lization from ethanol-water, weighed 0.25 g. (9.5%), m.p. 120-122°, and which was identified as the phenol-alcohol (I) by mixed melting point with authentic (I). (c) Addition of sodium hydroxide (15 g., 0.375 mole) in 20 cc. of water gave 1.65 g. (67.1%) of the furan (III), m.p. 94-96°, and 0.65 g. (24.6%) of the phenol-alcohol (I), m.p. 117-121°, both products being identified by mixed melting point determinations.

Preparation of 2-(2-Hydroxy-1-naphthyl)-2-phenylethanol (I).—The lactone of α-(2-hydroxy-1-naphthyl)-phenylacetic acid was prepared by a method similar to that given by Arventi.[8] A mixture of 2-naphthol (35 g., 0.243 mole) and mandelic acid (25 g., 0.164 mole) was heated to 190-195° for one hour. After the mixture was cooled to incipient solidification, 50 cc. of ethanol was added and the insoluble lactone filtered off, washed with ethanol and dried to give 27.1 g. (63.5%), m.p. 180-185°. When recrystallized from glacial acetic acid, the lactone melted at 186-187° in agreement with the literature values.[8,9]

The lactone (5 g., 0.0192 mole) was placed in the thimble of a Soxhlet extractor and reduced with lithium aluminum hydride (1.6 g., 0.042 mole) in 500 cc. of ether in the manner suggested by Nystrom and Brown[10] for ether-insoluble compounds. The product, initially obtained as an oil, was crystallized from isopropyl alcohol and water after charcoal treatment to yield 4.8 g. (95%), m.p. 121-121.5°. Purifying recrystallizations from chloroform-carbon tetrachloride mixtures gave fine, white needles, m.p. 121.5-122°, of 2-(2-hydroxy-1-naphthyl)-2-phenylethanol.

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.93; H, 6.26.

After 1 g. of this phenol-alcohol was refluxed with 50 cc. of 10% sodium hydroxide for one hour, it was recovered unchanged.

Preparation of 1-Phenyl-1,2-dihydronaphtho(2,1-b)furan (III) by Acid Catalysis.—A solution of 2-(2-hydroxy-1-naphthyl)-2-phenylethanol (I) (2.0 g.) and *p*-toluenesulfonic acid monohydrate (0.1 g.) in 100 cc. of benzene was refluxed for one hour with simultaneous removal of 50 cc. of benzene containing the water formed. Evaporation of the solvent and crystallization of the residue from ethanol-water gave long, white needles, 1.5 g. (80.6%), m.p. 95-96°, of 1-phenyl-1,2-dihydronaphtho(2,1-b)furan.

Anal. Calcd. for $C_{18}H_{14}O$: C, 87.77; H, 5.73. Found: C, 88.01; H, 5.89.

Summary

The intramolecular displacement of carboxylate ion from the ester (II) of 2-(2-hydroxy-1-naphthyl)-2-phenylethanol to form 1-phenyl-1,2-dihydronaphtho(2,1-b)furan (III) was observed to proceed under hydrolytic conditions at a faster rate than hydrolysis, a result believed to arise from a favorable spatial situation. This behavior was shown to be an outstanding example of facile alkylation by alkyl esters of carboxylic acids.

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[8] Arventi, *Ann. sci. univ. Jassy*, Pt. 1, **23**, 344 (1937).

[9] Bistrzycki and Flatau, *Ber.*, **30**, 124 (1897).

[10] Nystrom and Brown, THIS JOURNAL, **69**, 2548 (1947).

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF SYDNEY]

The Synthesis of Some Alkylated Cyclohexenones and Aromatic Compounds

BY ALAN M. DOWNES,[1] NAIDA S. GILL[2] AND FRANCIS LIONS

The present paper briefly describes the details of synthesis of some cyclohexenones and aromatic compounds according to a general method previously outlined.[3]

Condensation of the methiodide of 1-N-morpholinobutanone-3 with ethyl sodio-α-acetyl isovalerate in absolute ethanol yielded ethyl Δ^1-*p*-menthen-3-one-4-carboxylate, from which by decarbethoxylation under alkaline conditions *dl*-piperitone was obtained in 50% yield over-all. Mannich and Fourneau[4] previously failed to condense 1-dimethylaminobutanone-3 usefully with ethyl α-acetyl isovalerate in presence of small amounts of alkali, so that the advantage of using the Mannich base methiodide, a method due to du Feu, McQuillen and Robinson[5] is again emphasized. Piperitone has been already synthesized by Walker[6] from the not very accessible β-chloroethyl methyl ketone.

A similar condensation of the methiodide of a 3-dialkylaminomethyl-4-methylpentanone-2 with ethyl sodio-acetoacetate to ethyl Δ^1-*p*-menthen-3-one-6-carboxylate, followed by decarbethoxylation, should also yield piperitone. An attempt to effect such a synthesis starting from methyl isobutyl ketone failed because this ketone condensed with paraformaldehyde and morpholine hydrochloride to the hydrochloride of 1-N-morpholino-5-methyl-hexanone-3, the methyl group adjacent to carbonyl being attacked rather than the methylene group, in line with the experience of Mariella.[7] Condensation of the methiodide of this base with ethyl sodio-acetoacetate, followed by decarbethoxylation under alkaline conditions yielded 1-isobutyl-Δ^1-cyclohexen-3-one, as shown by dehydrogenation with palladium-charcoal to *m*-isobutyl-phenol and oxidation of the methyl ether of this to *m*-methoxybenzoic acid. Reduction of 1-isobutyl-Δ^1-cyclohexen-3-one yielded an oily pleasant-smelling mixture of stereoisomeric 1-isobutylcyclohexan-3-ols.

Condensation of the methiodide of 1-N-morpholino-4-methylpentanone-3 with ethyl sodio-α-acetyl propionate, followed by decarbethoxylation under alkaline conditions gave a product from which *dl*-carvenone (Δ^3-*p*-menthen-2-one) was obtained in poor yield.

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[3] Downes, Gill and Lions, *Aust. J. Sci.*, **X**, 147 (1948).

[4] Mannich and Fourneau, *Ber.*, **71**, 2090 (1938).

[5] du Feu, McQuillen and Robinson, *J. Chem. Soc.*, 53-60 (1937).

[6] Walker, *ibid.*, 1585 (1935).

[7] Mariella, THIS JOURNAL, **69**, 2670 (1947).

1-*t*-Butyl-Δ^1-cyclohexene-3-one, an oil with an odor similar to that of carvone, was readily prepared by condensing the methiodide of 1-N-morpholino-4,4-dimethylpentanone-3 (prepared from pinacolone) with ethyl sodio-acetoacetate and subsequent decarbethoxylation of the product. Dehydrogenation converted it to *m*-*t*-butylphenol, whilst reduction yielded an oily mixture of 3-*t*-butylcyclohexanols.

Condensation of the methiodide of 3-N-morpholinomethylbutanone-2 with ethyl sodio-α-acetyl propionate led to formation of 2,4,5-trimethyl-Δ^5-cyclohexenone-2(or 4)-carboxylate, decarbethoxylation of which yielded 2,4,5-trimethyl-Δ^5-cyclohexenone. Treatment of this ketone with methylmagnesium iodide yielded 1,2,4,5-tetramethyl-$\Delta^{2,4}$-cyclohexadiene, heat treatment of which with sulfur gave pure crystalline durene.

Abdullah's preparation[8] of 3-phenyl-Δ^2-cyclohexenone was improved and accelerated by condensing the methiodide of β-N-morpholinoethyl phenyl ketone with ethyl sodio-acetoacetate and then decarbethoxylation of the product. It could be readily dehydrogenated with palladium–charcoal to 3-hydroxybiphenyl. Treatment of it with methylmagnesium iodide followed by heating of the product with sulfur yielded 3-methylbiphenyl. Treatment with phenylmagnesium bromide followed by sulfur dehydrogenation gave pure *m*-terphenyl in good yield—an experiment suggesting that derivatives of *m*-terphenyl should thus be readily susceptible of synthesis.

Finally, it was found that the methiodide of the Mannich base formed in the interaction of 1-acetylcyclohexene, morpholine hydrochloride and paraformaldehyde could be condensed with diethyl sodio-malonate to diethyl 1-decalone-4,4-dicarboxylate, as shown by stepwise degradation of the product to the *trans*-α-decalone of Hückel.[9] This result indicates the occurrence of a dual Michael addition of diethyl malonate to the substituted divinyl ketone transitorily produced by alkaline decomposition of the Mannich base methiodide, and suggests that there is here available a very useful method of synthesis of cyclohexanone derivatives from suitably constituted α,β-unsaturated ketones *via* the Mannich reaction.

Experimental

No two of the Mannich bases described in this paper were prepared by exactly similar methods, individual variations of working detail being necessary for the best yields. Usually, the ketone (1 mole), morpholine hydrochloride (1 mole) and paraformaldehyde (1 mole) were added to absolute ethanol (about 250 ml. for each gram mole of morpholine hydrochloride) and the mixture then refluxed for a period of two to six hours. More paraformaldehyde (0.5 mole) was sometimes added after heating for two hours and, in one or two instances, yet a third addition of paraformaldehyde (0.25 mole) was made after four hours of heating. Sometimes much more than 1 mole of ketone was used, the excess being later recovered. If the hydrochloride of the Mannich base crystallized readily on cooling the product was isolated as its hydrochloric acid salt. Otherwise, the cooled reaction liquid was diluted with ice-water, extracted with ether to remove unreacted ketone, carefully basified with cold sodium hydroxide solution and the liberated Mannich base then recovered, washed and dried in ether, after which it was distilled *in vacuo*.

For the preparation of the Mannich base methiodides usually an equal bulk of dry ether was added to the purified Mannich base after which methyl iodide (1.2 moles) was added in the cold and the reaction mixture set aside overnight. Usually, the solution clouded fairly rapidly owing to the separation of quaternary salt. If this separated eventually in the crystalline state it was recrystallized from a suitable solvent, usually ethanol. Otherwise the crude pale yellow gum was washed several times with dry ether, drained and then used in the crude state.

1-N-Morpholino-5-methylhexanone-3.—(From methyl isobutyl ketone), colorless oil, yield 47%; b. p. 88–90° (1.5 mm.) or 102–103° (5 mm.).

Anal. Calcd. for $C_{11}H_{21}NO_2$: C, 66.3; H, 10.6; N, 7.0. Found: C, 65.9; H, 10.7; N, 6.9.

The hydrochloride (from dry ethereal solution with dry hydrogen chloride) was oily.

The picrate formed yellow plates, m. p. 115° (from ethanol).

Anal. Calcd. for $C_{17}H_{24}N_4O_9$: N, 13.1. Found: N, 13.0.

The methiodide (yield 80%) was a yellow gum.

1-N-Morpholino-4-methylpentanone-3.—(From methyl isopropyl ketone); colorless oil; yield 65%; b. p. 82–85° (1.5 mm.).

Anal. Calcd. for $C_{10}H_{19}NO_2$: C, 64.9; H, 10.3. Found: C, 64.5; H, 10.1.

The hydrochloride formed white prisms, m. p. 126–127°.

Anal. Calcd. for $C_{10}H_{20}ClNO_2$: C, 50.1; H, 9.2; N, 5.8. Found: C, 50.4; H, 9.2; N, 5.9.

The picrate formed yellow leaflets from ethanol, m. p. 158–159°.

Anal. Calcd. for $C_{16}H_{22}N_4O_9$: N, 13.5. Found: N, 13.5.

The methiodide formed colorless needles, m. p. 145°.

Anal. Calcd. for $C_{11}H_{22}INO_2$: C, 40.4; H, 6.8; N, 4.3. Found: C, 39.9; H, 6.8; N, 4.3.

This methiodide appeared to break down in an unexpected manner when its aqueous solution was made alkaline and then steam distilled. It was possible to extract a colorless oil b. p. 125° (18 mm.) from the distillate. This was 1-N-morpholino-4-methylpentanone-3, as was shown by the melting point of its picrate (m. p. 158°), alone or admixed with an authentic specimen. Vinyl isopropyl ketone did not appear to be formed.

1-N-Morpholino-4,4-dimethylpentanone-3.—(From pinacolone); colorless oil; yield 41%, b. p. 82–83° (1.5 mm.).

Anal. Calcd. for $C_{11}H_{21}NO_2$: C, 66.3; H, 10.6. Found: C, 65.1; H, 10.8.

The picrate formed yellow needles, m. p. 145–147°.

Anal. Calcd. for $C_{17}H_{24}N_4O_9$: N, 13.1. Found: N, 13.2.

The methiodide (yield 76%) was a gum.

1-N-Morpholine-2-methylbutanone-3 Hydrochloride.—(From methyl ethyl ketone); yield 90%; colorless needles from ethanol, m. p. 154°.

Anal. Calcd. for $C_9H_{18}ClNO_2$: C, 52.0; H, 8.7; N, 6.7. Found: C, 51.7; H, 8.8; N, 6.7.

The crude base corresponding to this salt gave the iodoform test. Its methiodide formed colorless needles, m. p. 147–148° (yield 90%).

Anal. Calcd. for $C_{10}H_{20}INO_2$: C, 38.4; H, 6.4; N, 4.5. Found: C, 37.9; H, 6.5; N, 4.3.

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[8] Abdullah, Thesis, Berlin, 1932; *J. Indian Chem. Soc.*, **12**, 62–66 (1935).

[9] Hückel, *Ann.*, **441**, 1–48 (1925).

β-N-Morpholinoethyl Phenyl Ketone Methiodide.—(From β-morpholinoethyl phenyl ketone[10] and methyl iodide in ether); colorless needles, m. p. 196–198° (from methanol).

Anal. Calcd. for $C_{14}H_{20}INO_2$: C, 46.5; H, 5.6; N, 3.9. Found: C, 46.0; H, 5.4; N, 3.7.

β-N-Morpholinoethyl Δ¹-Cyclohexenyl Ketone Hydrochloride.—(From 1-acetylcyclohexene) colorless prisms from absolute ethanol; m. p. 162–163°; yield 85%.

Anal. Calcd. for $C_{13}H_{22}ClNO_2$: C, 60.1; H, 8.5; N, 5.4. Found: C, 59.7; H, 8.7; N, 5.7.

The free base was an oil which could not be distilled.

The picrate formed yellow leaflets m. p. 130° from amyl alcohol.

Anal. Calcd. for $C_{19}H_{24}N_4O_9$: N, 12.4. Found: N, 12.5.

The methiodide (yield 84%) was obtained as a gum containing a few crystals.

***dl*-Piperitone.**—An absolute ethanolic solution of 30 g. of the gummy methiodide from 1-N-morpholinobutanone-3 was added to a warm ethanolic solution of ethyl sodio-α-acetylisovalerate [from sodium (3.4 g.), absolute ethanol (100 ml.) and ethyl α-acetylisovalerate (26 g.)]. After standing for about thirty minutes the solution was refluxed for four hours. A solution of potassium hydroxide (10 g.) in water (15 ml.) was then added and the refluxing continued for a further eight hours. Most of the alcohol was distilled off and water added to the residue. The precipitated oil was taken up and washed with water several times in ether, dried and distilled. After a small forerun *dl*-piperitone (7.8 g.), b. p. 111–113° (17 mm.), came over as a colorless oil with $n^{20}\mathrm{D}$. Its identity was proved by preparation of the α-oxime, m. p. 118°, alone or mixed with an authentic sample of *dl*-piperitone α-oxime prepared from natural piperitone from *E. dives* oil.

Anal. Calcd. for $C_{10}H_{17}NO$: N, 8.4. Found: N, 8.4.

The following cyclohexenones were prepared by methods substantially similar to that used to prepare piperitone.

***dl*-Carvenone.**—Yield 12% (from 1-N-morpholino-4-methylpentanone-3 methiodide and ethyl sodio-α-acetylpropionate); colorless oil, b. p. 115–116° (18 mm.) or 231–233° (764 mm.); $n^{23.5}\mathrm{D}$ 1.4806, d^{25}_4 0.9350.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.9; H, 10.5. Found: C, 78.5; H, 10.3.

The semicarbazone formed white leaflets m. p. 200–202° (from methanol).[11]

Anal. Calcd. for $C_{11}H_{19}N_3O$: N, 20.1. Found: N, 20.0.

3-Isobutyl-Δ²-cyclohexenone.—Yield 45% (from 1-N-morpholino-5-methyl-hexanone-3 methiodide and ethyl sodio-acetoacetate); colorless oil with pleasant mint-like odor; b. p. 77–82° (1.5 mm.) or 241–242° (760 mm.); $n^{27}\mathrm{D}$ 1.4835, d^{25}_4 0.9150.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.9; H, 10.6. Found: C, 78.4; H, 10.8.

The 2,4-dinitrophenylhydrazone formed small red plates, m. p. 135° (from ethanol).

Anal. Calcd. for $C_{16}H_{20}N_4O_4$: N, 16.7. Found: N, 16.9.

The **semicarbazone** formed white plates, m. p. 167–168° (from ethanol).

Anal. Calcd. for $C_{11}H_{19}N_3O$: N, 20.1. Found: N, 19.9.

3-*t*-Butyl-Δ²-cyclohexenone.—Yield 45% (from 1-N-morpholino-4,4-dimethylpentanone-3 methiodide and ethyl sodio-acetoacetate); colorless oil, b. p. 120–122° (20 mm.) or 238–240° (761 mm.).

Anal. Calcd. for $C_{10}H_{18}O$: C, 78.9; H, 10.5. Found: C, 78.6; H, 10.7.

2,4,5-Trimethyl-Δ⁵-cyclohexenone.—Yield, after prolongation of the alkaline decarbethoxylation process, 65% (from 1-N-morpholino-2-methyl-butanone-3 methiodide and ethyl sodio-α-acetyl propionate); colorless oil, b. p. 104–109° (8 mm.).

The 2,4-dinitrophenylhydrazone formed orange needles, m. p. 144–145° (from ethanol).

Anal. Calcd. for $C_{15}H_{18}N_4O_4$: N, 17.6. Found: N, 17.5.

The semicarbazone formed colorless needles, m. p. 202° (from aqueous alcohol).

Anal. Calcd. for $C_{10}H_{17}N_3O$: C, 61.5; H, 8.8; N, 21.5. Found: C, 61.1; H, 8.9; N, 21.7.

3-Phenyl-Δ²-cyclohexenone.—Yield 60% (from β-N-morpholinoethyl phenyl ketone methiodide and ethyl sodioacetoacetate); colorless needles, m. p. 64.5° (Abdullah[8] gives m. p. 64°).

The 2,4-dinitrophenylhydrazone formed red needles, m. p. 221° (from benzene).

Anal. Calcd. for $C_{18}H_{16}N_4O_4$: N, 15.9. Found: N, 15.7.

***m*-Isobutylphenol.**—Palladium-charcoal (1.5 g.) was added to a solution of 3-isobutyl-Δ²-cyclohexenone (5 g.) in diphenyl ether (15 ml.) and the mixture refluxed vigorously for two hours. After cooling to 50° the catalyst was filtered off and washed with four portions (5 ml.) of hot ethyl acetate which were added to the main filtrate. The combined filtrate was extracted once with 40-ml. and then twice with 20-ml. portions of Claisen solution.[11a] The combined extracts were washed with benzene (20 ml.) and this benzene extract added to the combined filtrate which was then extracted a further four times with the Claisen alkali solution (20-ml. portions). The combined alkaline extracts were washed with petroleum ether, diluted with water (160 ml.), acidified with hydrochloric acid and cooled. The liberated phenol was isolated with the help of ether, then distilled with steam. It was recovered from the steam distillate with ether and eventually obtained as a colorless oil (1.92 g.), b. p. 236–238° (759 mm.). It gave no color with ferric chloride solutions. Its acetyl, benzoyl and bromine-substitution derivatives were obtained only as oils. For characterization it was converted to ***m*-isobutylphenoxyacetic acid**, fluffy white needles m. p. 90° (from water).

Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.3; H, 7.7. Found: C, 68.8; H, 7.8.

***m*-Methoxybenzoic Acid.**—*m*-Isobutylphenol was converted to its methyl ether by treatment of its alkaline solution with dimethyl sulfate. This oily *m*-isobutylanisole [(1.1 g.; b. p. 216–218° (759 mm.)], was added to a solution of potassium permanganate (4 g.) in water (80 ml.) and the mixture refluxed for five hours, a further quantity of permanganate (2 g.) in water (40 ml.) being added in portions over the latter two and one-half hours of refluxing. The solution was cleared of precipitated manganese dioxide with sulfur dioxide and the acid liquid extracted with ether. Removal of the solvent from the dried extract left a small amount of oil which soon solidified. Recrystallized from hot water it yielded white plates of *m*-methoxybenzoic acid, m. p. 105°.[12]

Anal. Calcd. for $C_8H_8O_3$: C, 63.2; H, 5.9. Found: C, 62.9; H, 5.9.

3-Isobutylcyclohexanol.—Sodium (8 g.) was added in small pieces to a solution of 3-isobutyl-Δ²-cyclohexenone (6.4 g.) in absolute ethanol (100 ml.), heat being finally applied to assist solution of the metal. After cooling and diluting with water the liberated oil was extracted with ether, dried and distilled, a colorless, pleasant-smelling oil (4.1 g.), b. p. 219–221° (756 mm.) being collected, for which $n^{28}\mathrm{D}$ is 1.4654 and d^{25}_4 is 0.9034.

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[10] *Cf.* Harradence and Lions, *J. Proc. Royal Soc. N. S. W.*, **72**, 245 (1938).

[11] The melting point recorded in the literature varies from 200 to 205°; *cf.* "Beilstein," [IV], **7**, 79.

[11a] Made by dissolving potassium hydroxide (35 g.) in water (25 ml.) and then diluting with absolute methanol to 100 ml.

[12] The melting point recorded in the literature varies from 10[illegible]–110°; *cf.* Beilstein, [IV], **X**, 137.

Anal. Calcd. for $C_{10}H_{20}O$: C, 76.9; H, 12.8. Found: C, 76.4; H, 12.9.

1,2,4,5-Tetramethyl-$\Delta^{1,3}$-cyclohexadiene.—A solution of 2,4,5-trimethyl-Δ^{5}-cyclohexenone (10 g.) in dry ether was added slowly to an ethereal solution of methylmagnesium iodide (from 2.1 g. of magnesium), a vigorous reaction occurring. After gently refluxing for two hours the reaction mixture was poured onto ice and treated with ammonium chloride solution, the product being recovered with the help of ether as a colorless oil (7.7 g.), b. p. 73–76° (21 mm.).

Anal. Calcd. for $C_{10}H_{16}$: C, 88.2; H, 11.8. Found: C, 87.9; H, 11.7.

On warming a mixture of this hydrocarbon (0.7 g.) with maleic anhydride (0.5 g.) in a boiling water-bath the color changed through yellow to red and a vigorous reaction occurred, the color finally becoming yellow. However, the gummy reaction product could not be induced to crystallize.

1,2,4,5-Tetramethylbenzene (Durene).—The tetramethylcyclohexadiene (4 g.) and sulfur (0.96 g.) were heated together at 220° for five hours. On cooling the very dark product crystallized partially. When steam distilled the durene came over with the steam as an oil which solidified in the condenser. It was collected with the help of ether and obtained from ethanol in colorless leaflets, m. p. 80°.[13]

Anal. Calcd. for $C_{10}H_{14}$: C, 89.6; H, 10.4. Found: C, 89.4; H, 10.4.

3-Hydroxybiphenyl.—A solution of 3-phenyl-Δ^{2}-cyclohexenone (5 g.) in diphenyl ether (15 ml.) was heated at 270° with palladized charcoal (1.5 g.) for two hours. After cooling to 50° and filtering free from the catalyst the filtrate was extracted with Claisen alkali solution exactly as described above for *m*-isobutylphenol. The 3-hydroxybiphenyl (1.9 g., 40%) was finally steam distilled. It came over slowly and crystallized from the aqueous condensate in colorless needles, m. p. 79°,[14] unchanged after recrystallization from petroleum ether.

Anal. Calcd. for $C_{12}H_{10}O$: C, 84.7; H, 5.9. Found: C, 84.4; H, 6.0.

3-Methylbiphenyl.—A dry ethereal solution of methylmagnesium iodide (from 0.72 g. of magnesium) was added to a dry ethereal solution of 3-phenyl-Δ^{2}-cyclohexenone (4.3 g.), a vigorous reaction occurring. After refluxing for one and one-half hours the cooled solution was treated with ice-cold ammonium chloride solution and the oily 1-methyl-3-phenyl-Δ^{2}-cyclohexanol obtained by drying and then evaporation of the solvent from the ether layer. The oil was mixed with sulfur (0.82 g.) and heated at 220° for four and one-half hours, after which the product was steam distilled from accompanying tarry material. The steam-volatile oil was collected, dried and distilled, a yellow oil (2.4 g., 56%), b. p. 266–269° (761 mm.), being collected.[15]

Anal. Calcd. for $C_{13}H_{12}$: C, 92.9; H, 7.1. Found: C, 92.5; H, 7.0.

***m*-Terphenyl.**—A dry ethereal solution of 3-phenyl-Δ^{2}-cyclohexenone (43 g.) was added to an ethereal solution of phenylmagnesium bromide (from 0.78 g. of magnesium and 5.1 g. of bromobenzene). After one and one-half hours of refluxing the reaction mixture was decomposed in the usual way with ice and ammonium chloride solution and the 1,3-diphenyl-Δ^{2}-cyclohexenol recovered with the help of ether as an oil, which was then heated at 220° with sulfur (0.83 g.) for four and one-half hours. On cooling, the mixture set to a solid mass which was recrystallized from ethanol, yielding colorless needles of *m*-terphenyl, m. p. 87.5°.[16]

Anal. Calcd. for $C_{18}H_{14}$: C, 93.9; H, 6.1. Found: C, 93.4; H, 6.2.

Diethyl *trans*-1-Decalone-4,4-dicarboxylate.—A solution of the gummy methiodide of β-N-morpholinoethyl Δ^{1}-cyclohexenyl ketone (23 g.) in absolute ethanol (100 ml.) was added to an alcoholic solution of diethyl sodiomalonate [from diethyl malonate (15 g.), sodium (2.2 g.) and absolute ethanol (40 ml.)] and the mixture refluxed for two and one-half hours. Most of the ethanol was distilled off, water and dilute acid added and the separated oil collected, washed and dried in ether. On distillation it yielded a little unchanged diethyl malonate, b. p. 100–102° (24 mm.), and then a difficultly distillable oil (14.4 g., 77%), b. p. 170–175° (0.5 mm.).

Anal. Calcd. for $C_{16}H_{24}O_5$: C, 64.9; H, 8.1. Found: C, 64.5; H, 8.3.

The **2,4-dinitrophenylhydrazone** crystallized from ethanol in orange leaflets, m. p. 132°.

Anal. Calcd. for $C_{22}H_{28}N_4O_8$: N, 11.8. Found: N, 11.8.

***trans*-1-Decalone.**—A concentrated aqueous solution of potassium hydroxide (10 g.) was added to a solution of the above-described ester (10 g.) in ethanol (60 ml.) and the solution refluxed for four hours, after which most of the alcohol was distilled off and dilute hydrochloric acid added. With the help of ether a yellow-brown gum was isolated, but it could not be induced to crystallize. When heated at 200° for thirty minutes it lost carbon dioxide. The cooled residue of ***trans*-1-decalone-4-carboxylic acid** (4.5 g., 90%) solidified but resisted attempts at recrystallization. It readily yielded a **2,4-dinitrophenylhydrazone**, minute orange crystals, m. p. 200° (dec.) from ethanol.

Anal. Calcd. for $C_{17}H_{20}N_4O_6$: N, 14.9. Found: N, 14.9.

A portion of this keto-acid was dissolved in the minimum quantity of sodium carbonate solution which was then evaporated to dryness. The residue was intimately mixed with an excess of soda-lime and the mixture heated in a small side-arm test-tube. A few drops of *trans*-1-decalone with a strong menthol-like odor distilled. From them the **semicarbazone**, white needles, m. p. 230° (from benzene), was prepared (Hückel[9] gives m. p. 229–230°).

Anal. Calcd. for $C_{11}H_{19}N_3O$: N, 20.1. Found: N, 19.7.

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Summary

Syntheses of a series of cyclohexenones, including piperitone and carvenone, and aromatic substances, such as durene and *m*-terphenyl, are described, together with a synthesis of *trans*-α-decalone from 1-acetylcyclohexene.

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[13] Gissman, *Ann.*, **216**, 203 (1883), gives m. p. 80°.

[14] Jacobson and Loeb, *Ber.*, **36**, 4085 (1903), give m. p. 78°.

[15] v. Auwers and Julicher, *ibid.*, **55**, 2184 (1922), give b. p. 272–274°; Gomberg and Pernert, THIS JOURNAL, **48**, 1379 (1926), give b. p. 267–269°.

[16] Bachmann and Clarke, *ibid.*, **49**, 2093 (1927), give m. p. 87°.