129°). No other definite product was isolated from this reaction.

Dehydration of 8-*p*-Menthene-1,2-diol.—A solution of 34 g. (0.2 mole) of 8-*p*-menthene-1,2-diol in 700 g. of 5% aqueous oxalic acid was refluxed for 16.5 hours. The mixture was then steam distilled until oil ceased to pass over, and the distillate was extracted three times with 100-ml. portions of ether. The combined extracts were washed with 25 ml. of 5% sodium carbonate solution, then with water, and dried over anhydrous sodium sulfate. The ether was removed by distillation, and the residue was fractionally distilled through a Todd column with monel spiral packing to give 6.8 g. (37%) of *p*-cymene, b.p. 57–59° (10 mm.), $n^{26}\text{D}$ 1.4873, and 8.7 g. (26%) of carvenone, b.p. 101–101.6° (10 mm.), $n^{26}\text{D}$ 1.4797, m.p. of semicarbazone,[8] 201–202°, m.p. of hydroxylaminoöxime,[10] 165–166.5°.

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A New Route to 2-(β-Phenylethyl)-3-methyl-Δ²-cyclohexenones[1]

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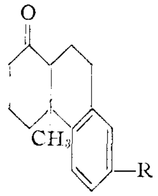
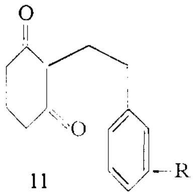
With a view to developing a method for the synthesis of diterpenoid resin acids represented by abietic acid and its congeners, we were in need of the tricyclic ketones I (R = H, OCH_3), the synthesis of which has been described briefly by Stork and Burgstahler.[2] While awaiting with interest the details of their experimental findings, we would like to record here a new synthesis of some of the intermediates leading to the synthesis of I (R = H, OCH_3) as our method differs substantially from that of the previous workers. 2-(β-phenylethyl)-cyclohexane-1,3-dione[3] and the corresponding methoxy derivative[4] II (R = OCH_3) have been utilized as our key intermediates for these synthetic attempts. We had some difficulty[5] in preparing the ethyl enol ether from the diketones II (R = H, OCH_3), but have been able to prepare the isobutyl ether[6] in a very good yield. The unsaturated isobutoxy ketones III (R = H, OCH_3) react readily with methylmagnesium iodide in ethereal solution. Decomposition of the reaction mixture with dilute acids leads to the formation of the unsaturated ketones IV (R = H, OCH_3). Measurement of absorption in the ultraviolet region of the ketones IV (R = H) ($\lambda^{\text{alc}}_{\text{max}}$ 242.5 mμ, log ε 4.0) and of the corresponding methoxy ketone IV (R = OMe) ($\lambda^{\text{alc}}_{\text{max}}$ 243.5 mμ, log ε 4.1) reveals a slight but significant hypsochromic shift of their absorption maxima from the values predicted by Woodward's rule.[7] Although no satisfactory explanation can be put forward to explain this shift, it may be of interest to compare a similar value $\lambda^{\text{alc}}_{\text{max}}$ 243 mμ recorded by Tishler, *et al.*,[8] for the compound V where the aromatic nucleus has been replaced by a carboxyl group.


I



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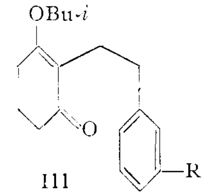

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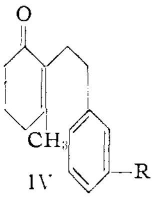

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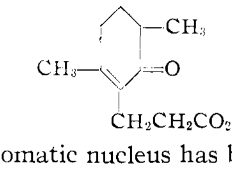

V

The identity of the ketones IV (R = H, OCH_3) has been established by comparison of the melting points of the solid dinitrophenylhydrazones with those of authentic samples prepared according to the published method. The structure of the unsaturated ketones has been further confirmed by cyclization to the tricyclic ketones I (R = H, OCH_3). It would be interesting to note that attempts at cyclization of the unsaturated ketone IV (R = H) with concentrated phosphoric acid at 165–170°[2] lead to product having a slightly bluish fluorescence and having practically no absorption in the 240–250 mμ region. Moreover, it was noticed that it was particularly difficult to obtain any solid ketonic derivative from this product and it led to an extremely poor yield of the desired condensation product in attempting the condensation of the cyclized ketone with ethyl cyanacetate according to Cragoe[9] in order to push the synthetic scheme further. These results are rather surprising because a closely analogous system, 10-methyldecalin-1-one has been synthesized and been found to undergo reactions with all ketonic reagents quite readily. As a result of further studies we have found that cyclization of IV (R = H) goes better at a lower temperature[10] and on heating for a longer period, and the product thus obtained in a much better yield is characterized readily by the yellow dinitrophenylhydrazone and by the absence of any typical ultraviolet absorption maxima in the 240–250 mμ.

It may be added that new methods[1b] have been successfully explored to build up the 1-methyl-1-carboxyl group in place of 1-carbonyl group as the former grouping is the characteristic of the diterpenoid resin acids.

Acknowledgments.—Ultraviolet measurements have been carried out by Dr. B. Mukherjee of the

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Department of Applied Chemistry, Indian Institute of Technology, Khargpur. Microanalyses for carbon and hydrogen have been carried out at Oxford by Drs. Weiler and Strauss and for nitrogen by Mrs. Chhabi Dutta, at the Chemical Laboratory of the University College of Science and Technology, Calcutta.

Experimental

2-(β-Phenylethyl)-3-keto-cyclohexenyl Isobutyl Ether (III, R = H).—A mixture of 2-(β-phenylethyl-cyclohexane-1,3-dione (102 g., 0.472 mole), isobutyl alcohol (170 cc.), dry benzene (680 cc.) and *p*-toluenesulfonic acid monohydrate (3.4 g.) was heated under reflux for seven hours and another lot of *p*-toluenesulfonic acid (1.7 g.) was added and refluxing continued for another seven hours. The water formed was removed by means of a water separator. The product was then poured into ice-cold sodium bicarbonate solution (5%) with stirring whereupon two layers separated. The upper benzene layer containing the enol ether was removed and the alkaline layer extracted with benzene once and combined with the previous benzene layer, washed with caustic soda solution (5%) repeatedly till the alkali-wash gave no precipitate on acidification with (6 *N*) hydrochloric acid. Finally the benzene extract was washed with water thrice and dried with anhydrous potassium carbonate. After removal of the solvent, the residue was distilled under vacuum affording a constant boiling colorless liquid, b.p. 195° (1.5 mm.), $n^{34}\text{D}$ 1.5343. The yield was 114.3 g. (88.2%). For analysis, it was twice distilled and a middle fraction was taken.

Anal. Calcd. for $C_{18}H_{24}O_2$: C, 79.41; H, 8.82. Found: C, 79.28; H, 8.74.

2-(β-Phenylethyl)-3-methyl-Δ²-cyclohexenone (IV, R = H).—To the ice-cold Grignard reagent prepared from magnesium (4.8 g., 0.2 atom), methyl iodide (28.4 g., 0.2 mole) and dry ether (100 cc.), was added slowly 2-(β-phenylethyl)-3-keto-cyclohexenyl isobutyl ether (27.2 g., 0.1 mole) in ether (20 cc.) with constant stirring (maintained for two hours) and then refluxed for one hour. After cooling, the complex was decomposed with ice and (6 *N*) sulfuric acid. The ether layer was removed, the acidic layer extracted thrice with ether and these extracts mixed with the original ether layer. The combined ether extract was washed with sodium bisulfite solution (2%) to remove dissolved iodine, then with sodium bicarbonate solution (5%) and finally with water until neutral. After removal of the solvent, the residue was hydrolyzed and dehydrated simultaneously by heating it with (10%) sulfuric acid (142 cc.) at 70–80° for 15 minutes. This was then cooled and extracted with ether and the ethereal layer washed with caustic soda solution (5%) several times till the alkali wash gave no precipitate on acidification with cold hydrochloric acid (6 *N*) and finally with water until neutral. The ether solution was next dried with anhydrous sodium sulfate. After removal of the solvent, the residue on distillation under reduced pressure gave a pale yellow liquid, b.p. 160–165° (3–4 mm.). The yield was 15.35 g. (71.1%). A small portion was redistilled under reduced pressure affording a pale yellow liquid, b.p. 163° (3 mm.). The middle fraction, $n^{34}\text{D}$ 1.5432, was analyzed.

Anal. Calcd. for $C_{15}H_{18}O$: C, 84.11; H, 8.41. Found: C, 84.27; H, 8.49.

The 2,4-dinitrophenylhydrazone prepared in the usual way was crystallized from ethanol–ethyl acetate in deep-red fine needles, m.p. 172° (lit.[2] 171–172°) alone or mixed with an authentic sample.

Anal. Calcd. for $C_{21}H_{22}O_4N_4$: C, 63.96; H, 5.58. Found: C, 63.93; H, 5.59.

Cyclization was carried out in (66%) yield by heating the unsaturated ketone (15 g.) with phosphoric acid (90 cc., 89% w./w.) in nitrogen atmosphere for 18 hours at 150–155°. The 2,4-dinitrophenylhydrazone on repeated crystallization from ethyl acetate separated in shining yellow needles melting at 195–196° (lit.[2] 193–195°).

Anal. Calcd. for $C_{21}H_{22}O_4N_4$: N, 14.21. Found: N, 13.98.

2-(β-*m*-Methoxyphenylethyl)-1,3-dimethoxy-2,5-dihydrobenzene.—To liquid ammonia (*ca.* 700 cc.) was added potassium (4 g., 0.102 atom) in small pieces at an interval of one minute with constant stirring when a blue solution was obtained. After the addition of potassium, 1,3-dimethoxy-2,5-dihydrobenzene (14 g., 0.1 mole) in ether (10 cc.) was added dropwise when the blue color disappeared and red color appeared. The whole solution was kept well-stirred as such for ten minutes. Then *m*-methoxyphenylethyl bromide (20 g., 0.09 mole) was added slowly whereupon the red color was discharged. The ammonia then was allowed to evaporate off and the residue decomposed with water whereupon a heavy oil separated which was extracted with ether. The ether solution was washed with water thrice and dried with anhydrous potassium carbonate. The solvent then was removed and the residue distilled under reduced pressure whereupon 2-(β-*m*-methoxyphenylethyl)-1,3-dimethoxy-2,5-dihydrobenzene (7.4 g.) passed over as a pale yellow liquid (b.p. 188–195° (1–2 mm.)).

Anal. Calcd. for $C_{17}H_{22}O_3$: C, 74.45; H, 8.03; OCH_3, 33.9. Found: C, 74.69; H, 7.80; OCH_3, 33.3.

2-(β-*m*-Methoxyphenylethyl)-cyclohexan-1,3-dione (II, R = OCH_3).—The above trimethoxy ether (7.5 g.) was treated with sulfuric acid (30 cc., 2 *N*) and heated with constant shaking in a water-bath at 80–85° for 25 minutes. The product, on cooling, solidified and the aqueous acidic layer was removed by decantation. The solid residue was again washed with water to remove mineral acid as far as possible since the moist diketone was found to turn brownish on standing in contact with acids. The residue was shaken vigorously with ether whereupon a white crystalline solid separated. This was collected, washed with ether and dried. The diketone (2.4 g.) thus obtained had the m.p. 149–150°. The ether extract and the washing were combined and washed with sodium hydroxide solution (5%) repeatedly until the alkali wash gave no precipitate on acidification with dilute hydrochloric acid. All the sodium hydroxide washings were combined and acidified with hydrochloric acid (6 *N*) affording a gummy substance which on trituration with ether gave another lot (0.6 g.) of the diketone having the m.p. 148–150°. The over-all yield was 3 g. For analysis, a small portion was thrice crystallized from chloroform–petroleum ether (90–100°) affording small prisms, m.p. 153–154° (lit.[4b] *ca.* 150°).

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 73.17; H, 7.31. Found: C, 72.90; H, 7.20.

2-(β-*m*-Methoxyphenylethyl)-3-keto-cyclohexenyl Isobutyl Ether (III, R = OCH_3).—A mixture of 2-(β-*m*-methoxyphenylethyl)-cyclohexane-1,3-dione (8 g.), isobutyl alcohol (13 cc.), thiophene-free benzene (54 cc.) and *p*-toluenesulfonic acid (0.5 g.) was refluxed in a water-separator for 18 hours. On working up in the usual way, the enol ether (7.5 g.) passed over at 205° (0.6 mm.). For analysis, it was redistilled and a middle fraction was collected.

Anal. Calcd. for $C_{19}H_{26}O_3$: C, 75.49; H, 8.60. Found: C, 75.68; H, 8.52.

2-(β-*m*-Methoxyphenylethyl)-3-methyl-Δ²-cyclohexenone (IV, R = OCH_3).—To the ice-cold Grignard reagent prepared from magnesium (1.1 g., 0.46 atom), methyl iodide (6.5 g., 0.46 mole) and dry ether (50 cc.), was added slowly with stirring, a solution of 2-(β-*m*-methoxyphenylethyl)-3-keto-cyclohexenyl isobutyl ether (7 g., 0.023 mole), in ether (20 cc.) and the mixture allowed to stand as such for two hours. On working up in the usual way, a pale yellow viscous liquid (4 g.) passed over at 160–164° (0.3 mm.).

Anal. Calcd. for $C_{16}H_{20}O_2$: C, 78.68; H, 8.19. Found: C, 78.48; H, 8.17.

The 2,4-dinitrophenylhydrazone crystallized from ethyl acetate–95% ethanol in deep-red prismatic crystals, m.p. 169–170° (lit.[2] 169–170°), alone or mixed with an authentic sample.

Anal. Calcd. for $C_{22}H_{24}O_5N_4$: N, 13.2. Found: N, 13.3.

Cyclization was carried out by heating for ten hours at 120° a mixture of the unsaturated ketone (2.5 g.) and phosphoric acid (10 cc., 89% w./w.), yield 1.8 g.

The 2,4-dinitrophenylhydrazone crystallized as orange-yellow small prisms melting at 205° (lit.[2] 203°).

Anal. Calcd. for $C_{22}H_{24}O_5N_4$: N, 13.20. Found: N, 13.21.

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