Tetrahedron Letters No. 31, pp 2821 - 2822. 0040-4039/78/0729-2821$02.00/0
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CYCLIC CONJUGATED ACETYLENES: THEIR UTILITY IN THE SYNTHESIS OF HETEROPHANES

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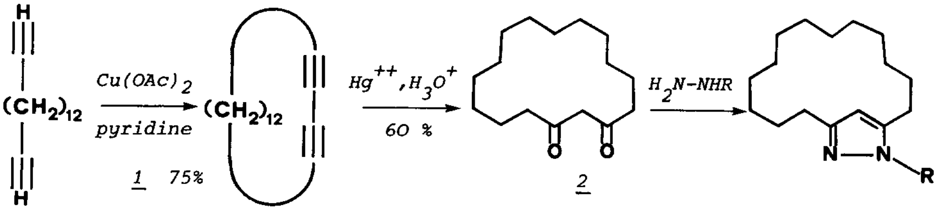
(Received in UK 26 May 1978; accepted for publication 2 June 1978)

The intramolecular oxidative coupling of α,ω-diynes catalysed by $Cu(OAc)_2$ is one of the most valuable and selective methods for the synthesis of large and functionalized rings. Nevertheless, the synthetic potential of the resulting cyclic conjugated acetylenes remains largely unexploited.

We have been especially interested in converting such compounds into heterophanes or their precursors because of the possibility, in principle, of obtaining phanes functionalized in the ansaring by starting with an appropriate chain.

Cyclohexadeca-1,3-diyne 1 was readily prepared by a standard procedure (75 %, conditions according to [1)]*. Hg^{++}-catalyzed hydratation affords cyclohexadeca-1,3-dione 2 in 60 % yield under the following controlled conditions* [2)]*:*

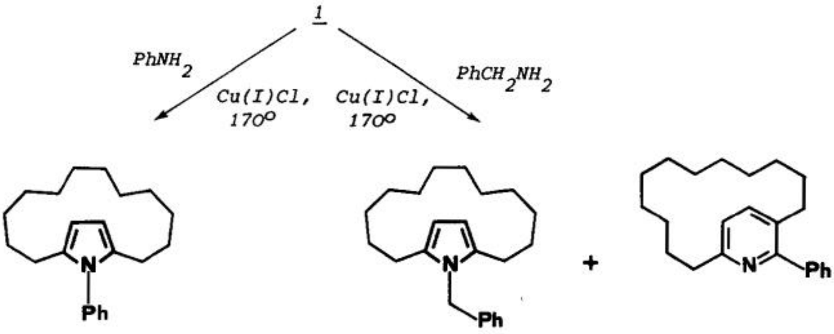
3 g Cyclohexadeca-1,14-diyne, 0.7 ml H_2SO_4 conc., 0.8 g $HgSO_4$ in 25 ml 90 % CH_3COOH were heated to reflux for 5 hours. The reaction mixture was poured into water and extracted with ethylacetate. After removal of solvent the residue was chromatographed on silica gel, yielding 2.1 g pure 2 (m. p. 40-45°) on elution with benzene.



R = H, 3 70 %
R = Ph, 4 50 %

This conversion seems to be of considerable potential value in view of the synthetic versatility of 1,3-diketones 3). 2, which exists mainly in the enol form, reacts readily with hydrazine hydrate (r. t., 15 min.) or phenylhydrazine (4 h, reflux) in ethanol to form the pyrazolophanes 3 (70 %, m. p. 125-26°) and 4 (50 %) respectively.

It is known from the work of Schulte et al. 4) and Chalk 5), that primary amines may be added to some conjugated acetylenes together with catalytic amounts of Cu(I)Cl to form pyrrols and/or pyridines. Application of this reaction to cyclic diynes should make possible the synthesis of appropriate heterophanes.



5 50 % *6* 31 % *7* 23 %

On heating (170°, Ar, 15 h) a solution of 1 in excess aniline (1:20) with 0.1 mole % Cu(I)Cl, 14-Phenyl-[12](2,5)-pyrrolophan 5 (m. p. 62-65°; NMR ($CDCl_3$): δ = 7,1 - 7,6 (5H); 5,9 (s,2H); 2,1 - 2,4 (4H)) is formed in 50 % yield. When benzylamine was taken as amine component, two products were isolated by column chromatography on silica gel. Elution with benzene yielded 31 % of 14-Benzyl-[12](2,5)-pyrrolophan 6 (NMR: δ = 7,15 - 7,35 (3H); 6,8 (m, 2H); 5,9 (s, 2H); 5,1 (s, 2H); 2,5 (m, 4H)). By further elution with benzene/ethyl acetate (98/2) 14-Phenyl-[12](2,5)-pyridinophan 7 (23 %; NMR: δ = 7,0 - 7,6 (7H); 2,3 - 3,2 (4H)) was obtained. Attemps to change the product ratio failed or diminished yields 6).

The skilful technical assistance of Miss W. GRANITZER is gratefully acknowledged.

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1) *W. McCrae, Tetrahedron 20, 1773 (1964)*

2) *Under slightly different reaction conditions small amounts of by products were isolated and characterized as cyclohexadeca-1,4-dione 8 (4 %) and [12](2,5)-furanophan 9 respectively.*

3) *H. Fliri, D. Scholz and A. Stütz,* **to be published.**

4) *K. E. Schulte, J. Reisch and H. Walker, Ber. 98, 98 (1965)*

5) *A. J. Chalk, Tetrahedron Lett., 3487 (1972)*
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6) *Satisfactory elementary analysis, mass spectral, IR, NMR and UV spectral data were obtained for all products herein.*