uct crystallized readily when cooled in an ice-bath but slowly liquefied on standing at room temperature.

Four recrystallizations of a specimen from 60–68° petroleum ether gave colorless needles, m.p. 54.4–54.7°.

Anal. Calcd. for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.64; H, 8.38.

Pyrolysis of VI.—The liquid acetate prepared as above was added dropwise from a pressure-equalized dropping funnel to the top of a vertical 80 × 2-cm. combustion tube packed with carbon-covered (from previous pyrolyses) glass beads and heated by an electric furnace. The reaction was conducted under a slight positive pressure of dry nitrogen and the pyrolysate collected in an ice-cooled filter flask attached to the lower, constricted end of the combustion tube. The results are summarized in Table I. The yields of I were calculated by comparing the extinction coefficients of the pyrolysates with that of pure I at 234 mμ (pure VI has $E_{\lambda 234}$ 15). Some dimeric product[9] crystallized from the pyrolysates on standing.

TABLE I

PYROLYSIS OF 2-ACETOXY-2-METHYLCYCLOHEXANONE

Temp., °C.	VI used, g.	Pyrolysate, g.	Estimated % of I in pyrolysate	Dimer, %
350	16.00	15.15	14	2.5
390	8.21	6.79	25	Not weighed
420	11.72	9.67	32	4.0
450	11.34	8.87	38	8.0

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The Dimer of 2-Methylenecyclohexanone

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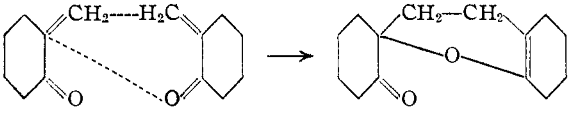
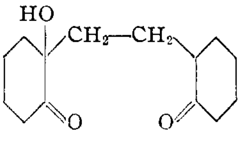
In 1920, Mannich and Braun[1] reported the formation of a compound, $C_{14}H_{22}O_3$, m.p. 149°, as a by-product in the Mannich reaction with cyclohexanone and dimethylamine hydrochloride. The normal product, 2-(dimethylaminomethyl)-cyclohexanone hydrochloride, on pyrolysis[2] gave, in addition to the expected 2-methylenecyclohexanone (I), substantial amounts of an oil from which the 149° compound was isolated by trituration with acid. It was later shown[2] that on standing I rapidly formed an oily dimer which was the product II of a heterocyclic Diels–Alder type reaction[3] between two molecules of I. This dimer underwent easy hydration in the presence of acid to give the 149° compound which was formulated as the diketo alcohol IIIa. It is noteworthy that in the later work[2] this substance was found to melt at 154–155°.

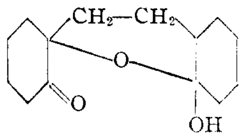
In the course of a study of the preparation of 2-methyl-2-cyclohexenone (IV),[4] 2-chloro-2-methylcyclohexanone (V) was dehydrochlorinated to give, in addition to the unsaturated ketone IV, a high-boiling oil which, on standing or trituration with aqueous solvents, partially crystallized to give colorless prisms, $C_{14}H_{22}O_3$, isolated in two forms, m.p. 146–147° and 141–142° (see discussion below) in yields as high as 20%. This same product was isolated in up to 8% yields from attempts to prepare IV by pyrolysis of 2-acetoxy-2-methylcyclohexanone (VI),[4] and was also encountered during an attempted condensation of acetylene and formaldehyde in cyclohexanone solution with a copper acetylide catalyst.[5] The identity of these specimens with the hydrated dimer of Mannich was established by mixture melting point determination and infrared spectroscopy.



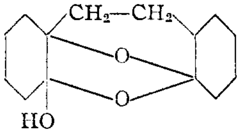
I II



IIIa



IIIb



IIIc

The formulation of the hydrated dimer as IIIa, however, is incompatible with the infrared spectrum which shows no carbonyl band, but instead a very intense hydroxyl absorption at 2.95 μ (Nujol mull). On this evidence the structure is preferably represented as IIIc rather than by either of the tautomeric possibilities IIIa or IIIb. The appearance of a very weak carbonyl absorption at 5.91 μ in chloroform solution suggests that in this medium there is some tautomerization to one of the ketonic modifications, the equilibrium, however, lying largely in favor of IIIc (since the hydroxyl band is intense). Additional evidence for a facile tautomerism (presumably acid-catalyzed) among IIIa, IIIb and IIIc in solution is the ready formation of biscarbonyl derivatives from the hydrated dimer.[2]

The higher melting specimens of III slowly changed to the lower melting form on standing and occasionally on crystallization. Apparently this is a case of polymorphism rather than a variation in the proportion of IIIa to IIIb to IIIc in a given sample since the infrared spectra (Nujol mull) of a somewhat higher and a lower melting form were identical and showed no band whatsoever in the carbonyl region. We have not obtained specimens melting as high as that reported by Mannich[2]; hence the possibility remains that he may have had one of the other tautomeric forms.

Additional support for the basic structure of III was provided by the following: (a) the compound had no ultraviolet absorption peaks from 215 to 340 mμ, (b) C-methyl determinations indicated the absence of any methyl groups, and (c) the molec-

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(1) C. Mannich and R. Braun, *Ber.*, **53**, 1874 (1920); *cf.* also K. Dimroth, K. Resin and H. Zetsch, *ibid.*, **73**, 1399 (1940).

(2) C. Mannich, *ibid.*, **74**, 554, 557 (1941).

(3) K. Alder, H. Offermans and E. Rüden, *ibid.*, **74**, 905 (1941).

(4) E. W. Warnhoff and William S. Johnson, THIS JOURNAL, **75**, 494 (1953).

(5) This experiment was carried out by Dr. A. W. Johnson of Cambridge University, who told us of his results during a discussion of this problem in the fall of 1951. We are grateful to Dr. Johnson for permitting us to mention his work, and for sending us a specimen of his product for comparison.

ular weight determined by the Rast method was 229 (calcd. for $C_{14}H_{22}O_3$, 238).

The hydrated dimer IIIc was not obtained when 2-methyl-2-cyclohexenone (IV) was subjected to the conditions used in the elimination reactions to prepare IV. Evidently the 2-methylenecyclohexanone necessary for the formation of II in the dehydrohalogenation and dehydroacetoxylation reactions arose by direct elimination toward the methyl group and not by isomerization of IV to I. In the case of the attempted acetylene condensation, I must have been formed by the β-elimination of 2-(hydroxymethyl)-cyclohexanone, a reaction reported by Dimroth, Resin and Zetsch.[1]

It seems most likely that the product recently described by Pfeiffer and Enders[6] as a diene adduct of acetaldehyde and 2-methylenecyclohexanone, is actually IIIc. The reported analytical data are in better agreement with IIIc than with $C_9H_{14}O_2$ and the m.p. (156–157°) is in satisfactory agreement with that observed by Mannich.[2]

Experimental[7]

Isolation of the Hydrated Dimer (IIIc). (a) From the Dehydrohalogenation Reaction.—The dark pot residue (48.7 g.) left after distillation of the 2-methyl-2-cyclohexenone prepared (from 196 g. of 2-methylcyclohexanone *via* the dehydrohalogenation reaction) by the procedure described in the accompanying note[4] was triturated with aqueous acetone containing a few drops of 10% hydrochloric acid. This treatment gave 41.5 g. (20% yield) of crude IIIc as a tan solid, m.p. 115–126°. Two recrystallizations of a sample from 60–68° petroleum ether gave colorless prisms, m.p. 142–144°. An analytical specimen obtained by repeated recrystallization melted at 146–147° just after preparation and at 141–142° six months later.

Anal. Calcd. for $C_{14}H_{22}O_3$: C, 70.55; H, 9.30; mol. wt., 238. Found: C, 70.64; H, 9.38; mol. wt. (Rast), 229.

This compound in 95% ethanol showed only end absorption in the 215 to 340 mμ region in a Beckman model DU spectrophotometer. Negligible C-methyl values of 0.11 and 0.06 C-methyl per mole were found by the Kuhn–Roth method.[8]

The sample supplied by Dr. A. W. Johnson[5] showed similar m.p. behavior alone or on admixture with our compound and the infrared spectra of the two specimens were identical.

(b) From the Pyrolysis of 2-Acetoxy-2-methylcyclohexanone (VI).—The solid which crystallized from the product of the pyrolysis of VI at 390°[4] was separated by filtration and washed with 60–68° petroleum ether.[9] One recrystallization from 60–68° petroleum ether gave colorless prisms, m.p. 148.5–150.5°. Further recrystallization gave material melting at 144–145° which also had the correct analysis for $C_{14}H_{22}O_3$, and showed no depression of the m.p. on admixture with the specimen described above (part a).

(c) From 2-(Dimethylaminomethyl)-cyclohexanone Hydrochloride (VII).—Four grams of VII, m.p. 146–147.5° (reported[1] 152°), prepared according to Mannich and Braun[1] was pyrolyzed according to the procedure of Mannich[2] in a two-bulb flask at 200°. The ether-soluble fraction (after extraction of the residue with water and ether) amounted to 1.49 g. (65% yield) of oily II, which crystallized on trituration with aqueous acetone containing a few drops of 10% hydrochloric acid. The oily crystals were separated by filtration, triturated twice with 33–37° petroleum ether and refiltered to give 0.39 g. (16% yield) of crude IIIc as a tan powder, m.p. 135–139°. Three recrystallizations from 60–68° petroleum ether (Norit used once) gave colorless prisms, m.p. 141–142°, undepressed on admixture with either of the samples described above (parts a and b).

Infrared Analysis.—The spectra of two samples of the hydrated dimer, one melting at 141.5–142.5° and the other at 144–146° (previous softening), determined in a Nujol mull on a Baird double beam, self-recording instrument were identical. There was a strong hydroxyl band at 2.95 μ but no band in the carbonyl region. The infrared spectrum of a sample, m.p. 144–145°, in chloroform solution showed a faint carbonyl band at 5.91 μ (92% transmission) and a strong hydroxyl band at 2.97 μ (50% transmission).

Attempts to effect dimerization of 2-methyl-2-cyclohexenone were carried out by (a) refluxing 3 g. of the ketone in 15 ml. of pyridine for 1 hour; (b) heating (as above) 4.9 g. of ketone in 10 ml. of pyridine which had been treated with a little anhydrous hydrogen chloride; (c) pyrolyzing 7.75 g. of ketone at 400° essentially as described for 2-acetoxy-2-methylcyclohexanone[4]; (d) pyrolyzing a mixture of 5.32 g. of ketone and 2.90 g. of glacial acetic acid as in (c). The products were worked up essentially as already described,[4] and in all of these experiments the 2-methyl-2-cyclohexenone was largely recovered, the higher-boiling fraction being practically negligible.

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(6) P. Pfeiffer and E. Enders, *Ber.*, **84**, 247 (1951).

(7) All melting points are corrected for stem exposure.

(8) Kindly determined by Mr. E. J. Eisenbraun.

(9) Apparently the small amount of water necessary for the formation of IIIc from II came from traces of moisture in the pyrolysate.