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PHOTOISOMERIZATION OF NORBORNADIENE TO QUADRICYCLANE IN THE PRESENCE OF COPPER(I)-NITROGEN LIGAND CATALYSTS

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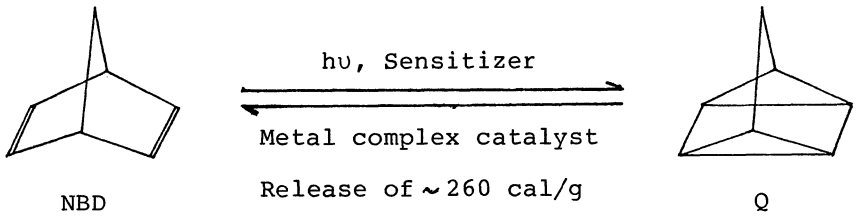
Use of copper(I)-nitrogen ligand catalysts, such as $Ph_3PCuCl.bipy$ (1), $Ph_3PCuCl.phen$ (2), $Ph_3PCuCl.phtha$ (3), and $Ph_3PCuBr.py$ (4), enables the photochemical isomerization of norbornadiene to quadricyclane in longer wavelength than 350 nm, in which CuCl catalyst itself can not induce such an isomerization.

Photochemical solar energy conversion has recently received wide attention. One of the most promising systems is the photoisomerization of norbornadiene (NBD) to quadricyclane (Q) (eq 1).[1)]



(eq 1)

Since norbornadiene does not absorb light in the wavelength region of solar radiation (>300 nm), an appropriate sensitizer is required to achieve the above transformation under solar irradiation. The most attractive and popular sensitizer is definitely CuCl, which has been studied principally by C. Kutal.[2)] An important problem that arises from this catalyst system is that the CuCl-NBD complex does not absorb light in longer wavelength than 350 nm (Fig 1). This causes a serious drawback for CuCl catalyst, since thermally utilizable range of the spectrum of the sun is >300 nm. From both practical and theoretical angles, it is highly desirable to develop a new catalyst which works in longer wavelength. We now wish to report that use of

copper(I)-nitrogen ligand catalysts (1 - 4)[3] solves some of the inherent problems associated with CuCl catalyst.

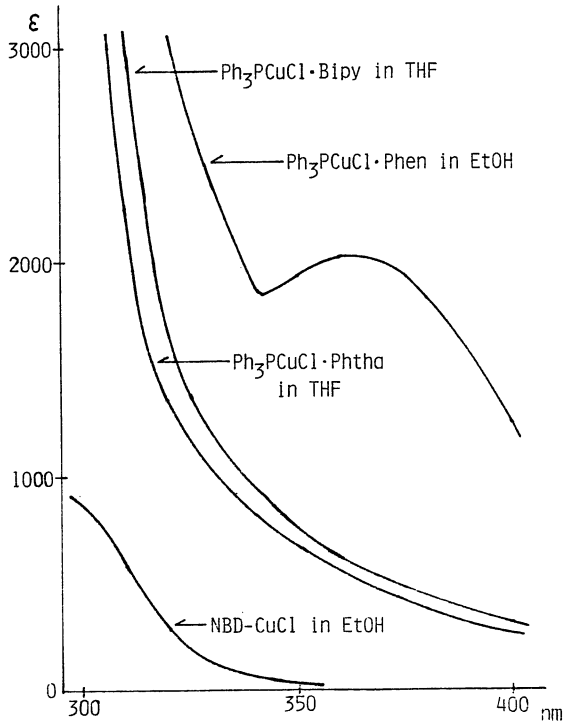
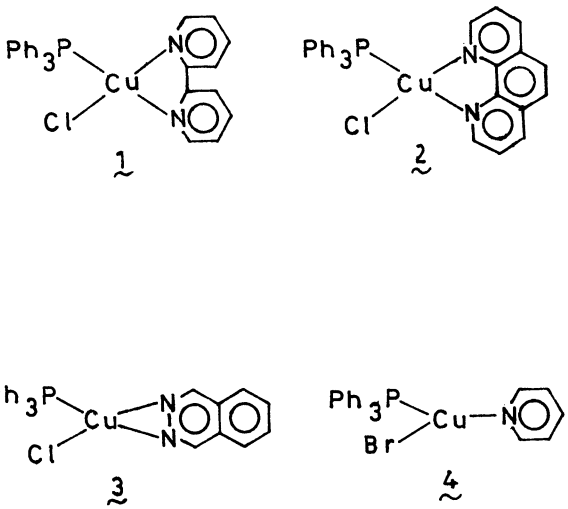


Fig 1. UV spectra of Cu(I)-nitrogen ligand complexes.



The results are summarized in Table 1. While the isomerization from NBD to Q is negligible with CuCl catalyst under the irradiation condition (>320 nm), copper(I)-nitrogen ligand complexes promote the isomerization without the formation of by-products. Among such complexes, $Ph_3PCuCl.phtha$ (3) is the most effective, and the turnover number increases with prolonged irradiation. Fig 2 indicates the UV spectra of a mixture of NBD and 1 in THF, and NBD and 3 in THF. It is clear that simple sum of the spectrum of NBD and that of individual Cu(I)-nitrogen ligand catalyst leads to the spectrum of the mixture, indicating that the formation of complex between NBD and the copper derivatives does not occur in the ground state. This is also supported by the fact that the isomerization proceeds smoothly even in CH_3CN (Table 1) which coordinates Cu(I) more strongly than NBD coordinates Cu(I).[4] Consequently, the mechanism is tentatively proposed which involves energy transfer from the excited Cu(I) complex to the ground state NBD.[5]

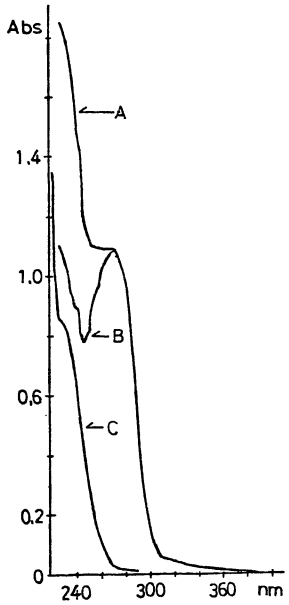
Table 1. Photochemical Isomerization of NBD to Q in the Presence of Copper Catalysts[a].

Cu (I)	Solvent	Turnover Number[b]
$Ph_3PCuCl.bipy$ (1)	THF	15
	CH_3CN	10
$Ph_3PCuCl.phen$ (2)	EtOH	7
$Ph_3PCuCl.phtha$ (3)	THF	8
	EtOH[c]	~17
$Ph_3PCuBr.py$ (4)[d]	THF	3
CuCl	THF	0.4

[a] All irradiations were performed for 120 h by using a tungsten-halogen lamp (>320 nm); [NBD] = 0.5 M, [Cu(I)] = 0.002 M. [b] Turnover number = (molar quantity of Q after 120 h)/(molar quantity of catalyst). [c] The solubility of 3 in EtOH at room temperature was quite low. On warming, the solution turned pale yellow and small amounts of white precipitates appeared. Since we used this supernatant liquid, the exact concentration of Cu(I) must be lower than 0.002 M.
[d] [NBD] = 0.2 M.

$$\text{Cu(I)} \xrightarrow{h\upsilon} \text{Cu(I)}^* \xrightarrow{\text{NBD}} [\text{Cu(I)}\cdot\text{NBD}]^* \longrightarrow \text{Q} + \text{Cu(I)}$$

The quantum yields for the isomerization at 313 nm were obtained; 0.063 for 1 in THF, 0.032 for 2 in EtOH, and 0.13 for 3 in EtOH.[6] These values are lower than the quantum yield for CuCl itself (0.27 - 0.42 at 313 nm).[2] However, the nitrogen ligand complexes are effective even at 366 nm in which CuCl can not be utilized, though the quantum yields are not high; 0.008 for 1 in THF and 0.011 for 3 in EtOH.[6]

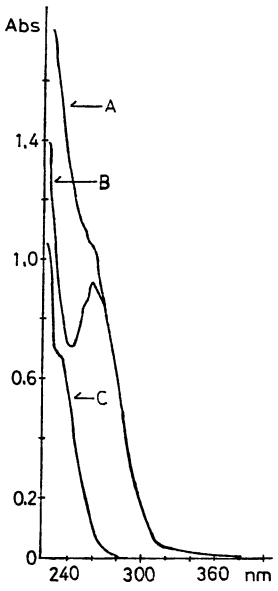


A; 4.3 X 10^{-5} M $Ph_3PCuCl.bipy$ (1) + 4.3 X 10^{-3} M NBD

B; 4.3 X 10^{-5} M $Ph_3PCuCl.bipy$ (1)

C; 4.3 X 10^{-3} M NBD

Solvent; THF



A; 5.0 X 10^{-5} M $Ph_3PCuCl.phtha$ (3) + 4.2 X 10^{-3} M NBD

B; 5.0 X 10^{-5} M $Ph_3PCuCl.phtha$ (3)

C; 4.2 X 10^{-3} M NBD

Solvent; THF

Fig 2. UV Spectra of NBD - Copper Complex System

References and Notes

1) T. Laird, Chem. and Ind., 1978, 176.

2) D. P. Schwendiman and C. Kutal, J. Am. Chem. Soc., 99, 5677(1977).

3) $Ph_3PCuCl.bipy$ (1), $Ph_3PCuCl.phen$ (2), and $Ph_3PCuBr.py$ (4) were synthesized from $[CuXPPh_3]_4$ (X = Cl or Br) and nitrogen ligands. See, J. H. Jardine, L. Rule, and A. G. Vohra, J. Chem. Soc., (A), 1970, 238. $Ph_3PCuCl.phtha$ (3) was synthesized similarly; mp 196 - 199 °C (decomp.); Found: C, 62.93; H, 4.19; N, 5.12%. Calcd: C, 63.55; H, 4.31, N, 5.70%.

4) Schwendiman and Kutal reported that use of CuCl catalyst in CH_3CN did not induce the isomerization. The reason was ascribed to the strong coordination of CH_3CN to Cu which inhibited the formation of CuCl - NBD complex.[2)]

5) Similar mechanism is proposed in the case of copper(I)-phosphine compound. See, P. A. Grutsch and C. Kutal, J. Am. Chem. Soc., 101, 4228(1979).

6) See Table 1 footnote c.

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