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STEREOCHEMISTRY AND ACID-CATALYZED RING OPENING REACTIONS OF THE CYCLOADDUCT OF CYCLOPROPENE WITH 1,3-DIPHENYLISOBENZOFURAN

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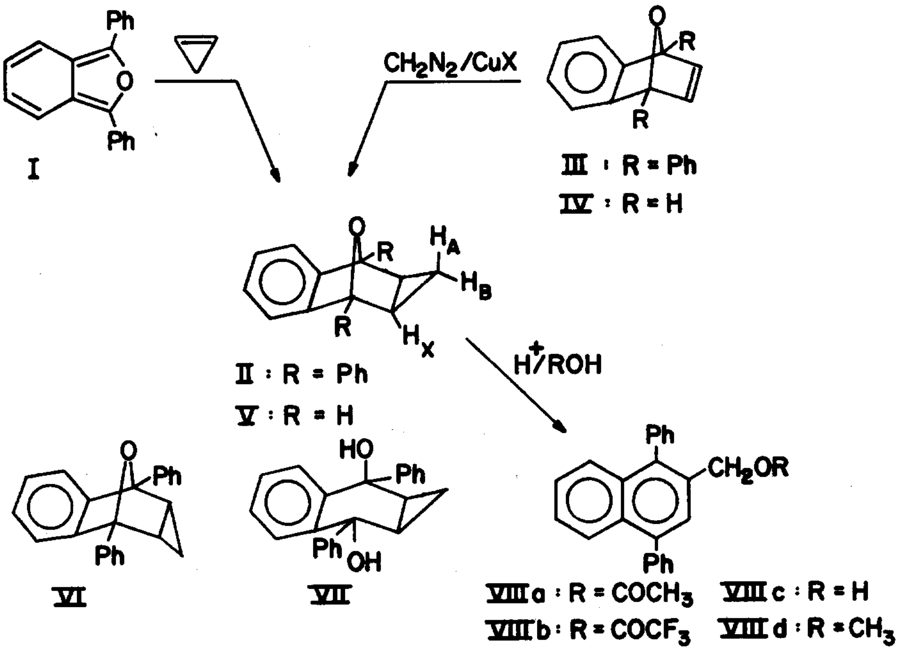
In the (4+2) cycloaddition of cyclopropenes to cyclic 1,3-dienes the commonly observed stereochemical course is endo-adduction.(2) Of late, however, several instances of predominantly exo cycloaddition have been reported for reactions of halogen bearing cyclopropenes with cyclopentadiene,(3a) tetracyclone,(3b) and 1,3-diphenylbenzisofuran.(3b) On the other hand the parent hydrocarbon, cyclopropene, had been observed to undergo only endo cycloaddition with all dienes including substituted cyclopentadienones(4) and 6,6-dimethylfulvene.(5) In connection with previous work on cycloaddition reactions of cyclopropenes(2c,4,6) we have examined the reaction of cyclopropene and several of its derivatives with the reactive furan 1,3-diphenylisobenzofuran (I).(7,8) A recent communication(9) describing the stereochemistry of cycloadducts of cyclopropene with I prompted us to describe our own results with this reaction which are in conflict with those of the earlier report.

Cyclopropene, generated by the procedure of Closs and Krantz(10) (acid wash trap omitted), was passed into a methylene chloride solution of I until the fluorescence of the solution was quenched. Column chromatography of the crude reaction product afforded a crystalline 1:1 adduct in 63% yield, m.p. 83-84°,(11) which was homogeneous according to the usual criteria. No additional crystalline products were found. The n.m.r. spectrum (100 MHz) of this adduct imme-



diately pointed to the *exo* structure II. Thus in deuteriobenzene the cyclopropyl methylene hydrogens were found as a pair of doublet of triplets at δ 0.84 (J_{AB} = 5.2 Hz, J_{BX} = 6.74 Hz) and 1.84 (J_{AB} = 5.2 Hz, J_{AX} = 3.7 Hz) with the cyclopropyl bridge protons (H_X) observed as a doublet of doublets at 1.62. The observation that the lower field geminal proton (H_A) has the smaller vicinal coupling constant, confirming its *trans* relationship with the bridge hydrogens (H_X), is in sharp contrast with the n.m.r. spectra for all known *endo*-tricyclo-[$3.2.1.0^{2,4}$]octenes where the highest field proton demonstrates the lower vicinal coupling constant ($J_{\text{trans}} \approx 3.5$ Hz).(2d,4) The relatively low chemical shift for H_A is consistent with steric deshielding by the bridge oxygen.(12,13)

Confirmation of the *exo* stereochemistry for adduct II was achieved by an alternant synthesis of this system starting with 1,4-diphenyl-7-oxabenznorbornadiene (III). Treatment of III with diazomethane-cuprous bromide, a reagent known to effect *exo*-cyclopropanation of benznorbornadiene and related bicyclic olefins,(13) afforded II as the only isolated product aside from recovered starting material. To verify that the oxygen bridge of III had not altered the usual course of cyclopropanation the parent bridged ether IV was subjected to the same reaction. Again only the exo stereoisomer product V was formed and in this case the stereochemistry was unequivocably established by the appearance of the C-1,C-5 bridgehead protons as a sharp singlet in the n.m.r.(14)

In their study of the reaction of cyclopropene (acid wash trap included) with I, Geibel and Heindl(9) report the isolation of three adducts in the ratio 75:13:12 to which they assign structures VI, II, and VII, respectively. Although no physical or spectral properties were reported for these adducts, the major adduct was observed to undergo acid-catalyzed aromatization in acetic acid to give 2-acetoxymethyl-1,4-diphenylnaphthalene (VIIIa) while the isomeric adduct, assigned the exo structure, gave a benzcycloheptadienone on similar treatment. We find that the exo-adduct II is quantitatively converted to trifluoroacetate VIIIb (n.m.r.) in $CHCl_3$-CF_3CO_2H. Hydrolysis yields the known(15) β-napthylmethanol VIIIc. Similarly methanolysis of II in the presence of CF_3CO_2H affords the methyl ether VIIId in ca 70% yields. On this basis we conclude that the original stereochemical assignments of Geibel and Heindl(9) are in error and should be reversed, i.e., their major adduct must have the exo structure II. The reassignments are likewise in better mechanistic accord with the expected mode of cyclopropane ring opening on bridge scission.

An attractive rationale for the apparent discrepancy regarding formation of endo adduct VI lies in the mode of generation of cyclopropene. Since trans diol VII was previously(9) suggested to arise from bridge opening of the original cyclopropene adduct catalyzed by acid carried over from the aqueous sulfuric acid trap, it would appear entirely feasible to us that reversible acid-catalyzed dehydration of VII with resultant regeneration of the oxygen bridge should lead to VI as well as II. Experiments designed to check this possibility of an acid-catalyzed equilibration of adducts II and VI via diol VII are in progress.

Similar adducts of I have been obtained with substituted cyclopropenes including 1-methyl-, 1,2,3-triphenyl-, and tetrachlorocyclopropene; however, discussion of the structural details and chemistry of these adducts will be postponed for the full report.

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7. We have previously inferred (footnote 7, ref. 8) *exo* stereochemistry for cycloadducts of II and some trisubstituted cyclopropenes based on work reported in this communication and ref. 1c. See ref. 3b regarding stereochemical assignments for adducts of II with chloro-, dichloro-, and trichlorocyclopropenes.

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11. Occassionally material having a higher, but sharp m.p. (92-93°) was isolated which was identical in all spectral details (n.m.r., i.r., mass spectral) with the original lower melting sample. This appeared to be a function of the history of the sample and recrystallization technique.

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