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 imporstant 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 biphenylyl 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.

Acknowledgement. This work was supported financially by the Basic Science Research Institute Program (1991).

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6. Spectral data for **5**: NMR($CDCl_3$) 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. $C_{19}H_{18}O$: C, 86.99: H, 6.92. Found: C, 87.24: H. 6.85.
7. Spectral data for **6**: NMR($CDCl_3$) 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. $C_{19}H_{18}O$: C, 86.99: H, 6.92. Found: C, 86.14: H. 6.60
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10. (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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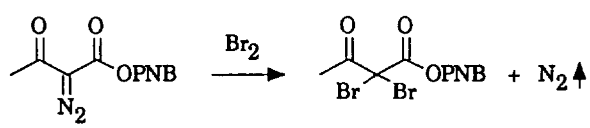
Received February 11, 1992

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 chemistry[1]. Recently rhodium (II) accetate mediated intramolecular metal-carbene insertion in the fields of β-lactam antibiotics[2] and natural products[3] receives a significant attention.

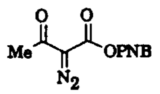
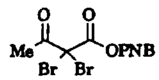
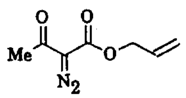
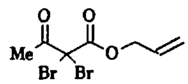
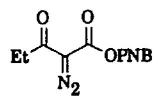
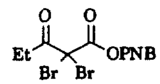
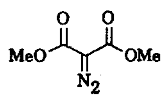
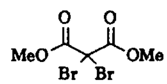
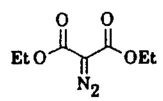
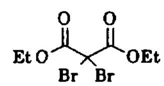
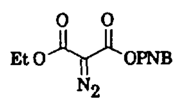
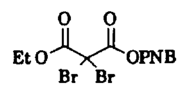
During the research of carbapenem antibiotics, we found that diazo compound can be converted to dibromide by the reaction of molecular bromine. Although a successful synthesis of *gem*-dihalide have been reported using various halogenation reagents, such as molecular halogens[4], sulfuryl chloride[5], *N*-bromosuccinimide[6], trifluoromethanesulfonyl chloride[7], and perchloryl fluoride[8], 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 oxadiazoles[4], and regioselective synthesis of dihydrofurans *via* 1,3-dipolar cycloaddition[6,9] or intermolecular trapping by olefin cycloaddition[10]. 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 diazomalonates.



1A 2A

When 2-diazo-*p*-nitrobenzyl (PNB) acetoacetate (1A) was treated with bromine, 2-dibromo acetoacetate (2A) was obtained as evidenced by IR and mass spectra[11]. Although the proton NMR spectroscopy for the two compounds looks similar, disappearance of $v=2130$ 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 diazomalonates (1A-C, F-H) were obtained from the corresponding acetoacetates and malonates by the diazo transfer reaction[12]. 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-

Table 1. *gem*-Dibromination of Diazo Compounds

Entry	Reactant(1)[a]	Product(2)[b]	Yield(%)[c]
A[d]			87
B			85
C			90
D	$N_2CHCOEt$ (C=O)	$Br_2CHCOEt$ (C=O)	75
E	Ph_2CN_2	Ph_2CBr_2	73
F			85
G			85
H			89

[a] see ref. 12. [b] all compounds were characterized by IR, MS, and NMR spectra. [c] isolated yields. [d] PNB = *p*-nitrobenzyl.

rough aqueous work up. Allyl acetoacetate was obtained by alcoholysis of diketene. Ethyl PNB malonate was prepared by the treatment of mono-potassium salt of ethyl hydrogen malonate[13] with *p*-nitrobenzyl bromide in the presence of catalytic amount of 18-crown-6. Commercially available ethyl diazoacetate (1D) was used and diphenyl diazomethane (1E) was prepared by oxidation of benzophenone hydrazone with yellow mercuric oxide[14].

A general procedure is as follows. To a solution of 1A (0.51 g, 1.93 mmol) in CH_2Cl_2 (20 m*l*) was added dropwise a solution of Br_2 (0.21 m*l*, 4.24 mmol) in CH_2Cl_2 (5 m*l*) at room temperature for 5 min. The reaction mixture gave the evolution of N_2. The mixture was additionally stirred for 30 min at the same temperature. The resulting solution was successively washed with 5% $NaHSO_3$ solution and water, and dried over anhydrous $MgSO_4$. Evaporation of the solvent *in vacuo* gave 2A (0.67 g, 87%) in oil.

Using the procedure described above, various diazo compounds were brominated to afford the corresponding dibromides. The results are shown in Table 1. As shown in the table, this pathway is quite general for the synthesis of dibromides from carbonyl or active methylene compounds containing diazo group, and applicable to synthesis of many heterocyclic compounds and hydrocarbons.

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11. IR(neat): v=1720, 1610, 1520, 1350 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ=2.64 (s, 3H), 5.43 (s, 2H), 7.58 (d, 2H, J=8.8 Hz), 8.26 (d, 2H, J=9.0 Hz). ^{13}C-NMR ($CDCl_3$): δ=23.1, 58.4, 123.5, 128.1, 141.0, 147.5, 162.9, 190.9. MS (70 eV): *m/z* (relative intensity)=394 (1.2), 396 (1.9), 398 (1.1). Anal. Calcd for $C_{11}H_9NO_5Br_2$: C, 33.4; H, 2.30; N, 3.50. Found: C, 34.4; H, 2.30; N, 3.70.
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A Synthetic Approach to Hydrindanes *via* the Homologous Michael Addition to Tricyclo[4.3.0.0^{1,5}]nonanes

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Received January 3, 1992

Since several efficient ways have been developed to synthesize cyclopropanes,[1] their transitory formation has been often employed in terpene synthesis.[2] Furthermore, recent advances in asymmetric cyclopropanations provide chiral cyclopropanes,[1,3] which can be appropriately transformed into chiral complex molecules. The most versatile chemistry of cyclopropanes certainly stems from their nucleophilic cleavage, which is known to occur in the presence of one or more electron-withdrawing groups on the ring. Since the nucleo-