Stigmastane-3α-carboxylic Acid.—In a 500-ml. Parr hydrogenation flask were placed 145 mg. of platinum dioxide (according to Adams) and 2.25 g. of 5-sitostene-3α-carboxylic acid in a solution of 300 ml. of absolute ether and 30 ml. of glacial acetic acid. Hydrogenation with vigorous shaking at 3 atm. was carried out for 17 hours. After removal of the catalyst by filtration, the ether was evaporated and crystallization proceeded upon cooling of the acetic acid to give colorless crystals, m.p. 240–242°, $[\alpha]^{25}\text{D}$ +29.7°, *c* 2.78 in chloroform. A total of 2.08 g. of the acid was secured by further crystallization of water–acetic acid mixtures.

Anal. Calcd. for $C_{30}H_{52}O_2$: C, 81.02; H, 11.79. Found: C, 81.58; H, 11.45.

3α-Carbomethoxystigmastane.—Stigmastane-3α-carboxylic acid, 0.900 g. (2.03 mmoles), was suspended in 200 ml. of absolute methanol containing 20 drops of concentrated sulfuric acid. The mixture was heated at reflux temperature under anhydrous conditions for two hours and then poured onto *ca.* 400 g. of ice. The insoluble ester was filtered at the pump, washed well with many portions of cold, distilled water, and then taken into solution with 150 ml. of hot methanol. Fractional crystallization from this solution gives 0.905 g. (98%) of the carbomethoxystigmastane as colorless crystals, m.p. 99–100°, $[\alpha]^{24}\text{D}$ +28°, *c* 4.53 in chloroform.

Anal. Calcd. for $C_{31}H_{52}O_2$: C, 81.52; H, 11.48. Found: C, 81.46; H, 11.71; C, 81.59; H, 11.62.

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2-Methyl-2-cyclohexenone

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In connection with another study we have had occasion to investigate the preparation of 2-methyl-2-cyclohexenone (I). This ketone has been obtained previously by a number of methods,[1] which suffer from either low over-all yields or lengthy procedures. Thus, the selenium dioxide[1a] or chromic acid[2] oxidation of 1-methylcyclohexene (II) led to difficultly separable mixtures of 2- and 3-methyl-2-cyclohexenone from which I has been obtained in low yield. The addition of nitrosyl chloride to II followed by dehydrochlorination and hydrolysis of the resulting oxime gave I in unspecified yield,[3,1b] whereas attempts to dehydrate 2-hydroxy-2-methylcyclohexanone by various procedures resulted in incomplete dehydration.[1a] The bromination of 2-methylcyclohexanone (III) with N-bromosuccinimide followed by dehydrobromination has given I in 17% yield.[1d] In the present work, a convenient synthesis of I from III in two operations (49% over-all yield) has been developed and is the subject of this note.

Since the reaction of sulfuryl chloride (IV) with methyl cyclohexyl ketone[4] and methyl isopropyl ketone[5] has been shown to effect chlorination exclusively at the methyne hydrogen, it was hoped that with 2-methylcyclohexanone (III) the product would be 2-chloro-2-methylcyclohexanone (V). This indeed proved to be the case, for on simply adding sulfuryl chloride to a solution of the ketone in carbon tetrachloride, V was produced in 84–86% yields. It is interesting to note that direct chlorination of III is apparently not selective.[6] The structure of V was shown by formation of I or its derivatives upon dehydrohalogenation. The action of 2,4-dinitrophenylhydrazine in methanol or ethanol at room temperature gave the 2,4-dinitrophenylhydrazone of the corresponding 2-alkoxy-2-methylcyclohexanone,[7] which on warming with dilute acid underwent elimination of alcohol to give the 2,4-dinitrophenylhydrazone of 2-methyl-2-cyclohexenone (I).[8]

For the preparation of I it was not necessary to isolate the chloro ketone which was simply obtained in a crude form and heated with collidine. An exothermic reaction occurred at 145–150°, and an almost quantitative yield of collidine hydrochloride separated. The filtrate yielded 49% of pure (redistilled) 2-methyl-2-cyclohexenone. The rest of the material was high boiling and has been shown[9] to consist mainly of the dimer of 2-methylenecyclohexanone, isolated in about 23% yield. The dehydrohalogenation thus occurred in both possible directions giving a mixture of isomers. When pyridine was used in place of collidine 2-methyl-2-cyclohexenone was produced in somewhat lower (36–38%) yields.

The purity and identity of 2-methyl-2-cyclohexenone (I) prepared as described above was confirmed by the constant boiling point and refractive index, by the high extinction (9,660) at 234 mμ, and by the fact that the known 2,4-dinitrophenylhydrazone was produced in 92% yield. Ozonization of I gave acetic and glutaric acids, isolated as the *p*-toluidides.

The unsaturated ketone I was also prepared by pyrolysis of 2-acetoxy-2-methylcyclohexanone (VI) which was produced by the action of potassium acetate on the chloro ketone. The yields, however, were not promising; so the study was not carried beyond the preliminary stages. It is interesting to note that the dimer of 2-methylenecyclohexanone was also produced in this reaction.[9]

Experimental[10]

2-Chloro-2-methylcyclohexanone (V).—To a solution of 224 g. (2.00 moles) of 2-methylcyclohexanone,[11] b.p. 162.5–

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[1] (a) For a list of references (except those listed here) to synthetic methods see L. W. Butz, B. L. Davis and A. M. Gaddis, *J. Org. Chem.*, **12**, 122 (1947); (b) W. N. Haworth, *J. Chem. Soc.*, **103**, 1242 (1913); (c) M. Mousseron, F. Winternitz and R. Jacquier, *Compt. rend.*, **224**, 1062, 1230 (1947); (d) W. W. Rinne, H. R. Deutsch, M. I. Bowman and I. B. Joffe, THIS JOURNAL, **72**, 5759 (1950); (e) A. J. Birch, *J. Chem. Soc.*, 593 (1946); (f) M. Godchot and P. Bedos, *Compt. rend.*, **181**, 919 (1925), report the preparation of I by the action of quinoline on 2-chloro-2-methylcyclohexanone, but the physical constants of their compound do not agree with those reported elsewhere.

[2] F. C. Whitmore and G. W. Pedlow, THIS JOURNAL, **63**, 758 (1941).

[3] O. Wallach, *Ann.*, **359**, 303 (1908).

[4] B. Tchoubar and O. Sackur, *Compt. rend.*, **208**, 1020 (1939).

[5] P. Delbaere, *Bull. soc. chim. Belg.*, **51**, 1 (1942).

[6] There are conflicting reports about the action of chlorine on III. A. Kötz and H. Steinhorst, *Ann.*, **379**, 1 (1911), report the formation of 2-chloro-6-methylcyclohexanone; M. Godchot and P. Bedos, ref. 1f, report the isolation of 2-chloro-2-methylcyclohexanone with physical properties which agree fairly well with those found in the present work; R. Cornubert and C. Borrel, *Bull. soc. chim.*, **43**, 804 (1928), report the formation of both the 2- and the 6-chloro isomers. *Cf.* ref. 1d for the action of bromine on III.

[7] *Cf.* the examples of analogous behavior: (a) K. von Auwers, *Ber.*, **50**, 1177 (1917); (b) V. R. Mattox and E. C. Kendall, THIS JOURNAL, **72**, 2290 (1950).

[8] *Cf.* ref. 7b; C. Djerassi, *ibid.*, **71**, 1003 (1949); F. Ramirez and A. F. Kirby, *ibid.*, **74**, 4331 (1952).

[9] E. W. Warnhoff and William S. Johnson *ibid.*, **75**, 496 (1953).

[10] All melting points are corrected for stem exposure.

[11] Prepared by chromic acid oxidation of 2-methylcyclohexanol.

163.5° (740 mm.), n^{25}_{D} 1.4459 and 1 l. of dry carbon tetrachloride in a 3-l., three-necked flask equipped with a glass stirrer, dropping funnel and tube connected to a gas absorption trap, was added during 1 hour with stirring a solution of 179 ml. (297 g., 2.20 moles) of sulfuryl chloride[12] in 300 ml. of dry carbon tetrachloride. The slightly exothermic reaction was moderated by cooling the flask in a water-bath at room temperature. After the addition was complete, stirring was continued for 2 hours to assist in the release of the sulfur dioxide and hydrogen chloride. After several hours, the yellow reaction mixture was washed with three 300-ml. portions of water, two 200-ml. portions of saturated sodium bicarbonate solution, one 200-ml. portion of saturated sodium chloride solution and dried with anhydrous magnesium sulfate. The solution was filtered and the solvent removed by distillation at atmospheric pressure through a 15-cm. Vigreux column. The residue was distilled through this column to give, after a small forerun, 246 g. (84%) of a clear, colorless liquid, b.p. 94–96° (27 mm.), n^{25}_{D} 1.4672, d^{25}_{4} 1.088 (reported[1f] b.p. 78–79° (14 mm.), n^{16}_{D} 1.4696, d^{16} 1.099). The chloro ketone is stable for long periods if stored in a brown bottle. The homogeneity of material thus prepared was shown by fractionation of such a product through a 37-cm. Fenske column packed with glass helices. The n^{25}_{D} of the various fractions ranged only from 1.4670 to 1.4675. A middle fraction, n^{25}_{D} 1.4671, was analyzed.

Anal. Calcd. for $C_7H_{11}OCl$: C, 57.34; H, 7.56; Cl, 24.19. Found: C, 57.84, 57.69; H, 7.71, 7.60; Cl, 23.89, 23.94.

Preparation of the 2,4-dinitrophenylhydrazone by the method of Shriner and Fuson[13] resulted in replacement of the chlorine atom by a molecule of solvent to give what was probably **2-ethoxy-2-methylcyclohexanone 2,4-dinitrophenylhydrazone** in 85% yield, m.p. 133.5–135°. Four recrystallizations from dilute alcohol gave golden platelets, m.p. 148–148.5°.

Anal. Calcd. for $C_{15}H_{20}O_5N_4$: C, 53.56; H, 6.00. Found: C, 54.01, 53.89; H, 5.93, 6.06.

When a sample of the derivative was warmed with dilute sulfuric acid, ethanol was eliminated to give 2-methyl-2-cyclohexenone 2,4-dinitrophenylhydrazone as red plates, m.p. 206–206.5° (reported[1a] 210°), after one recrystallization from ethanol. On admixture with the dinitrophenylhydrazone, m.p. 207.5–208°, of an authentic sample of I prepared essentially by the procedure of Wallach,[3] the m.p. was undepressed.

The use of methanol in place of ethanol in the derivative preparation gave what was probably **2-methoxy-2-methylcyclohexanone 2,4-dinitrophenylhydrazone** as golden needles m.p. 152–152.5°, after repeated recrystallization from ethanol.

Anal. Calcd. for $C_{14}H_{18}O_5N_4$: C, 52.17; H, 5.63. Found: C, 52.17; H, 5.75.

The action of semicarbazide hydrochloride and pyridine on the chloro ketone gave a semicarbazone which crystallized from ethanol as a colorless microcrystalline powder, m.p. 207–207.5°, undepressed on admixture with the semicarbazone (m.p. 209–210°) of authentic 2-methyl-2-cyclohexenone prepared by the method of Wallach.[3] This derivative is reported to melt at 207–208°.[3]

2-Methyl-2-cyclohexenone (I).—The crude 2-chloro-2-methylcyclohexanone, which remained after distillation of the carbon tetrachloride, in a preparation just like that described above, was freed of most of the solvent under diminished pressure and transferred to a 1-l., three-necked flask equipped with a strong Hershberg stirrer and two efficient condensers, one in each side neck. Two hundred and ninety milliliters (266 g., 2.20 moles) of 2,4,6-collidine was added with stirring and the contents of the flask heated by means of an oil-bath to 145–150°. A sudden exothermic reaction ensued, the residual carbon tetrachloride refluxing vigorously and the mixture set to a viscous suspension of collidine hydrochloride. After the reaction was over (about 1 minute), the oil-bath was removed, and as the reaction mixture cooled and became viscous enough that the stirrer slowed, 500 ml. of benzene was added cautiously (vigorous reflux) through a condenser in order to keep the reaction mixture fluid. The reaction mixture was then poured onto a 10-cm. sintered glass suction filter. The collidine hydrochloride on the filter was transferred to a beaker, triturated with 300 ml. of benzene and refiltered. After this treatment was repeated, the dried salt amounted to 303 g. (96% yield). The combined dark brown filtrates were washed twice with excess 10% hydrochloric acid in saturated sodium chloride solution, once with saturated sodium bicarbonate solution, once with saturated sodium chloride solution, dried over anhydrous magnesium sulfate, filtered, the benzene removed by distillation through a 15-cm. Vigreux column and all material boiling from 70–96° (56 mm.) was collected. The distillation residue amounted to 72 g. of dark oil, which distilled at 140–200° (1 mm.) and consisted largely of the dimer of 2-methylenecyclohexanone[9] (yield 51.3 g.). The crude 2-methyl-2-cyclohexenone was fractionated through a 20-cm. heated column packed with steel saddles. After a forerun of several milliliters of benzene, 108.7 g. (49% yield from III) of colorless 2-methyl-2-cyclohexenone was collected, b.p. 98–101° (77 mm.), n^{25}_{D} 1.4836, d^{25}_{4} 0.972, $\lambda_{\max}$ 234 mμ (E 9,660) (reported, b.p. 66–66.5° (14 mm.),[1a] $n^{19.8}_{\mathrm{D}}$ 1.4849,[1a] $\lambda_{\max}$ 235.5 mμ (E 10,000),[1a] d^{20} 0.966[3]).

The use of pyridine instead of 2,4,6-collidine in essentially the same procedure gave the unsaturated ketone in 36–38% yield.

The 2,4-dinitrophenylhydrazone, m.p. 202–204°, was prepared in 92% yield by the procedure of Shriner and Fuson.[13] Recrystallization from ethanol gave red plates, m.p. 207.5–208.5°, undepressed on admixture with an authentic sample, m.p. 207.5–208°, prepared from I made by the procedure of Wallach.[3]

Ozonization of I.—Ozone produced from oxygen flowing through a U. S. Air ozonizer was passed through a Dry Ice-cooled solution of 0.445 g. (4.05 moles) of the unsaturated ketone in 25 ml. of chloroform until iodine was liberated from an acidified solution of potassium iodide contained in a gas-washing bottle connected to the ozone exhaust. The ozonized solution was then added dropwise over a period of an hour to 50 ml. of a hot (steam-bath) 30% solution of hydrogen peroxide and the resulting aqueous solution was steam distilled until the distillate was neutral. The acid distillate required 29.6 ml. of 0.107 *N* sodium hydroxide solution for neutralization (79% yield of volatile acid). Both the titrated distillate and the neutralized steam distillation residue were evaporated to dryness and the sodium salts which remained were converted to the *p*-toluidides.

The *p*-toluidide of the steam volatile acid after crystallization from methanol gave 0.118 g. (19%) of derivative, m.p. 140–142.5°. The colorless platelets, m.p. 146.5–147.5°, obtained after recrystallization from ligroin did not depress the melting point of an authentic sample of aceto-*p*-toluidide, m.p. 148.5–149.5°.

The *p*-toluidide of the non-volatile acid gave 0.183 g. (14%) of tan needles, m.p. 215.5–218.5°, after crystallization from dilute alcohol. One recrystallization from the same solvent gave colorless needles, m.p. 220.5–221°, undepressed on admixture with authentic glutaro-bis-*p*-toluidide, m.p. 220–221°.

2-Acetoxy-2-methylcyclohexanone (VI).—A mixture of 108 g. (1.10 moles) of freshly fused, powdered potassium acetate, 300 ml. of glacial acetic acid and 15 ml. of acetic anhydride was refluxed in a 1-l. flask with attached condenser. After dissolution of the potassium acetate, 146 g. (1.00 mole) of 2-chloro-2-methylcyclohexanone was added through the condenser, whereupon precipitation of potassium chloride began almost immediately. The mixture was heated under reflux for 2 hours; then allowed to stand several hours. The potassium chloride was separated by filtration; yield 71.6 g. (96%). The acetic acid filtrate was distilled at reduced pressure to remove most of the acetic acid; water and ether were added and the water layer extracted with ether. The combined ethereal extracts were washed thoroughly with saturated sodium bicarbonate solution, then with saturated sodium chloride solution, dried over anhydrous magnesium sulfate, filtered and the ether removed by distillation. The residue was distilled and the fraction boiling at 105–107° (6 mm.) was collected to give 122 g. (72%) of a viscous liquid, n^{25}_{D} 1.4526 (reported[1a] b.p. 115–118° (15 mm.), $n^{20.3}_{\mathrm{D}}$ 1.4570). The prod-

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[12] Eastman Kodak Company practical grade.

[13] R. L. Shriner and R. C. Fuson, "Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.

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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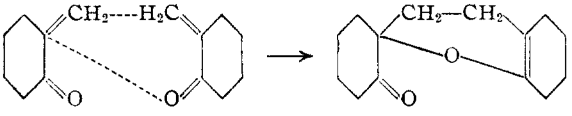
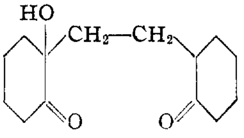
In 1920, Mannich and Braun[1] reported the formation of a compound, $C_{14}H_{22}O_3$, m.p. 149°, as a by-product in the Mannich reaction with cyclohexanone and dimethylamine hydrochloride. The normal product, 2-(dimethylaminomethyl)-cyclohexanone hydrochloride, on pyrolysis[2] gave, in addition to the 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°.

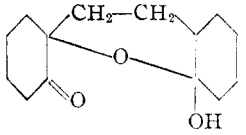
In the course of a study of the preparation of 2-methyl-2-cyclohexenone (IV),[4] 2-chloro-2-methylcyclohexanone (V) was dehydrochlorinated to give, in addition to the unsaturated ketone IV, a high-boiling oil which, on standing or trituration with aqueous solvents, partially crystallized to give colorless 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.



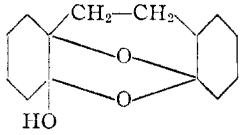
I II



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.