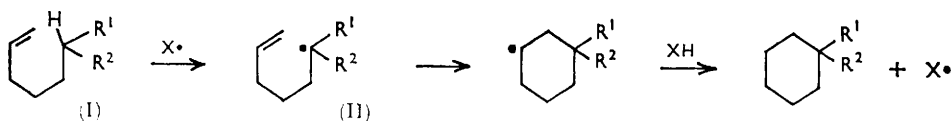


351. *Synthetic Aspects of Free-radical Addition. Part IV.¹ The Addition of Cyclohexane to Olefins*

By J. I. G. CADOGAN, D. H. HEY, and S. H. ONG

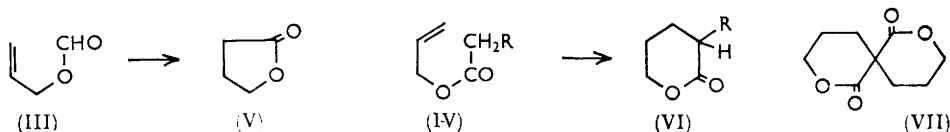
Conditions have been established for the addition of cyclohexane to allyl formate, allyl phenylacetate, diallyl malonate, pent-4-en-1-ol, allyl alcohol, and oct-1-ene, to give the corresponding 1:1 adducts. These reactions provide the first example of the free-radical addition of a saturated aliphatic hydrocarbon to an olefin under normal laboratory conditions. The radical-induced reaction between 2,2,4-trimethylpentane and allyl alcohol has also been investigated.

In Part III¹ it was reported that ethyl 2-acetylhept-6-enoate (I; $R^1 = \text{CO}\cdot\text{CH}_3$; $R^2 = \text{CO}_2\text{Et}$) and ethyl 2-cyanohept-6-enoate (I; $R^1 = \text{CN}$; $R^2 = \text{CO}_2\text{Et}$) undergo radical cyclisation, in high dilution in cyclohexane solution, in the presence of an appreciable quantity of benzoyl peroxide. This sequence of reactions was represented thus:



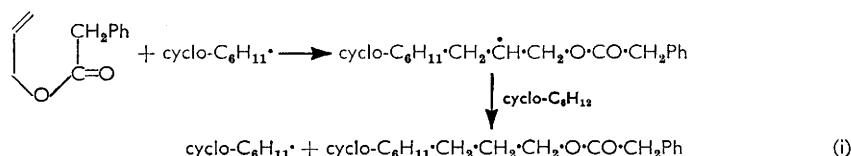
It was also shown that, under these conditions, the reactivity of the α -hydrogen atom of the methine group, which is governed by the substituents R^1 and R^2 , is critical in determining the extent of cyclisation, the relevant property of these substituents probably being their ability to stabilise the intermediate radical (II) formed by abstraction of the hydrogen atom.

It was therefore of interest to attempt to extend the scope of the intramolecular cyclisation reaction by allowing allyl formate (III), allyl phenylacetate (IV; $R = \text{Ph}$), and diallyl malonate (IV; $R = \text{CO}_2\text{C}_3\text{H}_5$) to react with benzoyl peroxide in a large excess of cyclohexane. In each of these cases, abstraction of a hydrogen atom would be expected to be facilitated by the possibility of resonance-stabilisation of the resulting intermediate radical, thus giving rise to the possibility of ring-closure to butyrolactone (V) and derivatives of valerolactone (VI):

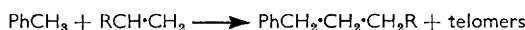


¹ Part III, Cadogan, Hey, and Ong, preceding Paper.

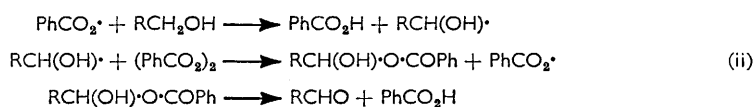
In the case of diallyl malonate, there remained the further possibility of subsequent reaction to give the spiro-dilactone (VII). In practice, however, reaction of these esters, as described above, gave 3-cyclohexylpropyl formate, 3-cyclohexylpropyl phenylacetate, and di-(3-cyclohexylpropyl) malonate as the major products, identified by comparison with authentic compounds. It is clear, therefore, that, under the conditions of high dilution in cyclohexane solution employed in these experiments, cyclohexane itself has undergone free-radical addition to the olefinic double bond, *e.g.*, with allyl phenylacetate:



These reactions provide the first example of the formation of a simple 1 : 1 adduct by radical-induced addition of an aliphatic hydrocarbon to an olefin under normal laboratory conditions. Ridgway² has reported that isobutane reacts with ethylene to give 2,2-dimethylbutane in 40% yield only at 750°r. It has also been reported that aromatic hydrocarbons, which can react by way of stabilised benzyl-type intermediate radicals, also add to alkenes in low yields:³



Such favourable resonance-stabilisation of the intermediate radicals does not exist in the examples described in this Paper. Further, the addition reaction of cyclohexane has been shown to be of general applicability. Thus, the benzoyl peroxide-induced reaction with oct-1-ene gave octylcyclohexane in 42% yield. This method of preparation has considerable advantage over the Wurtz synthesis (which was used to produce an authentic sample of octylcyclohexane in low yield), since the latter reaction is more difficult to carry out, and gives a mixture of products. It has been shown also that cyclohexane will add to unsaturated alcohols such as pent-4-en-1-ol and allyl alcohol to give saturated aliphatic alcohols [5-cyclohexylpentan-1-ol (41%) and 3-cyclohexylpropan-1-ol (33%), respectively], thus providing a new route to certain primary alcohols. The successful benzoyl peroxide-induced addition of cyclohexane to unsaturated alcohols is noteworthy, since Urry and his co-workers⁴ claimed that benzoyl peroxide does not initiate free-radical chains in alcohols, a situation attributed to the rapid induced decomposition of this peroxide which occurs in such solvents:⁵



Under the conditions of high dilution of the unsaturated alcohols in cyclohexane solution now used, unfavourable interaction between the alcohol and peroxide is suppressed, and the radical-addition reaction is able to proceed. In the presence of an unreactive hydrocarbon instead of cyclohexane, on the other hand, greater induced decomposition of benzoyl peroxide would be expected. Wibaut and Strang⁶ have shown that 2,2,4-trimethylpentane is relatively unreactive towards free radicals, remaining unchanged under conditions wherein ethylheptanes and dimethylhexanes were completely autoxidised. Hickinbottom and Fuller⁷ similarly reported the anomalous behaviour of 2,2,4-trimethylpentane

² Ridgway, *Ind. Eng. Chem.*, 1958, **50**, 1531.

³ Nikishin, Vorob'ev, and Petrov, *Doklady Akad. Nauk. S.S.S.R.*, 1960, **130**, 1256 (*Chem. Abs.*, 1960, **54**, 12020).

⁴ Urry, Stacey, Huyser, and Juveland, *J. Amer. Chem. Soc.*, 1954, **76**, 450.

⁵ Bartlett and Nozaki, *J. Amer. Chem. Soc.*, 1947, **69**, 2299.

⁶ Wibaut and Strang, *Proc. k. ned. Akad. Wetenschap.*, 1953, **54B**, 229.

⁷ Hickinbottom and Fuller, *Proc. Chem. Soc.*, 1963, 147.

during chlorination, when the major product was derived from attack on the *primary* rather than on the secondary or tertiary hydrogen atoms, which in this case are relatively inaccessible. Beckwith came to a similar conclusion.⁸ In accord with these observations, reaction of 2,2,4-trimethylpentane (600 mol.), allyl alcohol (1 mol.), and benzoyl peroxide (0.5 mol.) gave a low yield of volatile products, from which an aldehyde was isolated as its 2,4-dinitrophenylhydrazone. The molecular composition of this derivative ($C_{17}H_{26}N_4O_4$) indicated that the aldehyde had the composition $C_8H_{17}CH_2\cdot CH_2CHO$ and was probably derived by addition of 2,2,4-trimethylpentane, *via* a primary radical, to allyl alcohol. Reaction, as in eqns. (ii), between the resultant alcohol, $C_8H_{17}CH_2\cdot CH_2\cdot CH_2OH$, and benzoyl peroxide gives the aldehyde. The low yield of volatile products and the side-reaction of the alcohol further indicate the low reactivity of 2,2,4-trimethylpentane.

It is significant that, in the addition reactions of both cyclohexane and 2,2,4-trimethylpentane, neither are the initiating radicals produced stabilised by resonance, nor are the relevant C-H bonds made more prone to homolysis by the presence of activating substituents, conditions previously generally believed to be necessary for successful radical-addition reactions to be achieved. The realisation of the reactions described above indicates that these conditions are unnecessary, provided that suitable experimental procedures are employed. In such cases, high dilution is of greatest importance, in order that the destruction of the propagating radicals by radical-combination reactions be suppressed. Even under these conditions, the use of a large quantity (0.5 mol.) of peroxidic initiator to obtain measurable yields (40%) indicates that the kinetic chain-length is very short.

EXPERIMENTAL

Gas-liquid chromatography (g.l.c.) was carried out with the equipment described in Part III.¹

Reagents.—The following compounds were purified by distillation: 2,2,4-trimethylpentane, b. p. 100°, n_D^{22} 1.3900; allyl formate, b. p. 80–83°, n_D^{20} 1.3988 (Found: C, 56.0; H, 7.3. Calc. for $C_4H_6O_2$: C, 55.8; H, 7.0%); diallyl malonate, b. p. 110–113°/10 mm., n_D^{18} 1.4478 (lit.,⁹ b. p. 112°/9 mm., n_D^{20} 1.4478); and allyl 3-cyclohexylpropionate, b. p. 129.5°/15 mm., n_D^{23} 1.4595. Pent-4-en-1-ol (b. p. 130–139°) was prepared as described in Part III.¹

3-Cyclohexylpropan-1-ol. Sodium (5.78 g., 0.25 g.-atom) was added in two batches to a solution of allyl 3-cyclohexylpropionate (5.1 g., 0.028 mole) in sodium-ethoxide dried ethanol (50 ml.), and then ethanol (50 ml.) was added. The reaction mixture was boiled under reflux until all the sodium had dissolved (2 hr.) and was then concentrated. The residue was added to water, extracted with ether, and dried ($MgSO_4$). After the removal of ether, the residue (1.21 g.), on further distillation, yielded 3-cyclohexylpropan-1-ol (0.78 g., 20%), b. p. 116–122°/16 mm., n_D^{21} 1.4651 (lit.,^{10,11} b. p. 110–111°/11 mm., n_D^{25} 1.4675). The infrared (i.r.) spectrum was identical with that of the alcohol obtained by hydrogenation of cinnamaldehyde [ν_{max} 3279 cm^{-1} (alcohol OH)] (3,5-dinitrobenzoate, m. p. 80–80.5°).

3-Cyclohexylpropyl formate. A mixture of 3-cyclohexylpropan-1-ol (0.4 g., 2.8 mmole), formic acid (0.26 g., 5.6 mmole), *p*-toluenesulphonic acid (0.2 g.), and benzene (30 ml.) was boiled under reflux for 18 hr. A Dean and Stark apparatus was used to remove the water formed during the reaction. Work-up in the standard manner, followed by distillation, gave 3-cyclohexylpropyl formate (0.41 g., 86%), b. p. 107–108°/15 mm., $n_D^{23.5}$ 1.4505, ν_{max} 1727 (ester C=O) and 1176 (formate C–O) cm^{-1} (Found: C, 71.0; H, 10.6. $C_{10}H_{18}O_2$ requires C, 70.6; H, 10.7%).

Di-(3-cyclohexylpropyl) malonate. A mixture of 3-cyclohexylpropan-1-ol, (0.26 g., 1.8 mmole), malonic acid (0.091 g., 0.9 mmole), *p*-toluenesulphonic acid (0.2 g.), and benzene (30 ml.), after 16 hr. at the b. p., similarly gave di-(3-cyclohexylpropyl) malonate (0.273 g., 89%), b. p. 162–163°/0.05 min., n_D^{23} 1.4732, ν_{max} 1754 and 1739 cm^{-1} (ester C=O) (Found: C, 71.4; H, 10.5. $C_{21}H_{36}O_4$ requires C, 71.5; H, 10.3%).

⁸ Beckwith, *J.*, 1962, 2248.

⁹ Newman, Magertein, and Wheatley, *J. Amer. Chem. Soc.*, 1946, **68**, 2112.

¹⁰ Waser, *Helv. Chim. Acta*, 1925, **8**, 117.

¹¹ Bower, Cooke, and Hibbert, *J. Amer. Chem. Soc.*, 1943, **65**, 1192.

Octylcyclohexane. A mixture of bromocyclohexane (16.31 g., 0.1 mole) and 1-bromooctane (19.30 g., 0.1 mole), both previously dried (MgSO_4), was added to sodium (5.1 g., 0.22 g.-atom) about 5 ml. at a time. After the first 5 ml. had been added, the mixture was warmed. When the violent reaction had subsided, the mixture was shaken, which produced further reaction. After the addition of the bromides (45 min.), the mixture was allowed to stand for 75 min. Ethanol (20 ml.) was added, followed by 50% ethanol (20 ml.) and water (10 ml.), and the mixture was boiled under reflux for 3 hr. A large excess of water (300 ml.) was added, and the crude hydrocarbon was separated. The aqueous layer was shaken with ether (50 ml.) and the ether extract added to the main solution which was then dried (MgSO_4). After the removal of the ether, fractional distillation of the residue gave: (a) a fore-run (2.54 g.), b. p. 47–120°/15 mm., $n_D^{23.5}$ 1.4150; (b) a liquid (3.15 g.), b. p. 125–140°/15 mm., $n_D^{23.5}$ 1.4576; and (c) hexadecane (6.39 g.), b. p. 145–159°/15 mm., $n_D^{23.5}$ 1.4391 (lit.,¹² b. p. 143–145°/9 mm., n_D^{20} 1.435). Fraction (b) was analysed by means of g.l.c. (APL at 150°; flow, 60 ml./min.) and was shown to consist of two components. One was identified as bicyclohexyl (60%), and the other was assumed to be octylcyclohexane (lit.,¹³ b. p. 117–119°/11 mm., n_D^{20} 1.4507).

Addition of Cyclohexane to Olefins.—(i) *Addition to allyl formate.* A mixture of allyl formate (1.0 g., 11.6 mmole), cyclohexane (585 g., 7.0 mole), and benzoyl peroxide (1.41 g., 5.8 mmole) was boiled under reflux for 24 hr. The solution was washed with saturated sodium hydrogen carbonate solution (2 × 20 ml.) and with saturated sodium chloride solution (20 ml.) and dried (MgSO_4). Cyclohexane was removed by distillation, and the residue was fractionally distilled to give: (a) 3-cyclohexylpropyl formate (1.21 g.), b. p. 94–100°/10 mm., n_D^{17} 1.4569, i.r. spectrum identical with that of the authentic sample; (b) (0.18 g.), b. p. 103–174°/15 mm.; and (c) a residue (0.52 g.). Comparison of fraction (a) with an authentic specimen by means of g.l.c. (APL at 50°; flow, 60 ml./min., and PEGA at 150°; flow, 30 ml./min.) confirmed its identity as 3-cyclohexylpropyl formate. A portion (0.55 g.), on hydrolysis with methanolic sodium hydroxide, gave 3-cyclohexylpropan-1-ol (0.14 g., 31%), b. p. 112–113°/15 mm., n_D^{18} 1.4670 (lit.,^{10,11} b. p. 110–111°/11 mm., n_D^{25} 1.4675), i.r. spectrum identical with that of an authentic sample [ν_{max} 3279 (alcohol OH), 1057 (alcohol C–O) cm^{-1}] (3,5-dinitrobenzoate, m. p. and mixed m. p. 79–80°). Examination of fraction (b) by g.l.c. (APL at 150°; flow, 60 ml./min.) indicated that it consisted mainly of 3-cyclohexylpropyl formate (98%). The total yield, based on allyl formate, was 71%.

(ii) *Addition to diallyl malonate.* A mixture of diallyl malonate (0.92 g., 5 mmole), cyclohexane (252 g., 3.0 mole), and benzoyl peroxide (0.61 g., 2.5 mmole) was boiled under reflux for 24 hr. After treatment as described above, cyclohexane was removed and the residue distilled to give di-(3-cyclohexylpropyl) malonate (0.44 g., 25%), b. p. 160–165°/0.1 mm., $n_D^{21.5}$ 1.4810, i.r. spectrum identical with that of an authentic sample [ν_{max} 1754s and 1739 cm^{-1} (ester C=O)]. A portion (0.3 g.), on hydrolysis with methanolic potassium hydroxide, gave 3-cyclohexylpropan-1-ol (0.11 g.), b. p. 116–120°/15 mm., $n_D^{19.5}$ 1.4630, i.r. spectrum identical with that of an authentic sample. The identification of the di-(3-cyclohexylpropyl) malonate was confirmed by means of g.l.c. (APL at 150°; flow, 50 ml./min., and PEGA at 150°; flow, 30 ml./min.).

(iii) *Addition to allyl phenylacetate.* A mixture of allyl phenylacetate (1.82 g., 10 mmole), cyclohexane (503 g., 6.0 mole), and benzoyl peroxide (1.21 g., 5 mmole) was boiled under reflux for 45 hr. After treatment as described above and the removal of cyclohexane, the residue was distilled to give 3-cyclohexylpropyl phenylacetate (0.93 g., 35%), b. p. 110–120°/0.2 mm., $n_D^{19.5}$ 1.5100, ν_{max} 1751 (ester C=O) and 1616 and 1600 cm^{-1} (aromatic C=C) (Found: C, 78.3; H, 9.1. $\text{C}_{17}\text{H}_{24}\text{O}_2$ requires C, 78.5; H, 9.3%). A portion (0.51 g.) was hydrolysed to give: (a) 3-cyclohexylpropan-1-ol (0.12 g.), b. p. 113–115°/14 mm., $n_D^{22.5}$ 1.4645, i.r. identical with that of an authentic sample; and (b) phenylacetic acid (0.38 g.), m. p. and mixed m. p. 76–77°, i.r. spectrum identical with that of the authentic compound [ν_{max} (Nujol) 1678 (acid C=O) and 1605 and 1504 (aromatic C=C) cm^{-1}].

(iv) *Addition to allyl alcohol.* A mixture of allyl alcohol (1.16 g., 0.02 mole), cyclohexane (1006 g., 12 mole), and benzoyl peroxide (2.44 g., 0.01 mole) was boiled under reflux for 24 hr. After treatment as previously described and the removal of cyclohexane, the residue was distilled to give 3-cyclohexylpropan-1-ol (0.95 g., 33.4%), b. p. 104–116°/9 mm., n_D^{17} 1.4690. I.r. examination of the fraction indicated the presence of an aryl ester (weak absorption at

¹² Vogel, "Practical Organic Chemistry," Longmans, London, 1959, p. 235.

¹³ D'yakova and Lozovoi, *J. Gen. Chem. (U.S.S.R.)*, 1939, 9, 26.

1724 cm^{-1}). A portion was purified by hydrolysis with methanolic potassium hydroxide, from which the alcohol was distilled, b. p. 109–111°/10 mm., n_D^{19} 1.4655, i.r. spectrum identical with that of the authentic compound [ν_{max} 3279 cm^{-1} (alcohol OH)] (3,5-dinitrobenzoate, m. p. and mixed m. p. 78–79°).

(v) *Addition to pent-4-en-1-ol*. A mixture of pent-4-en-1-ol (2.0 g., 0.023 mole), cyclohexane (1160 g., 13.8 mole), and benzoyl peroxide (2.8 g., 0.0115 mole) was boiled under reflux for 24 hr. After treatment as described above and the removal of cyclohexane, the residue was distilled to give: (a) 5-cyclohexylpentyl alcohol (1.6 g., 41%), b. p. 124–128°/10 mm., n_D^{16} 1.4771; and (b) a residue (0.72 g.). I.r. examination of fraction (a) showed the presence of an aryl ester [ν_{max} 1706 cm^{-1} (aryl ester C=O)]. The fraction was purified by hydrolysis in methanolic potassium hydroxide, and the alcohol was distilled and collected at 125–128°/8 mm., n_D^{21} 1.4692 (lit.,¹⁴ b. p. 118–119°/4 mm., n_D^{25} 1.4638), ν_{max} 3278 cm^{-1} (alcohol OH) (Found: C, 77.7; H, 12.5. Calc. for $\text{C}_{11}\text{H}_{22}\text{O}$: C, 77.6; H, 13.0%).

(vi) *Addition to oct-1-ene*. A mixture of oct-1-ene (2.6 g., 0.023 mole), cyclohexane (1160 g., 13.8 mole), and benzoyl peroxide (2.8 g., 0.0115 mole) was boiled under reflux for 24 hr. The solution was concentrated to about 250 ml., washed with saturated sodium hydrogen carbonate solution (3×50 ml.), and dried (MgSO_4). After the removal of cyclohexane, the residue was fractionally distilled to give: (a) a fore-run (0.42 g.), $n_D^{21.5}$ 1.4370; (b) octylcyclohexane (1.81 g.), b. p. 128–130°/15 mm., n_D^{21} 1.4580; and (c) a residue (1.1 g.). Comparison of fractions (a) and (b), by means of g.l.c. (PEGA at 175°; flow, 7.9 ml./min., and APL at 150°, flow 60 ml./min.), with the mixture of hydrocarbons obtained from the Wurtz synthesis with bromocyclohexane and 1-bromo-octane indicated that octylcyclohexane had the same retention time as one of the products from Wurtz synthesis, and that fraction (a) contained 45% of octylcyclohexane and fraction (b) 94%. The total yield of octylcyclohexane, based on oct-1-ene, was 42%. I.r. examination of fraction (b) showed the presence of a small quantity of aryl ester [ν_{max} 1720 cm^{-1} (aryl ester C=O)]. Removal of the ester by hydrolysis and fractional distillation gave octylcyclohexane, b. p. 117°/14 mm., n_D^{21} 1.4529 (lit.,¹³ b. p. 117–119°/11 mm., n_D^{20} 1.4507), ester C=O peak absent from i.r. spectrum (Found: C, 86.1, H, 14.1. Calc. for $\text{C}_{14}\text{H}_{28}$: C, 85.6; H, 14.4%). The residue gave a precipitate (0.035 g.), m. p. 185–196°, ν_{max} 1678 (aryl acid C=O), 1608 and 1572 (aromatic C=C), which was probably a cyclohexyl-substituted benzoic acid.

The hydrogen carbonate extract was acidified and the acid extracted with ether (3×100 ml.) and dried (MgSO_4). After removal of the ether, a residue (1.08 g.), m. p. 85–100°, was obtained. This was probably a mixture of benzoic and cyclohexylbenzoic acids. It has previously been shown that cyclohexylbenzoic acids are formed on decomposition of dibenzoyl peroxide in cyclohexane.¹⁵

Reaction of 2,2,4-Trimethylpentane with Allyl Alcohol.—A mixture of allyl alcohol (1.16 g. 0.02 mole), 2,2,4-trimethylpentane (1368 g., 12 mole), and benzoyl peroxide (2.42 g., 0.01 mole) was boiled under reflux for 24 hr. 2,2,4-Trimethylpentane was distilled off and ether (100 ml.) was added to the cooled residue. The solution was washed with saturated sodium hydrogen carbonate solution (2×20 ml.) and water (20 ml.) and dried (MgSO_4). After removal of the ether, the residue was distilled to give: (a) (0.41 g.), b. p. 108–132°/9 mm.; (b) (0.17 g.), b. p. 111–118°/0.3 mm.; and (c) a residue (0.7 g.). I.r. examination of fraction (a) indicated the presence of an aliphatic aldehyde [ν_{max} 1730 cm^{-1} (aldehyde C=O)]; the 2,4-dinitrophenylhydrazone, purified by chromatography [bentonite-kieselguhr (4:1 w/w)], had m. p. 117–118° (from ethanol) (Found: C, 58.3; H, 7.4. Calc. for $\text{C}_{17}\text{H}_{26}\text{N}_4\text{O}_4$: C, 58.3; H, 7.4%).

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¹⁴ Hiers and Adams, *J. Amer. Chem. Soc.*, 1926, **48**, 2385.

¹⁵ Hermans and Van Eyk, *J. Polymer Sci.*, 1946, **1**, 407; Boeseken and Gelissen, *Rec. Trav. chim.*, 1924, **43**, 869; Gelissen and Hermans, *Ber.*, 1926, **59**, 662.