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VERSATILE SYNTHESES OF HETEROCYCLIC [n,3,4]PROPELLANES

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Pericyclic reactions of N-phenyl p-benzoquinone-2,3-dicarboxylic imide(PBI) with homo-diene and conjugated medium-ring polyenes have been examined. The high peri- and stereospecificity observed with dienes is explained using the frontier orbital model where the diene HOMO-PBI LUMO interaction predominates.

The cycloadducts of p-benzoquinone(BQ) with polyolefins are anticipated to be suitable precursors for the preparation of [$2\pi + 2\pi$]photocage compounds$^{1)}$. However, BQ is well known to act as a weaker dienophile in pericyclic reaction. In fact, BQ is proved to be inert to reaction with homo-diene and conjugated medium-ring polyenes such as norbornadiene, cycloheptatriene and tropone even at elevated temperature$^{2)}$. Recently we have reported$^{2)}$ that p-benzoquinone-2,3-dicarboxylic anhydride(PBA) behaves as a highly reactive dienophile in pericyclic reaction and also provides a simple synthetic route to new propellane molecule$^{3)}$. To provide some additional data for understanding these reaction modes, N-phenyl p-benzoquinone-2,3-dicarboxylic imide(PBI) as well as PBA seemed to be a highly reactive synthon for the pericyclic syntheses. Furthermore, the medicinal interest$^{4)}$ has prompted us to prepare the heterocyclic propellanes by the reaction of PBI.

In this communication, we present the results of our studies of the cycloaddition reactions of PBI with several polyolefins.

The LUMO energy of PBI was estimated 0.7 eV lower than that of BQ by means of Pariser-Parr-

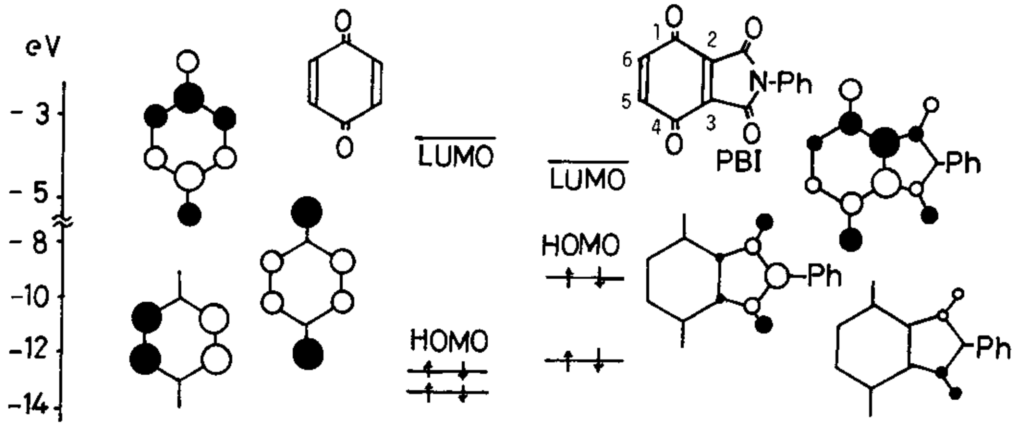


Figure 1. π Molecular orbitals of BQ and PBI.

Pople MO calculation[5)] as shown in Figure 1. It is predicted by using the energy and the relative coefficient magnitudes of LUMO that PBI behaves as highly reactive and LUMO controlled dienophile in the pericyclic reactions and also reacts predominantly at the sites of C_2-C_3 towards polyolefins.

Heating hydroquinone-2,3-dicarboxylic anhydride[6)] with an equimolor amount of aniline in acetic acid for 2 hr gave N-phenyl hydroquinone-2,3-dicarboxylic imide in 75 % yield, whose treatment with nitrogen dioxide in carbon tetrachloride at room temperature for 20 min afforded PBI[mp 235-238°(acetone), ir(cm^{-1}, nujol) 1730, 1660, nmr(acetone-d_6, δ) 7.12(s), 7.02-7,70(phenyl-H), mass(m/e) 253(M^+)] in quantitative yield.

When norbornadiene was added to PBI suspended in solvents such as nonpolar benzene and chloroform, and polar acetonitrile at reflux temperature, only a homo-Diels-Alder adduct 1 was formed in 90 % yield. It is to be noted that the exclusive formation of the adduct 1 could be explained as the result of the concerted fashion, since the reaction of norbornadiene with substituted acetylenic dienophile afforded homo-Diels-Alder adduct together with [2π + 2π] cycloadduct and Wagner-Meerwein rearrangement product *via* an ionic intermediate[7)].

In the similar manner, the reactions of quadricyclane, 6,6-dimethylfulvene and cycloheptatriene with PBI at room temperature gave the corresponding 1:1 adducts, 2, 3 and 4, in nearly quantitative yields. By contrast, more vigorous conditions were required for the reaction of tropone with PBI.

The results of the cycloaddition reactions are summarized in Table 1.

The stereochemistry of these adducts, 1-4, follows from the similarity of their NMR spectra(Table 1) to corresponding PBA adducts as previously reported by us[2)]. Further, the endo stereochemistry[8)] of 3 and 4 was confirmed by chemical transformation: irradiations of 3 and 4 in benzene solution formed the corresponding [2π + 2π]photocage compounds in excellent yields. The details about these photocage compounds will be mentioned in subsequent paper. On the other hand, the tropone adduct 5 was concluded to be normal [4π + 2π]cycloadduct: the NMR spectrum of 5 exhibits a characteristic pattern of the [4π + 2π]tropone adducts[9)]. Although no chemical evidence exists as to the endo or exo nature of the enedione moiety[8)] in 5 at the present stage, the HOMO-LUMO interactions and the secondary interactions[10)] as depicted in Figure 2 should favor the endo orientation.

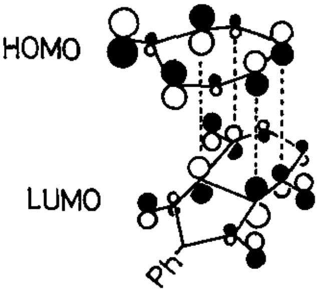
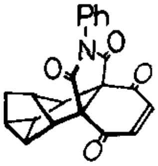
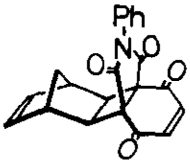
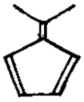
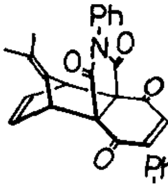
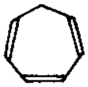
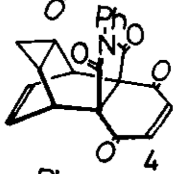
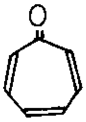
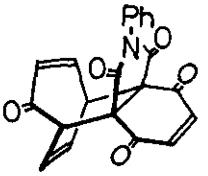


Figure 2. HOMO-LUMO interactions and secondary interactions for the cycloaddition of tropone with PBI.

Other aspects of the chemistry of PBI are currently under investigation in our laboratory.

Table 1. Cycloaddition of PBI with polyolefins.

Addend	Condition employed	Product	mp,°C	Yield	^{1}H NMR spectrum($CDCl_3$,δ)
	$CHCl_3$ refux 40 min.	 1	218 (decomp.)	90 %	1.21(d,J=4.0,2H) 1.50(m,1H) 1.57(s,2H) 2.00(bs,1H) 3.10 (bs,2H) 6.83(s,2H) 7.20-7.50 (phenyl-H)
	C_6H_6 room temp. 20 min.	 2	258	quant.	1.45(bs,1H) 1.59(s,1H) 2.60 (s,2H) 3.32(m,2H) 6.12(m,2H) 6.89(s,2H) 7.20-7.50(phenyl-H)
	$CHCl_3$ room temp. 10 min.	 3	214 (decomp.)	quant.	1.62(s,6H) 4.40(m,2H) 6.42(m, 2H) 6.68(s,2H) 7.02-7.45 (phenyl-H)
	$CHCl_3$ room temp. 30 min.	 4	210	quant.	0.20(m,1H) 0.35(m,1H) 1.25(m, 2H) 4.15(m,2H) 5.85(dd,J=8.5, 3.5,2H) 6.80(s,2H) 7.00-7.50 (phenyl-H)
	C_6H_5Cl reflux 2 hr.	 5	205 (decomp.)	76 %	4.30(dd,J=8.0,7.0,1H) 4.45(dd, J=7.5,1.8,1H) 5.76(dd,J=11.0, 1.8,1H) 6.44(t,J=8.0,7.5,1H) 6.76(t,J=8.0,7.0,1H) 7.10(q, J= 11.0,8.0,1H) 7.04(s,1H) 7.08(s,1H) 7.08-7.60(phenyl-H)

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