Tetrahedron Letters,Vol.30,No.45,pp 6193-6194,1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Pergamon Press plc

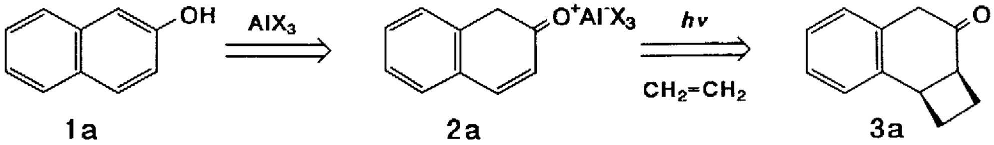
NOVEL PHOTOCYCLOADDITION OF 2-NAPHTHOLS TO ETHYLENE IN THE PRESENCE OF LEWIS ACID

Masaki Ue, Masahiko Kinugawa, Kiyomi Kakiuchi*, Yoshito Tobe, and Yoshinobu Odaira

Department of Applied Fine Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

Summary: The photoreaction of 2-naphthols **1a-e** with ethylene in the presence of aluminum halide gave the [2+2] cycloadducts **3a-e** in good yields.

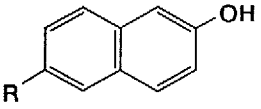
While [2+2] photocycloaddition of naphthalene derivatives to olefins has been extensively studied,1) such reaction of naphthols has been unknown except for that of 2-naphthol (**1a**) with acrylonitrile.2) On the other hand, it has been shown that phenol derivatives, for example, **1a** forms complex **2a** with aluminum halide involving α, β-unsaturated ketone moiety.3) In addition, photoisomerization of $AlBr_3$ complex of some phenol derivatives has been described.4) In view of the well-known photochemistry of α, β-enones,5) these observations led us to postulate that it would be possible to perform [2+2] photocycloaddition of 2-naphthol (**1a**) to olefin in the presence of aluminum halide to give cycloadduct **3a** by means of photoexcitation of the complex **2a**.6)



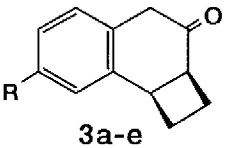
First, photoreaction of **1a** with ethylene was carried out. When CH_2Cl_2 solution of **1a**, $AlCl_3$ (2 equiv.), and ethylene (large excess) was irradiated with a high pressure mercury lamp through a Pyrex filter at -78 °C for 8 h, photoreaction proceeded smoothly (conv. >70%) to give [2+2] cycloadduct **3a** 7) in 49% yield along with some by-products including **4a** (3%).8) Moreover, with using 5 equiv. of $AlCl_3$, cycloadduct **3a** was obtained more efficiently in 70% yield with negligible amount of by-products except for **4a** (12%). Similar results were obtained when $AlBr_3$ (2 equiv.) was employed instead of $AlCl_3$ (**3a**: 63%, **4a**:15%). Of the Lewis acids examined ($TiCl_4$, $BF_3{\cdot}OEt_2$, $EtAlCl_2$), only $AlCl_3$ and $AlBr_3$ were effective for the reaction.

In order to investigate the effect of substituent and applicability of this reaction, we next examined reactions of 2-naphthols **1b-e** having a variety of substituents (OH, OMe, Br, CO_2Me) at 6-position under similar conditions (5 equiv. of $AlCl_3$). Importantly, it was found that regardless of the nature of the substituents, cycloadducts **3b-e** were obtained in good yields; **3b**: 49%, **3c**: 66%, **3d**: 68%, **3e**: 68%.7,9)

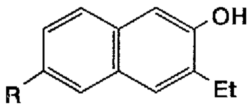
Thus, we have explored a novel type of [2+2] photocycloaddition of 2-naphthols which formally proceeds by way of its keto-tautomer form, though mechanistic detail of this reaction is yet to be clarified.



1a-e



3a-e



4a-e

a: R=H, b: R=OH, c: R=OMe, d: R=Br, e: R=CO_2Me

It is noteworthy that the obtained [2+2] cycloadducts possess bicyclo[4.2.0]octan-2-one moiety which has been demonstrated to be a useful building block in natural product synthesis.5)

Further application and mechanistic study of this novel photoreaction are in progress.

References

1) For a recent review; J. J. McCullough, *Chem. Rev*., **87**, 811 (1987).

2) I. A. Akhtar and J. J. McCullough, *J. Org. Chem* ., **46**, 1447 (1981).

3) V. A. Koptyug, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1968**, 2844; V. A. Koptyug, T. P. Andreeva, and V. I. Mamatyuk, *Zh. Org. Khim.*, **6**, 1848 (1970).

4) S. K. Chadda and R. F. Childs, *Can. J. Chem.*, **63**, 3449 (1985).

5) For recent reviews; S. W. Baldwin in *"Organic Photochemistry"* , Ed. by A. Padwa, Marcel Dekker, 1981, vol. 5, p 123; A. C. Weedon in *"Synthetic Organic Photochemistry"* , Ed. by W. M. Horspool, Plenum Press, 1984, p 61.

6) To make sure of our strategy, we measured IR spectrum of the complex **2a**. The spectrum of **1a** with $AlCl_3$ (5 equiv.) in CH_2Cl_2 solution revealed a new strong absorption at 1530 cm^{-1} probably due to the conjugated enone structure coordinated by $AlCl_3$. The C=O stretching vibration of 2-cyclohexenone (1670 cm^{-1}) was shifted up to 1570 cm^{-1} under similar conditions.

7) Yields are based on naphthols consumed. All new compounds gave satisfactory spectral and analytical data. Selected ^{1}H-NMR data (400MHz, δ, ppm) which were taken at Faculty of Engineering, Osaka University, are as follows:

3a ($CDCl_3$): 7.25-7.16 (m, 2H), 7.12 (d, J=8.3Hz, 1H), 7.06 (d, J=6.8Hz, 1H), 4.05 (br q, 1H), 3.68(ABq, J=16.0Hz, 2H), 3.31-3.24 (m, 1H), 2.68-2.49 (m, 1H), 2.43-2.33 (m, 1H), 2.26-2.16 (m, 1H), 2.13-2.04 (m, 1H).

3b (*d* $_6$-DMSO): 9.25 (s, 1H), 6.89 (d, J=8.2Hz, 1H), 6.60 (dd, J=8.2, 2.4Hz, 1H), 6.52 (d, J=2.0Hz, 1H), 3.97 (br q, 1H), 3.52 (ABq, J=16.0Hz, 2H), 3.26-3.20 (m, 1H), 2.57-2.35 (m, 1H), 2.28-2.19 (m, 1H), 2.09-1.92 (m, 1H), 1.91-1.86 (m, 1H).

3c ($CDCl_3$): 6.98 (d, J=8.3Hz, 1H), 6.76 (dd, J=8.3, 2.4Hz, 1H), 6.65 (d, J=3.0Hz, 1H), 4.02 (br q, 1H), 3.79 (s, 3H), 3.61 (ABq, J=16.0Hz, 2H), 3.30-3.23 (m, 1H), 2.67-2.58 (m, 1H), 2.42-2.32 (m, 1H), 2.26-2.17 (m, 1H), 2.12-2.04 (m, 1H).

3d ($CDCl_3$): 7.31 (dd, J=8.3, 2.0Hz, 1H), 7.27 (br d, J=ca. 2Hz, 1H), 6.94 (d, J=8.3Hz, 1H), 4.02 (br q, 1H), 3.62 (ABq, J=18.9Hz, 2H), 3.38-3.24 (m, 1H), 2.68-2.57 (m, 1H), 2.44-2.34 (m, 1H), 2.26-2.17 (m, 1H), 2.12-2.01 (m, 1H).

3e ($CDCl_3$): 7.85 (dd, J=8.1, 1.4Hz, 1H), 7.82 (br s, 1H), 7.15 (d, J=8.1Hz, 1H), 4.11 (br q, 1H), 3.91 (s, 3H), 3.73 (ABq, J=17.6Hz, 2H), 3.35-3.29 (m, 1H), 2.70-2.66 (m, 1H), 2.44-2.39 (m, 1H), 2.25-2.20 (m, 1H), 2.13-2.07 (m, 1H).

8) 1,1'- Bi-2-naphthol (22%), 2-tetralone (12%), and 3-ethyl-2-tetralone (3%) were also obtained.

9) Except for **1b**, 6-substituted 3-ethyl-2-naphthols were also produced; **4c**: 23%, **4d**: 17%, **4e**: 10%. In the case of **1b**, the reaction turned out to be slower and the conversion was lower (<50%) than the others (>70%) after similar irradiation time.

(Received in Japan 17 July 1989)