Tetrahedron Letters,Vol.24,No.50,pp 5591-5594,1983 0040-4039/83 $3.00 + .00
Printed in Great Britain

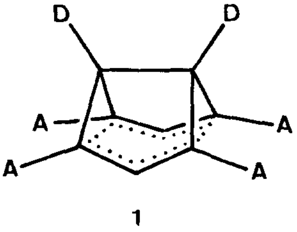
SYNTHESIS OF SOME 3,7-DICYANO-1,5-DIMETHYLSEMIBULLVALENES

Helmut Quast* and Yvonne Görlach

Institut für Organische Chemie der Universität Würzburg, Am Hubland, D-8700 Würzburg

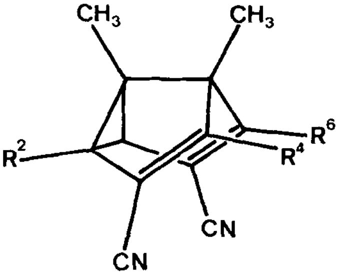
SUMMARY: The synthesis of 3,7-dicyano- (**2a**), 4-bromo-3,7-dicyano- (**2b**), and 2,6-dibromo-3,7-dicyano-1,5-dimethylsemibullvalene (**2e**) is reported; both **2a** and **2e** undergo the degenerate Cope rearrangement more slowly than the parent hydrocarbon.

In a synthetic exploration of semibullvalenes and barbaralanes related to donor-acceptor-substituted semibullvalenes which are predicted to exist in the nonclassical, homoaromatic ground state **1**[1] we recently synthesized 2,6-dicyanobarbaralane[2], 2,6-dicyano-1,5-dimethylsemibullvalene[3], and semibullvalene **2d**[4]. While the 2,6-dinitriles exhibited significantly *lower* activation barriers towards the degenerate Cope rearrangement than the parent hydrocarbons, in harmony with theoretical predictions[1], the substitution pattern of **2d** resulted in an unexpected *increase* of the Cope activation barrier. In order to further assess the effects of cyano and bromo substitution at the allylic part of semibullvalene we now report efficient syntheses of the related 3,7-dicyanosemibullvalenes **2a**, **2b** $\rightleftharpoons$ **2c**, and **2e**. The 3,7-dinitrile **2a** was previously obtained by Sauer and coworkers[5] from the corresponding 3,7-dimethylester[6].



1

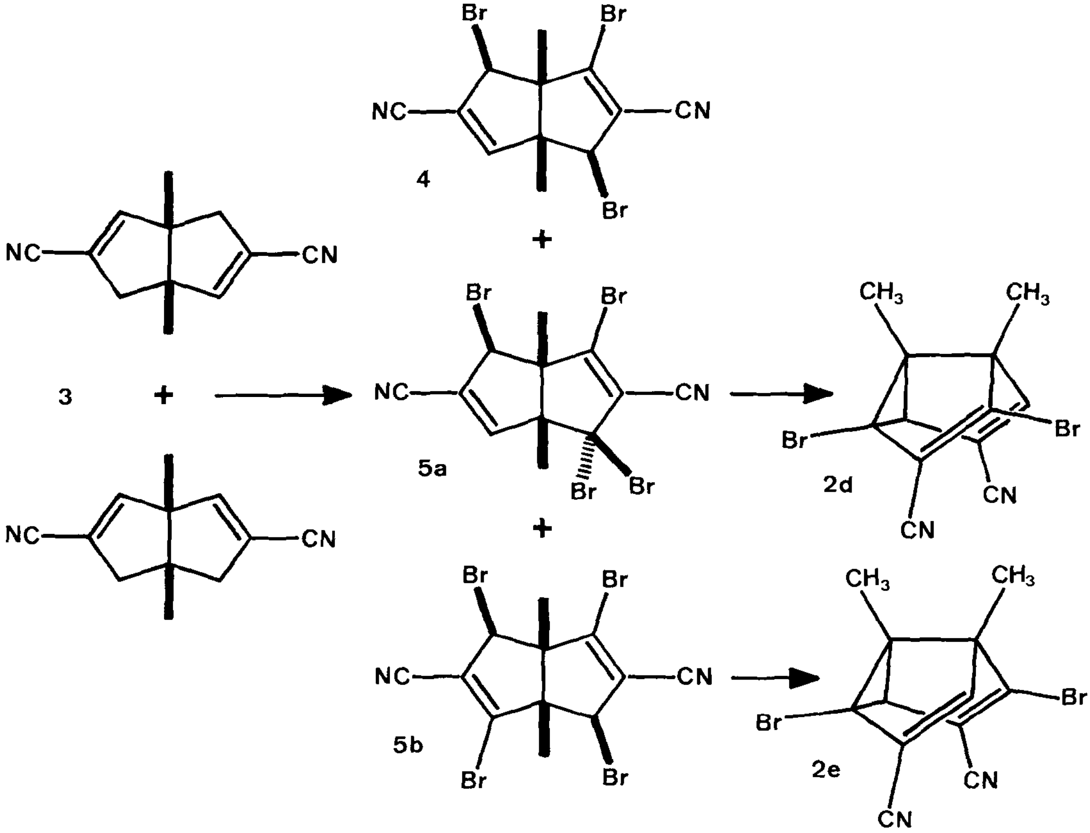
A = electron acceptor
D = electron donor



	R^2	R^4	R^6
2a	H	H	H
2b	H	Br	H
2c	Br	H	H
2d	Br	Br	H
2e	Br	H	Br

The large scale NBS bromination of the readily available unsaturated dinitriles **3**[4] under slightly less vigorous conditions afforded not only the previously reported tetrabromides **5**[4] but also substantial amounts of the tribromide **4** (**4**:**5a**:**5b** = 23:69:8) which was separated from the tetrabromides by column chromatography on silicagel using chloroform as eluant. While pure **5a** was obtained by a simple crystallization from ethyl acetate, attempts to separate **5b** by crystallization failed on preparative scale. Therefore, after removal of the bulk of **5a** the mixture of **5a** and **5b** (65:35) was treated in chloroform with diethylphosphite (1.2 moles) in the presence of triethylamine (1.9 moles, 0.5 h, 20 – 25 °C)[7]. This reagent converted the unsymmetrical tetrabromide **5a** to the 2,4-dibromosemibullvalene **2d**. The essentially unaffected symmetrical tetrabromide **5b** was readily separated from **2d** by crystallization from ethyl acetate (57% recovery). The structures of the brominated dinitriles **4** and **5b** were based on IR, carbon-13 (Table 1), and proton spectra [**4**: 1.50 (Me), 1.53 (Me), 4.91 (CHBr), 5.09 (CHBr), 6.53 (=CH –); **5b**: 1.56 (2 Me), 5.09 (2 CHBr) ($CDCl_3$)].

Zinc-copper reagent[8] in refluxing tetrahydrofuran debrominated **5b** in 2.5 h furnishing almost quantitatively the expected 2,6-dibromo-3,7-dicyanosemibullvalene **2e** as colourless crystals after crystallization from ethyl acetate. Unequivocal proof of structure **2e** was provided by an X-ray structure determination[9]. The NMR spectra revealed an extraordinary similarity between the dibromodicyanosemibullvalenes **2d** and **2e**. Thus, as in the case of **2d**[4] the 60 MHz proton spectrum of **2e** in [D]chloroform at ambient temperature consisted of two sharp singlets at 4.73 and 1.35 ppm corresponding to the rapidly exchanging protons H4/H8 and the methyl groups. Furthermore, the 100 MHz carbon-13 spectrum of **2e** in [D]chloroform exhibited significant broadening of the C2/C6 and C4/C8 resonances already at 30 °C due to slow Cope rearrangement. A similar increase of the Cope barrier over that of the parent hydrocarbon has already been found for the isomeric semibullvalene **2d**[4]. Therefore, we conclude that the 2,4-dibromo substitution, as in **2d**, and the 2,6-dibromo substitution, as in **2e**, differ only slightly if at all in their influence on the Cope barrier[10]. Further experiments are needed to verify this conclusion for other pairs of 2,4- and 2,6-disubstituted semibullvalenes.

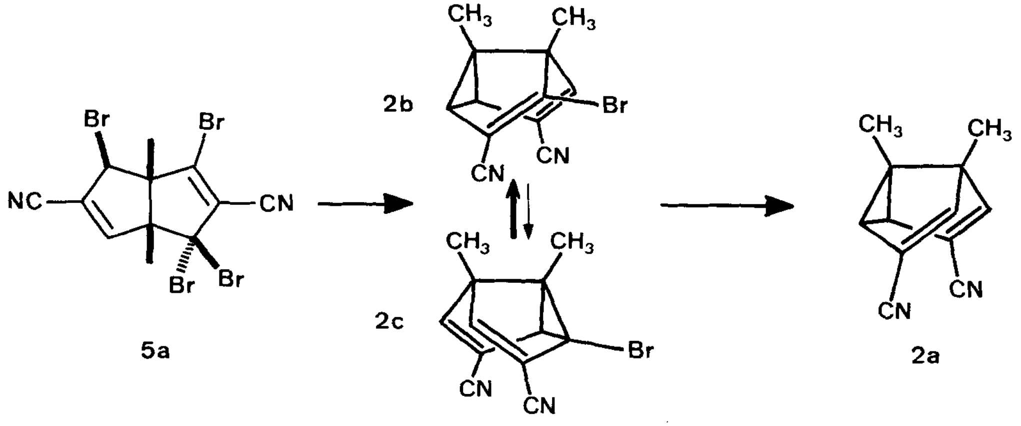


While zinc-copper reagent[8] in refluxing diethyl ether debrominated the unsymmetrical tetrabromide **5a** to the 2,4-dibromosemibullvalene **2d**, under more forcing conditions further debromination occurred. Thus, within 42 h in refluxing tetrahydrofuran **5a** was quantitatively converted into a mixture of the monobromosemibullvalene **2b** and the bromine free compound **2a** (93:7) from which **2b** was isolated in 57% yield by crystallization from chloroform or ethyl acetate. In tetrahydrofuran at −90 °C, the bromine atom of **2b** was smoothly exchanged by lithium by the action of t-butyllithium[11]. Quenching of the deep red solution of the lithiated semibullvalene with methanol afforded the dinitrile **2a** in 80% yield after sublimation at 130 – 170 °C/ 10^{-2} torr and crystallization from ethyl acetate. This product was identical with the dinitrile obtained from the corresponding 3,7-dimethylester[5, 6]. The last step completes a straightforward route to the set of 3,7-dicyanosemibullvalenes **2** starting from 1,5-dimethylbicyclo[3.3.0]octane-3,7-dione[4].

Table 1. Melting points, IR and 100.61 MHz carbon-13 spectral data of the bicyclo[3.3.0]octa-2,6-dienes **4**, **5b** and the 3,7-dicyanosemibullvalenes **2**.

Cpd.	m.p. [°C]	IR [cm^{-1}] (KBr) C≡N	C=C	^{13}C-NMR [ppm] C1,5	C2,6	C4,8	C3,7	CN	CH_3	Solvent	Temp. [°C]
4	142-143	2240	1615	63.7 59.9	149.1 153.0	56.4 57.3	112.7 113.1	117.5 117.6	19.3 19.9	$CDCl_3$	30
5b	252-253	2240	1614	63.2	148.0	56.1	112.5	118.1	20.0	$CDCl_3$	30
2a	197-197.5	2230	1564	62.0[a]	98.2[b]		106.0	115.9	14.5	CD_2Cl_2[c]	20
2b, 2c (94:6)	183-184	2225	1562	58.1 67.4	51.4 146.8	136.4 52.2	108.3 109.2	115.0 115.4	14.38 14.63	CD_2Cl_2[c]	20
2b				57.6 67.4	45.5 151.9	141.0 46.3	107.4 108.4	115.7 116.2	14.36 14.66	CD_2Cl_2[d]	− 110
2e	205 − 206 (dec.)	2235	1569 1557	64.1	98.3	102.1	111.2	113.6	13.9	$CDCl_3$	30
				59.5 67.5	52.0 144.1	150.6 52.4	108.0 111.1	113.8 114.1	12.6 13.9	CD_2Cl_2[c]	− 100

[a] Approximate halfwidth 2.5 ppm at − 130 °C in $CD_2Cl_2/CHClF_2$ (1:4). — [b] Approximate halfwidth 1.5 ppm at − 70 °C in $CD_2Cl_2/CHClF_2$ (1:4). — [c] CD_2Cl_2 as secondary standard at 53.80 ppm. — [d] The low temperature data are based on the average of the methyl signals at 20 °C (14.5 ppm) assumed to be temperature independent.



The C2,4,6,8 resonance in the 100 MHz carbon-13 spectrum of **2a** in $CD_2Cl_2/CHClF_2$ (1:4) shows the same broadening at − 70 to − 80 °C due to slow exchange as does the parent hydrocarbon 1,5-dimethylsemibullvalene only at − 123 °C[3]. Hence we conclude that *cyano groups in the 3,7-position of semibullvalenes considerably raise the Cope barrier* in striking contrast to cyano groups at C2 and C6[3]. Unequivocal structure proof of the monobromodicyanosemibullvalene was provided by an X-ray structure determination[9] which showed that only the valence tautomer **2b** was present in the crystalline state. However, the marked temperature dependence of the 100 MHz carbon-13 spectrum revealed an equilibrium between **2b** and **2c** in solution. Broadening of the signals of C2, C4, C6, and C8 in temperature range − 60 to − 100 °C is due to exchange with the minor isomer **2c**. However, at − 110 °C these signals are again sharp and correspond to the true chemical shift for **2b**. Assuming a chemical shift for C6 in **2c** as found for C4,6 in the low temperature spectrum of **2a** (147.7 ppm in $CHClF_2$[12]) and applying a correction of 0.6 ppm to account for the use of [D_2]dichloromethane as solvent and the average of the methyl signals (14.5 ppm) as internal temperature independent standard a ratio of **2b**:**2c** = 94:6 is calculated for the equilibrium at 20 °C from the C8 (**2b**)/C6 (**2c**) resonance (Table 1). The position of the **2b**/**2c** equilibrium is in accord with the reported predominance of 4-bromo- over 2-bromo-1,5-dimethylsemibullvalene[13].

ACKNOWLEDGEMENT: We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

REFERENCES AND FOOTNOTES

(1) Hoffmann, R.; Stohrer, W.-D. *J. Am. Chem. Soc.* **1971**, *93*, 6941. Dewar, M.J.S.; Lo, D.H. *J. Am. Chem. Soc.* **1971**, *93*, 7201. Dewar, M.J.S.; Náhlovská, Z.; Náhlovský, B.D. *J. Chem. Soc., Chem. Commun.* **1971**, 1377.

(2) Quast, H.; Görlach, Y.; Stawitz, J. *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 93.

(3) Quast, H.; Christ, J.; Görlach, Y.; von der Saal, W. *Tetrahedron Lett.* **1982**, 3653. The synthesis of this semibullvalene was simultaneously reported by Askani, R.; Littmann, M. *Tetrahedron Lett.* **1982**, 3651.

(4) Quast, H.; Görlach, Y.; Meichsner, G.; Peters, K.; Peters, E.-M.; von Schnering, H.G. *Tetrahedron Lett.* **1982**, 4677.

(5) Schuster, H.; Sellner, I.; Sichert, H.; Nöth, H.; Sauer, J. *Chem. Ber.*, in press. Schuster, H. *Diploma Thesis,* Universität Regensburg, FRG, 1981. We thank Professor Sauer for communicating his results prior to publication.

(6) Paske, D.; Ringshandl, R.; Sellner, I.; Sichert, H.; Sauer, J. *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 456.

(7) Hirao, T.; Masunaga, T.; Ohshiro, Y.; Agawa, T. *J. Org. Chem.* **1981**, *46*, 3745.

(8) Corbin, T.F.; Hahn, R.C.; Shechter, H. *Org. Synth. Coll. Vol. V,* **1973**, 328.

(9) Quast, H.; Görlach, Y.; Christ, J.; Peters, E.-M.; Peters, K.; von Schnering, H.G.; Jackman, L.M.; Ibar, G.; Freyer, A.J. *Tetrahedron Lett.* **1983**, 5595, following communication.

(10) The determination of the activation parameters of the Cope rearrangement of the isomeric semibullvalenes **2d** and **2e** is reported separately[9].

(11) Askani, R.; Kirsten, R. *Tetrahedron Lett.* **1979**, 1491.

(12) We thank Professor K. Müllen, University of Cologne, for the low temperature carbon-13 data of **2a**.

(13) Askani, R.; Sönmez, H. *Tetrahedron Lett.* **1973**, 1751.

(Received in Germany 16 July 1983)