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OBSERVATION OF REGIOSELECTIVITY IN CYCLOADDITION REACTION OF OXABENZONORBORNADIENE WITH 1,3-DIPHENYLISOBENZOFURAN [1]

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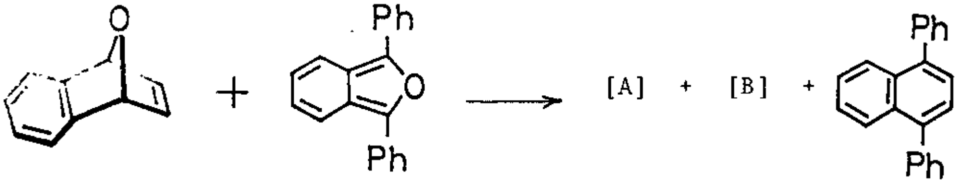
Cycloaddition reaction of oxabenzonorbornadiene with 1,3-diphenylisobenzofuran gave two 1:1 adducts accompanied with 1,4-diphenylnaphthalene. The structural elucidations of these adducts were accomplished by spectral inspections. The product distributions are observed to be dependent on the reaction temperatures.

Oxabenzonorbornadiene (1,4-epoxy-1,4-dihydronaphthalene) (1) has been proved to be useful as a dienophile and a dipolarophile for some cyclic olefins and dipolar compounds [2,3] as a 4π component, and for troponoide compounds as a 6π component.[4] These reactivities of 1 are presumably due to the ring strain and to the orbital participation of non-bonding electrons of the oxygen atom. In this communication, we have characterized the products of the thermal cycloaddition reaction of 1 with 1,3-diphenylisobenzofuran (2) as a

8π component.

Reaction of 1 with an equimolar 2 afforded two 1:1 adducts (A) (colorless needles, mp 216-217°) and (B) (colorless prisms, mp 275- 276°) accompanied with 1,4-diphenylnaphthalene (C) (mp 138-139°). The fragmentation patterns of mass spectra of A and B are very similar to each other; m/e 414 (M^+), 270 (base peak). The yields of the adducts under various conditions are summerized in Table 1.



(1) (2) [C]

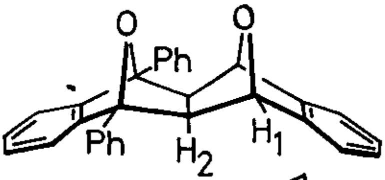
Table 1.

Solvent	Reaction Conditions		Product Distribution (Yield, %)		
	Temp.(°C)	Time(h)	(A)	(B)	(C)
Ether	0-20	100	69	12	trace
Benzene	30-40	60	71	1	3
Benzene	60-80	20	72	trace	5

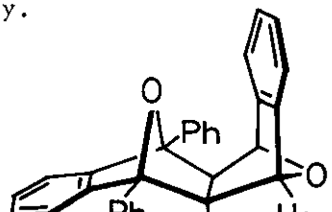
The structures of the adducts were eventually proved by the nmr inspections. The spectrum of major product (A) in $CDCl_3$ shows signals at δ 2.55 (s, 2H, center bridged-H between two dihydrofurans), 4.98 (s, 2H, oxygen bridgehead-H), and 6.9-7.8 (m, 18H, aromatic-H). On the other hand, the spectrum of minor product (B) exhibits signals at δ 3.10 (s, 2H, center bridged-H), 4.93 (s, 2H, oxygen bridged-H), and 6.8-7.7 (m, 18H, aromatic-H). The absence of vicinal couplings ($J_{1,2}$) for the adducts (A) and (B) indicated that the dihedral angles between the oxygen bridgehead protons and the protons of center bridge are to be approximately 90°.

Thus, [4 + 2] (or [8+2]) adducts (5) and (6) were ruled out for the structural possibilities because of the dihedral angles being approximately 40° by a stereo-model inspection. Besides, significant differences of the chemical shifts for the protons of center bridge at δ 2.55 and 3.10 are observed in the nmr spectra of (A) and (B), indicating clearly the anisotropy effects due to benzene ring or to the bridged oxygen.[5]

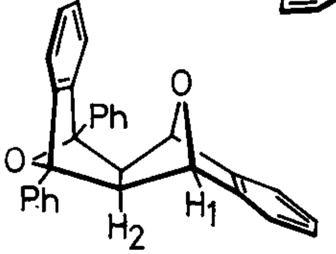
Therefore, the adducts (A) and (B) were assigned structures (3) and (4), that of thermally [4+2] (or [8+2]) cycloadducts with exo-configurations, respectively.



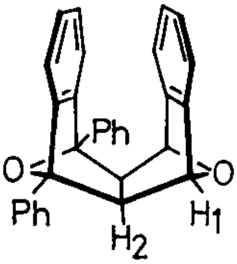
(3) (exo-exo)



(5) (endo-exo)

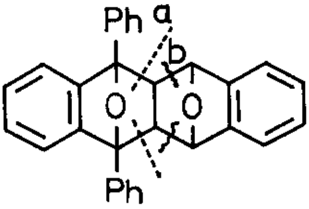


(4) (exo-endo)



(6) (endo-endo)

Surprisingly, both adducts (3) and (4) were thermally stable even under more drastic conditions (in chlorobenzene at 160-170° in a sealed tube) for much longer times, suggesting no interconversions of these adducts. Accordingly, the formation of compound (C) could be explained by no occurrance of the cycloreversion followed by dehydration of the adducts (3) and (4). Presumably, compound (C) was produced by decomposition followed by dehydration of other thermally unstable isomers.



The mass spectra of the adducts (3) and (4) support the above speculation, since the characteristic fragmentation of 1,3-diphenylisobenzofuran appears at m/e 270 as a base peak *via* a fission, but the isobenzofuran fragment at m/e 118 *via* b fission was not observed.

Thus, the formations of the thermal adducts (3) and (4) are presumably controlled by the steric effects in the transition states.

REFERENCES

1 Molecular Design by Cycloaddition Reactions. XX. Part XIX of this series, T. Sasaki, K. Kanematsu, and A. Kondo, submitted to Tetrahedron.

2 T. Sasaki, K. Kanematsu, and M. Uchide, Tetrahedron Letters, 4855 (1971).

3 T. Sasaki, K. Kanematsu, K. Hayakawa, and M. Uchide, J. Chem. Soc., Perkin 1, 2750 (1972).

4 T. Sasaki, K. Kanematsu, and K. Hayakawa, ibid., 1951 (1972).

5 M.P. Cava and F.M. Scheel, J. Org. Chem., 32, 1304 (1967).

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