

A PHENYL-GROUP PARTICIPATION IN THE ANTISYMMETRIC ORBITAL INTERACTION
FOR [8 + 2] CYCLOADDITION OF TROPOTHIONE WITH DIPHENYLKETENE

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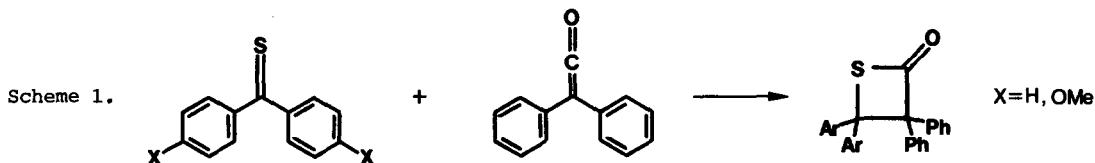
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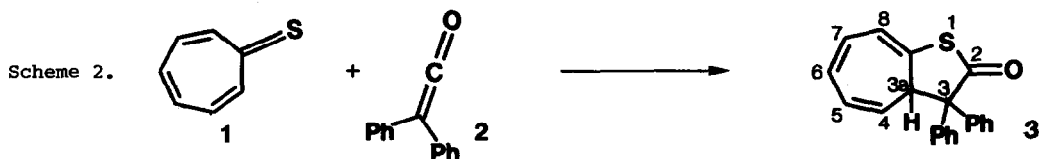
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Summary: Reaction of tropothione (1) with diphenylketene (2) gives regiospecifically an [8 + 2] cycloadduct (3) in high yield. Twisted phenyl groups in 2 intermix two vacant FMOs of the ketene moiety. This mixing brings about an appropriate site for the antisymmetric orbital interaction against the HOMO of 1. A phenyl carbon is found to assist this interaction.

Although there are numerous reports on the reaction of ketenes with carbonyl compounds,¹ those with thiocarbonyl compounds are rather few. Among these, Staudinger et al., in their early work on ketenes, noted that the addition of diphenylketene to thiobenzophenone and its 4,4'-dimethoxy derivative occurred quite readily at room temperature and 1:1 adducts were obtained in [2 + 2] manner.² As is shown in Scheme 1, Kohn et al. reinvestigated the reaction and reassigned the former product to the 3,3,4,4-tetraphenyl- β -thiolactone as opposed to the originally assigned 3-thietanone structure.³ We would like to report here that tropothione⁴ (1) undergoes cycloaddition readily with diphenylketene to form an enethiol lactone 3 of [8 + 2] adduct with high regioselectivity.⁵



Into a deep red solution of freshly prepared 1 in anhydrous benzene or carbon tetrachloride was added a freshly distilled diphenylketene⁶ dropwise with stirring, while the reaction temperature was maintained below 10 °C. The characteristic red color of 1 disappeared immediately after the completion of dropwise addition of diphenylketene. After solvent removal, chromatographic (silica gel, CCl₄) purification followed by recrystallization from benzene gave a cycloadduct (3) as the sole product (colorless prisms, mp 129-130 °C) in 84% yield (Scheme 2). ¹H NMR spectroscopic monitoring of the reaction (in CCl₄) proved the absence of significant amounts of other products.



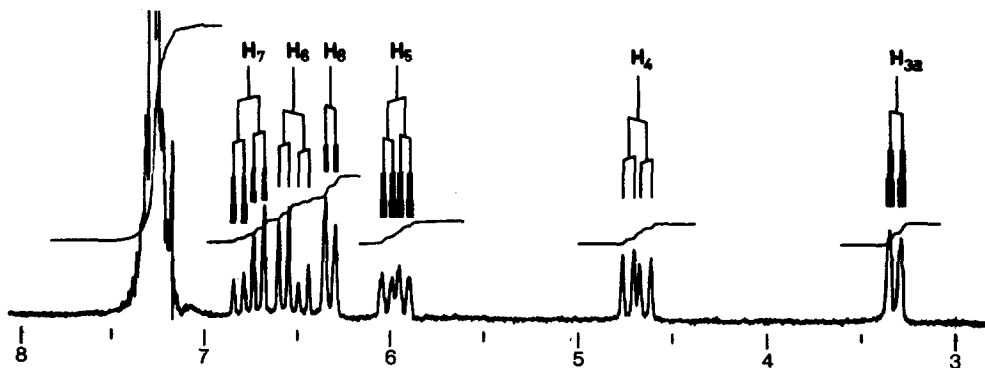


Figure 1. ^1H NMR spectrum (100 MHz, CDCl_3 , Me_4Si) of the adduct 3.

The structure of 3 is based on the following data.⁷ Elemental analysis and mass spectrometry (M^+ m/z 316) indicate that the product is a 1:1 adduct. The IR spectrum shows the very strong absorption of the carbonyl stretching vibration at 1711 cm^{-1} corresponding to an enethiol- γ -lactone. The ^1H NMR spectrum is amenable to the first-order ABCDEF pattern of six-spin systems (Figure 1), different from the obscure and complex one of the corresponding cycloadduct of tropone.⁸ The assignments and coupling constants are confirmed by double resonance experiments.⁹ The orientation of the cycloadduct is further supported through the analysis of nuclear Overhauser effect between phenyl protons, and H-3a and H-4 (35% and 13%, respectively).

In order to examine the orientation of the [8 + 2] cycloaddition, the optimized structure of the diphenylketene is determined with the Slater-type-orbital (STO-3G) MO calculation¹⁰ and is shown in Figure 2 to be nonplanar due to the phenyl-phenyl steric repulsion. The dihedral angle between the phenyl group and the ketene moiety is 33.69° . An interesting consequence of this rotation is found in the orbital mixing of two vacant frontier orbitals of the parent ketene, in-plane "lumo" (the lowest unoccupied molecular orbital in ketene) and out-of-plane "lumo + 1," which leads to lumo' and lumo+2' as is shown in Figure 3. The in-phase (symmetry-allowed) charge transfer (CT) interactions in our [8 + 2] cycloaddition are $\text{HOMO} \rightarrow \text{lumo}'$ and $\text{homo}' \rightarrow \text{LUMO}+2$. HOMO and homo' denote the highest occupied MO's of 1 and 2, respectively, and LUMO+2 stands for the third lowest unoccupied MO of 1. Since the STO-3G HOMO-lumo' energy gap 0.43 a.u. is smaller than the homo'-LUMO+2 one 0.64 a.u. (1 a.u. = 627.52 kcal/mol), the former CT is more dominant and consequently 2 acts as an electron acceptor.

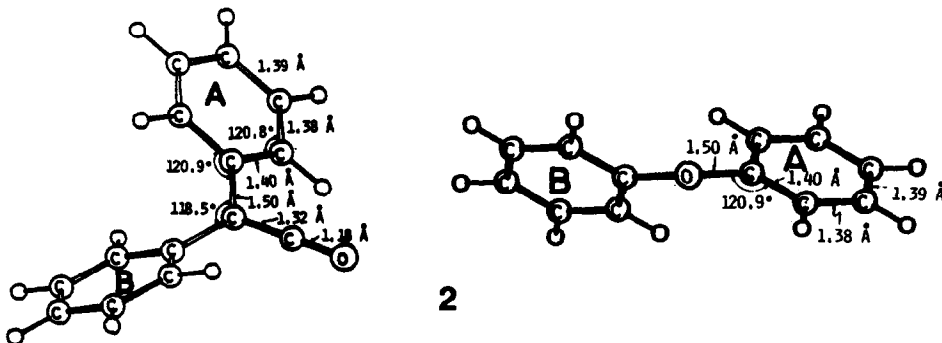


Figure 2. The STO-3G optimized structure of the C_2 -symmetry diphenylketene.

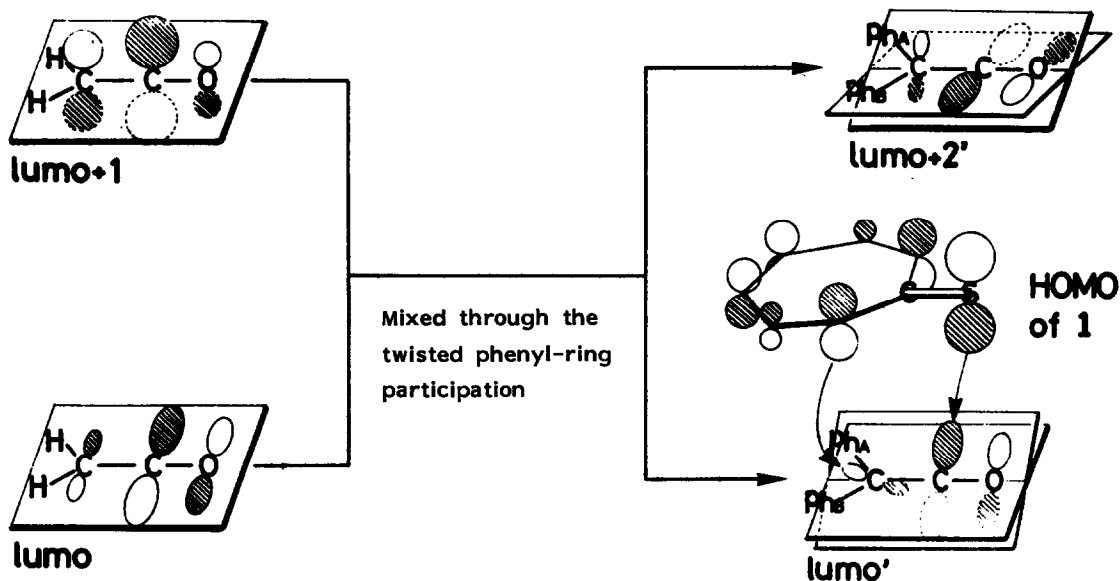


Figure 3. An orbital mixing of two FMOs from the parent ketene to diphenylketene. The charge transfer, HOMO \rightarrow lumo', leading to the $[\pi 8_s + \pi 2_s]$ path, is also shown.

The lumo' drawn in Figure 4 can match HOMO of 1 antisymmetrically. In the lumo', the C(sp²)-C(Ph) part is bonding, and the spatial extension on the carbonyl carbon deviates from the out-of-plane π direction (the inclined plane in Figure 3). In addition, the rotated phenyl ring "A" decreases the steric repulsion of the stack-approach of the tropothione plane along the bold-empty-arrow direction in Figure 4. These two conditions give rise to an effective antisymmetric HOMO \rightarrow lumo' CT interaction. Thus, the orientation of the present cycloaddition is $[\pi 8_s + \pi 2_s]$ ¹¹ through the phenyl-group assistance.

The second symmetry allowed $[\pi 8_a + \pi 2_a]$ approaching path is unfavorable due to the hindrance of a hydrogen at α position in the ring, and the $[\pi 8_s + \pi 2_s]$ route is better in the sense of the steric repulsion.

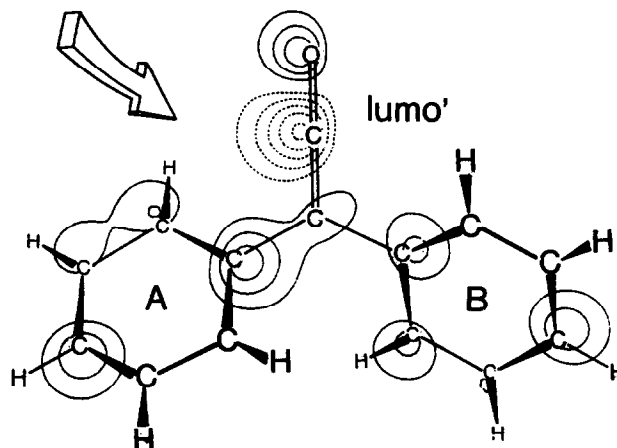


Figure 4. The contour line of the lowest unoccupied MO (lumo') of diphenylketene. In order to draw this π^* -type MO, the cut plane is set to 0.5 Å above the ketene molecular plane. The bold arrow indicates the direction of the tropothione approach.

Systematic study on the substituent dependence of the regioselectivity of the ketene cycloaddition is now under way.

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10. The GAUSSIAN 82 program is used. GAUSSIAN 82: J. S. Binkley, M. J. Frish, D. J. DeFrees, K. Raghavachari, R. A. Whiteside, H. B. Schlegel, E. M. Fluder, and J. A. Pople, Department of Chemistry, Carnegie-Mellon University, Pittsburg, PA 15213, U.S.A., 1982.
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