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PHOTOCYCLOADDITION OF PHENYLCYCLOALKENES

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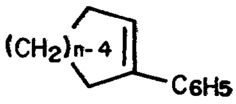
Phenylcyclopentene (I) dimerizes on irradiation at the same condition in which phenylcyclohexene (II) and phenylcycloheptene (III) give the adducts with methanol. Phenylcyclooctene (IV) does not give a dimer nor methanol adduct, but it isomerizes to trans-isomer at the same condition (1 - 3).

In the continuous work we tested the photocycloaddition of phenylcycloalkenes I, II, III, and IV to olefins, and found that those compounds do not give the cycloaddition products with simple olefins such as cyclopentene and cyclohexene but add to the more nucleophilic olefins such as dimethoxyethylene and furan.

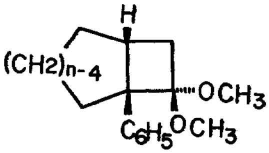
The solutions (10 ml) of phenylcycloalkenes in hexane (0.1 mol/l.) containing 18 equivalents of dimethoxyethylene were externally irradiated with a 450 W high pressure mercury lamp through a vycor filter under nitrogen for 5 hr. Most of the starting phenylcycloalkene disappeared in this period. The reaction mixtures were concentrated in vacuo and were purified by alumina chromatography. Elution with n-hexane and n-hexane - chloroform gave first small amount of the unreacted phenylcycloalkene and excess dimethoxyethylene, then the oily adduct. The adducts V, VI, VII, and VIII were further purified for the measurement of physical constants by carefull preparative vpc.

These adducts were thermally unstable and vpc at higher temperature (ca. 200°C) causes elimination of methanol giving enol ethers, especially easily with adducts VII and VIII. In the mass spectra of VII and VIII, strong peaks can be seen at m/e=228 and 242, respectively, which represent the fragment ions formed by elimination of methanol from the parent ions, and no parent peaks can be seen for these adducts.

Chemical shifts of two methoxy groups of adducts V, VI, VII, and VIII show a rather large difference (0.32 - 0.53 ppm), and this feature can be accounted for by magnetic anisotropy of the adjacent phenyl groups. Adduct VI acompanies an unidentified by-product (ca. 10%) having two methoxy groups (δ=3.12 and 3.28 ppm), which is most probably the orientational isomer IX of adduct VI.

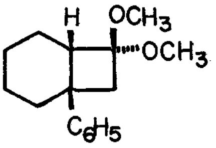


I : n=5
II : n=6
III: n=7
IV: n=8

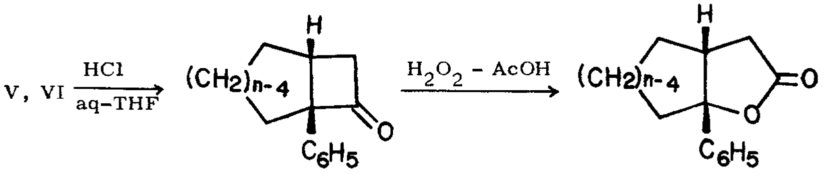


V : n=5
VI : n=6
VII : n=7
VIII: n=8

compound	mass (m/e)	nmr			yield (%)
		-OCH$_3^a$(δ)	-OCH$_3^b$(δ)	$\delta_a - \delta_b$	
V	232 (3 %, M^+) 144 (100 %, $C_{11}H_{12}$)	3.27	2.73	0.54	49
VI	246 (10 %, M^+) 158 (100 %, $C_{12}H_{14}$)	3.32	3.00	0.32	55
VII	228 (100 %, M^+- CH_3OH) 172 (24 %, $C_{13}H_{16}$)	3.30	2.77	0.53	33
VIII	242 (12 %, M^+- CH_3OH) 186 (52 %, $C_{14}H_{18}$)	3.30	2.77	0.53	64



IX



X : n=5
XI: n=6

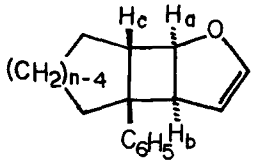
XII : n=5
XIII: n=6

Orientation of the methoxy groups of adducts V and VI was further confirmed by leading those adducts into lactones XII and XIII. The transformations were achieved by acid hydrolysis (4) of adducts V and VI followed by Bäyer - Villiger oxidation (5) of ketones X and XI. The lactones (M^+,m/e, 202 and 216, ir: 1780 and 1785 cm^{-1} for XII and XIII, respectively) have no nmr signal due to the α-hydrogen to lactonic oxygen.

cis -Junction of these adducts was inferred from the facts that the cycloaddition proceeds through a singlet state - described later - and stereoselectively giving a single adduct.

The solutions of phenylcycloalkenes in furan (0.4 mol/l.) were irradiated in the same manner as in the case of dimethoxyethylene for 24 hr, when considerable amount of the starting phenylcycloalkenes remained (20 - 30 %) but the reaction did not proceed appreciably thereafter due to the formation polymeric film on the wall of a reaction vessel. Purification of the products by alumina chromatography gave the oily adducts XIV, XV, XVI, and XVII.

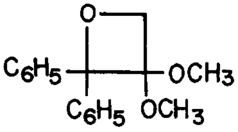
In the mass spectra of adducts XIV, XV, XVI, and XVII, prominent peaks are due to the ions of the phenylcycloalkenes which are formed by the rupture of furan moiety from the molecular ions, and those fragment ions are the heaviest ones in the spectra of XVI and XVII. The cis-anti-cis ring junction of adducts XIV, XVI, and XVII was deduced from the facts that the coupling constants of Ha with Hb and Hc are 7 - 8 Hz (Jab) and 2 - 4 Hz (Jac), and the cycloaddition proceeds stereoselectively giving a single adduct. Adduct XV must occupy a distorted conformation around the cyclobutane ring and the coupling constants do not allow the assignment of the mode of ring junction, but the same stereochemistry is assigned by analogy to other adducts.



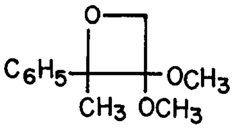
XIV : n=5
XV : n=6
XVI : n=7
XVII: n=8

compound	mass (m/e)	nmr			yield (%)
		Ha(δ)	Jab(Hz)	Jac(Hz)	
XIV	212 (1 %, M^+) 144 (100 %, $C_{11}H_{12}$)	4.36	8.0	2.0	39
XV	226 (1 %, M^+) 158 (100 %, $C_{12}H_{14}$)	4.93	6.0	6.0	29
XVI	172 (44 %, $C_{13}H_{16}$)	4.15	7.0	4.0	25
XVII	186 (30 %, $C_{14}H_{18}$)	4.44	8.0	4.0	24

In contrast to the photo-induced addition of methanol (1 - 3), the cycloaddition described in this paper shows no ring size effects. This difference suggests that these two reactions may take different excited states. The cycloadditions between phenylcyclopentene (I) and phenylcyclohexene (II) with dimethoxyethylene were subjected to sensitization by using benzophenone and acetophenone (50 equivalents to I or II), but no sensitization was observed and the aromatic ketones add to dimethoxyethylene giving oxetanes XVIII and XIX. The triplet energy of I and II must be about 62 kcal/mol (6), and the cycloaddition must be sensitized if the addition proceeds through a triplet state.



XVIII



XIX

The cycloaddition between phenylcyclopentene (I) (0.1 mol/l.) and dimethoxyethylene was not quenched by adding 1,3-pentadiene (0.01 - 0.5 mol/l.) to the reaction solution.

These results, absence of sensitization and quenching, imply that the cycloaddition takes place from a singlet state. This conclusion is in sharp contrast to the cycloaddition of indene (7) and diphenylethylene (8), which add to olefins by taking a triplet processes.

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