

complex formation between echinomycin and the DNA hexamer using solution NMR.

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Photochemistry of 4-Biphenyl-4-Methyl-2-Cyclohexenone: Solvent Effect on the Excited States

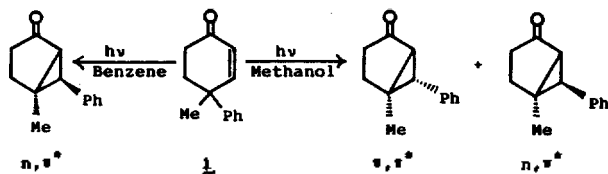
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The photochemical rearrangement of 4,4-disubstituted cyclohexenones¹⁻⁵ are well known, and mechanism involving solvent effects on the excited states of the enones were proposed in Dauben's earlier publication.⁴

Irradiation of the enone **1** in benzene, a nonpolar solvent, gave product arising from n, π^* triplet state, while in polar solvent such as methanol gave the product arising from the both of n, π^* and π, π^* triplet state.



Recently Zimmerman^{1,2} and his co-workers investigated the photochemical behavior of bichromophoric excited states of 4,4-dibiphenylcyclohex-2-enone (**2**)

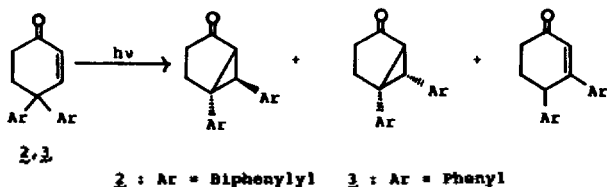


Table 1. Product Distribution on Irradiation of **4** in Different Solvent Polarity

Solvent	Φ			Relative Amounts (%)	
	4	5	6	5	6
Benzene	"	"	"	98	~2
Methanol	0.0070	0.0033	0.0007	82	18

Φ : quantum efficiency. "not determined"¹⁰.

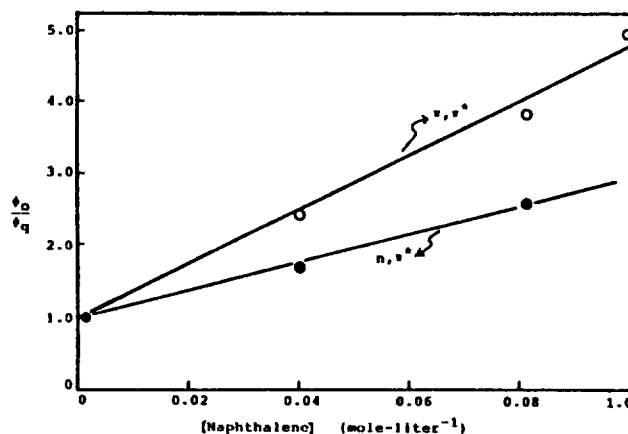
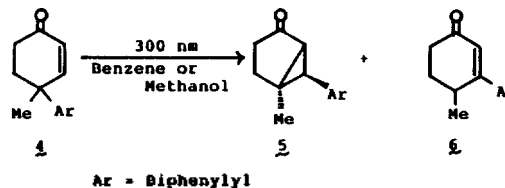


Figure 1. Stern-Volmer plot of triplet quenching of formation of **5** (●) and **6** (○) in methanol.

Since biphenyl groups on the C-4 position of the enone moiety produce the same type of photoproducts as 4,4-diphenylcyclohexenone (**3**) photochemistry¹¹, 4-biphenyl-4-methyl-2-cyclohexenone (**4**) was synthesized and the solvent effect on the excited state of the enone **4** involving the relative energy levels of n, π^* and π, π^* triplet states was investigated.

Direct irradiation of the enone **4** in benzene with 16 RPR-3000 Å lamps produced *trans*-5-methyl-6-biphenylbicyclo[3.1.0]hexan-2-one⁶ (**5**) and 3-biphenyl-4-methylcyclohex-2-enone (**6**) in trace.



When polar solvent such as methanol was used for irradiation of **4**, relative amount of the product⁷ **6** was increased as shown in Table 1.

Sensitized irradiation of the enone **4** with acetophenone produced the products as direct irradiation with the same product ratios.

Stern-Volmer type analysis for the products **5** and **6**, products possibly representative of the reactions from different triplet states, were undertaken in methanol using naphthalene ($E_T=91$ Kcal) as a quencher.

The results are shown in Figure 1 and the difference observed in the slopes for the quenching is indicative of the involvement of two excited states of different lifetimes^{12,9}.

It seems reasonable that there be a quantitative correlation between the lifetime of these excited states; n, π^* triplets have shorter lifetimes than π, π^* triplets. If this be the case, then the plots in Figure 1 further demonstrate the n, π^* character of the triplet involved in the formation of **5** and the π, π^* character of the triplet involved in the formation of the enone **6**. Undoubtedly, the solvent effect only becomes important when the n, π^* and π, π^* triplet states are very close in energy.

In the photochemistry of 2-cyclohexenone, not only the phenyl group on C-4 position of the enone shows solvent effects but also the aryl group such as biphenyl on C-4 position shows the same solvent effects. Some other substituents such as α -naphthyl and β -naphthyl on C-4 position of the enone with different solvent polarity are under investigation.

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- Spectral data for **5**: NMR(CDCl₃) δ 7.2-7.8 (m, 9H, biphenyl) 2.6-2.8 (d, 1H, cyclopropyl) 2.1-2.2 (d, 1H, cyclopropyl) 1.7-2.2 (m, 3H, cyclopentyl) 1.0-1.4 (m, 1H, cyclopentyl) 1.5 (s, 3H, methyl); IR 3100, 2900, 1715; Mass (m/e) 262, 221, 220, 219, 205, 204, 203; Anal. Calcd. C₁₉H₁₈O: C, 86.99; H, 6.92. Found: C, 87.24; H, 6.85.
- Spectral data for **6**: NMR(CDCl₃) δ 7.2-7.8 (m, 9H, biphenyl) 6.3 (s, 1H, cyclohexene) 3.0-3.4 (m, 1H, methine) 1.8-2.8 (m, 4H, methylene) 1.2 (d, 3H, methyl); IR 3100, 2900, 1665; Mass(m/e) 262, 234, 233, 205, 192, 189, 178, 165, 152; Anal. Calcd. C₁₉H₁₈O: C, 86.99; H, 6.92. Found: C, 86.14; H, 6.60
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- (a) Light output was monitored by potassium ferrioxalate actinometry according to the method of Hatchard and Parker, *Proc. Roy. Soc., A* 235, 518 (1956); (b) Quantum efficiencies for the compounds **4**, **5** and **6** in benzene were not determined since the reactions were reversible at room temperature.
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gem-Dibromination of Diazo Compounds

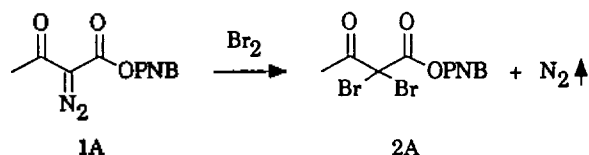
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Diazo chemistry has attracted considerable interests due to its broad applicability combined with facile reactivity. Furthermore, recent development of new synthetic methodology, such as diazo group transfer and diazoalkane substitution, has made these area of chemistry more feasible in the field of carbene and cycloaddition chemistry¹. Recently rhodium (II) acetate mediated intramolecular metal-carbene insertion in the fields of β -lactam antibiotics² and natural products³ receives a significant attention.

During the research of carbapenem antibiotics, we found that diazo compound can be converted to dibromide by the reaction of molecular bromine. Although a successful synthesis of *gem*-dihalide have been reported using various halogenation reagents, such as molecular halogens⁴, sulfuryl chloride⁵, *N*-bromosuccinimide⁶, trifluoromethanesulfonyl chloride⁷, and perchloryl fluoride⁸, their application has been rather limited to active methylene compounds. Therefore, further development of synthetic methods for various dihalides is still warranted. Dibromide has been used often for synthesis of resorcinols and oxadiazoles⁹, and regioselective synthesis of dihydrofurans *via* 1,3-dipolar cycloaddition^{6,9} or intermolecular trapping by olefin cycloaddition¹⁰. Because of its versatility, it can be further utilized for construction of the heterocyclic compounds. Here we report the new synthetic methodology of *gem*-dibromination utilizing diazo compounds, such as α -diazoester, diazomethane derivative, diazo acetoacetates, and diazomalونات.



When 2-diazo-*p*-nitrobenzyl (PNB) acetoacetate (**1A**) was treated with bromine, 2-dibromo acetoacetate (**2A**) was obtained as evidenced by IR and mass spectra¹¹. Although the proton NMR spectroscopy for the two compounds looks similar, disappearance of $\nu=2130 \text{ cm}^{-1}$ for the diazo group and the presence of two bromine by the examination of mass spectra clearly confirm the structure for the dibromo compound **2A**. Encouraged by this result, we applied this method to the preparation of various dibromides from diazo compounds. The diazo acetoacetates and diazomalونات (**1A-C**, **F-H**) were obtained from the corresponding acetoacetates and malonates by the diazo transfer reaction¹². PNB acetoacetate and PNB propionylacetate were obtained by transesterification of ethyl acetoacetate and ethyl propionylacetate, respectively, with *p*-nitrobenzyl alcohol. The starting ethyl propionylacetate was prepared by treating ethyl cyanoacetate with ethyl magnesium bromide followed by hydrolysis th-