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THE FORMATION OF 3(OR 5)-METHYLCYCLOPENT-2-EN-2-OL-1-ONE* FROM ACETONE

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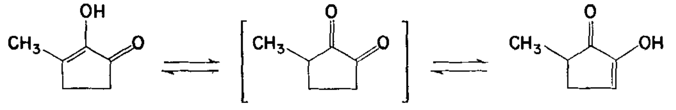
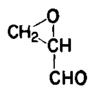
Abstract—The original observation that 3(or 5)-methylcyclopent-2-en-2-ol-1-one (I) was formed (in low yield) by the treatment of glycidaldehyde with acetone in the presence of aqueous alkali, and speculations concerning the reaction mechanism, led to the realization that the reaction could also be carried out with glyceraldehyde. This suggested an explanation for the previously known formation of I by drastic alkali-treatment of carbohydrates.

The treatment of glycidaldehyde (II)[3] with acetone and aqueous alkali afforded, in low yield, a crystalline solid of composition $C_6H_8O_2$, which was found to be identical with the known 3(or 5)-methylpent-2-en-2-ol-1-one (I).[1,2] This compound is a minor product of the destructive distillation of wood,[4] and has also been obtained from wood by the action of hot aqueous alkali under pressure.[5] It has previously been synthesized (a) by dehydrogenative cyclization of 3,4-dihydroxyhexa-1,5-diene (III) with copper,[6] (b) from 2-methylcyclopentanone (IV) by chlorination and subsequent hydrolysis of the resulting dichloro-derivative,[7] (c) from 3,5-diethoxycarbonylcyclopentan-1,2-dione (V) by methylation followed by ketonic hydrolysis,[8] and (d) by epoxidation of 3-methylcyclopent-2-en-1-one (VI) and isomerization of the resulting epoxide with boron trifluoride.[9]


Ib Ia Ic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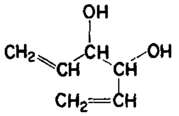
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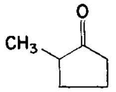
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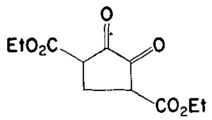
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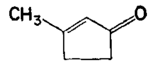
VI

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* The mono-enol form in which 3-methylcyclopentan-1,2-dione (Ia) exists was originally thought to have the structure of 3-methylcyclopent-2-en-2-ol-1-one (Ib).[1] Later investigators,[2] however, preferred to formulate the compound as 5-methylcyclopent-2-en-2-ol-1-one (Ic).

[1] C. A. Rojahn and F. Rühl, *Arch. Pharm.* **264**, 211 (1926).

[2] G. Hesse and K. Breig, *Liebigs Ann.* **592**, 120 (1955).

[3] G. B. Payne, *J. Amer. Chem. Soc.* **81**, 4901 (1959).

[4] J. Meyerfeld and C. Ohlgart, *Chem. Z.* **36**, 549 (1912).

[5] T. Enkvist, B. Alfredsson, M. Merikallio, P. Pääkkönen and O. Järvelä, *Acta Chem. Scand.* **8**, 51 (1954).

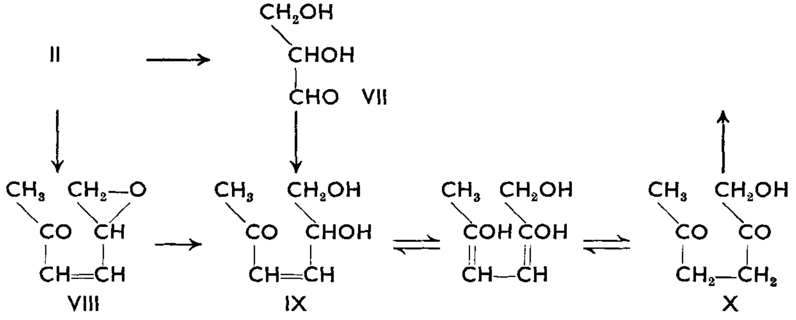
[6] G. Dupont and E. Urion, *C.R. Acad. Sci., Paris* **197**, 158 (1933); E. Urion, *Ann. Chim.* [11] **1**, 5 (1934).

[7] H. Gault and J. Burkhard, *C.R. Acad. Sci., Paris* **205**, 1416 (1937).

[8] G. Hesse and K. W. F. Böckmann, *Liebigs Ann.* **563**, 37 (1949).

[9] H. O. House and R. L. Wasson, *J. Amer. Chem. Soc.* **79**, 1488 (1957).

It was thought that the above reaction with glycidaldehyde (II) might have proceeded by initial hydration of the epoxy-group to afford glyceraldehyde (VII), followed by a condensation of the aldol type with acetone. Alternatively, or concurrently, condensation with acetone might have preceeded hydration, with the intermediate formation of the unsaturated epoxy-ketone (VIII). In either case, tautomeric rearrangement of the resulting product (IX) leading to the hydroxy-diketone (X), followed by an intramolecular aldol condensation,[10] could then have yielded the final product (I).



Support for the above mechanism was obtained by carrying out the reaction with glyceraldehyde (VII), which afforded I in similar yield. It seemed that this reaction provided an explanation for the production of I from wood by vigorous treatment with alkali, since alkaline degradation of the cellulose and other carbohydrate constituents could give rise to both acetone[11] and glyceraldehyde.[12]

It has been shown that I is formed not only from wood, but also (in very low yield) from galactose and glucose,* by the action of hot aqueous alkali under pressure.[5] Triose-reductone (XI) was also identified as a product of the galactose reaction, which was therefore explained on the basis of a disproportionation involving two molecules of the hexose:

$$2C_6H_{12}O_6 \rightarrow \underset{\mathrm{I}}{C_6H_8O_2} + 2\underset{\mathrm{XI}}{CH(OH){:}C(OH).CHO} + 4H_2O$$

However, it was found that, while none of the methylcyclopentenolone (I) was obtained by treatment of glucose with aqueous alkali at the reflux temperature, a similar reaction carried out in the presence of acetone produced an easily isolated amount of I.† This confirmed the view that the formation of 3(or 5)-methylcyclopent-2-en-2-ol-1-one (I) by the drastic treatment of carbohydrates with alkali results from a reaction between acetone and glyceraldehyde.

EXPERIMENTAL

3(*or* 5)-*Methylcyclopent-2-en-2-ol-1-one* (I)

(a) *From glycidaldehyde.* Glycidaldehyde‡ (20 g) in acetone (40 cc) was added gradually to a stirred mixture of sodium hydroxide (5 g), water (100 cc), and acetone (60 cc); a vigorous exothermic

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* In the reaction with glucose, the product (I) was not isolated in the pure state, but was detected by U.V. light absorption studies.

† The failure to isolate I in the absence of acetone could have been due to the small scale of the experiment, or possibly because the conditions were not sufficiently drastic to produce an appreciable amount of acetone *in situ*.

‡ Kindly supplied by Shell Development Company, Emeryville, California.

[10] *Cf.* H. Hunsdiecker, *Ber. Dtsch. Chem. Ges.* **75B**, 455 (1942).

[11] S. Odén and S. Lindberg, *Industr. Engng. Chem.* **19**, 132 (1927).

[12] G. N. Richards and H. H. Sephton, *J. Chem. Soc.* 4492 (1957).

reaction occurred, and the mixture refluxed. Stirring was continued for 2 hr, and then the dark solution was saturated with sodium chloride and washed well with ether. The aqueous layer was acidified with hydrochloric acid and extracted with ether, and the ethereal solution dried ($MgSO_4$) and evaporated. The tarry residue, which had a characteristic smell resembling that of burnt sugar, was extracted several times with boiling light petroleum (b.p. 40–60°); on cooling, the combined extracts deposited needles (0·63 g), m.p. 97–99°. Further purification of the product by sublimation at 90–100°/20 mm, followed by recrystallization from ether–light petroleum (b.p. 40–60°), afforded prisms, m.p. 105–106° (Found: C, 64·2; H, 7·2. Calc. for $C_6H_8O_2$: C, 64·3; H, 7·2%). The infra-red spectrum showed bands at 2·98 (O—H), 5·90 (C=O), and 6·07 μ (C=C). The product reduced Fehling's solution and ammoniacal silver nitrate solution, and gave a violet colour with aqueous alcoholic ferric chloride solution; it was identified as 3(or 5)-methylpent-2-en-2-ol-1-one by a mixed melting-point determination with an authentic specimen, and by comparison of the infra-red spectra.* The bis-phenylhydrazone was obtained as yellow needles (from aqueous ethanol), m.p. and mixed m.p. 140·5–141·5° (Rojahn and Rühl[1] recorded m.p. 138–139°).

Comparative experiments with other alkalis showed that while a similar yield could be obtained with potassium hydroxide in water, the yield was much reduced when potassium hydroxide in methanol was used, and with sodium ethoxide in dry ethanol none of the methylcyclopentenolone could be isolated.

(b) *From glyceraldehyde.* A mixture of glyceraldehyde dimer (5·0 g), acetone (35 cc), sodium hydroxide (1·0 g), and water (40 cc) was refluxed for 5 hr. Working-up as above afforded the crude product (0·11 g), m.p. 100–102°, and recrystallization then gave the methylcyclopentenolone, m.p. and mixed m.p. 105–106°. An equivalent amount of glycidaldehyde (4·0 g), under the same conditions, yielded 0·14 g of the crude product, m.p. 98–100°.

Comparative experiments were also carried out using a higher proportion of alkali and a shorter reaction time. Thus glyceraldehyde (5·0 g), acetone (75 cc), sodium hydroxide (3·0 g), and water (90 cc), refluxed for 5 min, afforded 0·07 g of crude product, m.p. 90–94°; glycidaldehyde (4·0 g) gave 0·06 g of the material, m.p. 93–98°.

(c) *From glucose.* A mixture of glucose (7·5 g), sodium hydroxide (2·0 g), water (45 cc), and acetone (35 cc), refluxed for 2½ hr, yielded 0·09 g of crude product, m.p. 80–84°, raised by recrystallization to 104–105° (undepressed on admixture with an authentic specimen of the methylcyclopentenolone).

A similar experiment was performed in the absence of acetone (using 80 cc of water); none of the methylcyclopentenolone could be isolated by the usual working-up procedure.

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* The identity of the product was kindly suggested by Dr. E. D. Morgan.