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# CYCLOADDITION REACTIONS OF CYCLOBUTENE WITH 7,9-DIALKYL-8H-CYCLOPENTA[a]ACENAPHTHYLEN-8-ONES. PHOTOAROMATIZATION AND VALENCE TAUTOMERISM[1]

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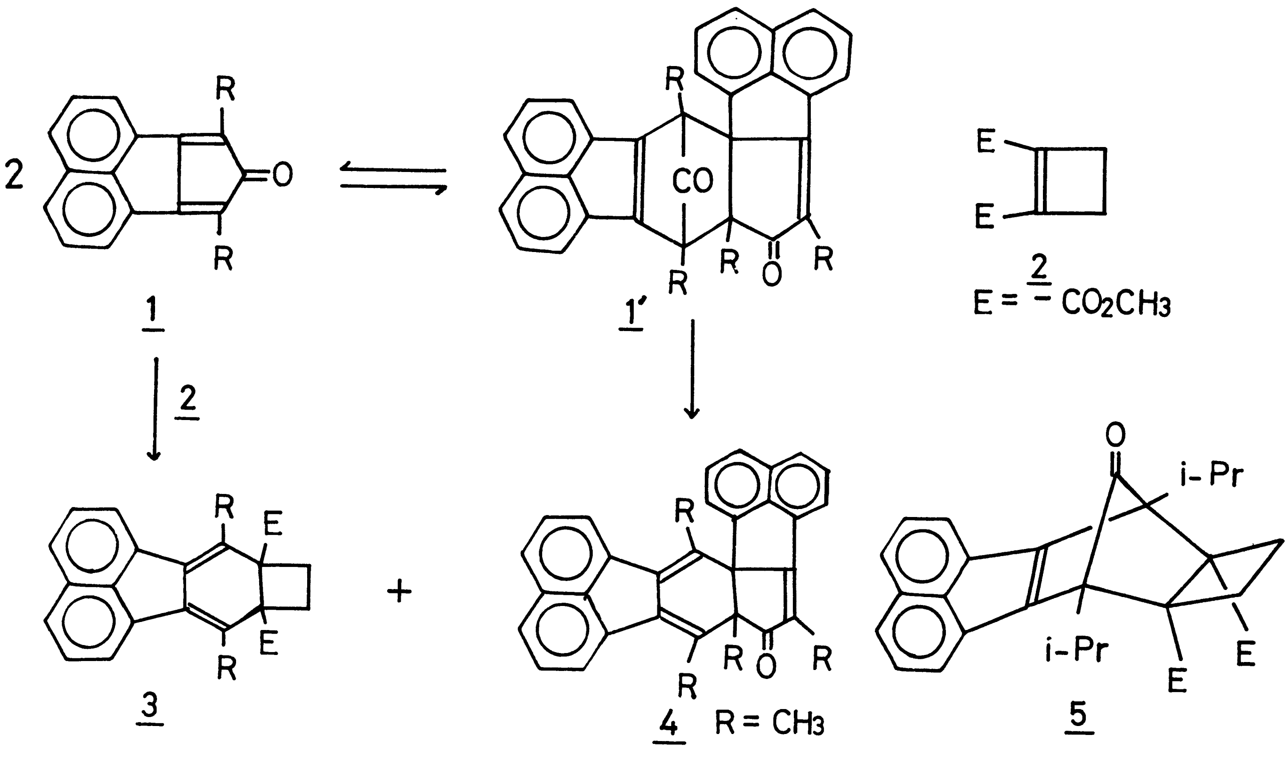
Reactions of 7,9-dimethyl-, 7,9-diethyl-, and 7,9-di-n-propyl-8H-cyclopenta[a]acenaphthylen-8-oneswith dimethyl 1-cyclobutene-1,2-dicarboxylate afforded the corresponding decarbonylated 1:1 adducts, while a similar addition of 7,9-diisopropyl-8H-cyclopenta[a]acenaphthylen-8-one onto the cyclobutene gave a 1:1 adduct. The photoaromatization and valence tautomerization of these adducts were examined.

Strained molecules such as cyclopropenes and cyclobutenes could be effective dienophile or dipolarophile, providing the synthetic potential to 6, 7, and 8-membered rings.[2] We wish to report the results on the thermal ( 4 + 2 )Π cycloadditions of 7,9-dialkyl-8H-cyclopenta[a]acenaphthylen-8-ones( 1 ) onto dimethyl 1-cyclobutene-1,2-dicarboxylate( 2 ), the adducts of which show some interesting chemical properties.

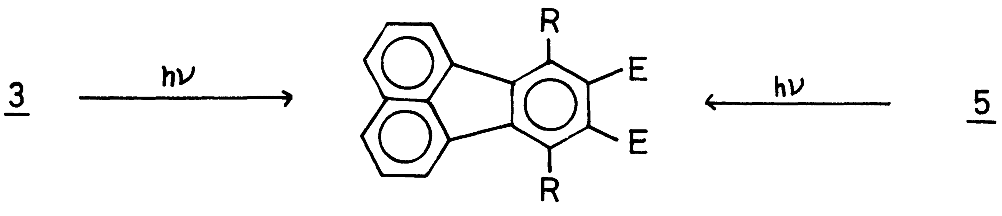
Heating a solution of 7,9-dimethyl-8H-cyclopenta[a]acenaphthylen-8-one ( 1; R=$CH_3$ )[3] and ( 2 ) in dry toluene under reflux for two days afforded a decarbonylated 1:1 adduct( 3; R=$CH_3$ ) and a decarbonylated dimer( 4; R=$CH_3$ ) in 45 % and 33 % yield, respectively; ( 3; R=$CH_3$ ) : mp 156 – 157°C[4], pmr $\delta_{TMS}(CDCl_3)$ 2.02 (6H, s), 2.1 – 2.4(2H, m), 2.8 – 3.2(2H, m), 3.67(6H, s), and 7.3 – 7.7(6H, m), ir(KBr) 1720 $cm^{-1}$; ( 4; R=$CH_3$ ): mp 278 – 280°C[4], pmr $\delta_{TMS}(CDCl_3)$ 1.15(3H, s), 1.53 (3H, s), 2.15(3H, s), 2.61(3H, s), and 7.1 – 8.0(12H, m), ir(KBr) 1648 and 1698 $cm^{-1}$. Similar reactions of 7,9-diethyl- and 7,9-di-n-propyl-8H-cyclopenta[a]acenaphthylen-8-ones ( 1; R=Et and n-Pr )[3] onto ( 2 ), on the other hand, gave only decarbonylated 1:1 adducts( 3; R=Et ) and ( 3; R=n-Pr ) in 77 % and 84 % yield, respectively; ( 3; R=Et ): mp 123 –124°C[4], pmr $\delta_{TMS}(CDCl_3)$ 1.19(6H, t, J=7.5 Hz), 2.0 – 3.2 (8H, m), 3.61(6H, s), and 7.3 – 7.8(6H, m), ir(KBr) 1729 $cm^{-1}$; ( 3; R=n-Pr ): mp 124.5 – 125°C[4] pmr $\delta_{TMS}(CDCl_3)$ 1.20(6H, t, J=8 Hz), 2.0 – 3.2(12H, m), 3.68(6H, s), and 7.4 – 7.8(6H, m), ir(KBr) 1730 $cm^{-1}$. The formation of the decarbonylated dimer in the case of ( 1; R=$CH_3$ ) may be due to the favoured equilibrium concentration of a dimeric form of ( 1'; R=$CH_3$ ). In fact, when R is replaced with a bulky isopropyl group, only a monomeric form of ( 1; R=iso-Pr ) exists.[3,5]



Reaction of the monomeric cyclopentadienone( 1; R=iso-Pr )[3] with ( 2 ) afforded the 1:1 adduct( 5 ) in 70 % yield; mp 153 − 154°C[4] , pmr $\delta_{TMS}$(CDCl$_3$) 1.13(6H, d, J=4.5 Hz), 1.25(6H, d, J=4.5 Hz), 2.2 − 3.0, 2.85(6H, m + broad s), 3.48(6H, s), and 7.2 − 7.9(6H, m), ir(KBr) 1723 and 1735(sh) cm$^{-1}$. The stereochemistry of methoxycarbonyl group was tentatively assigned as endo based upon chemical shifts of methoxycarbonyl protons.[6] The reluctance with which the adduct ( 5 ) decarbonylates thermally upto 250°C[7] is in striking contrast with the unstability of the corresponding methyl, ethyl, and n-propyl adducts, which decarbonylated spontaneously even in boiling benzene and therefore could not be isolated under the reaction conditions. The unusual reluctance for ( 5 ) to decarbonylate might be ascribed to steric hindrance to decarbonylation by isopropyl group which could veil a carbonyl group, and/or more probably to energetically unfavorableness for the decarbonylated adduct( 3; R=iso-Pr ) because of steric repulsion between methoxycarbonyl and isopropyl groups.[8]

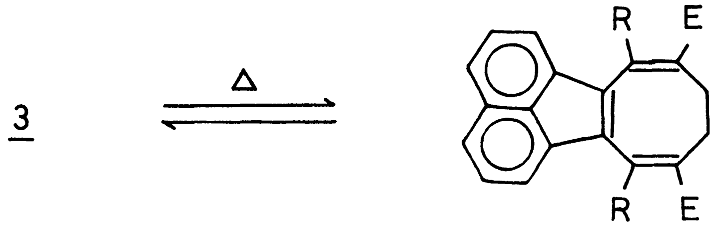
The irradiation[9] of the decarbonylated 1:1 adducts( 3; R=CH$_3$ ), ( 3; R=Et ) and ( 3; R=n-Pr ), and the 1:1 adduct( 5 ) in benzene or acetone gave moderate yields of the fluoranthene derivatives( 6a ), ( 6b ), ( 6c ), and ( 6d ), respectively; ( 6a ): mp 193 − 194°C[4,10], pmr $\delta_{TMS}$(CDCl$_3$) 2.66(6H, s), 3.92(6H, s), and 7.1 − 8.1 (6H, m), ( 6b ): mp 195 − 196°C(lit,[3] 195°C), ( 6c ): mp 161 − 162°C(lit,[3] 162°C), ( 6d ): 210 − 212°C[4,10], pmr $\delta_{TMS}$(CDCl$_3$) 1.53(12H, d, J=7 Hz), 3.88, 3.6 − 4.4(8H, s + m ), and 7.4 − 8,3(6H, m). Consequently, the photoaromatization of the bridged carbonyl compounds would proceed via the cyclohexadiene derivatives, the intermediate nature of which was previously suggested by Warrener et al.[9a]

The another interesting point is that the decarbonylated 1:1 adducts which crystallized out as ( 3 ) from ethanol could undergo thermal disrotatory valence



6a R = Me
b Et
c n-Pr
d iso-Pr

tautomerization[11] to the cyclooctatriene derivatives( 7 ), though slowly at room temperature, in chloroform, acetonitrile, DMSO etc. The presence of ( 7 ) was



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able to be seen from pmr chemical shifts of ester methyl protons observed at lower field and alkyl methyl protons in higher field in case of R=Et and n-Pr, and in lower field in case of R=Me, and further from ir ester carbonyl stretching frequency which appears at lower wave number( ca. 1710 $cm^{-1}$ ). The question about the relative stability of the cyclooctatriene and bicyclooctadiene remains essentially unsolved in spite of the elegant and rather systematic works of Huisgen et al.[12] and Cotton et al.[13] The preliminary examination of the equilibrium( 3 )$\rightleftharpoons$( 7 ) shows that the relative ratio ( 7 )/( 3 ) depends on R and temperature( Table ).

Table Percentage of ( 7 ) Determined by Pmr Analyses

| R | Me | Et | n-Pr |
|---|---|---|---|
| Solvent( Temp. ) | | | |
| Chloroform( 22°C ) | 9 | 26 | 28 |
| Dichlorobenzene( 22°C ) | 10 | 17 | 17 |
| ( 100°C ) | 15 | 33 | 33 |
| ( 150°C ) | 17 | 50 | 60 |

The increase in the concentration of ( 7 ) from R=Me to R=Et and n-Pr might be simply considered as steric effect, since the cyclooctatriene system is more mobile. This situation may be also reflected in larger temperature coefficient of the equilibrium for R=Et and n-Pr than for R=Me. The detailed investigation of these systems and heterocyclic analogue is in progress.

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7) The attempted thermal decarbonylation at 250°C resulted in the dissociation to the cyclopentadienone( 1; R=iso-Pr ).
8) Bicyclo[4,2,0]oct-7-ene, which is less substituted at reaction center, cycloadded onto ( 1; R=iso-Pr ), affording the decarbonylated 1:1 adduct, mp 89 – 90°C[4] ( 79 % yield ).
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