>  $n_{\text{D}}^{25}$  1.3842 ( $n_{\text{D}}^{16}$  1.3880).<sup>11</sup> NMR-spectrum ( $\text{CDCl}_3$ ):  $\delta=1.06$  (doublet,  $J=6.5$  Hz),  $\sum\text{H}=6$ ;  $\delta=2.06$  (singlet),  $\sum\text{H}=3$ ;  $\delta=2.49$  (septet,  $J=6.5$  Hz),  $\sum\text{H}=1$ . IR-spectrum (neat,  $\text{cm}^{-1}$ ): 2980(s), 1715(s), 1470(m), 1360(m), 1240(m).

*3-Hydroxy-3-methyl-2-butanone (IIa)*, b.p.  $137^{\circ}\text{C}$  ( $139^{\circ}$ ),<sup>12</sup>  $n_{\text{D}}^{24}$  1.4142 ( $n_{\text{D}}^{18}$  1.4160).<sup>13</sup> NMR-spectrum ( $\text{CDCl}_3$ ):  $\delta=1.30$  (singlet),  $\sum\text{H}=6$ ;  $\delta=2.19$  (singlet),  $\sum\text{H}=3$ ;  $\delta=3.8-4.0$  (broad singlet),  $\sum\text{H}=1$ . IR-spectrum ( $\text{CHCl}_3$ ,  $\text{cm}^{-1}$ ): 3450(s), 2970(s), 1700(s), 1450(m), 1340(s), 1220(m), 1160(s), 1110(m), 955(s).

*trans-4,5-Dimethyloct-4-ene-2,7-dione (III)*, m.p.  $17^{\circ}\text{C}$ . (Found: C 70.48; H 9.36. Calc. for  $\text{C}_{10}\text{H}_{16}\text{O}_2$ : C 71.39; H 9.59.) NMR-spectrum ( $\text{CDCl}_3$ ):  $\delta=1.66$  (singlet),  $\sum\text{H}=3$ ;  $\delta=2.08$  (singlet),  $\sum\text{H}=3$ ;  $\delta=3.12$  (singlet),  $\sum\text{H}=2$ . IR-spectrum (neat,  $\text{cm}^{-1}$ ): 2990(m), 2945(m), 1715(s), 1430(m), 1315(m), 1240(m), 1170(m).

*3-Acetyl-4-hydroxy-1,2,4-trimethylcyclopent-1-ene (IVa)*. NMR-spectrum ( $\text{CS}_2$ ):  $\delta=1.32$  (singlet),  $\sum\text{H}=3$ ;  $\delta=1.44-1.58$  (multiplet),  $\sum\text{H}=3$ ;  $\delta=1.58-1.70$  (multiplet),  $\sum\text{H}=3$ ;  $\delta=2.0$  (singlet),  $\sum\text{H}=3$ ;  $\delta=2.2-2.52$  (multiplet),  $\sum\text{H}=2$ ;  $\delta=2.90-3.15$  (broad singlet),  $\sum\text{H}=2$ . IR-spectrum (neat,  $\text{cm}^{-1}$ ): 3450(m), 2900(m), 1695(s), 1430(m), 1340(m), 1220(m), 1160(m), 1120(m), 945(m). Mass spectrum ( $m/e$  (%)): 39 (18), 41 (17), 43 (100), 51 (6), 53 (8), 55 (15), 65 (10), 77 (13), 79 (17), 83 (13), 91 (32), 93 (38), 107 (30), 108 (45), 110 (14), 125 (24), 150 (28), 166 (1), 168 (1).

*Acetylation of IVa*. Compound IVa (1380 mg) was dissolved in 5 ml of acetic anhydride and refluxed for 5 h. The cooled reaction mixture was then poured into an alkaline solution and made neutral with potassium hydroxide. The solution was extracted with methylene chloride, the organic layer washed with water, dried (magnesium sulphate), and the solvent removed *in vacuo*. The residue was separated on a column of silica with a mixture of methylene chloride and ether as eluent, starting with pure methylene chloride and ending with 10 % ether/methylene chloride. Isolated were 750 mg of:

*4-Acetoxy-3-acetyl-1,2,4-trimethylcyclopent-1-ene (IVb)*. NMR-spectrum ( $\text{CDCl}_3$ ):  $\delta=1.50-1.62$  (multiplet),  $\sum\text{H}=3$ ;  $\delta=1.59$  (singlet),  $\sum\text{H}=3$ ;  $\delta=1.62-1.72$  (multiplet),  $\sum\text{H}=3$ ;  $\delta=1.93$  (singlet),  $\sum\text{H}=3$ ;  $\delta=2.10$  (singlet),  $\sum\text{H}=3$ ;  $\delta=2.55-2.92$  (multiplet),  $\sum\text{H}=2$ ;  $\delta=3.32-3.48$  (broad singlet),  $\sum\text{H}=1$ . IR-spectrum (neat,  $\text{cm}^{-1}$ ): 2980(m), 2920(m), 2860(m), 1750(s), 1720(s), 1450(m), 1375(s), 1250(s), 1130(s), 1020(m). Mass spectrum ( $m/e$  (%)): 32 (32), 39 (15), 41 (21), 43 (100), 53 (11), 55 (11), 65 (13), 77 (19), 79 (35), 91 (51), 93 (75), 107 (83), 108 (100), 109 (31), 125 (21), 135 (5), 150 (68), 151 (11), 167 (3), 182 (<1).

*1,1,2,2-Tetraacetyethane (V)*, m.p.  $190^{\circ}\text{C}$  ( $189-191^{\circ}$ ).<sup>14</sup> NMR-spectrum ( $\text{CDCl}_3$ ):  $\delta=1.98$  (singlet),  $\sum\text{H}=6$ ;  $\delta=5.5$  (singlet),  $\sum\text{H}=1$ . IR-spectrum (KBr,  $\text{cm}^{-1}$ ): 2950(m), 1590(s), 1540(s), 1380(s), 1280(m), 1020(m), 960(m), 770(m).

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