DIALKYLBORYLMETHYLCYCLOBUTENE-1-(DIALKYLBORYL)-2-METHYLENECYCLOBUTANE: A NEW METALLOTROPIC SYSTEM. THE SYNTHESIS OF 2-SUBSTITUTED METHYLENE-CYCLOBUTANE AND CYCLOBUTENE DERIVATIVES

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The reaction of the metallation product of methylenecyclobutane (I) [1] and R_2BBr yielded the first cyclobutane allylboranes (II).



Boranes (II) are found in a state of constant allylic rearrangement (CAR) and neither form (IIA) nor (IIB) was detected by ¹H or ¹³C NMR spectroscopy at -50°C.

Similar to other allylboranes [2], (II) adds to aldehydes, ketones, and activated acetylenes in pentane at -70 to 0°C but in contrast to the analogous reactions of their fiveand six-membered analogs (which yield almost exclusively exo-methylene compounds [3]), the course of these reactions is highly dependent on the structure of the substrate. The reaction with acetone, cyclopentanone, cycloheptanone, and camphor gives 98-100% adducts with an exo-methylenic double bond (III) in 65-80% yield. The regioselectivity of these reactions is much lower in the case of aldehydes and cyclohexanone (see Table 1).



TEA = triethanolamine.

TABLE 1

Substrate	(III)/(IV) ratio	bp,°C (p,mnHg),	n_{D}^{20}	Substrate	(III)/(IV) ratio
Acetone Cyclopentanone Cycloheptanone Camphor	100 : 0 100 : 0 98 : 2 100 : 0	48-49(7) 57-58(2) 71-72(1) 82-84(1)	$1,4641 \\ 1,4945 \\ 1,5049 \\ 1,5092$	Cyclohexanone Benzaldehyde Acetaldehyde	90 : 10 60 : 40 53 : 47

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1918–1919, August, 1986. Original article submitted April 8, 1986. The reaction of (IIa) with ethoxyacetylene led to a ~4:1 mixture of dienes (V) and (VI) in about 80% total yield. The structures of (II)-(VI) were confirmed by elemental analysis and IR and 1 H and 13 C NMR spectroscopy.

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ELECTROCHEMICAL DEHYDROTRIMERIZATION OF DIMETHYL MALONATE TO THE HEXAMETHYL ESTER OF CYCLOPROPANEHEXACARBOXYLIC ACID

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We have discovered that the electrochemical oxidation of dimethyl malonate (I) in methanol in a diaphragmless cell in the presence of an alkali metal bromide, MBr, as an electron transfer catalyst at 50°C gives the hexamethyl ester of cyclopropanehexacarboxylic acid (II) in 50-60% yield.



The formation of ester (II) may be seen as an electrochemical dehydrodimerization of ester (I) to the tetramethyl ester of ethylenetetracarboxylic acid (III) [1] with the subsequent Michael addition of dimethyl bromomalonate formed under the electrolysis conditions and the cyclization of this adduct to ester (II). In all cases, ester (III) was detected in 10-15% yield and dimethyl dimethoxymalonate was detected in 15-20% at the end of the reaction.

The hexaethyl ester of cyclopropanecarboxylic acid has been obtained by the photolysis of isoquinolinium dicarboethoxymethylide in 25% yield [2] or by the reaction of the α, α' -dianion of the hexaethyl ester of propanehexacarboxylic acid with Br₂ [3] (the yield of the latter reaction was not reported).

A sample of 2.1 g (16 mmoles) ester (I) and 4 mmoles MBr were placed in a diaphragmless electrolyzer with a platinum anode and iron cathode and 4F current was passed permole of starting ester (I) at 50°C and 220 mA/cm² current density. Hexaester (II) crystallized at the end of the reaction and cooling to ~20°C. The product was separated by filtration and washed with cold methanol to give a 50-60% yield of (II) with 100% conversion of (I), mp 235-237°C (from acetone-methanol). PMR spectrum (δ , ppm): 3.86 s (CH₃O). ¹³C NMR (δ , ppm): 44.8 s [C(CO₂Me)₂], 53.6 q (CH₃O), 163.6 s (CO₂Me). Found, %: C 45.99, H 4.58. C₁₅H₁₈O₁₂. Calculated, %: C 46.15, H 4.61.

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