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2,6-DICYANO-1,5-DIMETHYLSEMIBULLVALENE AS A PROBE FOR HOMOAROMATIC MOLECULES OF THE DEWAR-HOFFMANN TYPE

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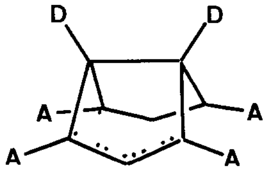
SUMMARY The 2,6-dicyano-1,5-dimethylsemibullvalene (**2d**) synthesized via the bicyclo[3 3 0]octanedione **7** exists as a classical ground state which is lower in energy by less than 5 kcal/mole than the homoaromatic transition state of the Cope rearrangement of **2d**

We report an efficient synthesis of 2,6-dicyano-1,5-dimethylsemibullvalene (**2d**) and show with the help of low temperature ^{13}C NMR that it possesses an even lower activation barrier (< 5 kcal/mole) towards degenerate Cope rearrangement [1,2] than the parent semibullvalene (**2a**) [1a] and **2b** [2f] Our results provide, therefore, the first experimental evidence in support of Dewar's [3] and Hoffmann's [4] prediction that electron accepting (A) substituents at the $C_{2,4,6,8}$ positions and electron donating (D) substituents at the $C_{1,5}$ positions should afford a non-classical homoaromatic semibullvalene **1** While for neutral, closed-shell π-systems such homoconjugative interaction was concluded to be destabilizing [5], our present results imply that open-shell systems, such as two interacting allyl fragments, may result in a stable homoaromatic semibullvalene **1**

Following Dewar's [3] and Hoffmann's [4] prediction we showed that the sterically unencumbered cyano group as π-electron acceptor indeed lowered significantly the activation barrier of barbaralane **3** [6] Consequently, we set out to prepare 2,6-dicyano-1,5-dimethylsemibullvalene (**2d**) as test system, in which the use of the two methyl substituents was dictated by synthetic necessity [2f] **2d** seemed most interesting in view of Dewar's expectation that already two cyano groups as in **2c** would suffice for homoaromaticity [3b]



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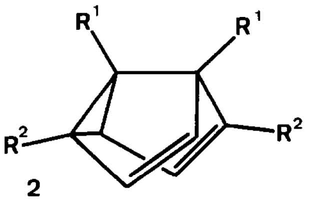

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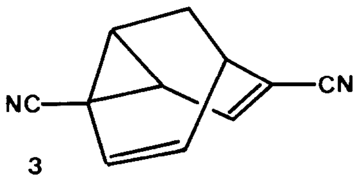

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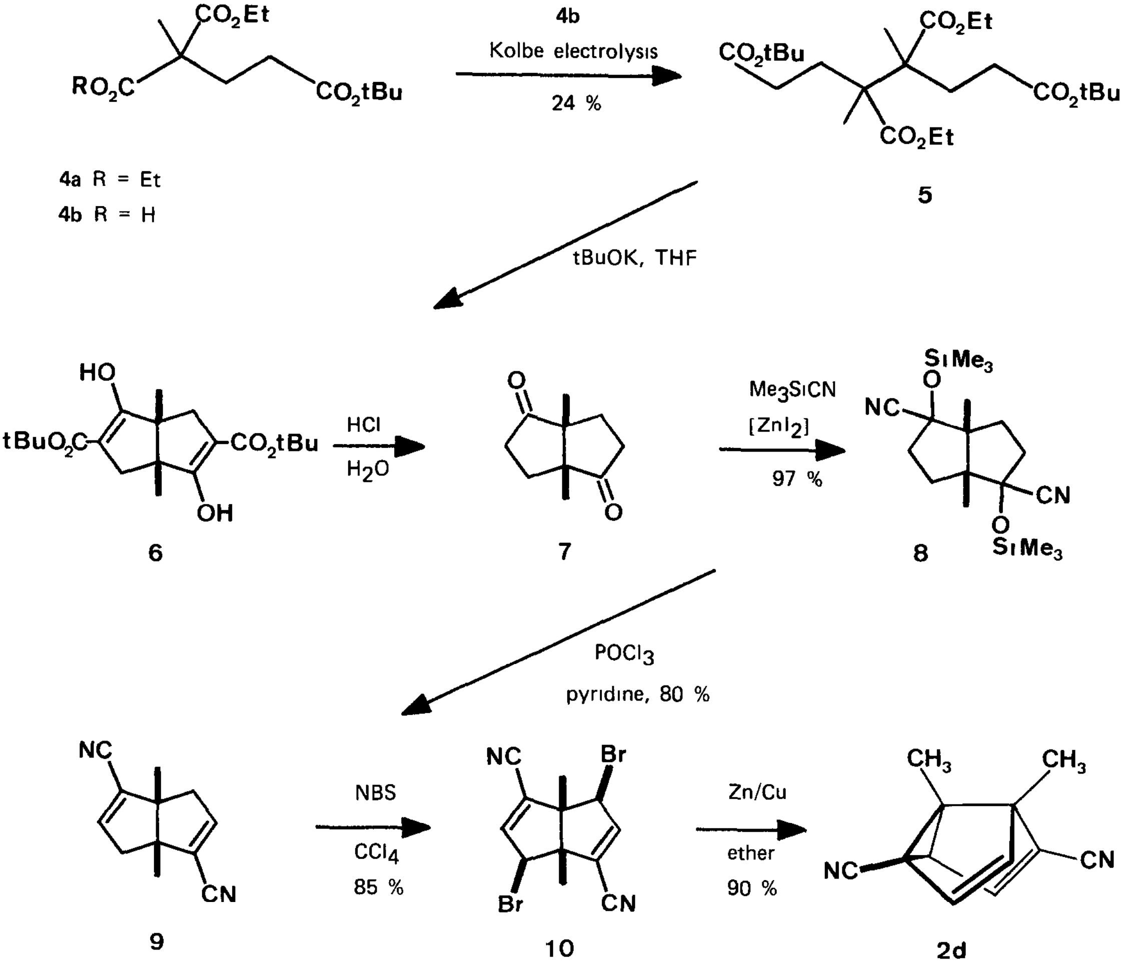
2a $R^1 = R^2 = H$, **2b** $R^1 = CH_3$, $R^2 = H$, **2c** $R^1 = H$, $R^2 = CN$, **2d** $R^1 = CH_3$, $R^2 = CN$

The key-intermediate for **2d**, the bicyclo[3 3 0]octane 2,6-dione **7**, had been obtained previously in low yield from the 1,5 dimethylbicyclo[3 3 0]octane-3,7 dione via a five step sequence [7] A more convenient access to substantial amounts of **7** seemed, therefore, mandatory To this end, diethyl methylmalonate was added to *tert*-butyl acrylate in the presence of small amounts of sodium hydride without use of a solvent to afford the triester **4a** [8] in 97 % yield [9] Selective partial hydrolysis of **4a** with one mole of potassium hydroxide in methanol [10] produced 82 % of the monoacid **4b** Without purification, **4b** was subjected to Kolbe electrolysis [11] (one mole of **4b** in 400 mL methanol in the presence of 0 1 mole potassium hydroxide), affording 24 % of the tetraester **5** as a colorless, viscous oil (b p 100 - 130°C/ 2 4 10^{-6} torr, 1 1 mixture of diastereomers [12]) Dieckmann condensation of **5** under the action of three moles of potassium *tert*-butoxide in tetrahydrofuran proceeded almost instantaneously [13], furnishing the expected bicylic ß-keto ester **6** which was hydrolyzed and decarboxylated under refluxing hydrochloric acid to the 2,6-dione **7** in 76 % yield (based on racemic **5** [14])

Conversion of the 2,6-dione **7** into the unsaturated dinitrile **9** was readily achieved [15] by addition of trimethyl silyl cyanide to **7** Using a twofold stoichiometric excess of the reagent in dichloromethane and 0 1 mole zinc iodide as catalyst, the bis(0-trimethylsilylcyanohydrin) **8** was produced in 97 % yield as a symmetrical diastereomer An excess of phosphorus oxychloride (20 moles) in boiling pyridine converted the cyanohydrin **8** into the dinitrile **9** in 80 % yield (after sublimation at 40 °C/14 torr) NBS bromination of **9** in carbon tetrachloride occurred



diastereoselectively affording the dibromide **10** in 85 % yield The exo, exo position of the bromine atoms in **10** was inferred in analogy to 4,8-dibromo-2,6-dicyanobicyclo[3 3 1]nona-2,6-diene, whose stereochemical assignement of the bromine atoms was confirmed by X-ray crystallography [6] Zinc-copper reagent [16] in refluxing ether debrominated **10** in 10 h furnishing 90 % of the 2,6-dicyanosemibullvalene **2d** as colorless crystals after sublimation at 40 50°C/10^{-5} torr, m p 142 - 144°C (decomposition) The 400 MHz proton NMR spectrum of **2d** in CDCl$_3$ at ambient temperature consisted of a sharp singlet at 1 28 (2 CH$_3$) and two dublets with $\underline{J}$ = 3 9 Hz at 4 61 (H$_{4,8}$) and 5 67 ppm (H$_{3,7}$), respectively

Of crucial importance for determining whether the cyano groups lower the Cope activation barrier in **2d** was the low temperature carbon spectrum The 100 61 MHz ^{13}C NMR spectrum of **2d** in CHClF$_2$ - CD$_2$Cl$_2$ (4 1) at 143°C consisted of six sharp signals [13 6 (2 CH$_3$), 65 5 (C$_{1,5}$), 84 5 (C$_{2,6}$), 100 2 (C$_{4,8}$), 118 9 (2 CN), 128 0 (C$_{3,7}$)], which did not show any signs of broadening For comparison we calculated the coalescence temperatures of the carbon signals of the parent semibullvalene (**2a**) at the same spectrometer frequency, using the reported low temperature (-160°C) ^{13}C NMR data and the rate constants of the Cope rearrangement [1a] Thus, in the 100 61 MHz carbon spectrum of semibullvalene the signals of C$_1$/C$_5$ (Δ v = 513 Hz) and C$_{2,8}$/C$_{4,6}$ (Δ v = 9015 Hz) would coalesce at 144°C and 126°C, respectively In harmony with the coalescence temperatures derived for **2a**, we found significant broadening of the $C_{2,4,6,8}$ signal in the 100 61 MHz carbon spectrum of the 1,5-dimethylsemibullvalene **2b** [2f] in CCl_2F_2-CD_2Cl_2 (4 1) already at -100°C At -123°C this signal had a half-width of 3 ppm Consequently, in view of the lack of all signs of line-broadening in **2d** down to -143°C, we conclude that *the activation barrier to Cope rearrangement must be considerably lower (< 5 kcal/mole) than that for semibullvalene (**2a**) itself*

A decisive probe for potential homoaromaticity of **2d** is offered by infrared spectroscopy At room temperature in tetrachloroethene the 2,6-dicyanosemibullvalene **2d** exhibits two C≡N bands of equal intensity at 2218 0 and 2230 5 cm^{-1} and a C=C frequency at 1578 8 cm^{-1} [17] For comparison, the 2,6-dicyanobarbaralane **3** shows two C≡N frequencies at 2216 8 and 2239 7 cm^{-1} and two C=C frequencies at 1610 4 and 1625 8 cm^{-1} corresponding to the conjugated and non-jugated functional groups, respectively Consequently, **2d** does not possess C_2-symmetry at the infrared time scale Thus, while homoaromaticity has not yet been reached by the introduction of two cyano groups, as in **2d**, the extremely low activation barrier towards the Cope rearrangement of **2d** and, perhaps, the significantly smaller difference between its C≡N frequencies compared to **3** may stimulate efforts to realize examples of the Dewar-Hoffmann type of homoaromaticity[18]

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Table 1 Melting points and IR ($CHCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$), data of the bicyclo[3 3 0]octanes 7 10 Literature data are given in brackets

Cpd	m p [°C]	IR [cm^{-1}]		^{13}C NMR [ppm]					
		C≡N	C=C	$C_{1,5}$	$C_{2,6}$	$C_{3,7}$	$C_{4,8}$	CN	Me
7[a]	97 - 98 (102)[7,18]	-	-	56 6 (56 9	221 1 221 4	35 9 36 2	28 8 29 2	- -	16 5 16 8)[7]
8	114	2228 5	-	54 6	81 7	37 5	29 9	121 4	21 2[b]
9	166 167 (173)[18]	2218 5	1622 0	58 2	115 2	144 2	43 0	123 4	19 9
10	189 - 190 (dec) (190)[18]	2223 3	1615 1	61 0	113 6	143 9	56 7	123 0	19 4

[a] IR 1735 (1735)[7] cm^{1} (KBr, C=O)

[b] 0 90 ppm (Me_3Si)

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(13) Cf Hagedorn III, A A , Farnum, O G *J Org Chem* **1977**, *42*, 3765

(14) Since the Michael addition affording **4a**, the partial hydrolysis of **4a**, and the Kolbe electrolysis of **4b** can be carried out easily on a scale of several moles using cheap starting materials and reagents, the 2,6 dione **7** is now conveniently available for preparative work Under the Dieckmann reaction conditions meso-**5** forms the anticipated trans-2,3-dimethylcyclopentanone triester, which is hydrolysed, decarboxylated and finally separated as trans 3-carboxy 2-(2-carboxyethyl)-2,3-dimethylcyclopentanone in 80 % yield (based on meso-**5**)

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(18) Professor Askani has kindly agreed to publish his work on **2d** in the same issue of this Journal R Askani, Littmann, M *Tetrahedron Lett* **1982**, 3651 The slightly different melting point of **2d** reported by these authors most probably results from different heating rates

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