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ACETYLENIC OXYGEN HETEROCYCLES[1]

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IN 1929 Lespieau[2] reported that dichlorodimethyl ether (I) on reaction with acetylenedimagnesium bromide yielded ca. 2% of 1,6-dioxa-3,8-cyclodecadiyne (II), a ten-membered heterocyclic diacetylene. Since no structure proof was given, this work has subsequently either been discounted[3] or else disregarded [e.g. by Treibs and Pester[4] who very recently described a synthesis of the related heterocycle (III, n = 6) by a method which could not be adapted to the preparation of (III, n = 4), a tetrahydro-derivative of (II)]. Some time ago we re-

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[1] This is Part XVI in the Series "Unsaturated Macrocyclic Compounds". For Part XV, see F. Sondheimer and Y. Gaoni, J. Amer. Chem. Soc. in press.

[2] R. Lespieau, Compt. rend. **188**, 502 (1929).

[3] See D.J. Cram and N.L. Allinger, J. Amer. Chem. Soc. **78**, 2518 (1956).

[4] W. Treibs and R. Pester, Tetrahedron Letters No. 17, 5 (1960).

investigated the reaction of Lespieau[2] and carried out a number of new reactions with the product corresponding in properties to those reported for (II). Our work conclusively shows the structural assignment of Lespieau to be correct and the credit for preparing the first cyclic acetylene must therefore be given to this investigator.

The reaction of (I) with an equimolecular amount of acetylenedimagnesium bromide in benzene afforded a product which on direct crystallization and chromatography of the mother liquors on alumina yielded a total of ca. 2% of (II) as colorless prisms (Anal. Calcd. for $C_8H_8O_2$: C, 70.57; H, 5.92; mol. wt., 136. Found : C, 70.55; H, 5.76; mol. wt., 136[5]). This substance showed m.p. 170-172° dec. when placed between two cover slides on a rapidly heated Fisher-Johns block at ca. 165° (decomposition without melting occurred if put on block before). A sample sublimed without melting when placed on an open cover slide in the range 100-180°, but from ca. 180° melting occurred; this corresponds to the observation of Lespieau[2] that (II) melted on the "bloc Maquenne" at about 180°. The infrared spectrum (in KBr) was compatible with structure (II) [strong bands at 9.03 and 9.37 μ (C-O vibration);

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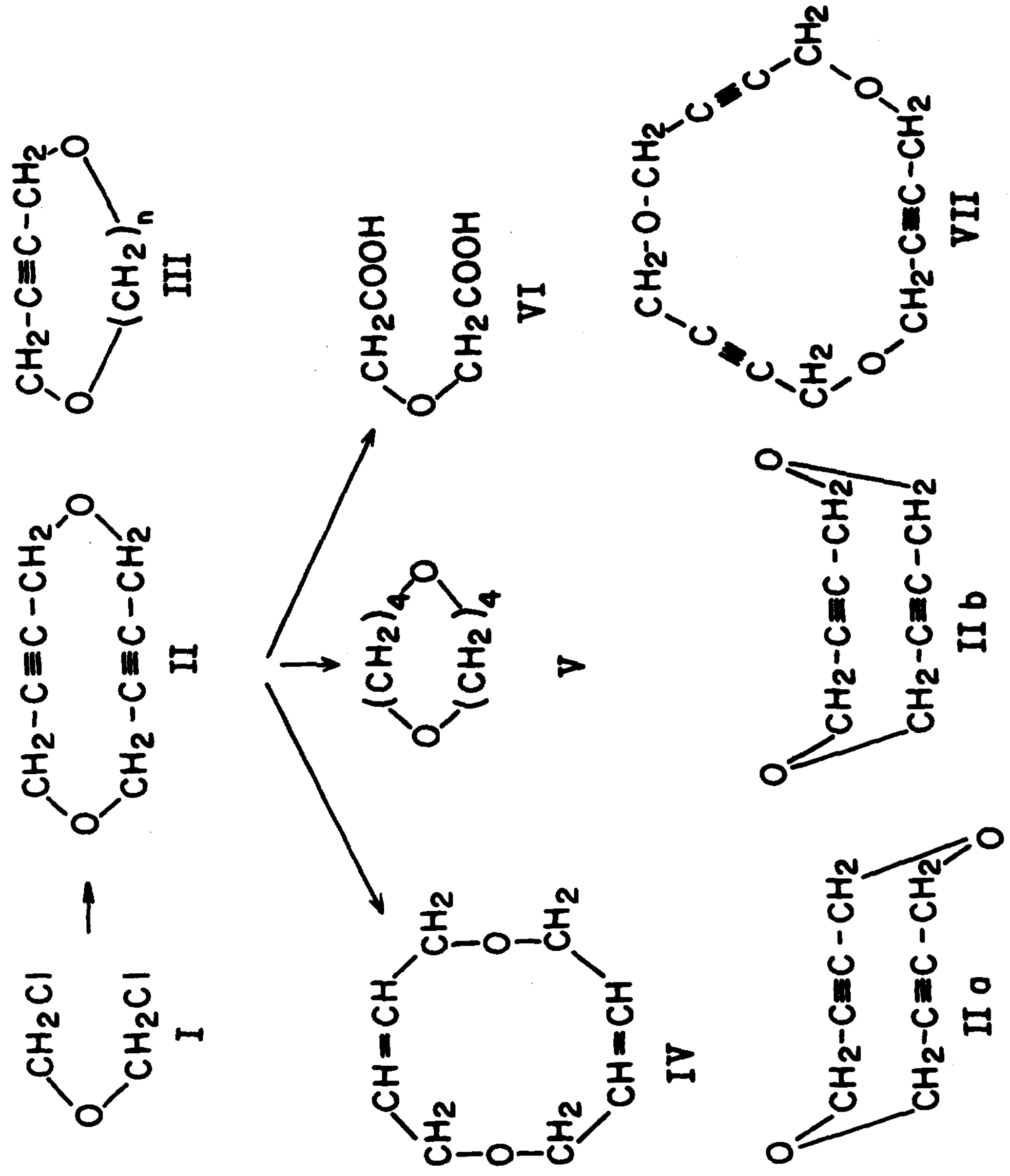
[5] Determined by the thermistor-drop technique, in methylene chloride (see B.R.Y. Iyengar, Rec. Trav. Chim. **73**, 789 (1954).


I
II
III
IV
V
VI
IIa
IIb
VII

weak band at 4.75 μ (disubstituted acetylene or overtone of the 9.37 μ band)] and showed the absence of allene or terminal acetylene groupings. There was only end-absorption in the ultraviolet.

Partial hydrogenation of (II) in benzene over a Lindlar palladium catalyst[6] led to cis-cis-1,6-dioxa-3,8-cyclodecadiene (IV) as prisms, m.p. 117-118° (between two cover slides; sublimes without melting at 70-80° on an open cover slide), showing a strong cis-ethylene band at 13.40 μ in the infrared (*Anal.* Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found : C, 68.53; H, 8.74). Full hydrogenation of (II) in ethyl acetate over platinum resulted in the uptake of exactly 4 molar equivalents of hydrogen and yielded 1,6-dioxacyclodecane (V), b.p. 90-100° (bath temp.) (25 mm.), n_D^{28} 1.4542 (*Anal.* Calcd. for $C_8H_{16}O_2$: C, 66.63; H, 11.18. Found : C, 66.48; H, 10.93).

Oxidation of (II) in acetone with aqueous potassium permanganate at 3° produced diglycolic acid (VI), m.p. 145-146°, identified with an authentic sample (m.p. 146-147°).

The two conformations (IIa) and (IIb) are possible for (II). The X-ray diffraction data (space group $P2_1/c$; $a = 6.82$ Å, $b = 7.72$ Å, $c = 6.98$ Å, $\beta = 113.8°$) and measured density of 1.33 identify the asymmetric unit in the unit cell as C_4H_4O. Symmetry requirements of the space group eliminate any multiple (n) of this unit higher than n = 2. Since n = 1

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[6] H. Lindlar, Helv. Chim. Acta 35, 446 (1952).

is ruled out by the molecular weight determination, the molecule is identified as $C_8H_8O_2$ having a molecular center of symmetry. Hence, in this particular crystal structure at least, the molecules are present in the chair conformation (IIa) and not in the boat (IIb).

The reaction of (I) with acetylenedimagnesium bromide in addition to (II) produced another substance in ca. 0.5% yield (eluted from the chromatogram directly after (II)), which crystallized as long colorless laths, m.p. 68-69°. This second product must be the fifteen-membered acetylenic heterocycle 1,6,11-trioxa-3,8,13-cyclopentadecatriyne (VII) in view of the elemental analysis and molecular weight determination (Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92; mol. wt., 204. Found : C, 70.68; H, 6.00; mol. wt., 192, 194[5]) as well as the similarity of the infrared spectrum to that of (II).

We are investigating at present the application of the Lespieau type of reaction for the synthesis of other heterocyclic and carbocyclic acetylenes.

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