CONVERSION OF CYCLOPENTADIENE INTO NEW BICYCLOPENTYL DERIVATIVES

Structure Determination with the Help of Proton Magnetic Resonance Spectroscopy

Diels–Alder diene associations, including the dimerization of cyclopentadiene, are susceptible to trichloroacetic acid catalysis[1], with carbonium ions as intermediates[2]. The catalysed formation of endo-dicyclopentadiene, $C_{10}H_{12}$, was studied at acid concentrations up to 0.16 M ($25°$). It has now been found that at higher acid concentration, for example, 0.5 M, cyclopentadiene is almost quantitatively converted into a trichloroacetic acid ester (I). $C_{12}H_{13}O_2Cl_3$, n_D^{25} 1.5085, $\lambda_{max.}$ (ethanol) 242 $m\mu$; $\varepsilon_{max.}$ 800 l./mol.-cm. This ester polymerizes so quickly on heating that it cannot be distilled, but purification by fractional thawing is possible. Alkaline hydrolysis produces an alcohol (II), $C_{10}H_{14}O$, b.p. $84-86°/0.2$ mm., n_D^{25} 1.5105, $\lambda_{max.}$ (ethanol) 243 $m\mu$, $\varepsilon_{max.}$ 400 l./mol.-cm., 3,5-dinitrobenzoyl ester m.p. $112-113°$, phenyl urethane m.p. $64-65°$. Bromination and hydrogenation established the presence of two double bonds in ester (I) and alcohol (II); the double bonds must be conjugated because of the specified position of the $\lambda_{max.}$ values.

There is no carbonyl frequency in the infra-red adsorption spectrum of alcohol (II), which excludes the possibility of hydroxyl being attached to unsaturated carbon. Hydrogenation of alcohol (II) produced a saturated alcohol (III), $C_{10}H_{18}O$, b.p. $95°/0.5$ mm., n_D^{25} 1.4844, 3,5-dinitrobenzoyl ester m.p. $79-82°$, phenyl urethane m.p. $88-92°$, acid phthalate m.p. $80-82°$, which was dehydrated to hydrocarbons $C_{10}H_{16}$, b.p. $112-115°/100$ mm., n_D^{25} 1.4796, the infra-red absorption spectrum of which was very similar to that of a mixture of cyclopentyl–cyclopentenes, prepared according to v. Braun and collaborators[3].

Hydrogenation of both hydrocarbons gave bicyclopentyl $C_{10}H_{18}$, which proves that the alcohols (III) and (II) and ester (I) are bicyclopentyl derivatives. Alcohol (III) was oxidized to a ketone, $C_{10}H_{16}O$, b.p. $74-75°/1.3$ mm., n_D^{25} 1.4743, 2,4-dinitrophenyl-hydrazone m.p. $129-131°$, semicarbazone m.p. $197-198°$, which was not identical with the well-known 2-cyclopentyl-cyclopentanone. Thus, the hydroxy-group of alcohols (III) or (II) cannot be attached to a carbon atom in juxtaposition to the junction points of the two five-membered rings. The proton magnetic resonance spectrum of pure liquid alcohol (II) is characterized by peaks A, B, C and D at -0.82, -0.05, 0.18 and 2.72 parts per million (p.p.m.). These chemical shifts (which are defined by the dimensionless number $[H_s - H_r/H_r] \times 10^6$ when H_s and H_r are the resonance fields of sample and reference (water)) are assigned as follows: A corresponds to hydrogen on unsaturated carbon, B to hydroxyl hydrogen, C to hydrogen bound together with hydroxyl to saturated carbon and D to the other hydrogens on saturated carbon. The assignment is consistent with the proton magnetic resonance spectra of alcohol (III) and cyclopentanol and with the relative peak positions in the pure liquid state

and in carbon tetrachloride solution. Peak area measurements showed that four hydrogens must be attached to unsaturated carbon. An investigation of the proton magnetic resonance spectra of ester (I) and of the trichloroacetic acid esters of alcohol (III), cyclopentanol and ethanol lead to similar conclusions.

All the observations taken together prove that alcohol (II) is 3-(cyclopenta-2′,4′-dienyl)-cyclopentanol.
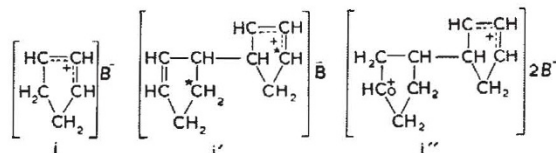
The new bicyclopentyl derivatives can be converted thermally and catalytically into polymers of unusual properties, which will be described elsewhere.

C. F. BLAKELY
R. J. GILLESPIE
L. ROUBINEK
A. WASSERMANN
R. F. M. WHITE

[1] Wassermann, J. Chem. Soc., 618 (1942).
[2] Rubin, Steiner and Wassermann, J. Chem. Soc., 3046 (1949).
[3] v. Braun, Kamp and Kopp, Ber., 70, 1756 (1937). Vapour phase chromatography showed that the 'cyclopentyl–cyclopentene' of these authors is a mixture of isomers.

Kinetics and Mechanism

THE rate, R_{ester}, of the trichloroacetic-catalysed reaction, 2-cyclopentadiene + trichloroacetic acid $\rightarrow$ trichloroacetic acid ester of 3-(cyclo-2′,4′-dienyl)-cyclopentanol (see previous communication), (ester (I)), has been measured. The results can be summarized by:

$$R_{ester} = k_{ester}[\text{cyclopentadiene}] \text{ [trichloroacetic acid]}^2 \quad (1)$$

where k_{ester} is $10^{4.3}\exp(-9900/RT)$(l./mole)^2 sec.$^{-1}$ in carbon tetrachloride and $10^{4.4}\exp(-9700/RT)$ (l./mole)^2 sec.$^{-1}$ in benzene. It has been shown before[1] that the rate, R_{dimer}, of the trichloroacetic acid catalysed dimerization, 2 cyclopentadiene $\rightarrow$ endo-dicyclopentadiene, is given by:

$$R_{dimer} = k_{dimer}[\text{cyclopentadiene}][\text{trichloroacetic acid}] \quad (2)$$

Using k_{ester} and k_{dimer}, relating to 25° and carbon tetrachloride, the ratios R_{dimer}/R_{ester} are 4.4 ± 0.8 and 0.022 ± 0.004 according to whether the trichloroacetic acid concentration is 0.0050 or 1.0 M. It is understandable, therefore, why the preparative isolation of ester (I) is only possible if the trichloroacetic acid concentration is sufficiently high (see previous communication).

Rate expression (1), the influence of polar aprotic solvents (nitrobenzene and nitromethane), which increase R_{ester}, and of proton acceptors (water, ethanol, acetone dioxan) which act as retarders, are compatible with a mechanism represented by: