##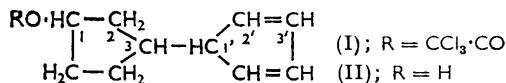 374. Conversion of Cyclopentadiene into New Bicyclopentyl Derivatives; Structure Determination with the Help of Proton Magnetic Resonance Spectroscopy.

By C. F. Blakely, R. J. Gillespie, L. Roubinek, A. Wassermann, and R. F. M. White.

Cyclopentadiene and trichloroacetic acid react, under specified conditions of concentration, to produce the trichloroacetate (I) of a new alcohol (II) containing two conjugated double bonds. Both the ester and the alcohol are unusually reactive and can be converted into novel polymers. Catalytic hydrogenation of the alcohol (II) gives 3-cyclopentylcyclopentanol which has been converted into 3-cyclopentylcyclopentanone, cyclopentylcyclopentenes, and bicyclopentyl. Proton magnetic resonance spectroscopy in conjunction with the above observations shows that alcohol (II) is 3-(cyclopenta-2,4-dienyl)cyclopentanol.

Diels–Alder diene associations, including the dimerisation of cyclopentadiene, are susceptible to catalysis by trichloroacetic acid [1] with carbonium ions as intermediates.[2] It is now shown that, at sufficiently high trichloroacetic acid concentrations, cyclopentadiene is converted into the trichloroacetate (I) of a new, unusually reactive bicyclopentyl

$$RO\cdot HC - CH_2 \qquad CH=CH$$
$$\overset{|}{\underset{H_2C - CH_2}{|}} \overset{1}{\underset{}{}}\ {}^{2}\!\!\overset{}{\underset{3}{}}CH - HC\overset{1'}{\underset{}{}}\ {}^{2'}\ {}^{3'}\overset{|}{\underset{CH=CH}{|}}$$

(I); R = CCl₃·CO
(II); R = H

alcohol (II). At low acid concentration [2] the formation of *endo*-dicyclopentadiene predominates. The main purpose of this investigation was to establish the structure of the new ester and of the corresponding alcohol with the help of proton magnetic resonance spectroscopy. In the following paper the mechanism of the reaction leading from cyclopentadiene to the bicyclopentyl derivatives will be discussed. It appears that the same carbonium ion, $C_5H_7^+$, plays a rôle as in the formation of the acid-catalysed Diels–Alder dimerisation.

EXPERIMENTAL

Cyclopentadiene concentrations were estimated by vapour pressure [3] or colorimetric [4] techniques. Trichloroacetic acid titrations were done in benzene, ethanol, or carbon tetrachloride–ethanol, with Bromophenol or Bromothymol Blue as indicator. The bicyclopentyl ester or the alcohol derived from it was used shortly after the final purification. The ester, usually prepared in 30 g. batches, was stored in absence of moisture over solid potassium hydrogen carbonate at −80°: exposure to air was as short as possible. The purification of cyclopentadiene, trichloroacetic acid, and the solvents has been described.[3] Cyclopentanol and ethyl trichloroacetate were commercial samples, dried and redistilled. The dehydration described on p. 1943 was done with activated alumina (type A, mesh $\frac{8}{16}$, of Peter Spence and Sons Ltd.). The catalyst was placed in a vertical tube, the top of which was connected with a separatory funnel from which the alcohol could be slowly released. The products passed through a water condenser, fitted to the lower end of the catalyst tubing, and were collected in traps at −80°. The molecular weight of the ester was estimated by measurements of light scattering and refractive-index increment on a Brice–Phoenix instrument,[4] with a vacuum-filter and light-scattering cell, and a Rayleigh interferometer, adapted for measurements with monochromatic light and for solutions free from molecular oxygen (partial pressure < 10⁻³ mm.). The electronic and infrared spectra were measured with Unicam, Perkin–Elmer, or Grubb–Parsons instruments. Proton nuclear magnetic resonance spectra were obtained with a Varian Associates V-4300 high-resolution instrument, with a 40 Mc./sec. oscillator: a capillary tube containing water

[1] Wassermann, *J.*, 1942, 618.
[2] Rubin, Steiner, and Wassermann, *J.*, 1949, 3046.
[3] Wassermann, *J.*, 1936, 1033.
[4] For calibration and other details see French, Roubinek, and Wassermann, *J.*, 1961, 1953.

was introduced into the sample tubes to provide an external reference. The spectra were calibrated by the side-band technique. The chemical shifts are given in terms of the dimensionless function δ, defined as $\delta = 10^6[(H_s - H_r)/H_r]$, where H_s and H_r are the resonance field for sample and reference respectively. Values of δ are given as parts per million. Broad lines are due partly to spin–spin interaction and partly to the high viscosity of some of the samples. Peak areas were measured with the help of a planimeter. By using substances of known structure, namely, cyclopentadiene, *endo-* and *exo*-dicyclopentadiene, *exo*-dicyclopentadienol, and cyclopentadienylidenecyclopentane, it was established that the peak-area measurements were accurate within 10—15%.

RESULTS

Stoicheiometry of Reactions between Cyclopentadiene and Trichloroacetic Acid.—Fig. 1 shows that the molar ratio, cyclopentadiene consumed: trichloroacetic acid consumed (α/β), is larger than two if the trichloroacetic acid concentration is below 0·3 mole l.$^{-1}$, while at higher acid
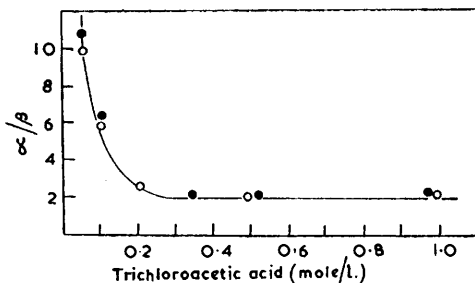

Fig. 1. *Stoicheiometry of reaction between cyclopentadiene and trichloroacetic acid: moles of cyclopentadiene consumed per mole of trichloroacetic acid consumed (α/β), plotted against trichloroacetic acid concentration.*

Temp. 20—25°; *Initial concn. of cyclopentadiene,* 1·00—1·31 *mole/l.; cyclopentadiene consumed,* 20·0—40·8%.

● CCl$_4$ *solution.*   ○ C$_6$H$_6$ *solution.*

concentrations $\alpha/\beta = 2$, within 5—10%. When α/β exceeded 2, product analyses showed that *endo*-dicyclopentadiene was predominantly formed. A typical experiment of this kind was as follows: A carbon tetrachloride solution (550 c.c.), 0·96M with regard to cyclopentadiene and 0·089M with regard to trichloroacetic acid, was left for 24 days at 20°; M-alcoholic potassium hydroxide (60 c.c.) was then added and the solution concentrated *in vacuo* to 400 c.c., any cyclopentadiene which had not reacted being thereby removed. After 24 hr. at 20° the solution was extracted with water, dried (Na$_2$SO$_4$), and fractionally redistilled, *endo*-dicyclopentadiene, b. p. 42°/2·0 mm., being isolated in over 80% yield. The identity of the product was established by its m. p. and mixed m. p. If, on the other hand, α/β is 2·0 $\pm$ 0·1, a new reaction, namely, 2 cyclopentadiene + trichloroacetic acid $\longrightarrow$ ester (I) occurs.

Ester (I).—A dry benzene solution, 0·50M with respect to trichloroacetic acid and 1·0M with respect to cyclopentadiene, was kept for 30 min. at 25° (a temperature rise being prevented by cooling); 40% of the cyclopentadiene was used up. Solid potassium hydrogen carbonate (2 moles per mole of acid) was added. Potassium trichloroacetate was filtered off. The filtrate,[5] was dried (Na$_2$SO$_4$) and freed from solvent *in vacuo* below 30°, finally at 1 mm. The residue was 3-*(cyclopenta-2,4-dienyl)cyclopentyl trichloroacetate* (>90%) (I), n_D^{25} 1·5085 $\pm$ 0·005 (mean of 8 determinations), d^{20} 1·29 [Found: C, 48·0; H, 4·4; Cl, 36·3%; equiv. (8 detns.), 290 $\pm$ 3. C$_{12}$H$_{13}$Cl$_3$O$_2$ requires C, 48·7; H, 4·4; Cl, 36·0%; equiv., 295·5]. Molecular-weight determinations in carbon tetrachloride at 20° indicated formation of double molecules. This was established by measurements of light scattering and refractive-index increment in absence of molecular oxygen, in carbon tetrachloride solution at 20°, with light of 546 mμ. The ratio R_{90}(solute)/c was (7·7 $\pm$ 1·5) $\times$ 10^{-5} cm.^{2} g.$^{-1}$ (R being the Rayleigh ratio), if the concentration (c) of ester was between 0·0678 and 0·0989 g. cm.$^{-3}$. The refractive-index increment, extrapolated to $c \longrightarrow 0$, was 0·110 $\pm$ 0·005 cm.^{3} g.$^{-1}$. The ester is easily soluble in light petroleum (b. p. 40—60°), ether, acetone, ethanol, chloroform, carbon tetrachloride, cyclohexane, benzene, pyridine, nitrobenzene, or acetic acid, but almost insoluble in water. $\lambda_{max.}$ was 242 mμ in ethanol and 244 mμ in cyclohexane, ϵ being respectively 802 and 773 l. mole^{-1} cm.$^{-1}$. The ester could not be purified by vacuum-distillation, owing to rapid polymerisation. It solidified

[5] Brown-red owing to a consecutive reaction discussed by Murphy, Roubinek, and Wassermann, *J.*, 1961, 1964.

at about $-180°$ to a glass; by fractional thawing, in the absence of moisture, four fractions were obtained, the equivalent weights, refractive indices, and electronic and nuclear magnetic resonance spectra of which were not significantly different.

Addition of bromine in carbon tetrachloride at 20° to (I) indicates two olefinic double bonds; the time of reaction was 20—120 min. and the initial concentration was $5·8$—$12·8 \times 10^{-3}$M with respect to ester and $0·056$—$0·11$N with respect to bromine. Some of the tests were done in absence of molecular oxygen. Hydrobromic acid was estimated (here and below) by the iodate method. In a typical experiment, when $1·28 \times 10^{-4}$ mole of ester and $11·24$ c.c. of $0·1$N-bromine reacted for 65 min., $6·24$ c.c. of bromine solution were used corresponding to the consumption of $4·9$ g.-atoms of bromine per mole of ester.

The Alcohol (II).—This was prepared by leaving ester (I) (60 g.) with benzene (20 ml.) and N-alcoholic potassium hydroxide (250 ml.) for 10 min. at 25°, 90% hydrolysis occurring. The mixture was added to aqueous sodium sulphate and extracted with ether; the extract, dried (Na_2SO_4) and evaporated, gave 3-(*cyclopenta-2,4-dienyl*)*cyclopentanol* (II), n_D^{25} $1·5105 \pm$ $0·0010$, d^{20} $1·025$, b. p. 84—86°/0·2 mm., 94—95°/2·0 mm., in ~50% yield if distillation was done quickly, the loss being due to polymerisation [Found: C, 79·9; H, 9·5%; M (Rast), 150. $C_{10}H_{14}O$ requires C, 80·0; H, 9·4%; M, 150]. The solubility of alcohol (II) is similar to that of ester (I), and $\lambda_{max.}$ in ethanol is 243 mμ (ϵ 400). A sample of the alcohol purified by steam-distillation had very similar physical constants to those given above. In carbon tetrachloride solution at 20°, it reacted in 2—60 min. with $4·0 \pm 0·1$ equiv. of bromine (mean of six experiments). The alcohol was converted in the usual way into a 3,5-*dinitrobenzoate*, m. p. 112—113° (from ethanol) (Found: C, 59·0; H, 4·8; N, 8·3. $C_{17}H_{16}N_2O_6$ requires C, 59·3; H, 4·7; N, 8·1%), and a *phenylurethane*, m. p. 64—65° [from light petroleum (b. p. 40—60°) and aqueous ethanol] (Found: C, 75·7; H, 7·2; N, 5·1. $C_{17}H_{19}NO_2$ requires C, 75·8; H, 7·1; N, 5·2%).

Formation of Novel Polymers.—The ester (I), if left at 20° in containers of glass, silica, porcelain, or various metals, with or without atmospheric oxygen or moisture, was gradually converted into bluish-black polymers. Similar reactions took place if the ester was mixed with one of the following substances: tri- or mono-chloroacetic acid, benzoyl peroxide, diphenyl phosphate, copper sulphide, copper or iron powder, various cation-exchangers (H^+ form), charcoal, stannous oxide, Raney nickel, or platinum oxide. The experiments with the last two added materials were done *in vacuo*, in air, and in hydrogen, with shaking. Analyses showed that in most cases the conversion into polymers is accompanied by a liberation of trichloroacetic acid. In no solvent is present, the gradual evaporation of the expelled acid is facilitated by low pressure. Some of the substances added to the ester increase the rate of polymer formation, the most efficient homogeneous catalyst being trichloroacetic acid.[6] The alcohol polymerises with liberation of water. The properties of the polymers prepared from the ester and the alcohol are similar,[7] but the alcohol is less reactive. Polymerisation of the alcohol catalysed by platinum oxide is so slow that during hydrogenation (see below) significant polymerisation did not occur.

Attempts to prepare Maleic Anhydride Adducts.—Dry benzene solutions, 0·3M with respect to ester or alcohol and 0·9M with respect to pure maleic anhydride, were refluxed for 9 hr., with exclusion of atmospheric moisture. In these reactions trichloroacetic acid is liberated from the ester and water from the alcohol. The acid was removed with solid potassium hydrogen carbonate; the water reacted with maleic anhydride and maleic acid crystallised. The solutions, freed from these acids, were evaporated *in vacuo*. The residues were viscous oils, probably polymers, giving neither crystals nor liquids of constant b. p. Similar observations were made when a benzene solution of the ester and maleic anhydride was left for 24 hr. at 20°.

Hydrogenation and Conversion of the Alcohol into a Ketone.—The alcohol (12·3 g.), platinum oxide (0·400 g.), and acetic acid (36 ml.) were shaken with hydrogen at 22°/753 mm. (absorption 3·81 g. per mole; half-time, 13 min.). After removal of the catalyst, and of 80% of the solvent *in vacuo*, the residue was added to an excess of 2N-potassium hydroxide and the product was extracted with ether, recovered, and treated with alcoholic potassium hydroxide to hydrolyse any ester formed. The solution was added to water, which was re-extracted with ether. The extract contained the hydrogenated alcohol and a ketonic impurity ($\nu_{max.}$ 1739 cm.$^{-1}$)

6 Murphy, Roubinek, and Wassermann, *J.*, 1961, 1964.
7 French, Roubinek, and Wassermann, *J.*, 1961, 1953.

forming a sparingly soluble 2,4-dinitrophenylhydrazone. The impurity, probably 3-cyclopentyl-cyclopentanone (see below) formed by reaction of the saturated and the unsaturated alcohol with the platinum oxide, was removed by reduction with sodium at 60—80° in absolute ethanol, added after removal of the ether. The resulting ethanol solution was added to water, and 3-*cyclopentylcyclopentanol* was taken up in ether, washed, dried, and recovered as liquid, b. p. 92°/0·5 mm., 98—99°/1·2 mm., n_D^{25} 1·4844 [Found: C, 78·1; H, 11·6%; *M* (Rast), 151. $C_{10}H_{18}O$ requires C, 77·9; H, 11·8%; *M*, 154].

The saturated alcohol was added, with stirring, to an aqueous solution (600 ml.) at 40°, 0·6M with respect to potassium dichromate and 0·5M with respect to sulphuric acid. After cooling to 20°, the product was taken up in ether, washed, and dried. Recovery gave 3-*cyclopentylcyclopentanone*, b. p. 74—75°/1·3 mm., n_D^{25} 1·4743 (Found: C, 79·1; H, 10·7. $C_{10}H_{16}O$ requires C, 78·9; H, 10·6%).

2-Cyclopentylcyclopentanone and 2-cyclopentylcyclopentanol, prepared as described by Wallach,[8] had b. p. 77°/1·5 mm., n_D^{25} 1·4757, and b. p. 91—92°/2 mm., n_D^{25} 1·4851, respectively.

FIG. 2. *Proton nuclear magnetic resonance spectra for pure liquids at about* 20° (*shifts in p.p.m.*).
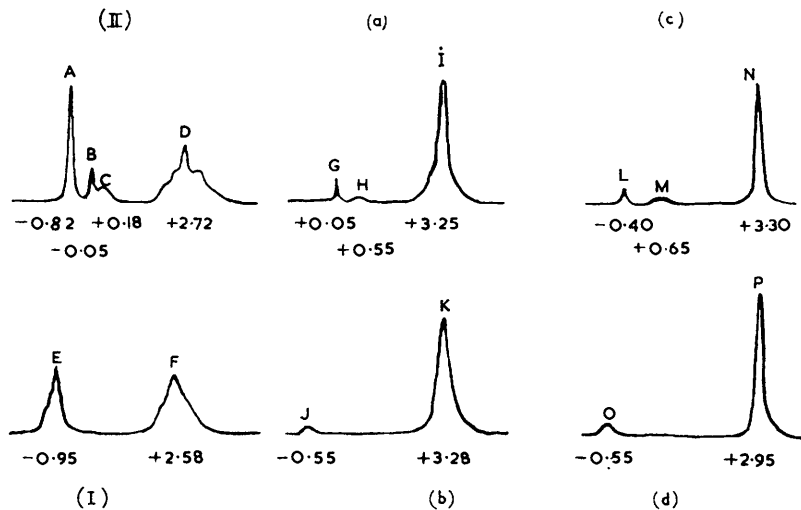
(I) *Ester prepared from trichloroacetic acid and cyclopentadiene.* (II) *Alcohol derived from* (I). (a) *Alcohol obtained by hydrogenation of* (II). (b) *Trichloroacetate of the hydrogenated alcohol.* (c) *Cyclopentanol.* (d) *Cyclopentyltrichloroacetate.*

The following derivatives were prepared by standard methods, *e.g.*, phthalates as indicated by Hückel and his collaborators.[9] Phthalates were recrystallised from pentane or light petroleum (b. p. 40—60°), other derivatives from ethanol or aqueous ethanol.

3- and 2-Cyclopentylcyclopentanol gave, respectively, a 3,5-*dinitrobenzoate*, m. p. 79—82° (Found: C, 58·7; H, 5·9; N, 8·4. $C_{17}H_{20}N_2O_6$ requires C, 58·6; H, 5·8; N, 8·05%) and m. p. 69—76° (mixed m. p. 64—68°) (Found: C, 58·1; H, 5·99; N, 8·3%), *phenylurethane*, m. p. 88—92° (Found: C, 74·7; H, 8·5; N, 4·8. $C_{17}H_{23}NO_2$ requires C, 74·6; H, 8·5; N, 5·1%) and m. p. 88—91° (mixed m. p. 82—86°) (Found: C, 74·5; H, 8·3; N, 5·4%), and *hydrogen phthalate*, m. p. 80—82° (from pentane) (Found: C, 71·6; H, 7·4. $C_{18}H_{22}O_4$ requires C, 71·5; H, 7·4%) and m. p. 85—86° (mixed m. p. 74—76°) (from light petroleum) (Found: C, 71·4; H, 7·3%).

3- and 2-Cyclopentylcyclopentanone gave, respectively, a 2,4-*dinitrophenylhydrazone*, m. p. 129—131°, $\lambda_{max.}$ (in EtOH) 232, 362 mμ (ε 20,000) (Found: C, 57·6; H, 5·8; N, 17·2. $C_{16}H_{20}N_4O_4$ requires C, 57·8; H, 6·1; N, 16·9%), and m. p. 158—160° (lit.,[10] 158—159°), $\lambda_{max.}$ and ε as above (Found: C, 57·7; H, 5·95; N, 16·9%), and a *semicarbazone*, m. p. 197—

[8] Wallach, *Annalen*, 1912, **389**, 178.
[9] Hueckel, Neunhoffer, Gercke, and Frank, *Annalen*, 1929, **477**, 135.
[10] Knight, Donald, and Cram, *J. Amer. Chem. Soc.*, 1954, **76**, 1643.

198° (Found: C, 63·4; H, 9·5; N, 20·3. $C_{11}H_{19}N_3O$ requires C, 63·1; H, 9·15; N, 20·1%) and m. p. 209° (mixed m. p. 184—186°) (lit.,[11] m. p. 208—209°).

The crude 3-cyclopentylcyclopentanol was oxidised to a crude ketone, whose dinitrophenylhydrazone and semicarbazone on systematic crystallisations gave only the derivatives of 3-cyclopentylcyclopentanone. It is concluded that the unsaturated alcohol is not contaminated with an isomer which, after hydrogenation, can be oxidised to 2-cyclopentylcyclopentanone. The interest of this is discussed in the following paper.

3-Cyclopentylcyclopentanol with trichloroacetyl chloride in pyridine and carbon tetrachloride at 20° (3·5 hr.) gave, on the usual working-up, its *trichloroacetate* as a colourless liquid (Found: C, 48·7; H, 5·4; Cl, 36·1. $C_{12}H_{17}Cl_3O_2$ requires C, 48·1; H, 5·7; Cl, 35·5%).

Dehydration of 3-Cyclopentylcyclopentanol and Conversion into Bicyclopentyl.—The alcohol (7 g.) was passed at 340°/41 mm. over activated alumina (100 g.), the reaction time being 17 min. The products were water and a mixture of cyclopentylcyclopentenes, b. p. 112—115°/100 mm., n_D^{25} 1·4796 (Found: C, 88·1; H, 12·0. Calc. for $C_{10}H_{16}$: C, 88·2; H, 11·8%). A similar mixture, prepared as described by von Braun *et al.*,[12] had b. p. 186°/763 mm., n_D^{25} 1·4738. Our mixture (3·8 g.), platinum oxide (0·14 g.), and ethyl acetate (14 ml.) were shaken with hydrogen for 18 hr. at 22°/767 mm. (absorption 1·8 g. per mole). After removal of the catalyst, and of the solvent *in vacuo*, the residue was dissolved in cyclohexane and treated with sulphuric acid, water, calcium chloride, and sodium at 80°. After filtration from sodium and removal of the solvent *in vacuo*, bicyclopentyl, b. p. 94—95°/46 mm., n_D^{25} 1·4631, was

TABLE 1. *Infrared absorption spectra* ($cm.^{-1}$; s = <50% *transmission*).

Key: I, 3-(Cyclopenta-2,4-dienyl)cyclopentyl trichloroacetate.
    II, 3-(Cyclopenta-2,4-dienyl)cyclopentanol.
    III, 3-Cyclopentylcyclopentanol.
    IV, 3-Cyclopentylcyclopentanone.
    V, 2-Cyclopentylcyclopentanone.
    VI, 2-Cyclopentylcyclopentanol.
    VII, Mixed cyclopentylcyclopentenes [from (III)].
    VIII,   ,,   ,,   (von Braun *et al.*).
    IX, Bicyclopentyl.

(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)	(IX)
3058	3279s	3333s	3448	3448	3333s	3049	3049	2944s
2941	2985s	2941s	2959s	2959s	2941s	2941s	2950s	2857s
2857	2907s	1443s	2857s	2857s	2857s	2865s	2857s	1471
1754s	2817s	1333s	1739s	1739s	1443s	1634	1613	1447s
1613	1618	1294	1449s	1449s	1333s	1600	1449s	1359
1238s	1445s	1238	1408s	1408s	1235	1437s	1370	1326
1010	1418	1190	1364	1361	1190	1335	1351	1299
1005	1355s	1163	1330	1333	1136	1312	1316	1250
971	1319	1101	1307	1316	1071s	1285	1289	1026
909								
877s	1266	1067s	1274s	1274s	1024s	1200	1220	963
833s	1205	1008s	1250	1242	971s	1157	935	926
826s	1183	990	1235	1208	917	1031	909	893
680s	1152	935	1156s	1193	900	943	893	
730	1109	900	1096	1156s	885	926	719s	
	1077	893	1018	1124	870	900		
	1053	840	1000	1081	781	893		
	1032		971	1020		800		
	1005s		935	1000		719s		
	943		893	935				
	909		885	909				
	734		826	893				
	725s		813	826				
	699s		758					

obtained (Found: C, 87·1; H, 13·1. Calc. for $C_{10}H_{18}$: C, 86·9; H, 13·1%). The cyclopentylcyclopentenes, prepared by the method of von Braun *et al.* gave, on hydrogenation, a product with identical analysis, b. p., n, and infrared spectrum.

[11] Hückel, Gross, and Doll, *Rec. Trav. chim.*, 1938, **57**, 557.
[12] von Braun, Kamp, and Kopp, *Ber.*, 1937, **70**, 1756. We have found by vapour-phase chromatography that the " cyclopentylcyclopentene " of these authors is a mixture of isomers; see also Roubinek, Ph.D. Thesis, London, 1960.

Cyclopentyl Trichloroacetate.—Prepared as above, this had b. p. 60—61°/0·4 mm. (Found: C, 36·8; H, 4·1; Cl, 45·2. $C_7H_9Cl_3O_2$ requires C, 36·3; H, 3·9; Cl, 45·9%).

Infrared Absorption Spectra.—These were determined at about 20° for the pure liquids without solvent. The results are in Table 1.

Proton Magnetic Resonance Spectra.—These are in Fig. 2, peaks being designated A—P. The spectra of cyclopentanol and its 3-substituted derivatives were measured both for the

TABLE 2. *Influence of carbon tetrachloride on proton magnetic resonance of 3-(cyclopenta-2,4-dienyl)cyclopentanol* (II) *at about* 20°.

	Position of peak (p.p.m.)			
	A	C	D	B
Pure liquid state	−0·82	+0·18	+2·72	−0·05
∼1 : 1 mixture with CCl_4	−0·90	+0·10	+2·65	+0·52

TABLE 3. *Observed peak area ratios of spectra in the pure liquid state.*

	A/(B + C)	D/(A + B + C)	F/E
Alcohol (II)	2·0	1·5	
Its trichloroacetate			1·8

pure liquid state and for CCl_4 solutions (about 50% by volume). The influence of this solvent on the spectrum of alcohol (II) is shown in Table 2. A similar effect was observed with the saturated bicyclic alcohol and cyclopentanol, the peaks which moved to higher field strength being G and L. Relative peak areas of the spectra of alcohol (II) and its trichloroacetate are recorded in Table 3. It was not possible to determine the areas of peaks B and C separately, because they overlap. For reasons explained below, we have also measured the proton magnetic resonance spectrum of ethyl trichloroacetate and compared it with that of ethanol; the methylene quartet and methyl triplet in the spectra of this ester are shifted respectively 1·20 and 0·60 p.p.m. to lower field relative to the corresponding peaks of ethanol.

DISCUSSION

The similarity, among the chemical classes, of the infrared spectra recorded in Table 1 for the various saturated alcohols, the ketones, and the hydrocarbons makes it probable that all these and therefore also the unsaturated alcohol (II) and its trichloroacetate (I), are bicyclopentyl derivatives. This is proved by the conversion of the saturated 3-cyclopentylcyclopentanol into bicyclopentyl. This alcohol is not identical with 2-cyclopentylcyclopentanol, nor is the ketone derived from the former identical with that derived from the latter, either in infrared spectra, refractive indices, and b. p., or in the m. p.s of the crystalline derivatives. The structures of the saturated alcohol (III) and ketone (IV) are thus proved.

The hydrogenation and bromination of the unsaturated alcohol (II) and its ester (I) prove that two double bonds per mole are present. These must be conjugated because the electronic spectra of both have peaks at 243—244 mμ.* Two conjugated double bonds can be incorporated into these bicyclopentyl derivatives in ten different ways. To decide between these possibilities, assignment of the peaks of the proton magnetic resonance spectra was considered. The alcohol (II) shows peaks A and D at −0·82 and +2·72 p.p.m., which are assigned [13] to hydrogen atoms bound respectively to unsaturated and saturated carbon. The corresponding hydrogenated alcohol showed no peak in the region −0·82 p.p.m. Addition of carbon tetrachloride to the pure liquid unsaturated alcohol (II) shifted peak B to higher field (see Table 2), while the other peaks move in the opposite direction. The former shift is characteristic of hydrogen-bonded alcoholic hydroxyl,[14]

* The relatively large $\varepsilon_{max.}$ value of ester, compared to that of alcohol, may be due to different stereochemical configurations.

[13] Meyer, Saika, and Gatowsky, *J. Amer. Chem. Soc.*, 1953, **76**, 4567.

[14] Cohen and Reid, *J. Chem. Phys.*, 1956, **25**, 790; Becker, Liddel, and Stoner, *J. Mol. Spectroscopy*, 1958, **2**, 1.

and therefore peak B is taken to be the signal of hydroxyl-hydrogen. To account for the ratio of line areas A/(B + C) (see Table 3), peak C must be due to a single hydrogen atom. The effect brought about by conversion of the alcohol (II) into its trichloroacetate shows that peak C must be assigned to a hydrogen atom bound, together with hydroxyl, to a saturated carbon atom.

This interpretation is confirmed by the spectra of the saturated bicyclic alcohol (III) and cyclopentanol itself: peaks G and L are assigned to hydroxyl-hydrogen, because of the effect produced by carbon tetrachloride, while peaks H and M are taken to correspond to C, peaks I and N being the signals of the other hydrogen atoms.

There are only two peaks, E and F, in the spectrum of the unsaturated ester, at -0.95 and $+2.58$ p.p.m., the signals corresponding to peaks B and C being absent. The disappearance, on esterification, of a peak due to hydroxyl-hydrogen is to be expected, but that of the other peak has to be explained with reference to the spectra of 3-cyclopentyl-cyclopentanol, cyclopentanol, and ethanol, and their trichloroacetates. For the spectra of these two cyclic alcohols and their esters peaks H, J, M, and O are assigned to hydrogen bound with either hydroxyl or trichloroacetoxyl to saturated carbon. Substitution of the electron-withdrawing trichloroacetoxyl group for hydroxyl produces a shift of the relevant peaks to lower field: this is 1.10 p.p.m. for the bicyclic alcohol (III) and its ester, 1.20 p.p.m. for the monocyclic alcohol and its ester (XI), the shifts on passing from ethanol to its ester having been specified on p. 1944. In view of all these observations it is assumed that in passing from the unsaturated alcohol (II) to its ester (I) the peak corresponding to C is shifted to about -1.00 p.p.m., so that it coincides in this ester with the peak due to hydrogen bound to unsaturated carbon. Peak E is assigned, therefore, to hydrogen at unsaturated carbon and to hydrogen bound together with trichloroacetate to saturated carbon, while peak F is due to the other hydrogen atoms.

These assignments exclude those four of the ten possibilities that have a double bond attached at positions 1 and 1'. Moreover, such formulæ should require keto–enol equilibrium for the alcohol and therefore a carbonyl frequency in its infrared spectrum, and this is not observed. To decide between the remaining six formulæ, their calculated peak-area ratios (Table 4) are compared with the observed values shown in Table 3. The last

TABLE 4. *Calculated peak-area ratios of proton nuclear magnetic resonance spectra for six of the ten possible doubly unsaturated derivatives of 3-hydroxybicyclopentyl.*

Posn. of double bonds	Calc. peak-area ratios			Posn. of double bonds		Calc. peak-area ratio		
	A/(B + C)	D/ (A + B + C)	F/E			A/(B + C)	D/ (A + B + C)	F/E
3'—4'; 1'—5'	1·5	1·8	2·25	3—4	1'—2'	1·0	2·5	3·33
4'—5'; 3—1'	1·0	2·5	3·33	2—3;	1'—5'	1·0	2·5	3·33
4—5; 3—1'	1·0	2·5	3·33	2'—3'; 4'—5'		2·0	1·33	1·6

structure in Table 4 is the only one for which the two sets of values agree within the limits of the experimental error. Further, the observed ratio of peak areas A/(B + C) is 2·0; since peak B is due to one hydrogen atom and there are only two double bonds in the molecule, peak A must be due to four hydrogen atoms and peak C to one hydrogen atom. The last structure in Table 4 is the only one having four hydrogen atoms attached to unsaturated carbon atoms. It is concluded, therefore, that the correct formula of the cyclopentadienylcyclopentanol is as shown in formula (II).

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