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HALOGENATED KETENES. XIII. ON THE STEREOCHEMISTRY OF PHENYLHALO- AND PHENYLMETHYLKETENE CYCLOADDITIONS WITH CYCLOPENTADIENE.[1]

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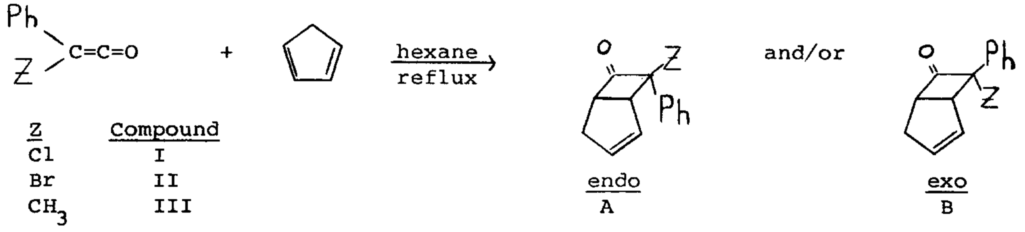
There are numerous reports on the cycloaddition of ketoketenes and olefins to produce substituted cyclobutanones. However, cycloadditions concerning unsymmetrical phenyl ketenes are rare. We have recently reported the preparation and subsequent *in situ* trapping of phenylchloroketene by 1,2-cycloaddition with cyclopentadiene.[3] We now wish to describe the stereochemistry of this reaction and that of other unsymmetrical phenyl ketenes.

The unsymmetrical nature of the ketenes involved introduces the possibility of two stereoisomers in this 1,2-cycloaddition reaction. It was anticipated that both isomers would be produced with a predominance of the *exo*-isomer B due to steric factors. However, nmr analysis indicated that the



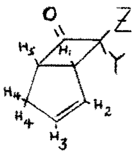
Z	Compound
Cl	I
Br	II
CH_3	III

cycloaddition proceeded stereospecifically to yield only the *endo*-isomer.

The preparation of the phenylchloroketene-cyclopentadiene adduct (I) has already been described.[3] The phenylbromoketene cycloaddition was accomplished by the dehydrochlorination of α-bromo-α-phenylacetyl chloride with triethylamine in the presence of cyclopentadiene under the same conditions to yield 53% of (II); bp 107° at 0.8 mm; ir, 1801 cm.$^{-1}$ (C=O), 1610 cm.$^{-1}$ (C=C). Calcd. for $C_{13}H_{11}BrO$: C, 59.4; H, 4.18. Found: C, 59.7; H, 4.06. Phenylmethylketene was prepared by the dehydrochlorination of 2-phenylpropanoyl chloride with triethylamine in hexane at room temperature, and distilled at 58° at 2.5 mm. A hexane solution of the ketene containing an excess of cyclopentadiene was refluxed for 6 hrs. Evaporation and recrystallization from ether afforded an 85% yield of (III); mp 29-30°; ir, 1773 cm.$^{-1}$ (C=O), 1603 cm.$^{-1}$ (C=C); Calcd. for $C_{14}H_{14}O$: C, 84.85; H, 7.07. Found: C, 84.9; H, 7.16.

The stereochemistry of the cycloadducts was determined from their nmr spectra. Table I reveals that an exo-halogen exerts a cross-ring deshielding effect on H_5 as compared to an exo-alkyl or aryl group. Moreover, an endo-phenyl group on C-7 exerts a shielding effect on the vinyl protons which are at least partially in its shielding cone. Since both effects are apparent for (I) and (II), these must be the endo-isomers. The vinyl resonance for (III) is as expected for an endo-phenyl. However, with no halogen on the number 7 carbon, the chemical shift of H_5 is no longer a clue as to the isomer involved.

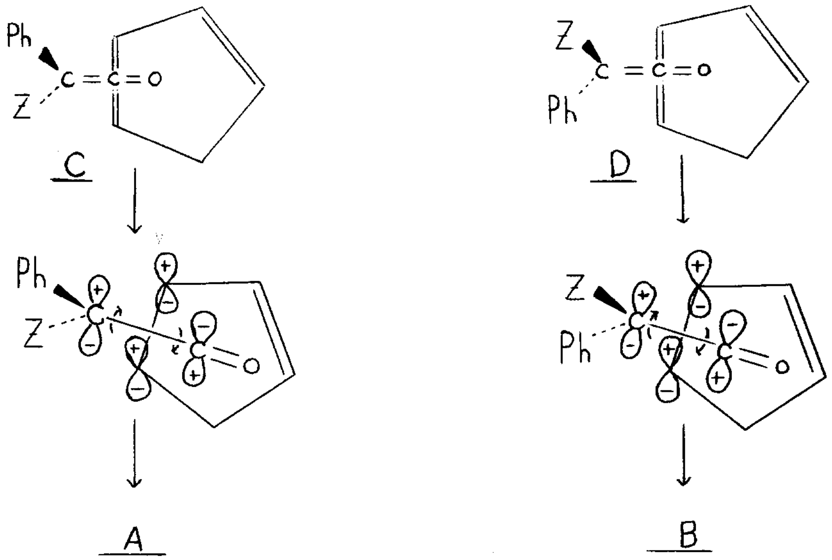
Table I. NMR Spectra



Compound	Z	Y	H_1	H_2 and H_3	H_4	H_5
I	Cl	C_6H_5	4.05	5.6	2.62	4.30
II	Br	C_6H_5	4.10	5.6	2.59	4.35
III	CH_3	C_6H_5	3.49	5.5	2.52	3.93
IV	C_6H_5	C_6H_5	4.23	5.6	2.67	3.78
V	CH_3	CH_3	3.15	5.8	2.70	3.95
VI	Cl	Cl	4.08	5.9	2.68	4.25

Nevertheless, a comparison of the methyl resonance of (III) with that of a brominated sample showed a shift from 1.61 δ to 1.63 δ. We have recently demonstrated[4] that the nmr spectrum of an exo-methyl group is essentially unchanged, while that of an endo-methyl is drastically altered upon bromination.

A thermal, concerted cycloaddition of ketenes to olefins must follow the $\left[{}_{\pi}2_{s} + {}_{\pi}2_{a}\right]$ path, according to the recent extension of the Woodward-Hoffmann rules for ketene cycloadditions.[5] Since this path involves an orthogonal approach of the ketene and olefin, a consideration of the two possible sterically preferred approaches is in order.[6] As these approaches become transition states, and cycloaddition occurs, it is apparent that orientation C (the sterically preferred geometry) will yield only the *endo*-isomer A, whereas orientation D will form only the *exo*-isomer B.



Thus, under the reaction conditions, it appears that the cycloaddition of phenylhalo- as well as phenylmethylketenes with cyclopentadiene results in the stereospecific formation of the *endo*-isomer. These results are most compatible with the recent revision of the Woodward-Hoffmann rules for ketene cycloadditions.

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6. The opposite orthogonal approach places the ketene substituents over cyclopentadiene, thus presenting a less favorable approach.