Thus, we have shown that β-substituted cyclohexenones such as 1–4 bearing sulfur leaving groups at the β′ position undergo substitution reactions with stabilized carbanions mainly by a radical mechanism. Especially in the case with $LiCMe_2NO_2$, distinct photochemical stimulation and radical inhibition were observed, and a very interesting radical-anion intermediate was detected.

Registry No. 1, 126319-19-5; **2**, 135823-73-3; **3**, 135823-74-4; **4**, 135823-75-5; **5**, 135852-94-7; **6**, 135823-76-6; **7**, 135852-95-8; **8**, 135823-77-7; **9**, 135823-78-8; **10**, 135823-79-9; **11**, 135823-80-2; **12**, 135823-81-3; **13**, 135823-82-4; **14**, 135823-83-5; **15**, 76047-55-7; **16**, 125066-15-1; *m*-DNB, 99-65-0; $NaCEt(CO_2Et)_2$, 18995-13-6; $NaCH(CO_2Et)_2$, 996-82-7; $LiCMe_2NO_2$, 3958-63-2; $LiCHMeNO_2$, 28735-55-9; $(CH_3)_3CNO$, 2406-25-9.

Supplementary Material Available: Complete experimental details and spectral data (5 pages). Ordering information is given on any current masthead page.

Novel Photochemical Ring Contraction of 1-Naphthols Promoted by Aluminum Halides

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Summary: Irradiation of 1-naphthol (**1a**) and its 2-alkyl and 6-methoxy derivatives **1b–d** with 5 equiv of $AlCl_3$ or $AlBr_3$ in CH_2Cl_2 gave (chloromethyl)indanones **4a–d** in 41–72% yields. Irradiation of **1a** with $AlBr_3$ in CH_2Br_2 afforded (bromomethyl)indanone **5a** in 54%. 3-Methyl derivative **1e** was unreactive and 4-methyl derivative **1f** underwent isomerization to **1e**.

Scheme I

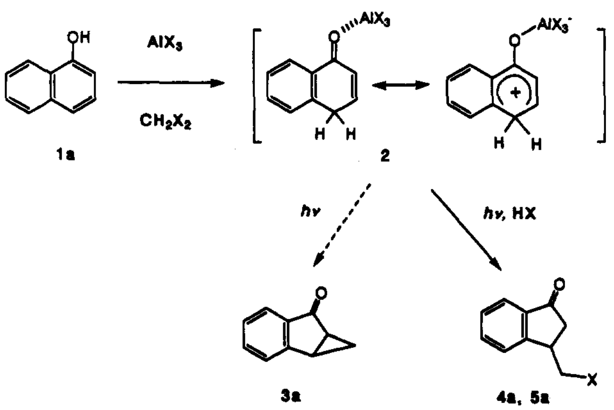

Table I. Product Distribution from Photoreaction of 1-Naphthols 1a–f in the Presence of AlX_3 in CH_2Cl_2

naphthol	AlX_3[a]	irradn time (h)	convn (%)	product (yield, %)[b]
1a	$AlCl_3$	2.5	95	**4a** (69)
	$AlBr_3$	2	85	**4a** (64), **5a** (trace)
	$AlBr_3$[c]	12.5	100	**5a** (54)
1b	$AlCl_3$	1.5	100	**4b** (72)
	$AlBr_3$	1	100	**4b** (41), **5b** (13)
1c	$AlCl_3$	6	100	**4c** (65)
	$AlBr_3$	6	100	**4c** (67)
1d	$AlCl_3$	10	91	**4d** (51)
	$AlBr_3$	7	93	**4d** (47), **5d** (trace)
1e	$AlCl_3$	7.5	0	no reaction
1f	$AlCl_3$	2	100	**1e** (81)

[a] 5 equiv of AlX_3 was used. [b] Yields are based on naphthols consumed. [c] In CH_2Br_2.

In the presence of Lewis or Brønsted acid, alkyl-substituted phenols have been shown to form C4-protonated species,[1,2c,d] which can be envisaged as AlX_3-coordinated or protonated cyclohexa-2,5-dienone. Childs has shown that these C4-protonated species undergo photochemical rearrangement to bicyclo[3.1.0]hex-3-en-2-ones,[2] which is analogous to the well-known lumiketone rearrangement of cyclohexa-2,5-dienones themselves.[3] Indeed, protonated cyclohexa-2,5-dienones are also known to undergo similar isomerization.[4] From synthetic points of view, this skeletal transformation is of great interest since it represents an aromatic to alicyclic transformation and it provides a useful way to prepare the bicyclo[3.1.0]hexenone system from readily available phenol derivatives. 1-Naphthol (**1a**) is also reported by Koptyug to form C4-protonated species **2** with $AlBr_3$.[1a,c] Since **2** is a 2,3-benzo homologue of the AlX_3 complex of C4-protonated phenol, it may well be anticipated to undergo a similar photochemical rearrangement leading to benzobicyclo[3.1.0]hexenone (**3a**) (Scheme I).[5,6] We report here that this is not the case but 1-naphthols **1a–d** undergo a novel photochemical ring contraction promoted by AlX_3 (X = Cl, Br) leading to the

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[1] (a) Koptyug, V. A.; Andreeva, T. P.; Mamatyuk, V. I. *Zh. Org. Khim.* **1970**, *6*, 1848. (b) Koptyug, V. A.; Golounin, A. V. *Zh. Org. Khim.* **1972**, *8*, 607. (c) Salakhutdinov, N. F.; Korobeinicheva, I. K.; Koptyug, V. A. *Zh. Org. Khim.* **1982**, *18*, 1894.

[2] (a) Childs, R. F.; Parrington, B. D.; Zeya, M. *J. Org. Chem.* **1979**, *44*, 4912. (b) Baeckstrom, P.; Jacobsson, U.; Koutek, B.; Norrin, T. *J. Org. Chem.* **1985**, *50*, 3728. (c) Chadda, S. K.; Childs, R. F. *Can. J. Chem.* **1985**, *63*, 3449. (d) Childs, R. F.; George, B. E. *Can. J. Chem.* **1988**, *66*, 1343. Recently we have found that 3-methoxyphenol also undergoes similar photorearrangement promoted by $AlBr_3$: Kakiuchi, K.; Ue, M.; Yamaguchi, B.; Nishimoto, A.; Tobe, Y. *Bull. Chem. Soc. Jpn.* In press.

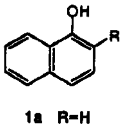
[3] (a) Zimmerman, H. E.; Schuster, D. I. *J. Am. Chem. Soc.* **1961**, *83*, 4486; (b) **1962**, *84*, 4527. For reviews, see: (c) Zimmerman, H. E. *Adv. Photochem.* **1963**, *1*, 183. (d) Chapman, O. L. *Adv. Photochem.* **1963**, *1*, 323. (e) Schaffner, K. *Adv. Photochem.* **1966**, *4*, 81. (f) Kropp, P. J. *Org. Photochem.* **1967**, *1*, 1. (g) Chapman, O. L.; Weiss, D. S. *Org. Photochem.* **1973**, *3*, 197. (h) Schaffner, K.; Demuth, M. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, p 281.

[4] Pauvlik, J. W.; Filipescu, N. *J. Am. Chem. Soc.* **1970**, *92*, 6062. Pavlik, J. W.; Pasteris, R. J. *J. Am. Chem. Soc.* **1974**, *96*, 6107.

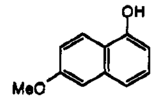
[5] Although it has been reported that 4,4-disubstituted 2,3-benzocyclohexa-2,5-dienones reacted differently, i.e., migration of an aryl group on the 4-position to give 1-naphthol derivatives, we think that the aryl group on the 4-position plays a crucial role in its facile 1,2-migration. The situation for **2**, which does not possess the C4-substituents, may well be different from the 4,4-disubstituted benzocyclohexadienones: Zimmerman, H. E.; Hahn, R. C.; Morrison, H.; Wani, M. C. *J. Am. Chem. Soc.* **1965**, *87*, 1138. Zimmerman, H. E.; Rieke, R. D.; Scheffer, J. R. *J. Am. Chem. Soc.* **1967**, *89*, 2033.

0022-3263/91/1956-5745$02.50/0

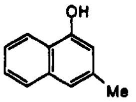
corresponding (chloromethyl)indanones **4a–d** rather than bicyclohexenones **3a–d**. Moreover, since the (chloromethyl)indanones **4a–d** were readily transformed to **3a–d** by treatment with LDA, an overall lumiketone-type transformation was accomplished in two steps.



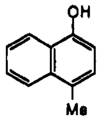
1a R=H
1b R=Me
1c R=Pr



1d

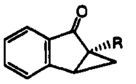


1e

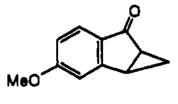


1f

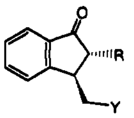
When a solution of 1-naphthol (**1a**) and 5 equiv[7] of $AlCl_3$ in CH_2Cl_2 was irradiated through a Pyrex filter at room temperature, (chloromethyl)indanone **4a** was obtained in 69% isolated yield after chromatography. Irradiation of 2-alkyl- and 6-methoxy-substituted derivatives **1b–d** under similar conditions afforded the corresponding (chloromethyl)indanones **4b–d** in 72, 65, and 51% yields, respectively. Since the stereochemistry of **4b** is assumed to be trans on the basis of NOE experiments[8] and the assumption that $AlCl_3$ would catalyze the isomerization to the more stable trans isomer, those of the other indanones **4c** and **5b** are believed to be the same. On the other hand, 3-methyl derivative **1e** was totally unreactive under the reaction conditions. 4-Methyl derivative **1f** afforded **1e** in 81% yield through 1,2-migration of the methyl group, but not ring contraction was observed. The ring contraction was also effected by $AlBr_3$. In CH_2Cl_2, the major products obtained from **1a–d** were the (chloromethyl)indanones **4a–d**. Only small amounts of (bromomethyl)indanones **5a**, **5b**, and **5d** were obtained. It is apparent that the solvent provided the source of halogen in the products due to the well-known halogen exchange between AlX_3 and haloalkanes.[9] (Bromomethyl)indanone **5a** was obtained in 54% yield from **1a** by irradiation with $AlBr_3$ in CH_2Br_2 (Table I).[10]



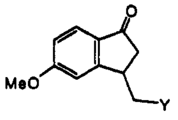
3a R=H
3b R=Me
3c R=Pr



3d



4a R=H, Y=Cl
4b R=Me, Y=Cl
4c R=Pr, Y=Cl
5a R=H, Y=Br
5b R=Me, Y=Br



4d Y=Cl
5d Y=Br

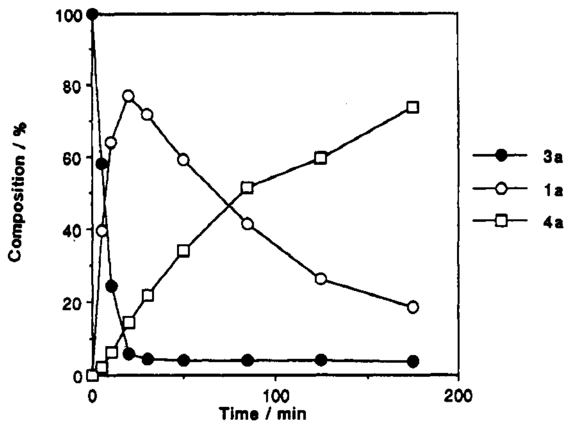
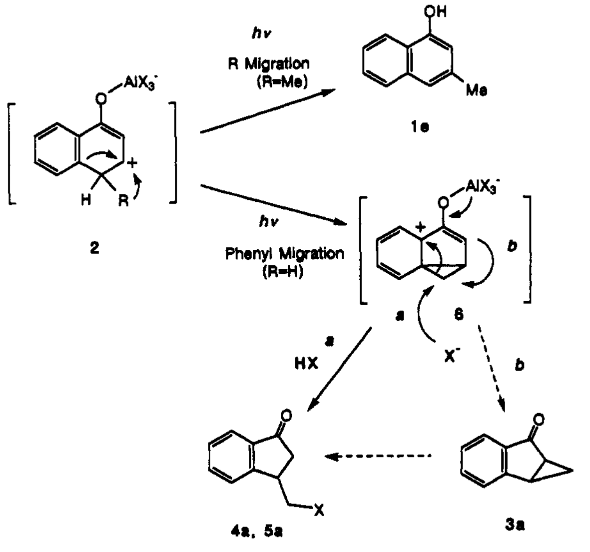


Figure 1. Photochemical cycloreversion of benzobicyclo[3.1.0]hex-3-en-2-one (**3a**) in the presence of $AlBr_3$ (5 equiv) in CH_2Cl_2.

Scheme II



The following experiments were undertaken in order to elucidate the mechanism of the ring contraction. First, cycloreversion of **3a** to **1a** was investigated because photocycloreversion of bicyclo[3.1.0]hex-3-en-2-ones in the presence[2] or absence[11] of acids has been known. Bicyclohexenone **3a** was thermally stable to $AlCl_3$ or $AlBr_3$ in CH_2Cl_2. However, irradiation of **3a** under the conditions similar to those of the reaction of **1a** (5 equiv of $AlBr_3$ in CH_2Cl_2) revealed that **3a** underwent rapid cycloreversion to **1a**, which then slowly reacted to afford **4a** as shown in Figure 1. In the absence of $AlBr_3$, the cycloreversion of **3a** to **1a** completed within 15 min. These results indicate that at least most of (chloromethyl)indanone **4a** is formed directly from **1a**. The possibility that **4a** is derived by photochemical addition of **3a** to HCl seems unlikely, though it cannot be excluded completely.

Next, the source of the hydrogen was examined. When the reaction of **1a** with $AlCl_3$ in CH_2Cl_2 was worked up with D_2O, mass and ^1H NMR spectra of the product **4a** showed no deuterium incorporated. On the other hand, when **1a** was irradiated under the conditions that generated DCl

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(6) We have reported that 2-naphthols underwent [2 + 2] photocycloaddition with ethylene in the presence of AlX_3. In this case 1-protonated species[1a,c] can be envisaged as 4,5-benzocyclohexa-2,4-dienone: Ue, M.; Kinugawa, M.; Kakiuchi, K.; Tobe, Y.; Odaira, Y. *Tetrahedron Lett.* **1989**, *30*, 6139.

(7) Use of excess AlX_3 has been shown to promote the formation of a phenol complex of the tautomeric keto form like **2**.[1c]

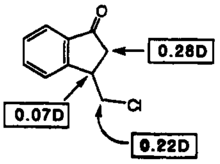
(8) Upon irradiation of the methyl group, a 6% intensity enhancement was observed for the benzyl methine proton.

(9) *Methoden der Organischen Chemie*; Müller, E., Ed.; Verlag: Stuttgart, 1955; Vol. IV/2, p 103; 1960; Vol. V/4, p 355, 758.

(10) 1-Naphthols **1a–f** did not react in the presence of AlX_3 without photoirradiation nor by irradiation in the absence of AlX_3.

(11) For example, (a) Wheeler, J. W.; Eastman, R. H. *J. Am. Chem. Soc.* **1959**, *81*, 2361. (b) Zimmerman, H. E.; Keese, R.; Nasielski, J.; Swenton, J. S. *J. Am. Chem. Soc.* **1966**, *88*, 4895. (c) Barber, L.; Chapman, O. L.; Lassila, J. D. *J. Am. Chem. Soc.* **1968**, *90*, 5933. For a review, see: (d) ref 3h, p 310.

during the reaction ($AlCl_3$ (5 equiv) and CH_3OD (1 equiv) in CH_2Cl_2) and the reaction was quenched with H_2O, the mass spectrum of the product **4a** indicated that it contained 40% monodeuterated and 10% dideuterated compounds. ^1H NMR showed that deuterium was incorporated at the methylene adjacent to the carbonyl (28%), the chloromethyl group (22%), and the benzyl methine (7%).[12] These results indicate clearly that the hydrogen was derived from hydrogen halides already present in the reaction mixture during irradiation but not from H_2O added after irradiation for workup.



These experimental results led us to propose the reaction mechanism shown in Scheme II, though the detail is still ambiguous. Thus irradiation of C4-protonated species **2** leads to migration of the fused phenyl group to give an intermediate such as **6**. Addition of HX to **6** gives indanone **4** or **5** (path a). Formation of benzobicyclohexenone **3** (path b), if any, is less likely since cycloreversion of **3** to the starting material takes place readily. Thus interception of **6** by a halide ion (X^-) seems to play a crucial role in this ring contraction. In the case of 4-methyl derivative **1f**, migration of R group predominates over that of phenyl to yield 3-methyl-1-naphthol (**1e**).[13] Lack of reactivity in **1e** can be readily understood from the tertiary character of the cationic center of **2** derived from **1e**.

Finally, treatment of (chloromethyl)indanones **1a–d** with LDA gave benzobicyclo[3.1.0]hex-3-en-2-ones **3a–d**[14] in 74–91% yields.[15] Thus, although the mechanism of this photochemical ring contraction of **1a–d** is yet to be clarified, an overall lumiketone-type transformation (from keto tautomers) of **1a–d** was accomplished in two steps.

Acknowledgment. We are grateful to the Ministry of Education, Science and Culture for the support of the NMR and Mass Spectral facilities used in this work at the Instrumental Analysis Center of the Faculty of Engineering, Osaka University, and for partial support of this work through a Grant-in-Aid.

Supplementary Material Available: Experimental procedures and spectral data for **3a–d**, **4a–d**, **5a**, **5b**, and **5d** (6 pages). Ordering information is given on any current masthead page.

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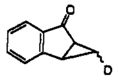
[12] The fact that a small amount of deuterium was found in the benzyl methine indicates that H3 of 1-naphthol (**1a**) was exchanged with deuterium during the photoreaction (see supplementary material). However, since this can be achieved by either 1,2-migration of a deuterium in the complex **2** (R = D in Scheme II) or cycloreversion of **3a** with a deuterium on the cyclopropyl methylene, i.e., i, the mechanism for this H/D exchange remains ambiguous.



i

[13] Similar 1,2-migration has been invoked in photoisomerization of 4,4-disubstituted benzocyclohexa-2,5-dienones.[5]

[14] **3a** has been known: House, H. O.; McDaniel, W. C.; Sieloff, R. F.; Vanderveer, D. *J. Org. Chem.* **1978**, *43*, 4316.

[15] For the related cyclopropane formation, see: House, H. O. *Modern Synthetic Reactions*, 2nd ed.; Benjamin: Menlo Park, 1972; p 542.

Extending the Scope of the Evans Asymmetric Aldol Reaction: Preparation of Anti and "Non-Evans" Syn Aldols[1]

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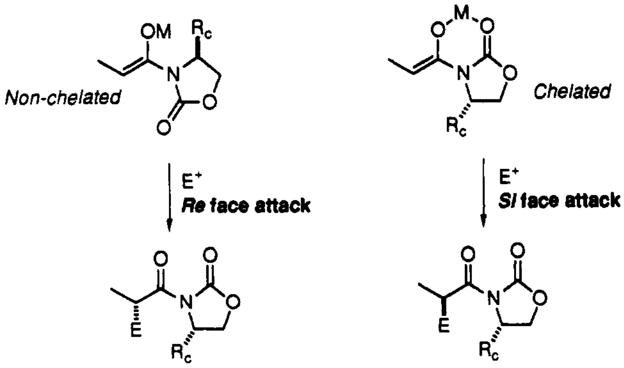
Received July 17, 1991

Summary: The Evans reagent, imide **1**, reacts with aldehydes under Lewis acid catalysis to give anti or "non-Evans" syn aldols **5** or **6**, depending on the reaction conditions. This discovery considerably amplifies the synthetic utility of these important reagents for asymmetric synthesis.

Scheme I



For some time an objective to this group has been to understand the factors that govern stereoselectivity in the aldol reaction and to apply this reaction to the stereocontrolled synthesis of chiral acyclic compounds.[2] The present research was undertaken with two goals in mind: (1) to find a convenient asymmetric, "anti aldol" method and (2) to develop methodology whereby several of the possible aldol stereoisomers can be synthesized from the same carbonyl precursor by simply changing reaction conditions.[3] This communication describes our discovery

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[1] Part 54 in a series of papers on Acyclic Stereoselection. For part 53, see: Van Draanen, N. A.; Arseniyadis, S.; Crimmins, M. T.; Heathcock, C. H. *J. Org. Chem.* **1991**, *56*, 2499.

[2] For general reviews on aldol stereoselectivity, see: (a) Heathcock, C. H. *Science* **1981**, *214*, 395. (b) Evans, D. A.; Nelson, J. V.; Taber, T. R. *Top. Stereochem.* **1982**, *13*, 1. (c) Mukaiyama, T. *Organic Reactions*; Wiley: New York, 1982; Vol. 28. (d) Heathcock, C. H. In *Comprehensive Carbanion Chemistry*, Buncel E., Durst, T., Eds.; Elsevier: Amsterdam, 1984; Part B, Chapter 4. (e) Heathcock, C. H. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3, Chapter 2. (f) Masamune, S.; Choy, W.; Petersen, J. S.; Sita, L. R. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1. (g) Braun, M. *Ibid.* **1987**, *26*, 24.

0022-3263/91/1956-5747$02.50/0