

A NEW APPROACH TO THE [6]PARACYCLOPHANE SYSTEM:

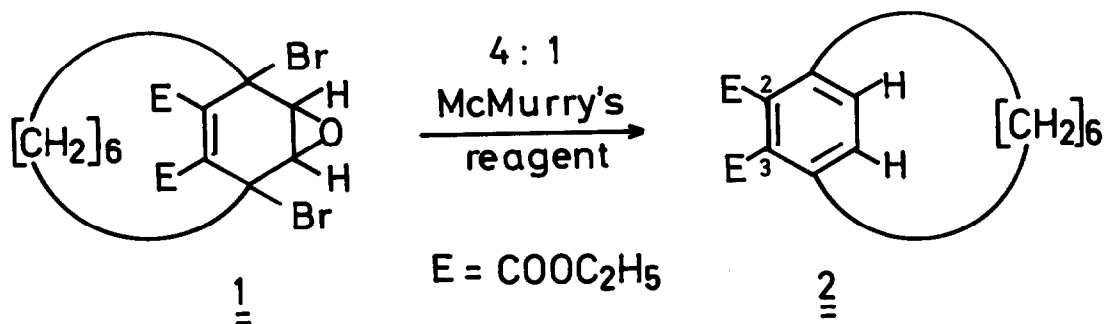
SYNTHESIS OF 2,3-DICARBETHOXY[6]PARACYCLOPHANE¹⁾

Jörg Liebe, Christian Wolff and Werner Tochtermann⁺

Institut für Organische Chemie der Universität, D-2300 Kiel, Germany

Abstract: The reaction of the dibromide 1 with McMurry's reagent gives 2,3-dicarbethoxy[6]paracyclophane (2) in about 40% yield.

[6]Paracyclophane has a high strain energy and a distorted benzene ring²⁾. The parent hydrocarbon, a liquid, has been synthesized first by M. Jones, Jr. and his group in about 5 - 10 % yield by a carbene route³⁾. Because of continuing interest in this field³⁻⁶⁾ a convenient synthesis of suitable crystalline derivatives would be desirable. Here we wish to report a new approach to this system from readily available starting materials.



A solution of the dibromide 1 (obtained from 4,5-dicarbethoxy-3,6-hexanooxepin and bromine in dichloromethane^{1,7)}) in tetrahydrofuran is added to McMurry's reagent, prepared in situ from $\text{TiCl}_3/\text{LiAlH}_4$ (4:1)⁸⁾. The reaction mixture is then heated for 4 hours under reflux. Hydrolysis and column chromatography of the crude product on alumina (act. II-III) with chloroform/dichloromethane/petroleum ether b.p. 30-60°C (1:1:1) gives 2 as colourless crystals (mp 47-48°C from n-pentane) in about 40% yield. The main by-product, the above mentioned oxepin, is separated by this procedure.

The structural assignment of 2 is based on molecular weight determinations (mass spectrum, m/e 304 (M^+ , 29%); osmometry: $M = 302, 306$), the elemental analysis and the NMR spectra (Table 1). In agreement with the data of the parent

hydrocarbon the ^1H -NMR-spectrum of 2 shows at room temperature broad signals in the high field region up to $\delta = -0.7$ ppm. Broad signals for the aliphatic and the benzene part of 2 are also observed in the ^{13}C -NMR-spektrum (30°C), which is sufficiently resolved at 60°C (Table 1). The ortho-isomer of 2, 2,3-dicarbethoxy-hexahydrobenzocyclooctene⁷⁾, shows quite different spectra. The simple nmr-spectra of 2 indicate a high symmetry of the molecule and would not be in agreement with a Dewar benzene⁹⁾ or with one of the possible isomeric [6]metacyclophanes⁹⁾.

Table 1. Spectroscopic data of 2

IR(KBr): 1715 cm^{-1} (CO). - UV($\text{C}_2\text{H}_5\text{OH}$): 233 (4.35), 265 sh (3.7), 330 nm (3.4).
 - ^1H -NMR (CDCl_3 , 34°C): $\delta = -0.7$ -2.2 (very broad, 14H, therein at 1.33 t with $J = 7\text{Hz}$ for 2CH_3), 2.2-2.7 (broad, 2H), 2.7-3.3 (broad, 2H), 4.31 (q, $J = 7\text{Hz}$, 2OCH_2), 7.34 (s, 2H). - ^{13}C -NMR (CDCl_3 , 60°C): 14.1 (q, CH_3), 26.4 (t, CH_2), 35.1 (t, CH_2), 35.3 (t, CH_2), 61.2 (t, OCH_2), 133.7 (s, $=\text{C}-$), 133.9 (d, $^1J_{\text{C-H}} = 156\text{ Hz}$, $=\text{CH}-$), 144.3 (s, $=\text{C}-$), 167.7 (s, $\text{O}-\text{C}=\text{O}$).

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