Tetrahedron Letters No.30, pp. 3387-3390, 1968. Pergamon Press. Printed in Great Britain.

TETRACYCLO$[3.3.0.0^{2,8}.0^{4,6}]$OCTANE-1,5-DICARBOXYLIC ACID

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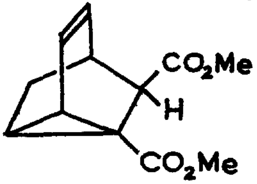
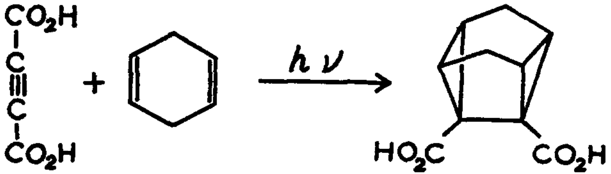
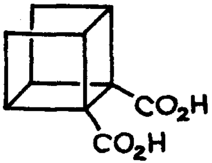
(Received in Japan 23 March 1968; received in UK for publication 29 April 1968)

The thermal reaction between dimethyl acetylene-dicarboxylate and cyclohexa-1,4-diene has been shown[1] to yield the unusual adduct I. In this communication we wish to report that the photochemical addition of acetylene-dicarboxylic acid (II) to cyclohexa-1,4-diene (III) affords tetracyclo$[3.3.0.0^{2,8}.0^{4,6}]$octane-1,5-dicarboxylic acid (IVa).


I


II III IVa


IVb

Internal irradiation of a dry ether solution [100 ml] of II [5 g] and III [25 g] in a quartz vessel under nitrogen atmosphere, with a 100 W high-pressure mercury lamp, afforded a solid dicarboxylic acid (IV), $C_{10}H_{10}O_4$[2], m.p. 259-262°C (decomp.), in 13% yield based on II.

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The photo-acid (IV) is transparent in the ultraviolet region and inert to permanganate. Esterification of IV with diazomethane gave a dimethyl ester (V), $C_{12}H_{14}O_4$, M^+ at m/e 222, m. p. 33-34°C, and treatment of IV with acetyl chloride or acetic anhydride readily afforded an anhydride m. p. 128-129°C [m/e 176 (M^+), 175 (M-H), 132 (M-CO_2), 104 (M-CO_2-CO), 103 (M-H-CO_2-CO) ; $\nu_{c=o}$ 1845, 1781 cm^{-1}].

The 100 MHz n. m. r. spectrum of the dimethyl ester (V) in C_6D_6 shows a six-proton singlet at 3. 68 (ester methyls), a four-proton triplet at 1. 91 (2. 6 Hz splittings), a two-proton doublet of quintets at 1. 62 (13 and 2. 6 Hz splittings), and a two-proton doublet (J = 13 Hz) at 1. 26 ppm, thus revealing a high-degree of symmetry in the molecule. This fact, when considered in conjunction with the mode of formation and other properties of the photo-acid, leads to only two feasible structures for the acid, namely, IVa and IVb, both of which possess two planes of symmetry. An examination of Dreiding models indicates that both the possible structures (Va and Vb) for the dimethyl ester could be expected to give rise to an $A_4B_2C_2$ spin-coupled system with J_{BC} = 13, $J_{AB} \approx J_{AB'} \approx 0$, $J_{AC} \approx J_{AC'}$ = ca 2. 6 Hz*, and hence these two structures cannot be distinguished unequivocally from the n. m. r. data. However, it is apparent that if one of the planes of symmetry were to be removed by making the groupings R_1 and R_2 non-identical, then Va and Vb would afford quite different spin-coupling patterns : Va with $R_1 \neq R_2$ would give an $A_2B_2C_2D_2$ pattern and Vb with $R_1 \neq R_2$ an A_2D_2BCEF pattern.

Treatment of the anhydride (m. p. 128-129°C) with absolute methanol afforded the half-ester (VI), m. p. 136-137°C [m/e 208 (M^+), 190 (M-H_2O), 176 (M-CH_3OH), 163 (M-COOH), 146 (M-$COOCH_3$), 131 (M-COOH-OCH_3-H), 105 (M-CO_2-$COOCH_3$) and 103 (M-COOH-$COOCH_3$-H)]. The 100 MHz spectrum of VI in C_6D_6 (see Fig. 1)[3] is characteristic of an $A_2B_2C_2D_2$ system, in which $|J_{AC} + J_{AC'}| = |J_{DC} + J_{DC'}| = 5.4$ and the previously unrevealed J_{AD} = ca 2. 5 Hz (indicative of a four-bond M-coupling, as in VIa, rather than a vicinal coupling as in VIb, $J_{AD'}$ is assumed to be zero), and thus is in accord with VIa but not with VIb. The methyl p-bromophenacyl ester (VII) [$C_{19}H_{17}O_5Br$, m. p. 132-133°C] was also prepared and its 100

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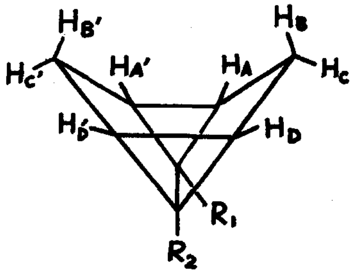
* The spectrum shows $|J_{AC} + J_{AC'}| = 5.4$ Hz. Models indicate that J_{AC} and $J_{AC'}$ could be approximately equal.



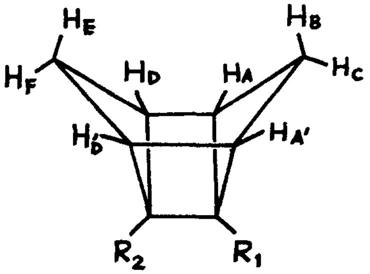
Va : $R_1 = R_2 = CO_2Me$

$H_A = H_D$

VIa : $R_1 = CO_2H$; $R_2 = CO_2Me$

VIIa : $R_1 = CO_2CH_2COC_6H_4Br$;

$R_2 = CO_2Me$



Vb : $R_1 = R_2 = CO_2Me$

$H_A = H_D$; $H_B = H_E$; $H_F = H_C$

VIb : $R_1 = CO_2H$; $R_2 = CO_2Me$

VIIb : $R_1 = CO_2CH_2COC_6H_4Br$;

$R_2 = CO_2Me$

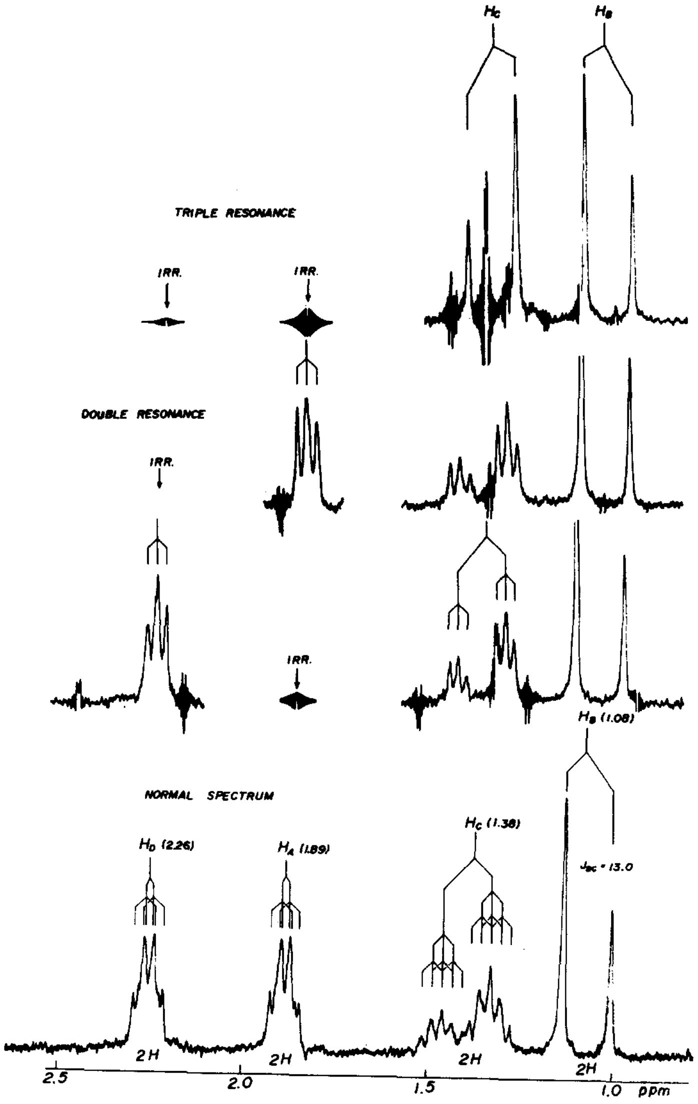
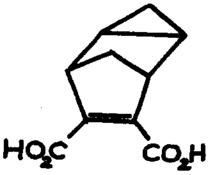


Fig. 1. 100 MHz n. m. r. spectrum of VIa in C_6D_6

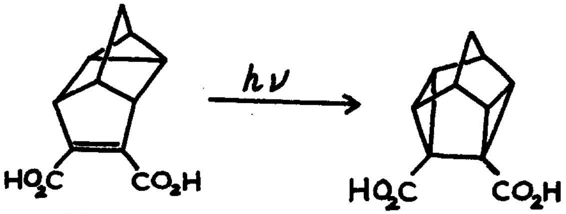
MHz n. m. r. spectrum similarly showed the presence of an $A_2B_2C_2D_2$ system [H_A at 1.94 (doublet of triplets), H_B at 1.29 (doublet), H_C at 1.69 (doublet of quintets), H_D at 2.25 ppm (doublet of triplet)] with the same splittings as before.3)

In accord with the correctness of structure Va, the dimethyl ester exhibits a C-H stretching vibration at 3050 cm^{-1}, a first overtone at 5967 cm^{-1}, and a second overtone at 8772 cm^{-1}, absorptions which are characteristic of a cyclopropyl hydrogen.4)

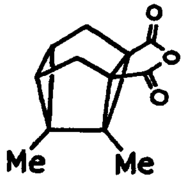
The photochemical cyclo-addition of acetylene-dicarboxylic acid to cyclohexa-1, 4-diene can be explained by either a one-step addition involving a transition state in which the two reactants are arranged orthogonally to each other or a two-step addition by way of the intermediate VIII followed by an intramolecular photochemical cyclo-addition to give IVa. Huebner and his co-workers have already reported the photochemical transformation of the related adduct IX to X.5) However, since examples of thermal 2+2+2 processes are known to occur,6)



VIII



IX X



XI

the photochemical formation of VIII is prohibited.7) Furthermore, Hoffmann and Woodward8) have predicted that the double addition of acetylene to a two pi-system, containing _m_ and _n_ pi-electrons, should be photochemical for $m + n = 4q (q = 1, 2, 3....)$, and hence it appears likely that the new sigma-bonds in IVa are formed in a concerted manner.

The only previous photochemical formation of a tetracyclo$[3.3.0.0^{2,8}.0^{4,6}]$octane system is that reported by Askani9) who prepared the photo adduct XI from cyclohexa-1, 4-diene-1, 2-dicarboxylic acid anhydride and 2-butyne.

N. m. r. spectra were measured on a Varian HA-100 with TMS(δ=0ppm) as lock-signal. We thank Mr. I. Miura for assistance in measurements.

REFERENCES AND FOOTNOTES

1) C. F. Huebner, E. Donoghue, L. Dorfman, F. A. Stuber, N. Danieli and E. Wenkert, Tetrahedron Letters 1185 (1966).

2) Satisfactory elemental analyses were obtained for all compounds synthesized.

3) The assignment of H_A and H_D is not unambiguous but this does not affect the argument.

4) H. Tanida, Y. Hata, Y. Matsui and I. Tanaka, J. Org. Chem. **30**, 2259 (1965). We are indebted to Mr. K. Iwatani of Shionogi Research Laboratory, Shionogi and Company, Ltd. for measurement of the near-infrared spectrum.

5) C. F. Huebner, E. Donoghue, L. Dorfman, E. Wenkert, W. E. Streth and W. Donely, Chem. Commun. 417 (1966).

6) A. T. Blomquist and Y. C. Meinwald, J. Am. Chem. Soc. **81**, 667 (1959) ; J. K. Williams and R. E. Benson ; J. Am. Chem. Soc. 84, 1257 (1962).

7) R. Hoffmann and R. B. Woodward, J. Am. Chem. Soc. **87**, 2046 (1965).

8) R. Hoffmann and R. B. Woodward, Accounts of Chem. Res. **1**, 17 (1968).

9) R. Askani, Chem. Ber. **98**, 3618 (1965).