

INTRAMOLECULAR [2 + 2] PHOTOCYCLOADDITION. 6.¹⁾
SYNTHESIS AND PROPERTIES OF OXACYCLOPHANES

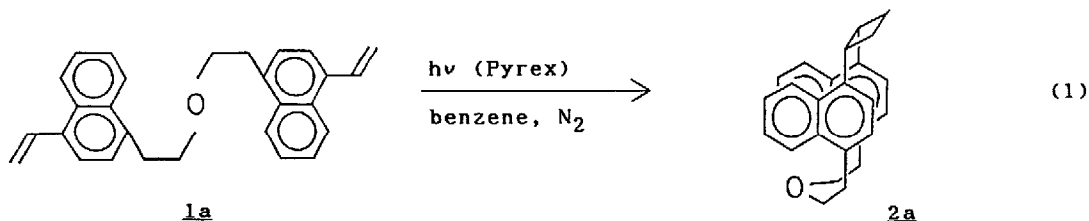
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Abstract: Several oxacyclophanes were prepared by a new photocyclization of styrene derivatives. Cyclophanes **2d** and **e** underwent C-O bond cleavage and gave olefin **6a** and **b** by subsequent transformations, respectively.

In order to modify cyclophanes at the linkages, heterocyclophanes are valuable intermediates. Generally such cyclophanes are afforded by the cyclization using facile carbon-heteroatom bond formations, whose examples are seen in many syntheses of dithiacyclophanes, etc.²⁾ There is, however, another one with the C-C bond formation using a material which has already heteroatoms at the linkage between aromatic nuclei. Recently we found the formation of oxacyclophanes along with the latter strategy, namely the photochemical C-C bond formation (1) of appropriate ethers. In this communication we would like to discuss the novel synthesis of some oxacyclophanes and their transformation at the ether linkages.



Starting materials **1**, styrene derivatives and a vinyl naphthalene derivative, were prepared in reasonable yields by the sequence of Grignard coupling³⁾ and dehydration⁴⁾ as reported.

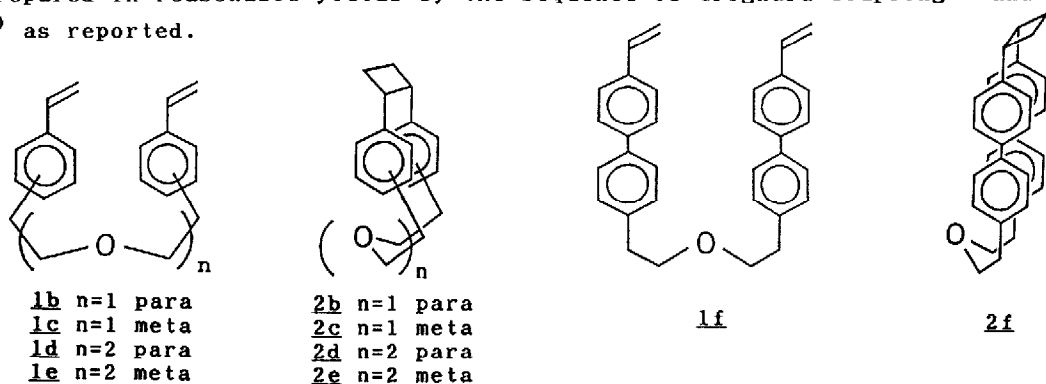


Table I Yields, Melting Points, and Analytical Data of Compounds Prepared

Compd	Isolated yield, % ^{a)}	Mp, °C	Anal. Calcd (Found) C, %; H, %	Ms (M ⁺ , m/z) Calcd (Found)
<u>2a</u>	46	164 - 165	-	378.1986(378.1987)
<u>2b</u>	85	124 - 125	-	278.1672(278.1666)
<u>2c</u>	40	oil	-	278.1672(278.1675)
<u>2d</u>	63	85 - 86	81.95(82.01); 8.13(8.27)	-
<u>2e</u> ^{cis}	26	oil	-	322.1933(322.1954)
<u>2e</u> ^{trans}	6	77 - 78	-	322.1933(322.1931)
<u>2f</u>	53	185 - 188	89.26(89.55); 7.02(7.11)	-

a) Reaction conditions: [1], 2 to 5 mM; 400 W high pressure mercury lamp; Pyrex filter; in dry benzene under a nitrogen atmosphere at rt for 12 - 24 h.

The photocycloaddition of olefin 1 was carried out in dry benzene under a N₂ atmosphere, using a Pyrex filter to eliminate the light of shorter wavelength than ca. 280 nm.⁵⁾ Reaction conditions and yields are summarized in Table I, together with physical and analytical data.

Olefins 1a, 1b, 1c, and 1f with ether linkage recorded better yields than those having pentamethylene linkage.^{5,6)} The relatively stable gauche conformation⁷⁾ of C-O bond is believed to be favorable for the cyclization.

Structures of oxacyclophanes were elucidated mainly by ¹H NMR spectroscopy, whose data are listed in Table II. Cyclophane 2b shows a high-field-shifted aromatic AB quartet at δ6.40, which clearly indicates the structure of the stacked aromatic nuclei. The characteristic methine proton peaks appear at δ3.99, so that the cis configuration of the cyclobutane ring is concluded.⁶⁾ The structures of 2d and 1 were determined in the same way.

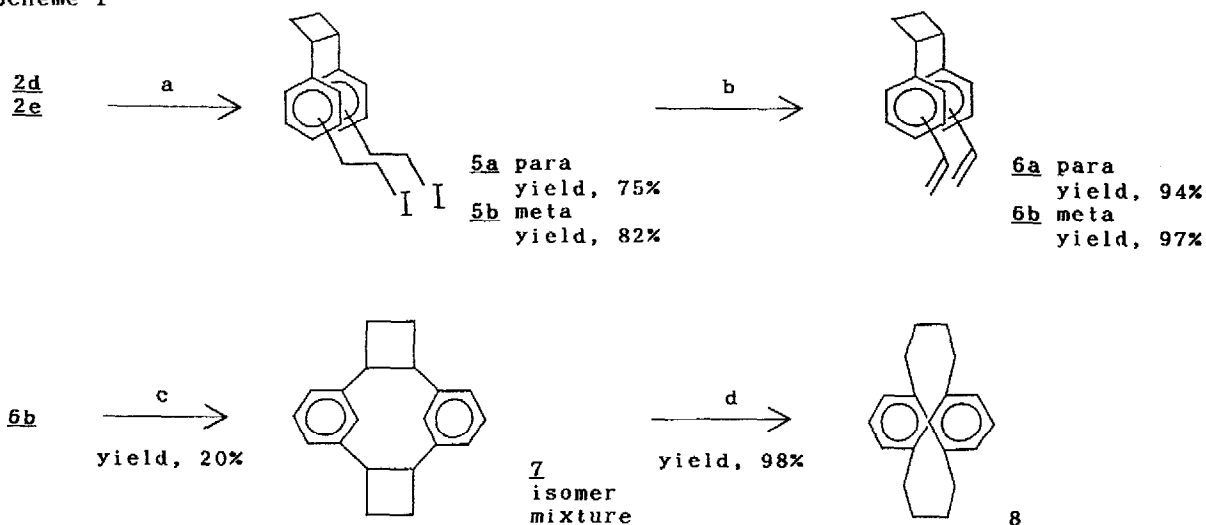
The structure of metacyclophane 2c was determined as just done for cis-(1,2)-ethano-syn-[2.5]metacyclophane 3⁶⁾: Chemical shift difference Δδ (+0.07) shows clearly that it exists predominantly as the syn conformer.⁸⁾

Cyclophane 2e contained cis and trans isomers whose ratio was 4.1:1.0. They were isolated by HPLC for the structural determination. Cis and trans isomers show characteristic cyclobutane methine proton peaks at δ3.98 (normal) and 3.56 (shielded), respectively, which indicate clearly their structures.⁶⁾

Naphthalenophane 2a is of exo configuration, because the non-bonding interaction between cyclobutane-methine hydrogens and naphthalene peri-hydrogens is apparent in its NOESY spectrum.⁵⁾

Trimethylsilyl iodide was used in order to cleave the ether linkage of the cyclophanes 2a, 1b, 1c, and 1f, but it resulted in the recovery of the starting materials. The reactivity of the ether linkage in these compounds is considered to be usual, so that the failure might be due to a steric reason that their oxygen lone pairs are hidden and not available for the attack of silyl iodide.⁹⁾ Accordingly the stable conformations of the cyclophanes were calculated by

the MM2 method,¹⁰⁾ which suggests the tail-in structures like one depicted for 2a and f. The structure is also independently proved by the ¹H NMR spectra of the parent cyclophanes, cis-(1,2)ethano[2.5]paracyclophane 4⁵⁾ and cis-(1,2)-

Scheme 1⁵⁾

a) Me_3SiCl , NaI, MeCN. b) $t\text{-BuONa}$, $t\text{-BuOH}$. c) $h\nu$ (Pyrex), benzene, N_2 .
 d) Na, NH_3 , EtOH.

Table II ¹H NMR Spectroscopic Data of New Cyclophanes^{a)}

Compd	¹ H NMR chemical shift δ (intensity, multiplicity, \underline{J} in Hz)
<u>2a</u>	7.81 (m, 2H), 7.37 (m, 4H), 6.96 (m, 6H), 5.13 (m, 2H), 3.80 (m, 4H), 3.25 (m, 4H), 2.81 (m, 4H).
<u>2b</u>	6.77 (ABq, 7.9, 2.0, 2H), 6.66 (ABq, 7.9, 2.0, 2H), 6.56 (ABq, 7.8, 2.0, 2H), 6.36 (ABq, 7.8, 2.0, 2H), 3.99 (m, 2H), 3.47 (m, 4H), 2.56 (t, 5.6, 4H), 2.42 (m, 4H).
<u>2c</u>	6.95 (s, 2H), 6.88 (t, 7.4, 2H), 6.71 (d, 7.7, 2H), 6.64 (d, 7.4, 2H), 3.93 (m, 2H), 3.33 (m, 4H), 2.58 (t, 5.5, 4H), 2.38 (m, 4H).
<u>2d</u>	6.78 (m, 8H), 3.99 (m, 2H), 3.41 (t, 5.9, 4H), 3.20 (s, 4H), 2.55 (t, 5.8, 4H), 2.43 (m, 4H).
<u>2e</u> ^{cis}	7.01 (t, 7.4, 2H), 6.87 (dt, 6.8 & 1.0, 2H), 6.77 (dt, 6.8 & 1.0, 2H), 6.70 (bs, 2H), 3.98 (m, 2H), 3.56 (s, 4H), 3.46 (t, 6.7, 4H), 2.67 (t, 6.7, 4H), 2.44 (m, 4H).
<u>2e</u> ^{trans}	7.29 (t, 7.5, 2H), 7.17 (dt, 7.9 & 1.0, 2H), 7.09 (bs, 2H), 7.03 (dt, 7.9 & 1.0, 2H), 3.71 (m, 4H), 3.56 (m, 2H), 3.51 (s, 4H), 2.81 (m, 4H), 2.31 (m, 2H), 2.16 (m, 2H).
<u>2f</u>	6.07 (ABq, 8.4, 6H), 6.99 (ABq, 8.4, 6H), 6.98 (ABq, 7.8, 2.0, 2H), 6.60 (ABq, 7.8, 2.0, 2H), 4.14 (m, 2H), 3.61 (t, 5.3, 4H), 2.79 (t, 5.4, 4H), 2.56 (m, 4H).

a) Taken in CDCl_3 by a Varian XL-200 NMR spectrometer, using TMS as an internal standard.

ethano-syn-[2.5]metacyclophane 3,⁶⁾ which show their central methylene groups in the linkages as the very high-field-shifted peaks at δ 0.40 and 0.58, respectively: i.e., the up-field shift is ascribed to their stable tail-in conformations.

On the other hand, 2d and e show relatively sharp singlets for methylene groups of oxyethylene units to suggest that these structural units rotate quite rapidly to expose the oxygen lone pairs for the attack of trimethylsilyl iodide. In fact, as shown in Scheme 1, compounds 2d and e reacted smoothly with this reagent to afford diiodides 5 exclusively.¹¹⁾ Diiodides 5 underwent E2 reaction with sodium t-butoxide in t-butanol to give unstable diolefins 6, which were purified by column chromatography (SiO₂, cyclohexane).

Olefin 6b gave desired cyclobutane-linked cyclophane 7 in a 20% yield after the photoirradiation (>280 nm) for 8 h, although p-substituted diolefin 6a easily polymerized itself under the same reaction conditions and did not give any desired cyclophanes. Cyclophane 7 was separated as an isomer mixture and reduced by Na/NH₃-EtOH to afford the known compound 8,¹²⁾ anti-[4.4]metacyclophane, in a 98% yield. Hence the photocyclization of 6b was confirmed.

Consequently, the photocyclization of olefins 1 afforded interesting oxacyclophanes 2, which lead some unique transformations of cyclophanes at their linkages.

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References and Notes

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- 10) We are indebted to Prof. Dr. Eiji Osawa, Hokkaido University, for providing the MM2 program.
- 11) The result is explained by the phenonium ion as the reaction intermediate. Ethylene glycol diphenethyl ether gave also β -phenethyl iodide exclusively, so that this selectivity is not specific for the cyclophane-skeletons.
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