

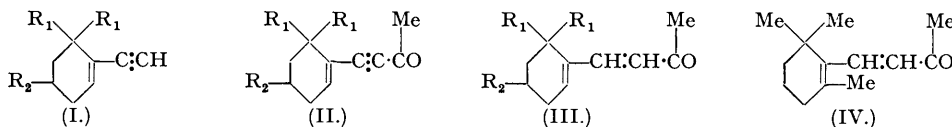
432. Studies in the Polyene Series. Part XXXII. Further Syntheses of Analogues of β -Ionone.

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In continuation of the schemes previously outlined for the preparation of compounds with modified β -ionone structures, 4-methyl-1-ethynylcyclohex-1-ene (I; $R_1 = H$, $R_2 = Me$) and 6:6-dimethyl-1-ethynylcyclohex-1-ene (I; $R_1 = Me$, $R_2 = H$) have been converted into the acetylenic ketones (II) which, on partial hydrogenation, yielded the diene ketones (III).

DEVELOPING the schemes previously described (Heilbron, Jones, Richardson, and Sondheimer, this vol., p. 737; Heilbron, Jones, Toogood, and Weedon, this vol., p. 1827) for the synthesis of analogues of β -ionone (IV), the diene ketones (III; $R_1 = H$, $R_2 = Me$) and (III; $R_1 = Me$, $R_2 = H$) have been prepared. As has already been reported (Braude, Jones, Koch, Richardson, Sondheimer, and Toogood, this vol., 1890), measurements of the light-absorption properties of these and related compounds have been of considerable value in revealing a plausible explanation for certain anomalies in the corresponding data for β -ionone.

Vapour-phase dehydration of 4-methyl-1-ethynylcyclohexanol over a supported aluminium phosphate catalyst at 300–310° (cf. Heilbron, Jones, and Richardson, this vol., p. 287) readily gave 4-methyl-1-ethynylcyclohex-1-ene (I; $R_1 = H$, $R_2 = Me$) in 75% yield. By condensation of the Grignard reagents derived from this hydrocarbon and from 6:6-dimethyl-1-ethynylcyclohex-1-ene (I; $R_1 = Me$, $R_2 = H$) (Heilbron, Jones, Lewis, and Weedon, preceding paper) with acetic anhydride at -60°, the acetylenic ketones (II; $R_1 = H$, $R_2 = Me$) and (II; $R_1 = Me$, $R_2 = H$) were obtained in 55 and 85% yield, respectively. Partial hydrogenation of the latter in the presence of a quinoline-poisoned palladium-charcoal catalyst gave the β -ionone analogues, 4-(4'-methylcyclohex-1'-enyl)but-3-en-2-one (III; $R_1 = H$, $R_2 = Me$) and 4-(6':6'-dimethylcyclohex-1'-enyl)but-3-en-2-one (III; $R_1 = Me$, $R_2 = H$), which were isolated in 40 and 5% yield, respectively, after regeneration from the semicarbazones.



The light-absorption properties of the diene ketones (III; $R_1 = H$, $R_2 = Me$) and (III; $R_1 = Me$, $R_2 = H$) have been discussed previously (Braude, Jones, Koch, Richardson, Sondheimer, and Toogood, *loc. cit.*), and the data for the acetylenic compounds described in this paper are very similar to those of the corresponding cyclohexenyl analogues (see Table).

EXPERIMENTAL.

Light absorption measurements were determined in ethanol, except where stated otherwise, and the data are given in the Table. All the operations were performed in an atmosphere of nitrogen.

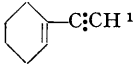
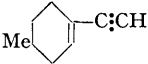
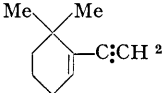
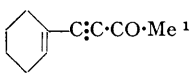
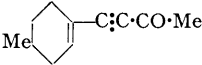
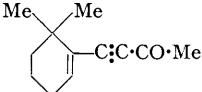
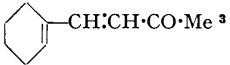
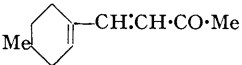
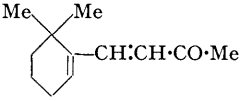
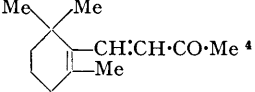
4-Methyl-1-ethynylcyclohexanol.—A solution of 4-methylcyclohexanone (156 g.) in ether (300 c.c.) was added dropwise during 2 hours to a solution of sodium acetylide [prepared from sodium (32 g.) by the procedure of Heilbron, Jones, and Weedon, *J.*, 1945, 83] in liquid ammonia (2 l.). After the mixture had been stirred for a further 5 hours, the reaction was terminated by the gradual addition of ammonium chloride (80 g.), and the ammonia evaporated. Isolation of the product in the usual way gave 4-methyl-1-ethynylcyclohexanol (118 g.), b. p. 100–103°/20 mm., m. p. 20° (Rupe and Kuenzy, *Helv. Chim. Acta*, 1931, 14, 701, give b. p. 73–75°/10 mm., m. p. 20°).

4-Methyl-1-ethynylcyclohex-1-ene (I; $R_1 = H$, $R_2 = Me$).—The above carbinol (40 g.) was slowly distilled (*ca.* 40 g./hr.) at 110–120° (bath temp.)/18 mm. through a Pyrex tube (70 × 2 cm.) maintained at 300–310° and containing a supported aluminium phosphate catalyst (prepared according to Heilbron, Jones, and Richardson, *loc. cit.*). The emergent gases were condensed in air- and water-condensers, and the product was collected in a flask cooled in ice-salt. After the water produced had been separated, the crude product was distilled and the fraction boiling below 80°/50 mm. was dried ($CaCl_2$) and fractionated, to give 4-methyl-1-ethynylcyclohex-1-ene (22 g.) as a colourless mobile liquid, b. p. 71.5°/40 mm., n_D^{20} 1.4836 (Found: C, 89.5; H, 10.55. C_8H_{12} requires C, 89.9; H, 10.1%). By distillation of the high-boiling residue, 4-methyl-1-ethynylcyclohexanol (7 g.) was recovered.

The hydrocarbon (2.133 g.) in methyl acetate (15 c.c.) was shaken in hydrogen in the presence of platinum oxide catalyst until absorption ceased. Hydrogen absorbed was 1160 c.c. at 20°/770 mm., equivalent to 2.75 double bonds.

4-(4'-Methylcyclohex-1'-enyl)but-3-en-2-one (II; $R_1 = H$, $R_2 = Me$).—A solution of 4-methyl-1-ethynylcyclohex-1-ene (30 g.) in dry ether (50 c.c.) was added dropwise to an ethereal solution of ethylmagnesium chloride (from 6.1 g. of magnesium), and the mixture heated under reflux for 2 hours. After cooling, the ethereal suspension of the Grignard reagent was slowly added with stirring to a solution

of acetic anhydride (26 g.) in ether (100 c.c.) at -60° . When addition was complete, the stirring was continued at -60° for an hour, and then the temperature of the mixture was allowed to rise to 20° during 2 hours. Ice was added, and the ethereal solution was separated, washed free from acid and dried.

	$\lambda_{\max.}, \text{A.}$	$\epsilon_{\max.}$	2 : 4-Dinitrophenyl- hydrazone. †		Semicarbazone.	
			$\lambda_{\max.}, \text{A.}$	$\epsilon_{\max.}$	$\lambda_{\max.}, \text{A.}$	$\epsilon_{\max.}$
	2230 2280 *	12,500 9,500				
	2250	11,500				
	2230 2280	9,000 9,000				
	2720 2220	11,000 6,000	3700	30,500	2820 2880 *	16,500 15,500
	2710	11,000	3860 †	31,000	2820 2910 *	19,000 17,000
	2710 2770 *	11,500 10,500	3790 †	27,500	2820 2910	16,000 15,000
	2810 2730 *	20,000 18,500	3950 †	32,000	2900 3000 *	35,000 32,000
	2790 2730	23,000 23,000	3930 †	34,500	2910 3000 *	37,000 35,000
	2810 2280 2910 *	13,000 4,000 12,500	3930 †	31,500	2910 2820	30,500 29,500
	2960 2230	10,700 6,500	3880 †	27,500	2820	22,300

* Inflexion.

† In chloroform.

‡ Main band only.

¹ Heilbron, Jones, and Richardson, *loc. cit.*² Heilbron, Jones, Lewis, and Weedon, *loc. cit.*³ Heilbron, Jones, Richardson, and Sondheimer, *loc. cit.*⁴ Braude, Jones, Koch, Richardson, Sondheimer and Toogood, *loc. cit.*

Distillation gave recovered 4-methyl-1-ethynylcyclohex-1-ene (8.3 g.), b. p. $60-65^{\circ}/20$ mm., and 4-(4'-methylcyclohex-1'-enyl)but-3-yn-2-one (15.5 g.) as a mobile liquid having a pleasant odour, b. p. $59^{\circ}/10^{-2}$ mm., n_D^{20} 1.5160 (Found: C, 81.65; H, 8.3. $C_{11}H_{14}O$ requires C, 81.45; H, 8.7%). The 2 : 4-dinitrophenylhydrazone crystallised from alcohol in orange needles, m. p. 167° (Found: C, 59.6; H, 5.5. $C_{17}H_{18}O_4N_4$ requires C, 59.6; H, 5.3%). The semicarbazone crystallised from aqueous alcohol in clusters of fine needles, m. p. 155° (Found: C, 65.55; H, 7.9. $C_{12}H_{17}ON_3$ requires C, 65.7; H, 7.8%).

4-(4'-Methylcyclohex-1'-enyl)but-3-en-2-one (III; $R_1 = H$, $R_2 = Me$).—A solution of the above ketone (9.7 g.) in methyl acetate (35 c.c.) was shaken with hydrogen in the presence of a palladium-charcoal catalyst (1.0 g.; containing 0.5 g. of quinoline and 4% of Pd) (*cf.* Isler, Huber, Ronco, and Kofler, *Helv. Chim. Acta*, 1947, **30**, 1911) until 1 molar proportion of hydrogen had been absorbed (1510 c.c. at $19^{\circ}/753$ mm.). After removal of the catalyst and solvent, fractionation gave a liquid (5.7 g.), b. p. $70-72^{\circ}/10^{-2}$ mm., n_D^{20} 1.5300. Treatment with semicarbazide acetate (from semicarbazide hydrochloride, 6 g.) in methanol (30 c.c.) gave the semicarbazone (6.6 g.) which crystallised from alcohol in needles, m. p. 212° (Found: C, 65.3; H, 8.65. $C_{12}H_{19}ON_3$ requires C, 65.1; H, 8.65%).

The semicarbazone (6.03 g.) was heated under reflux for 5 hours with light petroleum (60 c.c.; b. p. $60-80^{\circ}$) and 2N-sulphuric acid (40 c.c.). Isolation of the product in the usual manner gave 4-(4'-

methylcyclohex-1'-enyl)but-3-en-2-one (3.78 g.) as a pleasant-smelling, very pale yellow liquid, b. p. $82^{\circ}/5 \times 10^{-2}$ mm., n_D^{25} 1.5330 (Found: C, 80.25; H, 9.95. $C_{11}H_{16}O$ requires C, 80.5; H, 9.8%). The 2:4-dinitrophenylhydrazone crystallised from acetic acid in dark red prisms, m. p. 205° (Found: C, 59.35, H, 5.55. $C_{17}H_{20}O_4N_4$ requires C, 59.25; H, 5.85%).

4-(4'-Methylcyclohexyl)butan-2-one.—A solution of the acetylenic ketone (II; $R_1 = H$, $R_2 = Me$) (4.55 g.) in methyl acetate (10 c.c.) was shaken with hydrogen in the presence of a platinum oxide catalyst until absorption ceased. Hydrogen absorbed at 16° and 755 mm. was 1800 c.c. equivalent to 2.7 double bonds. Removal of the catalyst and solvent, and distillation of the residue, gave 4-(4'-methylcyclohexyl)butan-2-one (3.80 g.) as a pleasant-smelling liquid, b. p. $56-58^{\circ}/10^{-2}$ mm., n_D^{25} 1.4610 (Found: C, 78.4; H, 11.6. $C_{11}H_{20}O$ requires C, 78.5; H, 12.0%). The 2:4-dinitrophenylhydrazone crystallised from aqueous alcohol in yellow plates, m. p. 95° (Found: C, 58.25; H, 6.45. $C_{17}H_{24}O_4N_4$ requires C, 58.55; H, 6.95%). The semicarbazone crystallised from aqueous methanol in plates, m. p. 163° (Found: C, 63.85; H, 9.65. $C_{12}H_{23}ON_3$ requires C, 63.95; H, 10.2%).

4-(6':6'-Dimethylcyclohex-1'-enyl)but-3-yn-2-one (II; $R_1 = Me$; $R_2 = H$).—A solution of 6:6-dimethyl-1-ethynylcyclohex-1-ene (30 g.) (Heilbron, Jones, Lewis, and Weedon, *loc. cit.*) in dry ether (150 c.c.) was added dropwise to an ethereal solution of ethylmagnesium chloride (from 5.45 g. of magnesium), and the mixture was heated under reflux for $3\frac{1}{2}$ hours. After cooling, the ethereal suspension of the Grignard reagent was slowly added with stirring to a solution of acetic anhydride (46 g.) in ether (200 c.c.) at -60° . The temperature of the mixture was maintained at -60° for 1 hour and then allowed to rise to 10° . Ice was added, and the ethereal layer was separated, washed free of acid, and dried. Distillation gave (i) recovered 6:6-dimethyl-1-ethynylcyclohex-1-ene (13.7 g.), b. p. $60-62^{\circ}/20$ mm., and (ii) 4-(6':6'-dimethylcyclohex-1'-enyl)but-3-yn-2-one (18.4 g.) as a pleasant-smelling liquid, b. p. $68^{\circ}/0.05$ mm., n_D^{25} 1.5110 (Found: C, 82.05; H, 9.35. $C_{13}H_{18}O$ requires C, 81.75; H, 9.15%). The 2:4-dinitrophenylhydrazone crystallised from alcohol in orange needles, m. p. 148° (Found: C, 61.2; H, 5.6. $C_{13}H_{20}O_4N_4$ requires C, 60.8; H, 5.65%). The semicarbazone crystallised from aqueous methyl alcohol in needles, m. p. 115° (Found: C, 66.9; H, 8.1. $C_{13}H_{19}ON_3$ requires C, 66.9; H, 8.2%).

4-(6':6'-Dimethylcyclohex-1'-enyl)but-3-en-2-one (III; $R_1 = Me$, $R_2 = H$).—A solution of the above ketone (10.3 g.) in methyl acetate (60 c.c.) was shaken with hydrogen in the presence of a palladium-charcoal catalyst (1.0 g.; containing 0.5 g. of quinoline and 4% of Pd) (*cf.* Isler *et al.*, *loc. cit.*) until 1 molar proportion of hydrogen had been absorbed (1435 c.c. at $20^{\circ}/758$ mm.). After removal of the catalyst and solvent, the product was distilled and collected in several fractions (b. p. $52-70^{\circ}/10^{-2}$ mm.) of which only that with b. p. $65-70^{\circ}/10^{-2}$ mm., n_D^{25} 1.5060 (1.7 g.), gave a solid derivative on treatment with semicarbazide acetate (from semicarbazide hydrochloride, 1.5 g.) in methanol (10 c.c.). Recrystallisation of the solid from alcohol gave the semicarbazone (0.9 g.) in plates, m. p. 191° (Found: C, 66.35; H, 9.05. $C_{13}H_{21}ON_3$ requires C, 66.3; H, 9.0%).

The semicarbazone (0.7 g.) was heated under reflux for 30 minutes with light petroleum (50 c.c.; b. p. $60-80^{\circ}$) and 2*N*-sulphuric acid (75 c.c.). Isolation of the product as usual gave 4-(6':6'-dimethylcyclohex-1'-enyl)but-3-en-2-one (0.5 g.) as a pleasant-smelling, very pale yellow liquid, b. p. $62^{\circ}/10^{-2}$ mm., n_D^{25} 1.5178 (Found: C, 80.55; H, 10.35. $C_{12}H_{18}O$ requires C, 80.85; H, 10.2%). The product was collected in 5 fractions which differed but slightly in their light-absorption intensities. The 2:4-dinitrophenylhydrazone crystallised in dark red plates from acetic acid, m. p. 153° (Found: C, 60.3; H, 6.15. $C_{13}H_{22}O_4N_4$ requires C, 60.45; H, 6.1%).

4-(2':2'-Dimethylcyclohexyl)butan-2-one.—A solution of the acetylenic ketone (II; $R_1 = Me$, $R_2 = H$) (1.42 g.) in methyl alcohol (10 c.c.) was shaken in hydrogen in the presence of a palladium-calcium carbonate catalyst (0.2 g.; 10% of Pd) until absorption ceased. Hydrogen absorbed at 20° and 770 mm. was 570 c.c., equivalent to 2.95 double bonds. Removal of the catalyst and solvent, and distillation of the residue, gave 4-(2':2'-dimethylcyclohexyl)butan-2-one (1.2 g.), as a pleasant-smelling liquid, b. p. $60.5^{\circ}/10^{-2}$ mm., n_D^{25} 1.4648 (Found: C, 78.9; H, 12.25. $C_{12}H_{22}O$ requires C, 79.05; H, 12.15%). The semicarbazone crystallised from methyl alcohol in needles, m. p. 186° (Found: C, 65.15; H, 10.05. $C_{13}H_{22}ON_3$ requires C, 65.2; H, 10.5%).

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