Tetrahedron Letters No.10, pp. 1017-1021, 1966. Pergamon Press Ltd.
Printed in Great Britain.

STRAINED SYSTEMS. VII.[1]

PENTACYCLO[4.2.2.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]DECA-9-ENE, BASKETENE.

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(Received 16 December 1965)

The special geometrical disposition of the two double bonds of the Diels-Alder adduct (I) of cyclooctatetraene and maleic anhydride[2] is particularly suited for the study of interaction of the double bonds. In view of revived interest in this system[3] we wish to describe our investigation in this field.

A solution of 10 g. of I in 1100 ml. of acetone was irradiated with a Hannovia 450 w. mercury lamp, using a Vycor filter. The double bonds disappeared completely within eight hours (n.m.r. analysis). Silicic acid chromatography of the product provided an approximately 40% yield of anhydride (II), m.p. 126-130°*, (Anal. Found C, 71.2; H, 5.2). The n.m.r. (no olefinic protons, but two broad peaks at τ 6.78 and 6.87)

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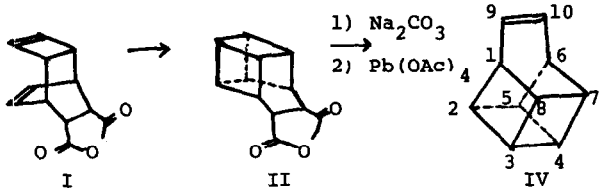
* Most compounds described in this paper showed a wide range of melting point, although they were gas-chromatographically pure.

and infrared (1782 cm^{-1}, 1856 cm^{-1}) spectral evidence is consistent with the structure shown in II. This photo-sensitized intramolecular cyclization is analogous to those recently reported for less strained systems.[4] A definite proof for structure II is given below:



I II IV

Treatment of the corresponding cis-dicarboxylic acid* (III) with lead tetraacetate in pyridine at 60-65° afforded in 30% yield an unsaturated hydrocarbon (IV), m.p. 58.5-59°, Anal. C, 91.9, H, 7.6, ** $\lambda_{max.}^{Chl.}$ 2970 cm^{-1} (s), 1620 (w) 1388 (w), 1315 (w), 1267 (w), 1184 (w), 948 (w), 865 (w) and 854 (w). Molecular weight, 130 (mass spectrum). The analysis of the n.m.r. spectrum (see FIG. I) and decoupling experiments provided the following data: $\tau_1 = 6.32$, $\tau_2 = 7.35$, $\tau_3 = 6.75$, $\tau_4 = 3.52$; $J_{1,6} = 0.0$, $J_{9,10} = 8.5$, $J_{1,10} = 1.0$

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* Compound II was converted to the cis-acid III, m.p. 162-165° with sodium carbonate in boiling water. The methyl ester of III was epimerized to the trans acid, m.p. 225-226°, with methanolic potassium hydroxide.

** Compound IV showed an appreciable vapor pressure at room temperature. Repeated elemental analyses always gave slightly lower values both in carbon and hydrogen contents.

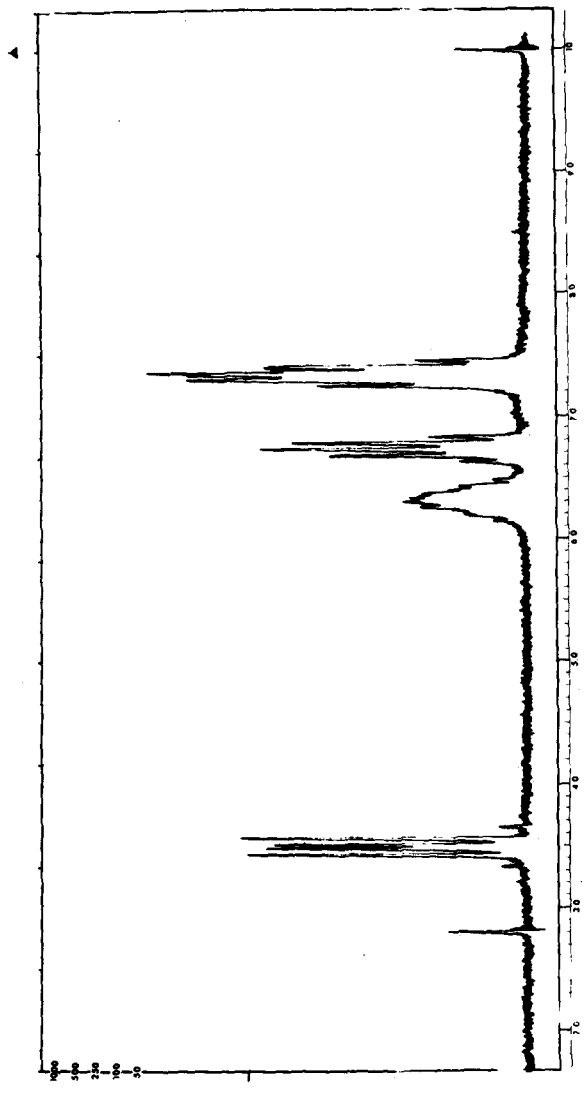
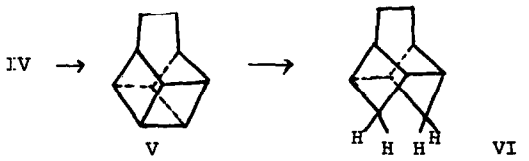


FIG. 1. The 60 Mc. n.m.r. spectrum of compound (IV).

$J_{1,9}$=6.8 , $J_{1,2}$= 2.9, $J_{1,5}$= 2.9, $J_{2,4}$ = 3.0 and $J_{2,3}$ = 3.0 . It is interesting to note $J_{2,3} = J_{2,4}$ and $J_{1,2} = J_{1,5}$. For simplicity we will hereafter use the name "basketene" for compound IV and "basketane" for the corresponding saturated compound (V) with the numbering system shown in IV.

Hydrogenation of IV with 10% Pd on carbon proceeded at one atmospheric pressure (1 mole uptake, 10 mins; 2 moles, 3 hours) and provided an 85% yield of dihydrobasketane (VI), m.p. 48-52°, which was slightly contaminated with tetrahydrobasketane as evidenced by its mass spectrum. Likewise, compound II afforded the corresponding dihydro compound (VII), m.p. 114-118°. Estimating the relative p-character of each



V VI

C-C bond of basketane V on the basis of the unique stereochemistry of the compound, we infer that the σ bond ruptured would be the C_3-C_4 bond. The above examples presumably represent the first cases where the system consisting of four-membered or larger rings are cleaved under mild hydrogenation conditions. The interruption of hydrogenation of IV immediately after one mole uptake of hydrogen provided the parent compound basketane, m.p. 58-61°, in 80% yield.[5]

Acknowledgement: The authors are grateful to the National Research Council of Canada for financial support.

References:

1. Part VI, S. Masamune, K. Fukumoto, Y. Yasunari and D. Darwish, Tetrahedron Letters, in press.

2. W. Reppe, O. Schlichting, K. Klages and Toepel, Ann., 560, 1 (1948).

3. D. G. Farnum and J. P. Snyder, Tetrahedron Letters, 3861 (1965).

4. G. O. Schenk and R. Steinmetz, Ber., 96, 520 (1963) and references quoted therein.

5. We have just learned through the Nov. 22, 1965 issue of Index Chemicus that G. O. Schenk, J. Kuhls and C. H. Krauch have mentioned compound II neither with the physical properties nor with a proof of structure. Zeit. Naturforsch., 20a 635 (1965).