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[2.2]PARACYCLOPHANE BY PHOTOEXTRUSION OF CARBON DIOXIDE FROM A CYCLIC DIESTER

Martin L. Kaplan* and Elizabeth A. Truesdale*
Bell Laboratories
Murray Hill, New Jersey 07974 USA

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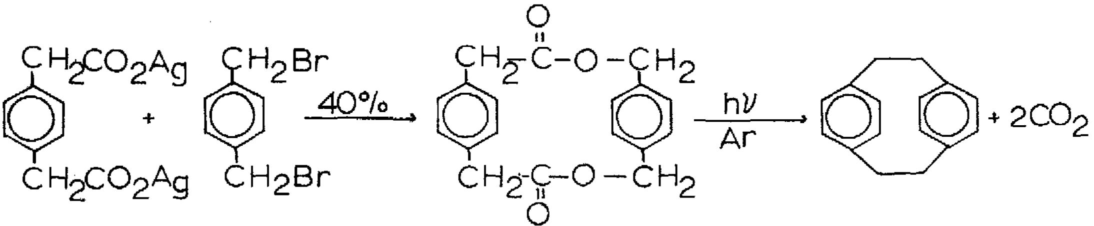
For the past quarter century organic chemists have sought the means to study highly strained systems of the cyclophane type, in which the benzene rings actually deviate from planarity and assume a boat-like conformation. The synthetic route described permits us to introduce such strain by starting with an unstrained molecule which under appropriate conditions decomposes to form intermediates which can then react by one major pathway. We have demonstrated this technique with the preparation of [2.2]paracyclophane (I) in good yield by the photodecarboxylation of a cyclic diester.

The literature of the last few years has been replete with studies of the photo-reaction of benzylic esters. In particular we noted that the photolysis, at 300 nm, of α-naphthalenemethyl phenylacetate gave 65% isolated yields of naphthalenemethyl and benzyl hydrocarbon coupling products (1,2). In a like manner it was found that benzyl phenylacetate upon irradiation with wavelengths above 210 nm, in the absence of oxygen, gave 91% yields of bibenzyl. The quantum yield at 26° was 0.19 (3).

By taking advantage of the high yields and simplicity of the photodecarboxylation reaction we reasoned that a useful synthetic route to cyclophane type compounds could be developed. The preparation of p-xylylene-1,4-benzenediacetate (II) was accomplished by heterogeneously reacting diargentous 1,4-benzenediacetate (III) and α, α′-dibromo-p-xylene (IV) in refluxing acetonitrile. The diester II was isolated chromatographically, recrystallized from ethyl acetate or ethyl alcohol and exhibited the following physical properties: m.p. 238-239°C; nmr spectrum, $CDCl_3$(TMS), four singlets of equal intensity at τ's 2.98, 3.09, 4.94 and 6.64 assigned to the aromatic alcohol, ring protons, aromatic acid ring protons, alcohol methylene protons and acid methylene protons respectively; i.r. spectrum (KBr), 3025 (w), 1740(s), 1530(m), 1460(m), 1430(m), 1350(m), 1330(w), 1275(m), 1250(s), 1230(m), 1220(w), 1190(w), 1120(s), 1090(w),



III IV II I

1020(w), 980(s), 962(w), 940(m), 865(w), 843(w), 813(s), 782(s), 750(s), 720(w) and 680(m) cm^{-1}; u.v. spectrum, $\lambda_{max}^{CH_2Cl_2}(\varepsilon)$, 240(3400), 264(530), 268(530) and 273(450)nm; analysis of the material (Calc. $C_{18}H_{16}O_4$:C, 72.96; H, 5.44. Found: C, 72.82; H, 5.46) and its mass spectrum (m/e for molecular ion 296) are entirely consistent with the assigned structure.

When II was irradiated at ambient temperatures in either methanol or 1,2-dimethoxyethane(4) high yields of I were realized. The properties of isolated I (m.p., i.r. and n.m.r.) were identical in all respects with those of authentic material. The yields of I approached 70% when 1,2-dimethoxyethane was used but were somewhat lower in methanol and compare favorably with the currently available synthetic routes to I. For example, the standard procedure of preparing I by the decomposition of p-methylbenzyl-trimethyl ammonium hydroxide (5) is relatively tedious and results in overall yields of about 10%. Other methods resulting in even lower yields of cyclophanes involve pyrolysis of p-xylene (6,7), dimerization of p-xylylene (8) and intramolecular Wurtz reactions (9). Recently good yields of [2.2] bridged cyclophanes have been achieved by the photoextrusion of sulfur from dithia [3.3] bridged precursors in the presence of trimethylphosphite (10,11). The present method appears to afford access to cyclophanes unattainable by the more classical schemes, and the potential of this photochemical decarboxylation technique is currently being explored.

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