292. Acetolysis of 4-*endo*-diazoacetyl-bicyclo[3.1.0]hexene: a new synthesis of semibullvalene

Preliminary communication¹)

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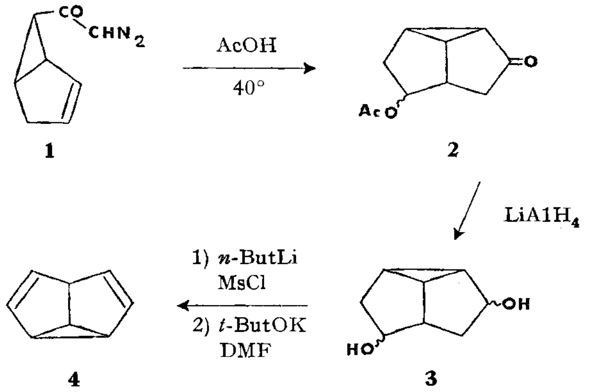
Summary. Acetolysis of diazoketone **1** gives in good yield 6-acetoxy-tricyclo[3.3.0.0^{2,8}]octan-3-one (**2**) which is converted into semibullvalene in a three-step sequence. Compound **2** is potentially a good starting material for 3,6-substituted semibullvalenes.

Owing to its unique geometry, semibullvalene (**4**) is capable of undergoing a facile *Cope* rearrangement [1]. There is considerable current interest in this process and the development of improved routes to the parent compound [2]. We report a new synthesis which also offers possibilities for the preparation of 3- or 6-substituted semibullvalenes.

We have previously reported that primary 5,6-unsaturated diazoketones undergo intramolecular acid catalyzed hydrolysis to give a high yield of cyclic products [3]. Acetolysis of 4-*endo*-diazoacetyl-bicyclo[3.1.0]hexene (**1**) [4] (glacial acetic acid, 40°), followed by neutralisation and vacuum distillation yielded **2**, b.p. 90–91°/10^{-3} Torr (70–80%)³). The IR. spectrum, $\nu_{C=O}$ 1735 (acetate), 1715 cm^{-1}, is very similar to that of tricyclo[3.3.0.0^{2,8}]octan-3-one, $\nu_{C=O}$ 1723 cm^{-1} [5], and is typical of an unstrained five membered ring ketone.

Analysis by gas chromatography showed the presence of two isomers. The main product, **2b** (55%), a low melting solid isolated by preparative gas chromatography



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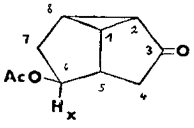
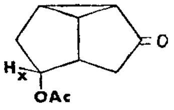
³) All new compounds gave satisfactory elemental analyses and spectral data.

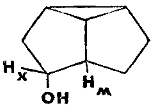
(Carbowax, 180°), was assigned the *endo*-configuration by comparison of its NMR. spectrum with that of alcohol **5**, in particular the characteristic signal from H(6) ($\delta = 5.27$, X of $AA'MX$ system, $J_{AX} = J_{A,X} = 3$ Hz, $J_{MX} = 2.5$ Hz) [6]. The minor isomer, 6-*exo*-acetoxy-tricyclo[3.3.0.0^{2,8}]octan-3-one (**2a**) (45%), was isolated as a white crystalline compound, m.p. 84–86°, and gave a broad singlet at $\delta = 4.99$ for H(6); the higher field position relative to the corresponding proton in **2b** is consistent with the structural assignments and the magnetic anisotropy of the carbonyl group.



2a



2b



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The initial mixture of isomers **2a** and **2b** was reduced with an excess of lithium aluminium hydride to give the mixture of diols **3**, m.p. 167–174° (65%), probably by *exo*-attack of the reagent [6]. Attempts to separate the components by G.C. were unsuccessful; under the conditions of analysis (SE 30, 130°) the material isomerised to two compounds, each with *m/e* 140, and NMR. and IR. spectra indicating a *cis*-olefinic linkage.

The diols **3** were treated with 2 equiv. of *n*-butyllithium at –40° followed by 2 equiv. of methanesulfonyl chloride. A double elimination with an excess of potassium *t*-butoxide in DMF at 60° gave semibullvalene (**4**), identified by comparison with spectral data from the literature [2], in 25% overall yield from **3**[4]).

Acetate **2** could be hydrolysed in alkaline solution and the resulting keto-alcohols oxidised by *Collins* reagent to give the dicarbonyl compound, tricyclo[3.3.0.0^{2,8}]octan-3,6-dione (**6**), m.p. 69–70° (from CCl_4/petroleum ether), $\nu_{C=O}$ 1712, 1748 cm^{-1}. Compounds **2** and **6** should provide a simple entry to 3- and/or 6- substituted semibullvalenes.

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REFERENCES

[1] *H. E. Zimmerman & G. L. Grunewald*, J. Amer. chem. Soc. *88*, 183 (1966); *H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald & M. A. Sherwin*, ibid. *91*, 3316 (1969); *M. J. S. Dewar & W. W. Schoeller*, ibid. *93*, 1481 (1971); *M. J. S. Dewar & D. H. Lo*, ibid. *93*, 6941 (1971); *R. Hoffmann & W. D. Stohrer*, ibid. *93*, 6941 (1971).

[2] *H. E. Zimmerman & H. Iwamura*, J. Amer. chem. Soc. *90*, 4763 (1968); *J. Meinwald & D. Schmidt*, ibid. *91*, 5877 (1969); *H. E. Zimmerman, J. D. Robbins & J. Schantl*, ibid. *91*, 5878 (1969); *L. A. Paquette*, ibid. *92*, 5766 (1970); *R. Askani*, Tetrahedron Letters *1970*, 3349; *R. Askani*, ibid. *1971*, 447; *R. M. Moriarty, C. L. Yeh & N. Ishibe*, J. Amer. chem. Soc. *93*, 3085 (1971).

[3] *R. Malherbe, Nguyen Thi Thanh Tam & H. Dahn*, Helv. *55*, 245 (1972).

[4] *P. K. Freeman & D. G. Kuper*, Chem. Ind. *1965*, 424; *J. Meinwald & G. H. Wahl*, ibid. *1965*, 425.

[5] *S. A. Monti, D. J. Bucheck & J. C. Shepard*, J. org. Chemistry *34*, 3080 (1969).

[6] *J. S. Haywood-Farmer & R. E. Pincock*, J. Amer. chem. Soc. *91*, 3020 (1969).

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[4]) Determined by GC. (internal standard); no attempt has been made to optimize yield.