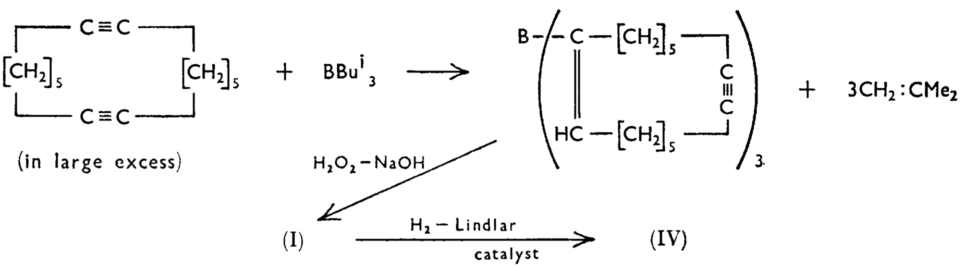
# **1240.** *Macrocyclic Compounds. Part XI.*[1] *A Novel Synthesis of Civetone Homologues*

By A. J. Hubert

Macrocyclic alkadiynes can be partially converted into monoketones by means of an insufficient quantity of trialkylborane and subsequent oxidation of the formed non-volatile tri(cycloalkynenyl)borane. The remaining triple bond is partially reduced to a *cis*-double bond on a Lindlar catalyst.

It was shown recently [2] that trialkylboranes react irreversibly and cleanly with acetylenic hydrocarbons to give trialkenylboranes, which can be hydrolysed to *cis*-olefins or oxidised to ketones. This route to ketones has now been applied in a simple novel synthesis of homologues of the valuable perfume civetone [3] from readily available macrocyclic alkadiynes.[4] One of the triple bonds is selectively transformed to an alkenylborane group by working with a large excess of cycloalkadiyne. The excess of diyne can be easily recovered by distillation, as the formed tri(cycloalkynenyl)borane is very much less volatile. The final selective reduction of the remaining triple bond cannot be performed with alkylboranes because of the presence of the carbonyl group, and the Lindlar catalyst [5] was used. As an example, the synthesis of *cis*-cyclotetradec-7-en-1-one according to the Scheme gave an overall yield of 50%.



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[1] Part X, A. J. Hubert and J. Dale, preceding Paper.

[2] A. J. Hubert, *J.*, 1965, 6669,

[3] E. Lederer, *Fortschr. Chem. Org. Naturstoffe*, 1950, **6**, 87.

[4] J. Dale, A. J. Hubert, and G. S. D. King, *J.*, 1963, 73.

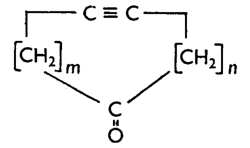
[5] H. Lindlar, *Helv. Chim. Acta*, 1952, **35**, 446.

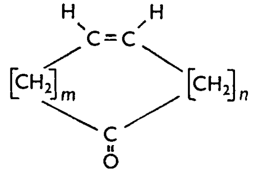
Civetone homologues and acetylenic precursors

| | | | Found (%) | | | | | Required (%) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | B. p. | C | H | N | O | Formula | C | H | N | O |
| Ketones | (I) | 125°/0·1 mm. | 81·7 | 10·7 | — | 7·8 | $C_{14}H_{22}O$ | 81·5 | 10·75 | — | 7·8 |
| | (II) | 150—155/1 mm. | 82·2 | 11·45 | — | 7·15 | $C_{16}H_{26}O$ | 82·0 | 11·2 | — | 6·8 |
| | (III) | 145—150/0·1 mm. | 82·0 | 11·4 | — | 6·6 | $C_{18}H_{30}O$ | 82·4 | 11·5 | — | 6·1 |
| | (IV) | 120/0·01 mm. | 80·7 | 11·3 | — | 7·8 | $C_{14}H_{24}O$ | 80·7 | 11·6 | — | 7·7 |
| | (V) | 145—150/1 mm. | 81·6 | 11·6 | — | 5·8 | $C_{16}H_{28}O$ | 81·3 | 11·9 | — | 6·8 |
| | (VI) | 140—143/0·01 mm. | 82·6 | 12·0 | — | 5·3 | $C_{18}H_{32}O$ | 81·75 | 12·2 | — | 6·05 |
| | | M. p. | | | | | | | | | |
| Dinitrophenylhydrazones of | (I) | 124 | 61·7 | 6·7 | 14·5 | — | $C_{20}H_{26}N_4O_4$ | 62·2 | 6·8 | 14·5 | — |
| | (II) | 120—125 | 63·7 | 7·3 | 13·3 | — | $C_{22}H_{30}N_4O_4$ | 63·75 | 7·3 | 13·5 | — |
| | (III) | 103—106 | 65·3 | 7·8 | 12·3 | — | $C_{24}H_{34}N_4O_4$ | 65·1 | 7·7 | 12·7 | — |
| | (IV) | 116—118 | 61·8 | 7·2 | 14·4 | — | $C_{20}H_{28}N_4O_4$ | 61·8 | 7·3 | 14·4 | — |
| | (V) | 102—105 | 63·7 | 7·7 | 13·9 | 15·7 | $C_{22}H_{32}N_4O_4$ | 63·4 | 7·7 | 13·45 | 15·4 |
| | (VI) | 78—79 | 64·4 | 8·0 | 12·3 | — | $C_{24}H_{36}N_4O_4$ | 64·8 | 8·2 | 12·6 | — |
| | | M. p. | | | | | | | | | |
| Semicarbazones of | (I) | 188—192 | 68·4 | 9·6 | 15·6 | — | $C_{15}H_{25}N_3O$ | 68·4 | 9·6 | 16·0 | — |
| | (II) | 174—175 | 69·6 | 10·3 | 14·1 | — | $C_{17}H_{29}N_3O$ | 70·1 | 10·0 | 14·4 | — |
| | (III) | 180—182 | 70·6 | 10·1 | 12·5 | — | $C_{19}H_{33}N_3O$ | 71·4 | 10·4 | 13·15 | — |
| | (IV) | 179—182 | 67·9 | 10·1 | 15·5 | — | $C_{15}H_{27}N_3O$ | 67·9 | 10·3 | 15·8 | — |
| | (V) | 169—171 | 69·6 | 10·6 | 14·5 | — | $C_{17}H_{31}N_3O$ | 69·6 | 10·65 | 14·3 | — |
| | (VI) | 170—172 | 70·7 | 10·8 | 12·6 | — | $C_{19}H_{35}N_3O$ | 71·0 | 11·0 | 13·1 | — |

As civetone itself is the symmetrical *cis*-cycloheptadec-9-en-1-one, it can only be obtained by this method mixed with the unsymmetrical 8-en-1-one isomer, starting from the less readily available unsymmetrical cycloheptadeca-1,9-diyne. Of the unsymmetrical civetone homologues the representatives (IV), (V), and (VI) were prepared by reduction of the acetylenic precursors (I), (II), and (III). The properties of these ketones and their derivatives are given in the Table. The odour of (IV) was between that of musk and that of mushroom, of (V) musk (but hard), and of (VI) very weak.

| | $m$ | $n$ |
|---|---|---|
| (I) | 5 | 6 |
| (II) | 6 | 7 |
| (III) | 7 | 8 |





| | $m$ | $n$ |
|---|---|---|
| (IV) | 5 | 6 |
| (V) | 6 | 7 |
| (VI) | 7 | 8 |

Compounds (V) and (VI) have already been reported,[6] but with an undefined configuration of the double bond; as they were reported to be solids, the configuration is probably *trans*. Our *cis*-compounds are all liquid and their semicarbazones have lower melting points.

## EXPERIMENTAL

Tri-isobutylborane (1·8 g., 0·01 mole) was heated to 160—170° with a 12-fold excess (0·08 mole) of the symmetrical cycloalkadiyne.[4] When the calculated quantity of isobutene had escaped (determined by the weight loss), the excess of diyne was recovered by distillation *in vacuo*. The tri(cycloalkenyl)borane remained as a glassy residue in the flask. It was dissolved in tetrahydrofuran and oxidised [7] with hydrogen peroxide–sodium hydroxide. Extraction with ether and distillation gave the liquid cycloalkynones [(I), (II), and (III) in Table 1] in 50% yield calculated on consumed diyne. The infrared spectrum showed a very weak band at 4·54 μ (C⋮C) and a strong band at 5·83 μ (C=O). The cycloalkynones readily formed 2,4-dinitrophenylhydrazones and semicarbazones (Table 1). Hydrogenation on a Lindlar catalyst [5] under conditions described earlier [4] was selective and furnished the liquid cis-*cycloalkenones* (IV), (V), and (VI) (Table 1), whose infrared spectra showed bands at 3·35, 6·04, and 14·73 μ

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[6] L. Ruzicka, M. Stoll, W. Scherrer, H. Schinz, and C. F. Seidel, *Helv. Chim. Acta*, 1932, **15**, 1459; A. T. Blomquist and J. Wolinsky, *J. Amer. Chem. Soc.*, 1955, **77**, 5423.

[7] H. C. Brown, *Tetrahedron*, 1961, **12**, 117.

(*cis*-double bond), and at 5·84 μ (ketone). The cycloalkenones also readily formed 2,4-dinitrophenylhydrazones and semicarbazones (Table 1).

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