crystallized from petroleum ether (b.p. 35–65°). V solidified when the solvent-free reaction material was chilled in ice. Recrystallization from pentane afforded pure material. VI was isolated in the same way as V, employing petroleum ether for the recrystallization. I–III are colorless oils with a pleasant odor. IV–VI are colorless, waxy solids. The infrared spectra of I–VI conform with their structures. The more volatile I–III were shown to be homogeneous by vapor phase chromatography.

The effect of air on the decomposition of 1-phenylcyclopentyl hypochlorite. The hypochlorite was prepared according to the general directions given earlier using methylene chloride as the immiscible phase. After separation and drying of the methylene chloride solution of the hypochlorite, the solvent was removed by evaporation under reduced pressure. A sample of the crude, yellow hypochlorite was then heated in an open test tube at 75–96° for 3.25 hr. After this time the potassium iodide test was still strongly positive and no change in the appearance of the sample was noticed. A stream of nitrogen was bubbled through another sample of the material held at 85–88°. In 47 min. the material was colorless and the potassium iodide test was very weakly positive. Higher temperatures led to darkened material and hydrogen chloride evolution.

Characterization of I–VI. All the ω-chloro ketones formed 2,4-dinitrophenylhydrazones easily in the usual fashion. In their reaction with sodium iodide in acetone, I–III gave precipitates within 6 min. at 50°, while IV–VI required approximately 30 min. at this temperature. All the ω-chloro ketones except IV and V developed precipitates within 30 min. in acetone solution when admixed with 5% aqueous silver nitrate solution at 25°. IV and V required 30 min. at 50° for evidence of reaction with this reagent.

Attempted cyclization of V. To V (7.83 g., 0.04 mole) in ethanol (150 ml.) there was added sodium carbonate (8.85 g., 0.08 mole) in water (150 ml.). On heating to reflux, the solution became homogeneous and some darkening took place. After 1 hr. of reflux, a cooled, acidified (nitric acid) portion of the material gave a precipitate with alcoholic silver nitrate. After 4 hr. of reflux the material was poured onto an equal volume of ice and extracted with benzene (3 times 100 ml.). The extracts were dried and the benzene removed. The residual oil (7.0 g.) was fractionated under reduced pressure. Wide boiling ranges were observed for the series of fractions obtained. Infrared examination of the fractions indicated that the lowest boiling cut (0.1 g., b.p. 106–116° at 0.5 mm., n_{D}^{20} 1.5295) was olefinic. The other fractions consisted of unchanged V and hydroxylic material, probably the ketol. No further examination of these substances was made.

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5,5-Dimethylcyclopentadiene[1]

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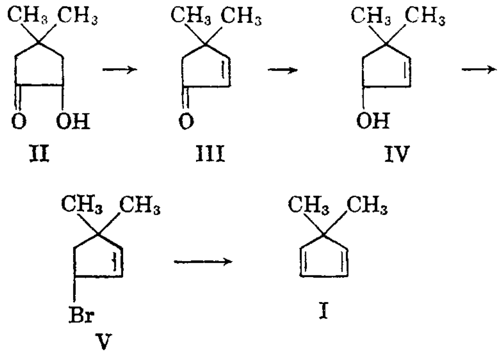
The recently reported synthesis[3] of 5,5-dimethylcyclopentadiene (I) prompts the recording of our independent and more convenient route to I, which seems well suited as a building block for the synthesis of bicyclic terpenes and related compounds. An earlier synthesis of I, b.p. 108–110° (atm. press.) has been reported[4]; however, comparison of the atmospheric boiling points of the known cyclopentane, methyl cyclopentanes, and their unsaturated derivatives shows clearly (for details, see Ref. 3) that the substance obtained by Zonis is most probably not the desired I. That this is in fact the case has been demonstrated by repetition of Zonis's work in which we obtained a material boiling in his reported range whose ultraviolet spectrum has maxima at 238, 247, 258, and 268 mμ and is wholly incompatible with the single maxima observed in the ultraviolet spectra of cyclopentadiene (240 mμ),[5] 1-methylcyclopentadiene (249.6 mμ),[6] and I as prepared below (250 mμ). Vapor liquid partition chromatography also confirms this situation.

By an adaptation of Sheehan's method[7] for the preparation of the D-ring of the steroid nucleus in an acyloin condensation, using sodium in ether–liquid ammonia, we have prepared 4,4-dimethylcyclopentan-2-ol-1-one (II) from dimethyl β,β-dimethylglutarate in 80% yield. Subsequent to this work, the preparation of II has been reported by two other groups of workers using essentially the same method.[8,9]



The sequence of reactions used is outlined below. Dehydration of II proceeds in about 80% yield using polyphosphoric acid in ten weight parts excess. When less polyphosphoric acid is used, the yield of III is considerably lower. The significance of this result lies apparently in the degree of hydration of the acid since dehydration of II using polyphosphoric acid prepared from phosphorus

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[1] This work, from the dissertation presented by W. E. T. to the graduate faculty of Lehigh University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, October 1960, was also presented before the Division of Organic Chemistry, 138th meeting of the American Chemical Society, New York, N. Y., September 1960.

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pentoxide and 85% phosphoric acid and which is 105% phosphoric acid resulted in an 85% recovery of II.

Lithium aluminum hydride reduction of III proceeds in 90% yield using diethyl ether as solvent. The 4,4-dimethyl-2-cyclopenten-1-ol (IV) is converted to 3,3-dimethyl-5-bromocyclopentene (V) in 70% yield with 48% hydrobromic acid containing 2% sulfuric acid at room temperature for two days. The allylic bromide V is presumed to have the structure indicated inasmuch as the other possible allylic isomer would have the bromine atom in bond opposition to the methyl group and would thus be less stable than the structure drawn above. As with some halides of this type structure, V discolors on standing unless purified. Once distilled V rapidly turns green followed by a slow change to dark blue at room temperature. These changes are completely obviated by repeated vacuum distillation, giving material which is stable at room temperature for several days.

When either the crude V or carefully purified V is heated with a four-fold excess of quinoline at about 140°, practically pure I distills from the reaction mixture in over 70% yield. On catalytic reduction of I thus obtained, two moles of hydrogen are absorbed to give 1,1-dimethylcyclopentane, infrared identical with an authentic sample[10] and identical in other physical properties. In the work-up of the hydrogenation mixture, we encounter an azeotrope of acetic acid and 1,1-dimethylcyclopentane, b.p. 83.5–84°.

An ether solution of I reacts slowly with maleic anhydride to give a nearly quantitative yield of an adduct. This reaction is quite in contrast with the very rapid and exothermic reaction of maleic anhydride with cyclopentadiene.[11] In addition, redistillation of I, which has been stored at 0° for three months, under which conditions cyclopentadiene almost completely dimerizes, gives a 96% recovery of pure I. Thus, it appears that the geminal-dimethyl group exerts a marked steric hindrance to the approach of dienophiles.

EXPERIMENTAL[12]

β,β-Dimethylglutaric acid. The diacid was prepared by the Guareschi reaction as described by Vogel[13]; however, the hydrolysis of the Guareschi imide was performed according to Reid and Gompf.[14]

Dimethyl β,β-dimethylglutarate. The dimethyl β,β-dimethylglutarate was prepared according to Komppa[15] in 85–90% yield, b.p. 80° (4 mm.)

4,4-Dimethylcyclopentan-2-ol-1-one (II). The acyloin was prepared according to the method used by Sheehan[7] (see also Refs. 8 and 9) in 81% yield, b.p. 69–70° (2 mm.).

4,4-Dimethyl-2-cyclopenten-1-one (III). To 500 g. of cold polyphosphoric acid (equivalent to 115% orthophosphoric acid) 35 g. (0.274 mole) of II was added with cooling, and the yellow solution was let stand at room temperature overnight. The reaction mixture was then heated on a boiling water bath for 10 hr., and after cooling, the dark brown, viscous mass was poured into 500 ml. of ice water, extracted with five 200-ml. portions of ether, and the combined ether extracts dried over magnesium sulfate. Removal of the ether by distillation followed by vacuum distillation of the residue gave 25.4 (84%) of colorless liquid, b.p. 75° (45 mm.).

This III was characterized as the 2,4-dinitrophenylhydrazone m.p. 163–164° (from absolute ethanol) (lit.[16] 163–164°).

4,4-Dimethyl-2-cyclopenten-1-ol (IV). In a 500-ml. three-necked flask fitted with stirrer, dropping funnel, and reflux condenser protected with a calcium chloride drying tube, 200 ml. of anhydrous ether and 17 g. (0.46 mole) of powdered lithium aluminum hydride were placed, and refluxed with stirring for 2 hr. After cooling to room temperature, a solution of 17 g. (0.154 mole) of III in 50 ml. of anhydrous ether was added dropwise with stirring over the course of 30 min., whereupon the mixture was refluxed and stirred for 4 hr. After cooling to room temperature, 7 ml. of water were added dropwise, followed by 7 ml. of 15% sodium hydroxide solution, and 21 ml. of water. The precipitate was removed by suction filtration, and the ether solution dried over magnesium sulfate. The ether was removed by distillation, and vacuum distillation of the residual liquid gave 15.5 g. (90%) of IV as a colorless liquid, b.p. 41–42° (1.5 mm.), n_D^{20} 1.4532, d_4^{20} 0.9037.

Anal. Calcd. for $C_7H_{12}O$: C, 74.95; H, 10.79. Found: C, 74.10; H, 11.02.

IV-α-Naphthyl-urethane was prepared in the usual manner,[17] m.p. 93–93.5° (from 60–70° petroleum ether).

Anal. Calcd. for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81. Found: C, 76.90; H, 7.08.

3,3-Dimethyl-5-bromocyclopentene (V). This procedure was adapted from one given by Young and co-workers.[18] In a 200-ml. round-bottomed flask, 100 ml. of 48% hydrobromic acid and 10 ml. of concd. sulfuric acid were mixed with cooling. To the cold acid mixture 16.8 g. (0.15 mole) of IV was added with cooling. After standing at room temperature for 2 days with occasional shaking, the dark mixture was poured into an equal volume of cold water and extracted with four 100-ml. portions of commercial pentane (b.p. 30–40°). The combined pentane solutions were dried over magnesium sulfate, the pentane removed by distillation, and the residual liquid vacuum distilled to give 18.5 g. (70%) of V, b.p. 76° (50 mm.), n_D^{20} 1.4903, d_4^{20} 1.2571. The colorless V thus obtained darkened on standing overnight even in a nitrogen atmosphere; however, by repeated vacuum distillation the analytical sample of the above physical constants was obtained which remained colorless for several days.

Anal. Calcd. for $C_7H_{11}Br$: C, 48.02; H, 6.33; Br, 45.65. Found: C, 48.50; 6.70; Br, 45.50.

5,5-Dimethylcyclopentadiene (I). In 100-ml. Claisen flask fitted with a capillary bubbler which reached to the bottom of the flask were placed 60 ml. of quinoline and 18.5 g. (0.108

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(11) O. Diels and K. Alder, *Ann.*, **460**, 98 (1928).

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mole) of V. Dry nitrogen was passed through the bubbler until the air had been displaced, and this nitrogen stream was continued throughout the reaction. The flask was heated in an oil bath to a bath temperature of 140°, at which point evidence of reaction appeared in bubbling of the reaction mixture and in the appearance of distillate. Over the course of 20 min., the bath temperature was raised from 140° to 190° and maintained at the latter point for 5 min. During this period material was collected of b.p. 60–80°. Redistillation of the liquid product gave 8.2 g. (72%) of I, b.p. 70°, n_{D}^{20} 1.4253, d_{D}^{20} 0.7670, $\lambda_{\max}$ 250 mμ, log ε 2.32 (hexane).

Anal. Calcd. for C_7H_{10}: C, 89.25; H, 10.71. Found: C, 89.50; H, 10.73.

When 5.1 g. of I was redistilled after having been stored at 0° for 3 months, 4.9 g. (96%) of I, b.p. 69–71.5° was obtained and 0.1 g. of residue (2%) was left.

Adduct of I *with maleic anhydride.* To 0.98 g. (0.01 mole) of maleic anhydride dissolved in 20 ml. of ether contained in a 125-ml. Erlenmeyer flask was added 0.94 g. (0.01 mole) of I. No heat was evolved and no precipitate formed on standing overnight at room temperature; however, when the solution was cooled in a refrigerator, the adduct crystallized as white needles, 1.90 g. (99%), m.p. 91–92° (petroleum ether, b.p. 30–40°).

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29. Found: C, 68.80; H, 6.56.

1,1-Dimethylcyclopentane from I. In a 500-ml. hydrogenation bottle were placed 50 ml. of glacial acetic acid, 8.1 g. (0.093 mole) of I, and 0.30 g. of platinum oxide. This mixture was hydrogenated at 3 atm. at room temperature, and in 15 min. 17 lb. of hydrogen pressure was taken up corresponding to 98% reaction. The reaction mixture was filtered, and the solution fractionally distilled using a Precision Distillation GE-118 concentric tube column. An azeotropic mixture, constant boiling at 83.5–84°, was obtained. The azeotrope plus material boiling to 92° was washed with three 15-ml. portions of water, five 15-ml. portions of saturated sodium bicarbonate solution, and three 15-ml. portions of water. After drying the hydrocarbon over phosphorus pentoxide, distillation gave 5.07 g. of 1,1-dimethylcyclopentane, b.p. 87–88°, n_{D}^{25} 1.4097, d_4^{25} 0.7487 (lit.[4] n_{D}^{25} 1.4091, d_4^{25} 0.7599). The infrared spectrum of this sample was identical in all respects with that[10] reported for authentic 1,1-dimethylcyclopentane.

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Cyclic Products from Hydrazines. I. Nitroindoles, Nitrotetrahydrocarbazoles, Nitroindolenines, and Nitrotetrahydrocarbazolenines

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The present investigations have been restricted to a study of the behavior of some nitrophenylhydrazones of ketones[1,2] in the presence of different condensing reagents. It has been found that cyclization of 2-nitro-, 4-nitro-, 2-chloro-4-nitro-, 4-chloro-2-nitro-, 2-iodo-4-nitro-, 4-iodo-2-nitro-, 2,4-dinitro-, and 4,6-dinitro-3-methylphenylhydrazones of methyl ethyl, diethyl, and methyl propyl ketones to the corresponding indoles and those of unsubstituted and 4-methylcyclohexanones to the corresponding tetrahydrocarbazoles takes place whether the phenylhydrazone has one or two nitro groups. But in case of nitrophenylhydrazones of methyl isopropyl ketone and 2-methylcyclohexanone (where the ring closure yields the corresponding indolenines and tetrahydrocarbazolenines, respectively), cyclization takes place only when one nitro group is present. Attempts to prepare dinitroindolenines and dinitrotetrahydrocarbazolenines have not been successful under similar experimental conditions.

Of the different condensing agents used[3-5] concentrated hydrochloric acid functions best for cyclizing the mononitrophenylhydrazones to indoles, tetrahydrocarbazoles, indolenines, and tetrahydrocarbazolenines while a mixture of concentrated sulfuric acid and acetic acid is preferable for preparing the dinitroindoles and dinitrotetrahydrocarbazoles from the corresponding phenylhydrazones.

Two differently substituted indoles can be obtained from the phenylhydrazones of unsymmetrical ketones of the type $RCH_2CH_2COCH_3$, as one or the other α-carbon atom is linked with the benzene ring. Only one isomer, however, could be isolated in each case. The structure of such compounds has been assigned by methylating[6,7] them. Thus, the product of methylation of the indole from 4-nitrophenylhydrazone I of methyl ethyl ketone is either IV or V as its structure is II or III. It has been found to be identical with IV obtained from the cyclization of VI and different from the isomeric product V, the cyclization product of VII. The indole formed from I is, therefore, II.

Similar studies, carried out with the indoles obtained from 2-nitro-, 4-chloro-2-nitro-, 2-chloro-4-nitro-, 4-iodo-2-nitro-, and 2-iodo-4-nitrophenylhydrazones of methyl ethyl ketone, confirm the pre-

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