Tetrahedron Letters Vol. 21, pp 1837 - 1840
© Pergamon Press Ltd. 1980. Printed in Great Britain

0040-4039/80/0501-1837$02.00/0

CONVENIENT NEW SYNTHESIS OF SNOUTENE [1] UTILIZING A DIPOLAR CYCLOADDITION OF 4-PHENYL-1, 2, 4-TRIAZOLIN-3, 5-DIONE [**]

Ihsan Erden und Armin de Meijere [*]

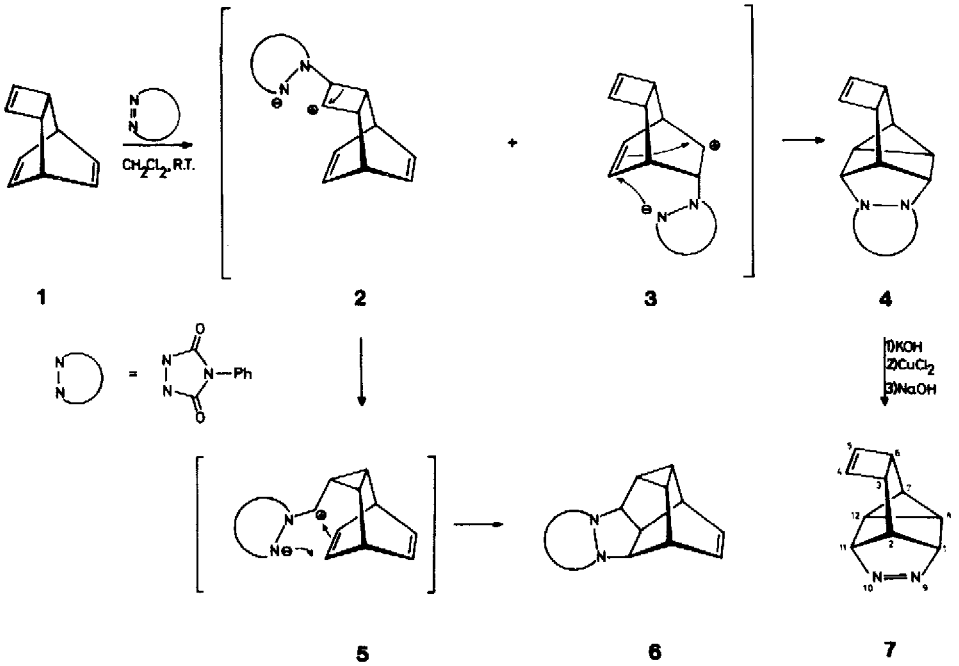
Institut für Organische Chemie und Biochemie der Universität Hamburg
Martin-Luther-King-Platz 6, D-2000 Hamburg, West-Germany

Summary: 4-Phenyl-1, 2, 4-triazolin-3, 5-dione readily cycloadds to Nenitzescu's hydrocarbon 1 [6] with skeletal rearrangement. The major adduct 6 can conveniently be transformed to the azo compound 8, which upon photolysis or thermolysis yields up to 80 % pentacyclo[3.3.2.$0^{2,4}$.$0^{3,7}$.$0^{6,8}$]dec-9-ene (" snoutene ").

Snoutene 9 [2] is an interesting member of the (CH)$_{10}$ family [3] and an important precursor to others [3,4] in this group. It has previously been obtained by silver ion catalyzed rearrangement of basketene [2], which in turn is accessible from the Diels-Alder-adduct of cyclooctatetraene and maleic anhydride in a four step sequence. Upon studying the various modes of 4-phenyl-1, 2, 4-triazolin-3, 5-dione (PTAD) cycloadditions [5] to strained polycyclic olefins we found a useful new access to 9.

Tricyclo[4.2.2.$0^{2,5}$]deca-3, 7, 9-triene ("Nenitzescu's hydrocarbon") [6] in methylene chloride reacted with PTAD at room temperature within 6 hrs to give an almost quantitative yield (92 % total) of a 1:1 mixture of 2 products, which were separated by column chromatography (SiO$_2$, CH$_2$Cl$_2$/ether 4/1). Their 270 MHz ^{1}H-NMR spectra (see table 1) and their further chemical reactions (see below) unequivocally characterized them as 4 and 6.

The adduct 6 with its skeleton resembling snoutene (9) more than 1, can only arise by a dipolar attack of PTAD on the cyclobutene double bond in 1 to give the intermediate zwitterion 2, which can undergo a cyclobutyl to cyclopropylcarbinyl cation ring contraction to 5 [7] and subsequent ring closure with π participation. 4, however, is apparently formed by attack of PTAD on the 1, 4-diene unit of the bicyclo[2.2.2]octadiene skeleton



in 1 either via a dipolar intermediate like 3 or more probably by a concerted [2+2+2]-cycloaddition. This is in accord with the observation, that 6 becomes the predominant product (ratio 70 : 30) in a more polar solvent like acetone.

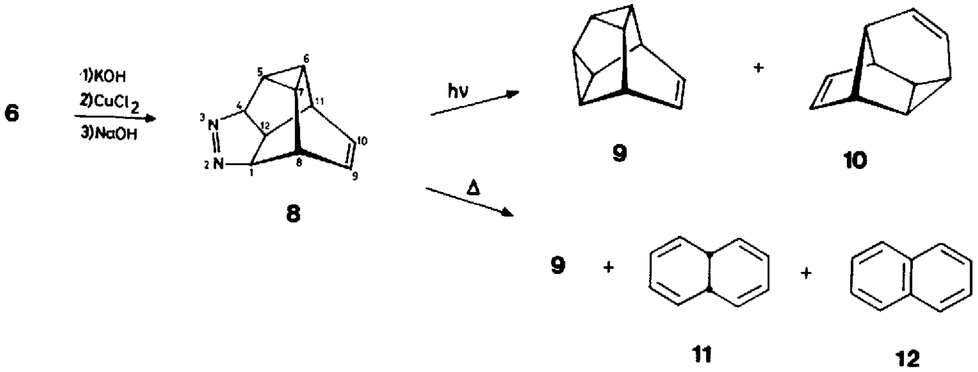
The polycyclic urazoles 4 as well as 6 can be transformed to the corresponding azo compounds 7 and 8 respectively following a well documented scheme of reactions [8]. Thus, almost pure 2,3-diazapentacyclo[6.4.0.$0^{4,12}$.$0^{5,7}$.$0^{6,11}$]dodec-9-ene (8) was obtained as a slighthly yellow oil in 90 % yield; further purification by preparative gc afforded an analytically pure sample (spectral data see table 1).

Whereas 8 is stable up to 150 °C, the azo compound 7 slowly decomposes even at room temperature to give 1, as should be expected for its type of structure [9]. 7 can, however, be liberated from its cuprous chloride complex at 0 °C and identified by ^{1}H-NMR spectroscopy (see table 1).

Upon irradiation of 8 (ether solution, 150 W Hg lamp, Corex filter) 90 % snoutene (9) and 10 % of the known hydrocarbon 10 [4c] were obtained. Also, snoutene was the main product (87 %), when 8 was sublimed (0.01 torr) through a hot glass tube at 350 °C,

Table 1. Spectroscopic data of new compounds

Compd. (m.p.)	^{1}H-NMR (270 MHz, $CDCl_3$, TMS)	IR (KBr or film)[cm^{-1}]
4 (203 °C)	1.29 (m,H^7); 1.71 (m,$H^{8,12}$); 2.42 (m,H^2); 2.97 (AB system, $H^{3,6}$); 4.61, 4.73 (2s,$H^{1,11}$); 6.17 (AB system, $H^{4,5}$); 7.22 - 7.43 (m, 5H).	3100, 3040, 2920 (νC-H); 1770, 1710, (νC=O); 1500 (νC=C).
6 (161 °C)	1.16 (m,H^6); 1.96 (m,H^7); 2.08 (m,H^5); 3.23 (m,H^{11}); 3.43 (m,H^8); 3.67 (m,H^1); 4.87 (m,H^4); 6.39 (AB system, $H^{9,10}$); 7.33 - 7.50 (m, 5H).	3060, 2990, 2970 (νC-H); 1760, 1710 (νC=O); 1495 (νC=C).
7 (-)	1.25 (m,H^7); 1.55 (m,$H^{8,12}$); 2.52 (m,H^2); 2.77 (m,$H^{3,6}$); 5.12 (m,H^1); 5.19 (m,H^{11}); 6.11 (AB system, $H^{4,5}$).	
8 (-)	0.87 (m,H^6); 1.79 (m,H^7); 1.90 (m,H^5); 2.25 (m,H^{12}); 2.96 (m,H^{11}); 3.24 (m,H^8); 4.31 (m,H^1); 5.09 (m,H^4); 6.43 (AB system, $H^{9,10}$).	3060, 2970 (νC-H); 1605 (νC=C); 1535 (νN=N)



cis-9,10-dihydronaphthalin (11) [3] (11 %) and naphthalin (12) (2 %) occured as by-products.

Several attempts to bring about an intramolecular $[{}_{\pi}2 + {}_{\sigma}2]$cycloaddition in 6 or 8 either photochemically or under rhodium(I) catalysis [10], have failed so far.

Following the above convenient sequence, snoutene (9) can be prepared from the Diels-Alder adduct of maleic anhydride and cyclooctatetraene with an overall yield of 25-30 %. This compares favorably with the 12 % at best achievable by the earlier published procedure [2].

References and Footnotes

[*] Author to whom correspondence should be addressed .

[**] This work was supported by the Deutsche Forschungsgemeinschaft (Project Me 405/11), the Fonds der Chemischen Industrie and the BASF AG, Ludwigshafen.

[1] This is considered as no. XII in a series on the chemistry of (CH)$_{10}$-hydrocarbons. For preceeding papers see: D. Bosse, A. de Meijere, Chem. Ber. 111, 2223, 2243 (1978).

[2] W. G. Dauben, C. H. Schallhorn, D. L. Whalen, J. Amer. Chem. Soc. 93, 737 (1971); L. A. Paquette, J. C. Stowell, ibid. 93, 2459 (1971).

[3] For reviews see: S. Masamune, N. Darby, Acc. Chem. Research 5, 272 (1972); L. T. Scott, M. Jones jr., Chem. Rev. 72, 181 (1972); A. T. Balaban, Rev. Roum. Chimie 17, 865 (1972).

[4] A. de Meijere, D. Kaufmann, O. Schallner, Angew. Chem. 83, 404 (1971); Angew. Chem. Int. Ed. Engl. 10, 417 (1971); D. Kaufmann, H.-H. Fick, O. Schallner, W. Spielmann, L.-U. Meyer, A. de Meijere, Liebigs Ann. Chem. 1980, in press; b) A. de Meijere, L.-U. Meyer, Tetrahedron Lett. 1974, 1849; c) L.-U. Meyer, A. de Meijere, ibid. 1976, 497.

[5] I. Erden, O. de Lucchi, W. Adam, Angew. Chem. 91, 512 (1979); Angew. Chem. Int. Ed. Engl. 18, 468 (1979); I. Erden, D. Kaufmann, Tetrahedron Lett. 1980, in press; W. Weber, I. Erden, A. de Meijere, Angew. Chem. 92, in press (1980); Angew. Chem. Int. Ed. Engl. 19, in press (1980).

[6] cf. W. G. Dauben, G. T. Rivers, R. J. Twieg, W. T. Zimmermann, J. Org. Chem. 41, 887 (1976) and references cited therein.

[7] A similar skeletal rearrangement has been observed upon treatment with lead tetraacetate and thallium(III) salts. T. Sasaki, K. Kanematsu, A. Kondo, K. Okada, J. Org. Chem. 41, 2231 (1976).

[8] L. A. Paquette, M. J. Wyvratt, H. C. Berk, R. B. Moerck, J. Amer. Chem. Soc. 100, 5845 (1978).

[9] Cf. E. L. Allred, J. C. Hinshaw, A. L. Johnson, J. Amer. Chem. Soc. 91, 3383 (1969); E. L. Allred, K. J. Voorhees, ibid. 95, 620 (1973) and earlier papers cited therein.

[10] Cf. T. J. Katz, S. A. Cerefice Tetrahedron Lett. 1969, 2509; A. de Meijere, L.-U. Meyer, ibid. 1974, 1849 and ref. cited therein.

(Received in USA 29 February 1980)