A Pentacyclononanedicarboxylic Acid

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THE ready availability of the adduct (Ia) of norbornadiene and dimethyl acetylenedicarboxylate[1] prompted an investigation of its chemistry. In the hope of preparing cage-like substances the ester (Ia) and its hydrolysis product (Ib), m.p. 217—219°, were pyrolysed and photolysed. While the ester proved to be inert to pyrolysis, the acid underwent decomposition on heating. Photolysis of the ester produced a mixture of liquid products, whereas exposure of the acid (in 1·2% solution in 7 : 3 ether–tetrahydrofuran) to an unfiltered, medium-pressure, 100 w mercury lamp afforded a mixture from which a solid $C_{11}H_{10}O_4$ dicarboxylic acid, m.p. 245—249° (on crystallization from acetone), could be isolated in 33% yield.

In contrast to the starting compounds (I) (λ_{max} 257 mμ; ϵ, 6120) the photo-acid was inactive in the ultraviolet region. The ratio of dissociation constants (pK_1 = 3·2, pK_2 = 10·6 in 20% ethanol) was high and characteristic of compounds possessing proximate carboxyl groups.[2] Prolonged treatment of the photo-acid with acetyl chloride yielded a succinic anhydride (ν_{CO} 1777, 1840 cm.$^{-1}$), m.p. 104—106°, further confirming the vicinal nature of the carboxyl groups. Esterification of the photo-acid with diazomethane produced a dimethyl ester, m.p. 63—65°. The photo-acid and its derivatives were surprisingly inert. Exposure of the acid or the ester to hydrogenation over platinum in acetic–hydrochloric acid solution at 60° caused no change. Pyrolysis of the ester or anhydride at 250° for *ca.* 1·5 hr. led to recovery of starting material. The photo-acid could be isolated in high yield from its solution in concentrated sulphuric acid which had been left standing at 5° for two months.

The proton magnetic resonance spectrum of the photo-acid is depicted in the Figure. The spectrum of a deuterochloroform solution of the ester revealed a six-proton singlet at 3·68 p.p.m. (methoxyl hydrogens), a broad two-proton multiplet at *ca.* 2·81 p.p.m., a four-proton multiplet at 2·69 p.p.m., and a two-proton multiplet at 1·91 p.p.m. (half-height width 2·7 c./sec.). The mass spectrum of the anhydride of the photo-acid was very similar to that of anhydride (II) (ν_{CO} 1748, 1825 cm.$^{-1}$), m.p. 73°, prepared by the treatment of (Ib) with acetic anhydride, and exhibited intense peaks at 188 (*M*, parent), 187 ($M - H$), 144 ($M - CO_2$), 116 ($M - CO_2 - CO$), and 115 ($M - H - CO_2 - CO$).[3]

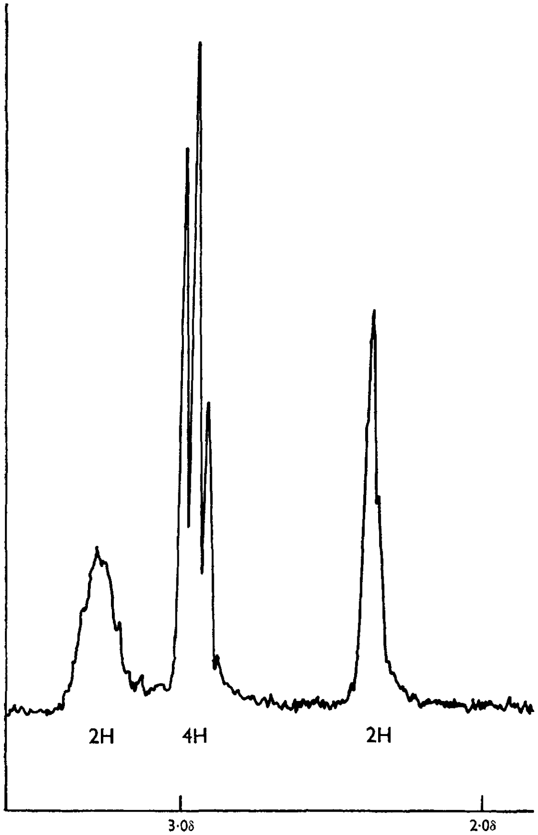
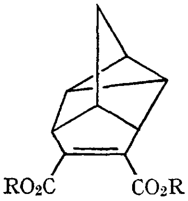
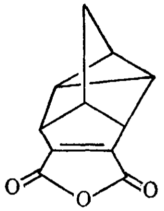


FIGURE. *Proton magnetic resonance spectrum of the photo-acid* (III) *in* 3N-NaOD–D_2O. *Varian* *A*-60 *spectrometer*, Me_4Si *external standard.*

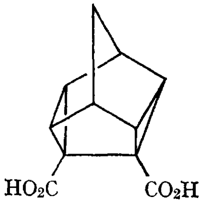
The above data, especially the simplicity of the p.m.r. spectra and their revelation of only three types of hydrogen in 2 : 4 : 2 ratio, limit the photoproduct to two structures, (III) and (VI). While the four cyclopropyl hydrogens of (III) might have been expected at higher field than that observed and hence (VI) be considered the preferred structure, the corresponding hydrogens of quadricyclanedicarboxylic acid, a close model for (III) in the literature,[4] also appear at low field (about 2·5 p.p.m. as the sodium salt in D_2O). Reminiscent photoisomerization of a simpler system also involving interaction of double bond and cyclopropyl grouping have been recently reported.[5–7] Since mechanistic interpretation of the photochemical process could account for either structure, an *X*-ray crystal structure determination, reported below, was undertaken to make a rigorous assignment. Photoexcitation of the maleic acid moiety of (Ib) could lead to bond reorganization by internal attack on the proximate cyclopropane σ-bond in a direct or "criss-crossing" manner. The direct interaction would yield (III), while the more complex reaction path would lead first to an isomer (V) of the starting compound by way of the intermediate (IV) (or its diradical equivalent)



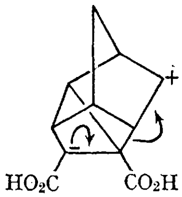
(I)



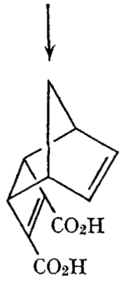
(II)



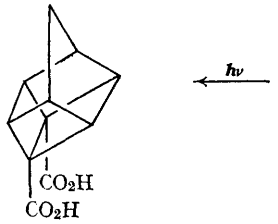
(III)



(IV)



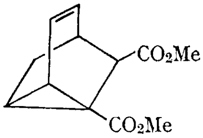
(V)



(VI)

and subsequently to (VI) by intramolecular photochemical cyclo-addition.

The infrared spectrum of the photo-acid exhibited peaks characteristic of cyclopropyl hydrogen absorptions,[8] a fundamental stretching vibration at 3041 cm.$^{-1}$, a first overtone at 5988 cm.$^{-1}$, and a second overtone at 8827 cm.$^{-1}$, reminiscent of those of other caged cyclopropane systems [(Ia): 3064, 8850 cm.$^{-1}$; (Ib anhydride): 3067, 6013, 8820 cm.$^{-1}$; (VII)[1]: 3062, 5999, 8827 cm.$^{-1}$]. These data and the absence of fundamental stretching vibration bands at >3000 cm.$^{-1}$ in the infrared spectra of homocubanecarboxylic esters derived from acids kindly supplied by Professors P. E. Eaton and W. G. Dauben suggest that the photo-acid should be assigned structure (III).



(VII)

A three-dimensional *X*-ray-diffraction study of the anhydride of the photo-acid, which is crystallographically more convenient than the photo-acid itself, has proved structure (III) correct. The crystal was found to be monoclinic, space group $P2_1/c$, using photographic *X*-ray data collected at room temperature. The intensity data were collected on a G. E. single crystal counter diffractometer at approximately $-125°$ c. The low-temperature cell constants are $a = 7{\cdot}82$, $b = 6{\cdot}95$, $c = 15{\cdot}17$ Å, $\beta = 92° \ 14'$, with four molecules per unit cell. The intensity data were adjusted to an absolute scale by means of a *K*-curve[9] and normalized structure factor magnitudes, $|E|$, were calculated. Phases were assigned to 123 reflections having $|E|$ values $\geqslant 1{\cdot}5$ using the symbolic addition procedure.[10] The 14 largest peaks in an *E*-map computed using this assignment, corresponded to a molecular model of structure (III) (anhydride). A difference Fourier revealed all of the hydrogen-atom positions. The structure has been refined with isotropic temperature factors, the residual *R*-value = 0·103.

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