

Dehydrogenation of Hexamethyl-Dewar-benzene to its Tetramethyl-*o*-dimethylene Derivative: Synthesis and Cycloreversion of 1,2,3,4-Tetramethyl-5,6-bismethylene-bicyclo[2.2.0]hex-2-ene**

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Abstract: The allylic bromination of hexamethyl-Dewar-benzene (1) followed by dehydrobromination yields tetramethyl-Dewar-«xylylene» (3). The cycloreversion of 3 to the reactive monocyclic isomer 4 proceeds smoothly upon irradiation or heating above 60°C.

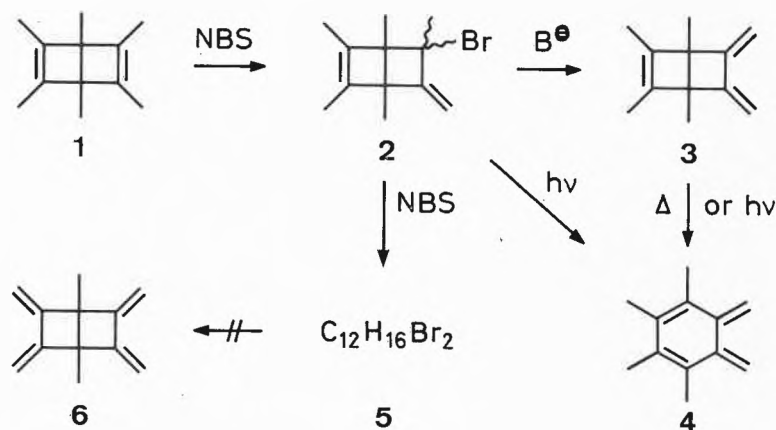
The highly reactive «*o*-xylylenes» (*o*-quinodimethane and derivatives) are important intermediates in chemical synthesis^[1] which have in recent years been characterized by various spectroscopic techniques^[2]. Benzocyclobutene derivatives are readily available precursor compounds^[3], but they require temperatures up to 200°C for activation. In contrast, the «Dewar» valence isomer of «*o*-xylylene» reacts smoothly at temperatures above 60°C, but is hard to synthesize^[4]. It has been speculated that the «forbidden» but facile cycloreversion of the Dewar isomer might proceed by thermal activation to an electronically excited state^[5]. We report here a simple two-step synthesis (Scheme 1) for «tetramethyl-Dewar-xylylene» (1,2,3,4-tetramethyl-5,6-bismethylenebicyclo[2.2.0]hex-2-ene 3)

and preliminary results on its photochemical and thermal cycloreversion to «tetramethyl-*o*-xylylene» (1,2,3,4-tetramethyl-5,6-bismethylenecyclohexa-1,3-diene 4).

The bromination of hexamethyl-Dewar-benzene (1) with *N*-bromosuccinimide (NBS) proceeded spontaneously at room temperature to give predominantly a single stereoisomer of constitution 2. Subsequent elimination of HBr with strong base then afforded the «Dewar-xylylene» 3 as a colourless liquid in 25% overall yield. Neat 3 polymerized within a few days, but could be kept for prolonged periods in dilute solution.

Our attempts to synthesize the elusive 1,4-dimethyl-2,3,5,6-tetrakis-methylenebicyclo[2.2.0]hexane (6) by the same method have failed. Further bromination of

Scheme 1:



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2 with NBS at 77°C did yield a mixture of three dibromides 5 along with the diastereomer of 2 (2'). The ¹H-NMR data of the labile compounds 5 did not allow an unambiguous structural identification, but indicated that the second bromine atom is introduced at either one of the remaining vinylic methyl groups. How-

ever, treatment of the mixture **5** with strong base at temperatures down to -100°C invariably gave intractable polymers.

The irradiation of a glassy solution of **3** in a hydrocarbon mixture (2,2-dimethylbutane:pentane = 8:3) at 77 K with a low-pressure mercury arc ($\lambda = 254\text{ nm}$) rapidly produced a yellow, highly fluorescent compound **4** (Fig. 1) which disappeared upon thawing. The same product was formed less efficiently upon irradiation of **2** under the same conditions. The decay kinetics of **4** at ambient temperature were monitored by conventional flash photolysis of deaerated 10^{-4} M hexane solutions of **3**. The transient absorption of **4** ($\lambda_{\text{max}} = 370\text{ nm}$) decayed by a second order rate law, $k_2/\epsilon = 0.05\text{ cm s}^{-1}$, on a time scale of minutes. In the presence of acrylonitrile, the decay of **4** was accelerated and obeyed a pseudo-first order rate law. This rate constant was proportional to the dienophile concentration, i.e. $k_2 = 0.9\text{ M}^{-1}\text{ s}^{-1}$.

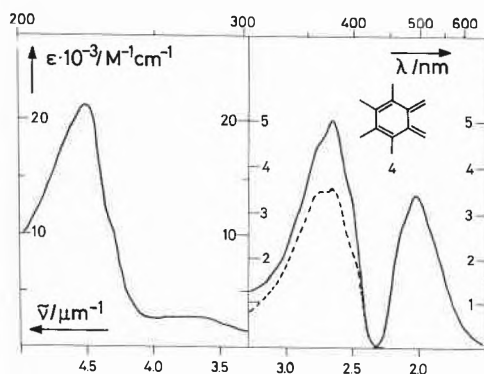


Fig. 1. Absorption (—) and corrected fluorescence excitation (---) and emission (—) spectra of **4** in a hydrocarbon glass at 77 K. Ordinate scales (fluorescence): relative quanta per wavenumber; (absorption): estimated using ϵ (**3**) determined at room temperature and assuming 100% photochemical conversion to **4**.

All of these observations strongly suggest that the reactive intermediate **4** is «tetramethyl-*o*-xylylene». This assignment is supported by the close similarity of the optical spectra shown in Fig. 1 with those of parent «*o*-xylylene» and its methyl derivatives^[2].

The thermally activated cycloreversion **3**→**4** in tetrachloroethene solution was monitored by $^1\text{H-NMR}$ spectroscopy. The decay of the signals due to **3** was first order in [3] and did not depend on the amount or nature of the added trapping reagents (*p*-benzoquinone, norbornadiene, or diethyl maleate) within the limits of error, $k_1(80^{\circ}\text{C}) = (14 \pm 2) \cdot 10^{-5}\text{ s}^{-1}$. Thin layer chromatography indicated the formation of a single product in each case and the spectroscopic data ($^1\text{H-NMR}$) were consistent with the expected Diels-Alder addition products. The same

decay rate of **3** was found in the absence of trapping agents but the product NMR was complex and no simple dimers could be isolated.

Preparative Part

5-Bromo-1,2,3,4,5-pentamethyl-6-methylenebicyclo[2.2.0]hex-2-ene (**2**): A solution of 2.0 g **1** (Aldrich, 12 mmol) in 25 cm³ dry tetrachloromethane was treated with 3.1 g NBS (17.4 mmol) and stirred under a nitrogen atmosphere at ambient temperature. The reaction caused a perceptible temperature increase within 15 min. The suspension was filtered after one hour and the solvent evaporated under reduced pressure (2000 Pa) at room temperature. The residue was distilled to a cold trap in vacuo ($\leq 0.1\text{ Pa}$) yielding 1.37 g (46%) of solid **2** which melted on warming. Liquid **2** decomposed slowly at room temperature, rapidly (yielding **3**) at its *b.p.* of $80\text{--}85^{\circ}\text{C}/2000\text{ Pa}$. Chromatography was destructive. $^1\text{H-NMR}$ (CCl_4): $\delta = 1.14$ (s, 3H), 1.28 (s, 3H), 1.45–1.60 (m, 6H), 1.75 (s, 3H), 4.82 (d, 1H, $J = 1\text{ Hz}$), 5.02 (d, 1H, $J = 1\text{ Hz}$). UV (hexane): end absorption only. MS: 242, 240 (M^+ , 5 each), 227, 225 (4 each), 161 (100). — Diastereomer **2'**: $^1\text{H-NMR}$ (CCl_4): $\delta = 1.06$ (s, 3H), 1.10 (s, 3H), 1.5–1.7 (m, 6H), 1.72 (s, 3H), 4.85 (d, 1H, $J = 1\text{ Hz}$), 5.05 (d, 1H, $J = 1\text{ Hz}$). 1,2,3,4-Tetramethyl-5,6-bismethylenebicyclo[2.2.0]hex-2-ene (**3**): A solution of potassium *tert*-butoxide (1.8 g, 16 mmol) in dry dimethyl sulfoxide (10 cm³) was added dropwise to a stirred and cooled (0°C) solution of **2** (1.3 g, 5.4 mmol) in dry tetrahydrofuran (20 cm³) under an

inert gas atmosphere. The mixture was warmed to room temperature, quenched with ice, diluted with pentane (20 cm³), and washed with salted water until the extracts were neutral. Evaporation of the solvent and chromatography of the residue on active basic alumina with pentane gave 0.47 g of **3** (54%) as a colourless liquid which polymerized within a few days, but could be kept indefinitely as a dilute solution. For analytical purposes, **3** was crystallized (*m.p.* $16\text{--}17^{\circ}\text{C}$) from pentane at -80°C . $^1\text{H-NMR}$ (CDCl_3): $\delta = 1.16$ (s, 6H), 1.55 (s, 6H), 4.79 (s, 2H), 5.13 (s, 2H). UV (hexane): $\lambda_{\text{max}} = 240\text{ nm}$ ($\lg \epsilon = 3.9 \pm 0.1$). IR (neat): 3080 (m), 3000–2850 (s), 1685 (w), 1640 cm⁻¹ (w). MS: 160 (M^+ , 10), 145 (11), 86 (100).

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