Novel Photochemical Reactions of 1- and 2-Naphthols with Ethylene Promoted by Aluminum Halides

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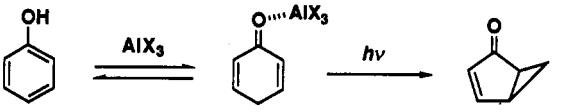
Novel photoreactions of 1- and 2-naphthols with ethylene promoted by aluminum halides are described. Irradiation of 2-naphthol (**2a**) with AlX_3 (X = Cl, Br) and ethylene in CH_2Cl_2 gave the corresponding [2 + 2] cycloadduct **7a** in good yields. The major side product was 2-ethyl-1-naphthol (**8a**). Of the Lewis acids and alkenes examined, only $AlCl_3$ and $AlBr_3$ effected the reaction and only ethylene gave satisfactory results, although allene can also be employed. Naphthols **2b–e** having different electron-attracting substituents on C-6 afforded [2 + 2] adducts **7b–e** in moderate to good yields, while the reactions of C-3-alkyl-substituted derivatives **8a** and **15b** were unsuccessful. By contrast, 1-naphthol (**1a**) and its derivatives **1b–e** exhibited diverse reactivities depending on the substituent on C-2, C-3, or C-6. Namely **1a** and 3-methyl derivative **1b** afforded [2 + 2] cycloadducts **16a** and **16b** in moderate yields. On the other hand, 2-methyl and 2-propyl derivatives **1c** and **1d** yielded unusual products like indenones **22a** and **22b** and cyclopropyl ketones **23a** and **23b**, respectively. 6-Methoxy derivative **1e** also gave indenone **30**. Plausible reaction mechanisms leading to the observed products are presented.

Introduction

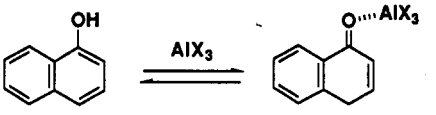
Koptyug has demonstrated based on spectroscopic investigations that phenol and its derivatives form C-4 protonated complexes with aluminum halides which possess cross-conjugated cyclohexadienone structures coordinated by AlX_3 to the carbonyl oxygen.[1] Childs has investigated the photochemistry of these and related complexes and found that some alkyl-substituted derivatives underwent novel rearrangement to afford bicyclo[3.1.0]hex-3-en-2-ones (Scheme I).[2] Recently we have also found that 3-methoxyphenol underwent similar photorearrangement promoted by $AlBr_3$.[3] The reaction is formally analogous to the lumiketone rearrangement of the parent cyclohexa-2,5-dienones which has been extensively studied.[4]

It has been also shown by Koptyug that 1-naphthol (**1a**) produces the cross-conjugated benzocyclohexadienone type complex **3**, and 2-naphthol (**2a**) gives the linearly conjugated complex **4** (Scheme II).[1a,b,5] Since **3** is a 2,3-benzo homologue of the AlX_3 complex of C-4 protonated phenol, we anticipated a similar photochemical rearrangement to that observed for the phenol complex leading to benzobicyclo[3.1.0]hexenone (**5**). We found, however, that irradiation of **1a** in the presence of aluminum halides brought about a novel ring contraction to yield halomethyl indanones **6a** or **6b** instead of **5**.[6] Although the products are formal hydrogen halide adducts of **5**, mechanistic investigations suggested that **6a** and **6b** were not secondary products derived from **5** but formed directly from polarized intermediates like **20a** and **21a**.

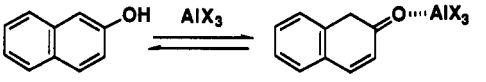
Scheme I



Scheme II



1a **3**



2a **4**

Recently Lewis reported the pronounced effect of Lewis acid in the efficiency and regiochemistry of [2 + 2] photodimerization and cross-cycloaddition of coumarin.[7] As to the linearly conjugated complex **4** of 2-naphthol (**2a**), therefore, we focused our attention to photocycloaddition to an alkene because of the structural similarity between

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(1) (a) Koptyug, V. A.; Andreeva, T. P.; Mamatyuk, V. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1968**, 2844. (b) *Zh. Org. Khim.* **1970**, *6*, 1848. (c) Golounin, A. V.; Koptyug, V. A. *Zh. Org. Khim.* **1972**, *8*, 2555.

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(3) Kakiuchi, K.; Ue, M.; Yamaguchi, B.; Nishimoto, A.; Tobe, Y. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 3468.

(4) (a) Zimmerman, H. E.; Schuster, D. I. *J. Am. Chem. Soc.* **1961**, *83*, 4486; (b) *Ibid.* **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.

(5) (a) Koptyug, V. A.; Golounin, A. V. *Zh. Org. Khim.* **1972**, *8*, 607. (b) Salakhutdinov, N. F.; Korobeinicheva, I. K.; Koptyug, V. A. *Zh. Org. Khim.* **1982**, *18*, 1894.

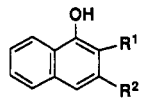
(6) Kakiuchi, K.; Yamaguchi, B.; Tobe, Y. *J. Org. Chem.* **1991**, *56*, 5745.

(7) Lewis, F. D.; Barancyk, S. V. *J. Am. Chem. Soc.* **1989**, *111*, 8653.

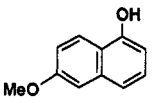
0022-3263/93/1958-2797$04.00/0

4 and the coumarin–Lewis acid complex. Also we anticipated the [2 + 2] photochemistry in view of the cyclohexenone substructure of **4**, since [2 + 2] photocycloaddition of α,β-enones has been extensively studied and has been demonstrated to be of substantial synthetic utility.[8] The corresponding [2 + 2] chemistry of the parent 2,4-cyclohexadienones, to our knowledge, is unknown, although they have been shown to undergo photochemical α-cleavage to give ketene intermediates.[4f,h,9]

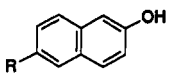
We found that, when **2a** and its derivatives **2b–e** were irradiated with ethylene in the presence of AlX_3, [2 + 2]



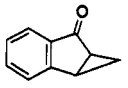
1a $R^1 = R^2 = H$
1b $R^1 = H$, $R^2 = Me$
1c $R^1 = Me$, $R^2 = H$
1d $R^1 = nPr$, $R^2 = H$



1e



2a R = H
2b R = Br
2c R = OMe
2d R = OH
2e R = CO_2Me



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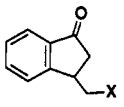

6a X = Cl
6b X = Br

adducts **7a–e** were obtained in moderate to good yields.[10] This represents a new type of photochemical [2 + 2] reaction in the chemistry of naphthols.[11] In this paper, we describe the scope and limitation of this novel photoreaction with the main focus on the effect of Lewis acid, alkene, and the substituents on C-6 of **2a**.

In contrast with α,β-enones, the photocycloaddition of the cross-conjugated 2,5-cyclohexadienones had been unknown until Schultz reported recently the first examples of intra- and intermolecular [2 + 2] photocycloaddition of some 2,5-cyclohexadienone derivatives.[12] These findings moved us to investigate the photoreaction of 1-naphthol (**1a**) with ethylene in the presence of aluminum halides. We found that **1a** underwent [2 + 2] photocycloaddition with ethylene to give the adduct **16a**, which provided an additional example of [2 + 2] reaction in phenol chemistry. 3-Alkyl-substituted derivatives **1c** and **1d**, however, did not give [2 + 2] adducts but the ring-contracted indenones **22a** and **22b** and the cyclopropyl ketones **23a** and **23b** in which two molecules of ethylene were incorporated. In this context, we describe herein also the results of photoreaction of **1a** and its derivatives **1b–e** with ethylene promoted by AlX_3.

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(9) (a) Barton, D. H. R. *Helv. Chim. Acta* **1959**, *42*, 2604. (b) Barton, D. H. R.; Quinkert, G. *J. Chem. Soc.* **1960**, 1. For a review: (c) Quinkert, G. *Pure Appl. Chem.* **1973**, *33*, 285.

(10) Preliminary results on photoreaction of 2-naphthols **2a–e** have been reported: Ue, M.; Kinugawa, M.; Kakiuchi, K.; Tobe, Y.; Odaira, Y. *Tetrahedron Lett.* **1989**, *30*, 6193.

(11) For the only precedent, to our knowledge, of [2 + 2] cycloaddition of 2-naphthol (**2a**): Akhtar I. A.; McCullough, J. J. *J. Org. Chem.* **1981**, *46*, 1447.

(12) (a) Schultz, A. G.; Plummer, M.; Taveras, A. G.; Kullnig, R. K. *J. Am. Chem. Soc.* **1988**, *110*, 5547. (b) Schlutz, A. G.; Taveras, A. G. *Tetrahedron Lett.* **1988**, *29*, 6881. (c) Schultz, A. G.; Geiss, W. *J. Am. Chem. Soc.* **1991**, *113*, 3490.

Table I. Photoreaction of 2-Naphthols 2a–e with Ethylene in the Presence of AlX_3

naphthol	AlX_3	reaction time (h)	conversion (%)	product (yield, %)[a]
2a	$AlCl_3$[b]	8	73	**7a** (49), **8a** (3), **9a** (12), **9b** (3), **10** (22)
	$AlCl_3$[c]	5	88	**7a** (70), **8a** (12), **9a** (1), **9b** (3)
	$AlBr_3$[b]	7.5	86	**7a** (63), **8a** (15), **9a** (3), **9b** (3)
2b	$AlCl_3$[c]	3	100	**7b** (68), **8b** (17)
2c	$AlCl_3$[c]	4.5	90	**7c** (66), **8c** (23)
2d	$AlCl_3$[c]	9	52	**7d** (49), **8d** (10)
2e	$AlCl_3$[c]	10	70	**7e** (68), **8e** (10)

[a] Yields are based on naphthols consumed. [b] Two equivalents. [c] Five equivalents.

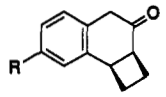
Results and Discussion

Photoreaction of 2-Naphthols. First, photoreaction of 2-naphthol (**2a**) with ethylene in the presence of AlX_3 is described in some detail (Table I). Irradiation of a solution of **2a** and $AlCl_3$ (2 equiv) in CH_2Cl_2 saturated with ethylene (large excess) at −78 °C through a Pyrex filter for 8 h gave [2 + 2] adduct **7a** in 49% yield after chromatographic purification. Besides **7a**, 3-ethyl-2-naphthol (**8a**, 3%), 2-tetralone (**9a**, 12%), 3-ethyl-2-tetralone (**9b**, 3%), and 1,1′-bi-2-naphthol (**10**, 22%) were obtained along with unreacted **2a** (73% conversion). The position of the ethyl group in **8a** was determined unambiguously by comparison with an authentic sample prepared independently.[13] When 5 equiv of $AlCl_3$ was used (not all $AlCl_3$ dissolved), the reaction proceeded more rapidly and 88% of **1a** was consumed after 5 h. Moreover, the reaction was cleaner and **7a** was obtained in 70% yield. The major side product was **8a** (12%) and only negligible amount of redox products **9a** and **9b** were obtained. Similarly, when 2 equiv of $AlBr_3$ was employed instead of $AlCl_3$, **7a** was obtained as the major product (63%) along with **8a** (15%). Reaction of **7a** under similar conditions as described above (with 5 equiv of $AlCl_3$) resulted in the recovery of **7a**, indicating that **8a** is a primary photoproduct and is not a secondary product derived from **7a**. No reaction was observed when **2a** was treated with $AlCl_3$ and ethylene in the dark at −78 °C. Moreover, AlX_3 and ethylene were essential to this reaction, since **2a** was recovered when it was irradiated in the absence of $AlCl_3$ or ethylene. In the absence of ethylene, the formation of [2 + 2] dimers was not detected although it may well be expected.

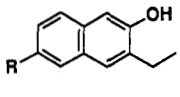
The formation of **7a** can be explained by a concerted [2 + 2] cycloaddition of excited complex **4** or a stepwise reaction through a diradical intermediate **11** or **12** as shown in Scheme III. The initial bond formation occurs at the α- or β-position of the carbonyl to generate the intermediate **11** or **12**, and the subsequent ring closure gives **7a**. Although the radical center of **11** located on the benzyl position would suffer from considerable stabilization and **8a** can only come from **11** as described below, it would be appropriate to consider the other possibility (i.e., **12**), by analogy with the photocycloaddition reactions of cyclic enones with alkenes.[8,14]

The formation of the byproducts **8a–10** may deserve comment: Firstly, 3-ethyl-2-naphthol (**8a**) can be derived

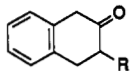
(13) Wahl, H.; Fraemohs, J. *Compt. Rend.* **1947**, *224*, 573.



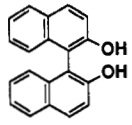
7a R = H
7b R = Br
7c R = OMe
7d R = OH
7e R = CO_2Me



8a R = H
8b R = Br
8c R = OMe
8d R = OH
8e R = CO_2Me



9a R = H
9b R = Et



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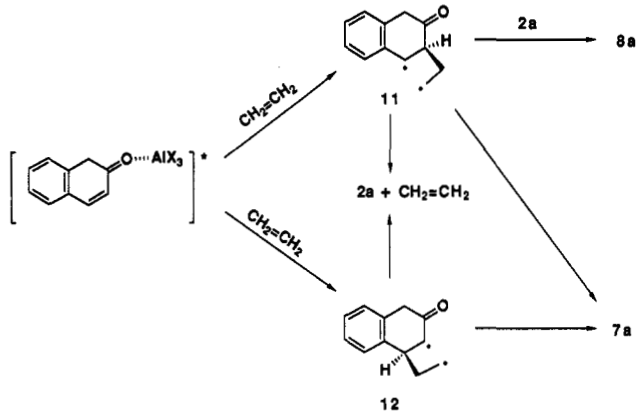
by the Friedel–Crafts type alkylation of **2a** with ethylene. However, it has been demonstrated that the Friedel–Crafts alkylation of **2a** took place selectively at C-1 or C-6 of the naphthol ring.[15] This implies that **8a** is not an electrophilic alkylation product. Since the amount of **8a** parallels that of **7a** with regard to the amount of $AlCl_3$, **8a** and **7a** might be formed through a common intermediate. We consider, therefore, that **8a** is formed by intermolecular disproportionation[16] of the diradical intermediate **11** with 2-naphthol (**2a**) (Scheme III). Next, when 2 equiv of $AlCl_3$ was used, substantial amount of the formal redox products **9a** and **10** were formed. Although oxidative coupling of **2a** with a Lewis acid such as $FeCl_3$ is well known to give **10**,[17] such reaction does not take place with AlX_3. Moreover, in the present case, no reaction occurred in the absence of ethylene indicating that ethylene is essential to the redox process. The reason for this is not fully understood at this time.

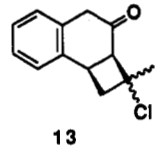
In order to investigate the effect of Lewis acid on this reaction, irradiation was undertaken with $EtAlCl_2$ (5 equiv), $TiCl_4$ (2 equiv), or $BF_3{\cdot}OEt_2$ (2 equiv) under otherwise similar conditions. However, no reaction was observed with these acids, in contrast with the photocycloaddition of coumarin in the presence of Lewis acid.[7] Since we did not observe significant change in the IR spectra of **2a** (CH_2Cl_2 solution) when $TiCl_4$ and $BF_3{\cdot}OEt_2$ (up to 10 equiv) were added to a solution of **2a**, these acids were not strong enough to form a complex like **4**. On the other hand, with $EtAlCl_2$ we observed appearance of a new absorption band at 1530 cm^{-1} in the IR spectrum, which can be assigned to a complex like **4**.[18] This implies that, although cyclohexadienone type complex is formed with $EtAlCl_2$, [2 + 2] cycloaddition is promoted with only AlX_3. The reason for this is uncertain.

Next, we examined reactions with alkenes other than ethylene. However, the choice of alkene is limited because of the propensity of most olefins to undergo the Friedel–Crafts alkylation of naphthol promoted by AlX_3. For example, with cyclopentene, a complex mixture of products

Scheme III



resulted after irradiation under otherwise similar conditions (1 equiv of $AlCl_3$). With allene, however, we were able to observe the formation of cyclobutane-containing products. When **2a** was irradiated with $AlCl_3$ (5 equiv) and allene (large excess) under similar conditions, **2a** was consumed rapidly (2 h) to give cycloadducts **13** (35%) and **14** (18%) and methallylnaphthol **15a** (9%). The fact that



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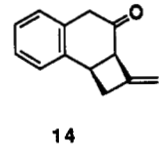

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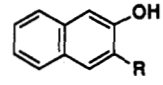


15a R = $C(Me)CH_2$
15b R = Me

cycloadducts **13** and **14** decomposed gradually precluded complete confirmation of their regio- and stereochemistry. The regiochemistry of **13** and **14** was tentatively assumed to be head-to-head in view of the selectivity observed in the related reaction of α,β-enones with allene.[8] The stereochemistry of **13** was not determined. Thus it turned out that, although the major product was a formal HCl adduct to the primary cycloadduct, allene could be employed besides ethylene as an alkene in this reaction.

Finally, in order to examine the effect of substituents on the naphthol ring, photoreaction of the derivatives **2b–e** having a variety of substituents on C-6 with ethylene was undertaken using 5 equiv of $AlCl_3$. As shown in Table I, **2b–e** afforded the corresponding [2 + 2] cycloadducts **7b–e** in moderate to good yields. The major byproducts were 3-ethylnaphthols **8b–e** as in the case of the parent **2a**. Thus it has been found that $AlCl_3$-promoted [2 + 2] cycloaddition proceeded nicely regardless of the electronic properties of the C-6 substituent of 2-naphthol. This is

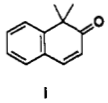
(14) (a) de Mayo, P. *Acc. Chem. Res.* **1971**, *4*, 41. (b) Loutfy, R. O.; de Mayo, P. *J. Am. Chem. Soc.* **1977**, *99*, 3559. (c) Schuster, D. I. In *The Chemistry of Enones*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1989; p 623.

(15) Patinkin, S. H.; Friedman, B. S. In *Friedel-Crafts and Related Reactions*; Olah, G. A., Ed.; Wiley-Interscience: New York, 1964; Vol. II, Part 1, p 222.

(16) Hastings, D. J.; Weedon, A. C. *J. Am. Chem. Soc.* **1991**, *113*, 8525 and references cited therein.

(17) Mihailović, M. L.; Čeković, Ž. In *The Chemistry of the Hydroxyl Group*; Patai, S., Ed.; Wiley-Interscience: New York, 1971; Part 1, p 505.

(18) The IR spectrum of **2a** showed a new absorption at 1530 cm^{-1} on addition of 5 equiv of $AlCl_3$. Since 1,1-dimethyldihydronaphthalenone (i)



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also exhibited an absorption at 1530 cm^{-1} with 5 equiv of $AlCl_3$, this absorption was assigned to the enone carbonyl coordinated by a Lewis acid to the oxygen.

Table II. Photoreaction of 1-Naphthols 1a–e with Ethylene in the Presence of AlX_3

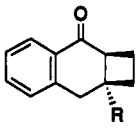
naphthol	AlX_3	reaction time (h)	conversion (%)	product (yield, %)[a]
1a	$AlBr_3$[b]	8	90	16a (46), 17a (10)
1b	$AlBr_3$[b]	12	60	16b (73)
1c	$AlBr_3$[b]	10	85	17b (13), 22a (38), 23a (14), 24 (8)
1d	$AlBr_3$[b]	6	93	17c (18), 22b (17), 23b (12), 25b (26)
1e	$AlBr_3$[c]	12	45	30 (11), 31b (28)
	$AlCl_3$[b]	10	65	30 (30), 31a (12), 32 (29)

[a] Yields are based on naphthols consumed. [b] Five equivalents. [c] Two equivalents.

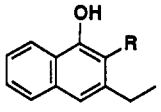
in accord with the proposed mechanism of the reaction shown in Scheme III in which the diradical intermediates 11 or 12 is involved. The substituents in the [2 + 2] adducts 7b–e would allow further manipulation of the remaining benzene ring that would extend synthetic utility of this reaction.

We also undertook reactions with 3-methyl-2-naphthol (15b) and 3-ethyl derivative 8a. However, the consumption of the starting materials was very slow and we were unable to isolate any products. The inefficiency may be due to steric interference by the alkyl group during the formation of a diradical intermediate like 11 or in the bond-forming step in a diradical like 12.

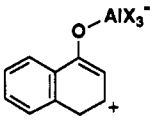
Photoreaction of 1-Naphthols. Next, we investigated photoreactions of 1-naphthol (1a) and its derivatives 1b–d with ethylene in the prescence of AlX_3. According to the information obtained from the reactions with 2-naphthol (2a), we employed only ethylene as an alkene and AlX_3 as a Lewis acid. Since reaction with $AlCl_3$ turned out to be impractically sluggish, $AlBr_3$ was used in most cases (Table II). Irradiation of a solution of 1a and $AlBr_3$ (5 equiv) in CH_2Cl_2 saturated with ethylene for 8 h (90% conversion) afforded [2 + 2] cycloadduct 16a in 46% yield along with 3-ethyl-1-naphthol (17a, 10%). The 1,3-relationship between the hydroxy and ethyl groups of 17a is established based on the coupling constant (J = 1.5 Hz) between H-2 (δ 6.67) and H-4 (δ 7.23) in the ^1H NMR spectrum. Control experiments with 16a revealed that 17a was not a secondary photoproduct derived from 16a.



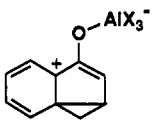
16a R = H
16b R = Me



17a R = H
17b R = Me
17c R = nPr



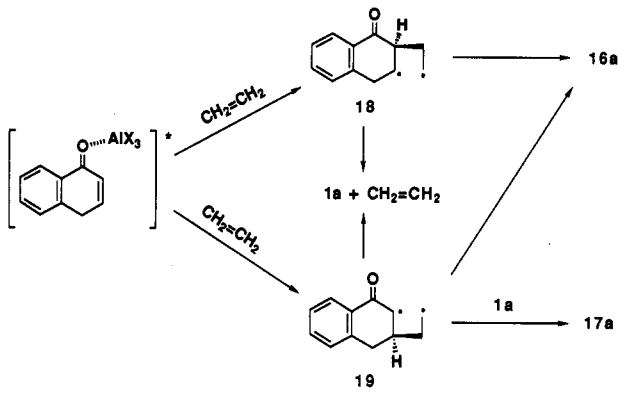
20a



21a

It should be noted that (chloromethyl)indanone (6a), which was obtained in good efficiency in the absence of ethylene,[6] was not detected. Similarly 3-methyl derivative 1b afforded the corresponding adduct 16b in 73% yield. We

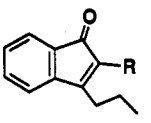
Scheme IV



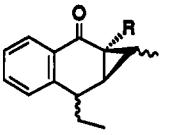
have already shown that 1b was unreactive in the absence of ethylene.[6]

The formation of these products is explained in terms of a diradical mechanism through an intermediate 18 or 19 (Scheme IV) as in the case of 2-naphthols. Previously we assumed polarized species 20a and 21a as the key intermediates leading to the ring-contracted products 6a and 6b.[6] In the present case, however, we prefer the nonpolar mechanism shown in Scheme IV because 6a or 6b was not detected.

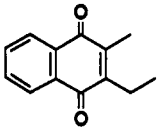
By contrast, we were surprised to find that irradiation of 2-methyl derivative 1c did not give any [2 + 2] adduct but unusual products like 22a and 23a (Table II). Thus irradiation of 1c yielded ring-contracted indenone 22a as a major product (38%). As byproducts cyclopropyl ketone 23a (14%) was obtained along with naphthol 17b and naphthoquinone 24.



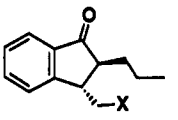
22a R = Me
22b R = nPr



23a R = Me
23b R = nPr



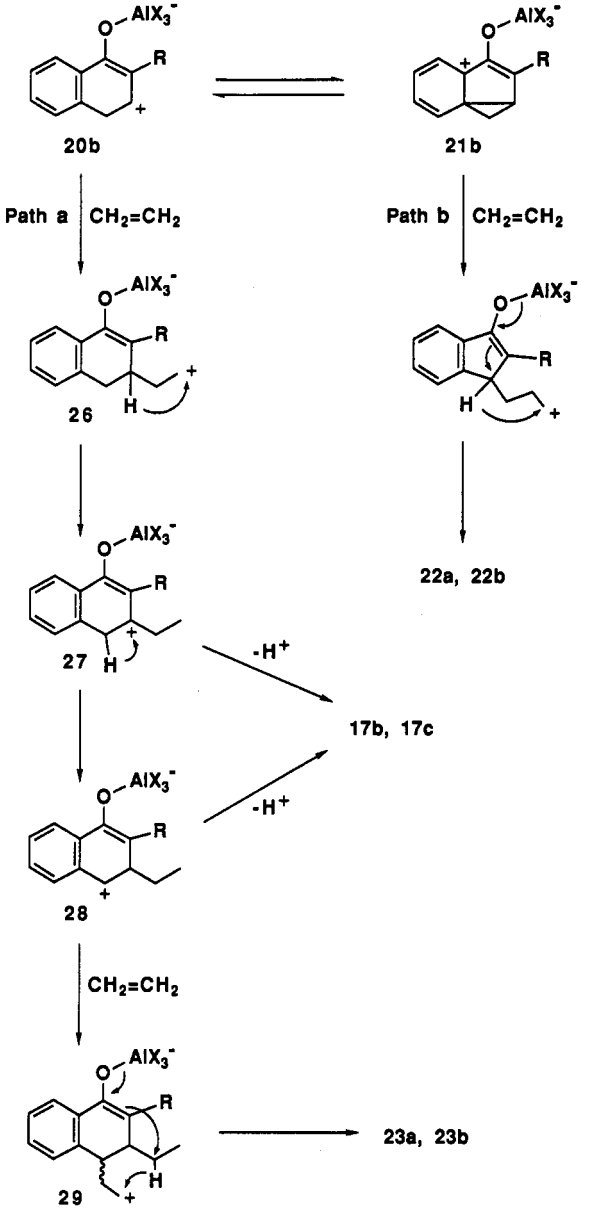
24



25a X = Cl
25b X = Br

The structure of indenone 22a was elucidated on the basis of the IR (ν_{CO} = 1700 cm^{-1}) and ^1H NMR spectra which indicated the presence of an n-propyl group (δ 2.52 (t), 1.65 (tq), 1.01 (t)). The mass spectrum and elemental analysis of 23a indicated that two molecules of ethylene had added to 1c. Carbonyl absorption was observed at 1660 cm^{-1} in the IR spectrum. The ^{13}C NMR showed seven sp^2 signals including carbonyl and three methyl (δ 13.3, 13.1, 10.3), one methylene (δ 32.9), three methine (δ 40.3, 34.9, 26.0), and one quaternary (δ 33.3) sp^3 carbon signals. The ^1H NMR spectrum of 23a indicated the presence of an ethyl group which was attached to a methine. We assumed that 23a might contain a cyclopropane ring, because the ^{13}C NMR signals of quaternary and methine carbons were observed at relatively high fields. Since the structure of 23a was not elucidated solely from these data,

Scheme V

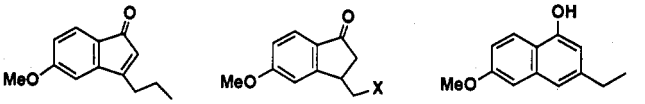


the connectivity was finally established as illustrated by the 2D ^{13}C-INADEQUATE spectrum. The stereochemistry of the methyl and ethyl groups still remains uncertain. So far we were not able to prepare derivatives of **23a** suitable for X-ray crystallographic structure analysis.

Similarly, irradiation of 2-propyl derivative **1d** gave indenone **22b** and cyclopropyl ketone **23b**, along with naphthol **17c**. In this case, however, considerable amount of (bromomethyl)indanone **25b** was also obtained. By contrast, in the absence of ethylene, we found that (chloromethyl)indanone **25a** was formed efficiently.[6,19]

One of the possible reaction mechanisms leading to these products is shown in Scheme V. In this case, we assume a polar mechanism which is similar to that proposed previously because of the formation of the ring-contracted products **22a** and **22b**. Thus nucleophilic attack of ethylene takes place either at C-3 of intermediate **20b** or C-4 of **21b**. The cation center of these intermediates may be stabilized by the electron-donating property of the C-2 alkyl group. Attack of ethylene to **21b** leads straightforwardly to indenones **22a** or **22b** by a formal 1,4-hydride shift (path b). On the other hand, the former process produces the intermediate **26**. Cyclization at this stage may well produce cyclobutane products, but this may be precluded by steric interference by the C-2 alkyl group. 3-Ethylnaphthols **17b** and **17c** are formed after a formal 1,3-hydride shift to give **27**. Another 1,2-hydride shift would produce the benzyl cation **28**. Attack of the second ethylene molecule at C-4 of **28** and the subsequent hydride shift in the resulting intermediate **29** followed by cyclization could give the final products **23a** and **23b** (path a).

Lastly photoreaction of 6-methoxy derivative **1e** was examined. Since irradiation of **1e** with 5 equiv of $AlBr_3$ gave a complex mixture of products, reaction was undertaken with 2 equiv of $AlBr_3$ or 5 equiv of $AlCl_3$. With $AlBr_3$, we obtained indenone **30** (11%) and (bromomethyl)indanone **31b** (28%),[6,19] while with $AlCl_3$, **30** (30%), (chloromethyl)indanone **31a** (12%),[6] and ethylnaphthol **32** (29%) were obtained. It is noteworthy that **1e**



30 **31a** X = Cl **32**
31b X = Br

underwent similar reaction to that of 2-alkyl derivatives **1c** and **1d** to give the ring-contracted products. This reactivity is certainly due to the electron-donating effect of the methoxyl group which stabilizes the cation centers of the intermediates.

Conclusion

We have found novel photocycloadditions of 1- and 2-naphthols with ethylene which were promoted by aluminum halides. 2-Naphthol (**2a**) and its 6-substituted derivatives **2b–e** gave the corresponding [2 + 2] cycloadducts **7a–e** in moderate to good yields. The major side products were 3-ethyl-2-naphthols **8a–e**. Of the Lewis acids and alkenes examined, only $AlCl_3$ and $AlBr_3$ effected the reaction and only ethylene gave satisfactory results, although allene could also be employed. While the substituents on C-6 did not exert appreciable effect on the reaction, C-3 alkyl groups markedly depressed the reactivity. By contrast, 1-naphthol (**1a**) and its derivatives exhibited diverse reactivities depending on the substituent on C-2, C-3, or C-6. Namely **1a** and 3-methyl derivative **1b** afforded [2 + 2] cycloadducts **16a** and **16b** in moderate yields. On the other hand, 2-methyl and 2-propyl derivatives **1c** and **1d** yielded unusual products like indenones **22a** and **22b** and cyclopropyl ketones **23a** and **23b**, respectively. 6-Methoxy derivative **1e** also gave indenone **30**. These anomalous products may be derived by nucleophilic attack of ethylene to polarized intermediates **20b** and **21b**, respectively. Though the mechanistic details are not fully understood at present, these reactions represent a new aspect in both the mechanistic and synthetic chemistry of phenols.

Experimental Section

All melting points are uncorrected. IR spectra were recorded on a Hitachi 260-10 spectrometer as liquid films unless otherwise

(19) We reported that irradiation of **1d** and **1e** with $AlBr_3$ in CH_2Cl_2 (in the absence of ethylene) gave *(chloromethyl)indanones* **25a** and **31a**, respectively, probably due to rapid halogen exchange between $AlBr_3$ and the solvent (ref 6). Irradiation of **1d** and **1e** in the presence of ethylene, however, afforded (bromomethyl)indanones **25b** and **31b**, respectively. We assume that in the presence of ethylene the halogen exchange reaction is precluded due to coordination of ethylene to the Lewis acid.

stated. Mass spectra were measured with a Hitachi RMU-6E or JEOL JMS-DX303 spectrometer and are given in terms of *m/e* (relative intensity). ^{1}H NMR (90 MHz, 100 MHz, 400 MHz, or 600 MHz) and ^{13}C NMR (22.5 MHz, 100 MHz, or 150 MHz) spectra were taken on a JEOL JNM-FT-90Q, JNM-PS-100, JNM-GSX-400, or Bruker AM-600 spectrometer in $CDCl_3$ with Me_4Si as an internal standard unless otherwise stated. Analytical GLC was carried out on a Hitachi 163 gas chromatograph with a 10% FFAP or 30% SE-30 column. Column chromatography was performed with Wako C-200 silica gel.

Naphthols **1a**, **2a**, and **2d** are commercially available and used without further purification. Naphthols **1b**,[20] **1c**,[21] **1e**,[22] **2b**,[23] **2c**,[24] and **2e**[25] were prepared according to the literature. 2-Propyl-1-naphthol (**1d**)[26] was prepared from **1a** by allylation and subsequent Claisen rearrangement followed by hydrogenation. 3-Methyl-1-naphthol (**15b**)[27] was prepared from commercially available reagent 3-hydroxy-2-naphthoic acid by the literature method.[28] 2-Oxo-1,2,3,4-tetrahydronaphthalene (**9a**) and 1,1'-bi-2-naphthol (**10**) are commercially available.

General Procedure of Photoreaction of Naphthols with Ethylene in the Presence of Lewis Acid. To a solution of 1.0 g of naphthol in 100 mL of CH_2Cl_2 in Pyrex tube was added a Lewis acid (equivalent indicated in Tables I and II). The mixture was stirred for 30 min at room temperature and then was immersed in a dry ice–ethanol bath. Ethylene was bubbled into the mixture for 20 min, and then the mixture was irradiated with a 500-W high-pressure mercury lamp (Eikoshya, EHB-W-500) at −78 °C for a period shown in Tables I and II under a slow stream of ethylene. After irradiation, the mixture was carefully poured into crushed ice. The mixture was extracted with ether, and the combined organic layers were washed with $NaHCO_3$ solution and brine and dried ($MgSO_4$). Column chromatography of the crude material gave products. The results are summarized in Table I and II. Reaction of 400 mg of 2-naphthol (**2a**) with $EtAlCl_2$ (5 equiv) for 8 h gave unreacted **2a** (390 mg). Similarly, reaction of 1.0 g of **2a** with $TiCl_4$ (2 equiv) or BF_3·OEt_2 (2 equiv) for 8 h resulted in the recovery of unreacted **2a** (0.98 g or 0.96 g, respectively).

(1*S,6*R**)-4,5-Benzobicyclo[4.2.0]oct-4-en-2-one (7a)**: IR 1700, 1480, 1440, 850, 830 cm^{-1}; MS 172 (M^+, 15), 144 (100); ^{1}H NMR δ 7.3–7.2 (m, 2 H), 7.12 (d, *J* = 8.3 Hz, 1 H), 7.06 (d, *J* = 6.8 Hz, 1 H), 4.05 (br q, 1 H), 3.68 (ABq, *J* = 16.0 Hz, Δν = 16.5 Hz, 2 H), 3.28 (m, 1 H), 2.59 (m, 1 H), 2.38 (m, 1 H), 2.21 (m, 1 H), 2.09 (m, 1 H); ^{13}C NMR δ 210.4 (s), 138.3 (s), 133.1 (s), 128.4 (d), 126.9 (d), 126.6 (d, 2C), 44.1 (d), 43.7 (t), 40.3 (d), 28.5 (t), 21.9 (t). Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.42; H, 7.07.

(1*S,6*R**)-4,5-(4'-Bromobenzo)bicyclo[4.2.0]oct-4-en-2-one (7b)**: IR 1705, 1480, 900 cm^{-1}; MS 252 (M^+ + 2, 20), 250 (M^+, 21), 222 (100); ^{1}H NMR δ 7.31 (dd, *J* = 8.3, 2.0 Hz, 1 H), 7.27 (br d, *J* = ca. 2 Hz, 1 H), 6.94 (d, *J* = 8.3 Hz, 1 H), 4.02 (br q, 1 H), 3.62 (ABq, *J* = 18.9 Hz, Δν = 18.9 Hz, 2 H), 3.31 (m, 1 H), 2.63 (m, 1 H), 2.39 (m, 1 H), 2.22 (m, 1 H), 2.11 (m, 1 H); ^{13}C NMR δ 210.5 (s), 140.7 (s), 132.3 (s), 130.4 (d), 140.0 (d), 129.9 (d), 120.9 (s), 44.1 (d), 43.6 (t), 40.2 (d), 28.8 (t), 22.2 (t). Anal. Calcd for $C_{12}H_{11}BrO$: C, 57.40; H, 4.41; Br, 31.82. Found: C, 57.37; H, 4.03; Br, 31.69.

(1*S,6*R**)-4,5-(4'-Methoxybenzo)bicyclo[4.2.0]oct-4-en-2-one (7c)**: IR 1700, 1250, 1230 cm^{-1}; MS 202 (M^+, 50), 174 (100); ^{1}H NMR δ 6.98 (d, *J* = 8.3 Hz, 1 H), 6.76 (dd, *J* = 8.3, 2.4 Hz, 1 H), 6.65 (d, *J* = 3.0 Hz, 1 H), 4.02 (br q, 1 H), 3.79 (s, 3 H), 3.61 (ABq, *J* = 16.0 Hz, Δν = 16.0 Hz, 2 H), 3.27 (m, 1 H), 2.63 (m, 1 H), 2.37 (m, 1 H), 2.22 (m, 1 H), 2.08 (m, 1 H); ^{13}C NMR δ 211.6 (s), 158.9 (s), 139.7 (s), 129.7 (d), 125.3 (s), 113.0 (d), 111.9 (d), 55.3 (q), 44.3 (d), 43.4 (t), 40.8 (d), 28.8 (t), 22.2 (t). Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 76.76; H, 7.07.

(1*S,6*R**)-4,5-(4'-Hydroxybenzo)bicyclo[4.2.0]oct-4-en-2-one (7d)**: mp 107–109 °C; IR (KBr) 3400–3100, 1670, 1590, 1500, 1160 cm^{-1}; MS 188 (M^+, 38), 160 (100); ^{1}H NMR (d_6-DMSO) δ 9.25 (s, 1 H), 6.89 (d, *J* = 8.2 Hz, 1 H), 6.60 (dd, *J* = 8.2, 2.4 Hz, 1 H), 6.52 (d, *J* = 2.0 Hz, 1 H), 3.97 (br q, 1 H), 3.52 (ABq, *J* = 16 Hz, Δν = 32.5 Hz, 2 H), 3.23 (m, 1 H), 2.24 (m, 1 H), 2.1–1.95 (m, 2 H), 1.89 (m, 1 H); HRMS calcd for $C_{12}H_{12}O_2$ 188.0837, found 188.0850.

This sample was also obtained from **7c**. A mixture of 84 mg (0.42 mmol) of **7c**, 3 mL of 48% HBr, and 3 mL of acetic acid was heated at reflux for 40 min. Water was added to the cooled mixture and the mixture was extracted with ether. The combined organic layer was washed with $NaHCO_3$ solution and water and dried ($MgSO_4$). Evaporation of solvent followed by column chromatography on silica gel of the crude material gave **7d** (30 mg, 38%).

(1*S,6*R**)-4,5-(4'-Methoxycarbonylbenzo)bicyclo[4.2.0]-oct-4-en-2-one (7e)**: IR 1710, 1600, 1270, 1190 cm^{-1}; MS 230 (M^+, 8), 202 (100); ^{1}H NMR δ 7.84 (d, *J* = 7.9 Hz, 1 H), 7.81 (s, 1 H), 7.14 (d, *J* = 7.9 Hz, 1 H), 4.10 (m, 1 H), 3.90 (s, 3 H), 3.72 (ABq, *J* = 17.4 Hz, Δν = 25.8 Hz, 2 H), 3.31 (m, 1 H), 2.67 (m, 1 H), 2.41 (m, 1 H), 2.22 (m, 1 H), 2.09 (m, 1 H); ^{13}C NMR δ 209.9 (s), 166.8 (s), 138.8 (s), 138.7 (s), 129.3 (s), 128.9 (d), 128.3 (d), 128.0 (d), 52.0 (q), 44.3 (t), 44.2 (d), 40.3 (d), 28.8 (t), 22.2 (t); HRMS calcd for $C_{14}H_{14}O_3$ 230.0942, found 230.0948.

3-Ethyl-2-naphthol (8a):[13] mp 76–77 °C (lit. 78 °C);[13] IR (KBr) 3500–3100, 870, 750 cm^{-1}; ^{1}H NMR δ 7.9–7.0 (m, 6 H), 5.19 (s, 1 H), 2.85 (q, *J* = 8 Hz, 2 H), 1.37 (t, *J* = 8 Hz, 3 H).

6-Bromo-3-ethyl-2-naphthol (8b): mp 120–121 °C; IR (KBr) 3400–3100, 1625, 1585, 1230 cm^{-1}; MS 252 (M^+ + 2, 98), 250 (M^+, 100); ^{1}H NMR δ 7.89 (s, 1 H), 7.6–7.3 (m, 3 H), 7.01 (s, 1 H), 5.09 (s, 1 H), 2.80 (q, *J* = 8 Hz, 2 H), 1.32 (t, *J* = 8 Hz, 3 H). Anal. Calcd for $C_{12}H_{11}BrO$: C, 57.40; H, 4.41; Br, 31.82. Found: C, 57.68; H, 4.49; Br, 31.63.

3-Ethyl-6-methoxy-2-naphthol (8c): mp 84–85 °C; IR (KBr) 3400–3100, 1610, 1385, 1220 cm^{-1}; MS 202 (M^+, 100), 187 (56); ^{1}H NMR δ 7.7–7.5 (m, 2 H), 7.2–6.9 (m, 3 H), 4.97 (s, 1 H), 3.90 (s, 3 H), 2.81 (q, *J* = 8 Hz, 2 H), 1.35 (t, *J* = 8 Hz, 3 H). Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.18; H, 6.95.

3-Ethyl-2,6-naphthalenediol (8d): mp 160–165 °C; IR (KBr) 3500–3100, 1610, 1230, 900, 880 cm^{-1}; MS 188 (M^+, 100), 173 (71); ^{1}H NMR δ 7.54 (d, *J* = 8.8 Hz, 1 H), 7.43 (s, 1 H), 7.06 (d, *J* = 2.6 Hz, 1 H), 7.04 (s, 1 H), 7.00 (dd, *J* = 8.8, 2.6 Hz, 1 H), 4.9–4.8 (m, 2 H), 2.78 (q, *J* = 7.6 Hz, 2 H), 1.32 (t, *J* = 7.6 Hz, 3 H); HRMS calcd for $C_{12}H_{12}O_2$ 188.0837, found 188.0832.

3-Ethyl-6-(methoxycarbonyl)-2-naphthol (8e): mp 128–129 °C; IR (KBr) 3550–3100, 1700, 1620, 1270 cm^{-1}; MS 230 (M^+, 100), 215 (56); ^{1}H NMR δ 8.50 (br d, 1 H), 7.93 (dd, *J* = 8.5, 2 Hz, 1 H), 7.68 (s, 1 H), 7.62 (d, *J* = 8.5 Hz, 1 H), 7.13 (s, 1 H), 5.84 (s, 1 H), 3.96 (s, 3 H), 2.82 (q, *J* = 8 Hz, 2 H), 1.30 (t, *J* = 8 Hz, 3 H); HRMS calcd for $C_{14}H_{14}O_3$ 230.0943, found 230.0950.

3-Ethyl-1,2,3,4-tetrahydronaphthalen-2-one (9b): IR 1710, 1490, 1450, 850 cm^{-1}; MS 174 (M^+, 45), 146 (54), 131 (38), 104 (100); ^{1}H NMR δ 7.4–7.0 (m, 4 H), 3.59 (s, 2 H), 3.05 (dd, *J* = 14, 7 Hz, 1 H), 2.96 (dd, *J* = 14, 9 Hz, 1 H), 2.5–2.2 (m, 1 H), 2.1–1.8 (m, 2 H), 0.98 (t, *J* = 8 Hz, 3 H); ^{13}C NMR δ 211.6 (s), 136.1 (s), 133.3 (s), 127.9 (d), 127.8 (d), 126.73 (d), 126.68 (d), 48.7 (d), 44.6 (t), 33.7 (t), 22.8 (t), 11.4 (q). Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.83; H, 8.11.

(1*S,6*S**)-3,4-Benzobicyclo[4.2.0]oct-3-en-2-one (16a)**: IR 1675, 1600, 1270 cm^{-1}; MS 172 (M^+, 100), 144 (76); ^{1}H NMR δ 7.97 (dd, *J* = 7.7, 1.5 Hz, 1 H), 7.50 (td, *J* = 7.7, 1.5 Hz, 1 H), 7.34 (t, *J* = 7.7 Hz, 1 H), 7.25 (d, *J* = 7.7 Hz, 1 H), 3.3–3.1 (m, 2 H), 3.04 (dd, *J* = 16.5, 6.2 Hz, 1 H), 2.75 (dd, *J* = 16.5, 4.0 Hz, 1 H), 2.55 (m, 1 H), 2.14 (m, 1 H), 1.99 (m, 1 H), 1.87 (m, 1 H); ^{13}C NMR δ 200.8 (s), 141.9 (s), 133.0 (s and d), 129.0 (d), 126.7 (d), 126.2 (d), 42.7 (d), 31.0 (d and t), 24.1 (t, 2C). Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.84; H, 6.93.

(1*S,6*S**)-6-Methyl-3,4-benzobicyclo[4.2.0]oct-3-en-2-one (16b)**: IR 1660, 1580, 1285 cm^{-1}; MS 186 (M^+, 32), 158 (100); ^{1}H NMR δ 7.95 (m, 1 H), 7.7–7.1 (m, 3 H), 3.1–1.6 (m, 7 H), 1.34 (s, 3 H); ^{13}C NMR δ 201.7 (s), 142.6 (s), 133.3 (d), 133.0 (s), 129.1

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(d), 127.1 (d), 126.7 (d), 49.2 (d), 39.1 (t), 37.1 (s), 30.4 (t), 27.8 (q), 20.9 (t). Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.83; H, 7.62.

3-Ethyl-1-naphthol (17a): IR 3550–3100, 1600, 1400, 1280, 1070 cm^{-1}; MS 172 (M^+, 92), 157 (100); ^{1}H NMR δ 8.10 (dd, J = 8.1, 1.1 Hz, 1 H), 7.73 (dd, J = 7.3, 1.5 Hz, 1 H), 7.5–7.4 (m, 2 H), 7.23 (d, J = 1.1 Hz, 1 H), 6.67 (d, J = 1.5 Hz, 1 H), 5.31 (br s, 1 H), 2.72 (q, J = 7.7 Hz, 2 H), 1.29 (t, J = 7.7 Hz, 3 H). Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.60; H, 6.97.

3-Ethyl-2-methyl-1-naphthol (17b): IR 3550–3100, 1600, 1380, 1100, 750 cm^{-1}; MS 186 (M^+, 90), 157 (100), 129 (51); ^{1}H NMR δ 8.02 (m, 1 H), 7.70 (m, 1 H), 7.40–7.35 (m, 2 H), 7.25 (s, 1 H), 5.27 (s, 1 H), 2.75 (q, J = 7.7 Hz, 2 H), 2.31 (s, 3 H), 1.27 (t, J = 7.7 Hz, 3 H); ^{13}C NMR δ 148.5 (s), 141.6 (s), 132.8 (s), 127.2 (d), 125.4 (d), 124.5 (d), 122.9 (s), 120.7 (d), 118.7 (d), 116.3 (s), 27.2 (t), 14.6 (q), 11.3 (q); HRMS calcd for $C_{13}H_{14}O$ 186.1045, found 186.1040.

3-Ethyl-2-propyl-1-naphthol (17c): IR 3550–3100, 1600, 1570, 1460, 1380, 1100, 750 cm^{-1}; MS 214 (M^+, 47), 185 (100); ^{1}H NMR δ 8.03 (m, 1 H), 7.68 (m, 1 H), 7.4–7.3 (m, 2 H), 7.25 (s, 1 H), 5.66 (br s, 1 H), 2.76 (q, J = 7.3 Hz, 2 H), 2.74 (t, J = 7.8 Hz, 2 H), 1.60 (qt, J = 7.3, 7.3 Hz, 2 H), 1.28 (t, J = 7.3 Hz, 3 H), 1.02 (t, J = 7.3 Hz, 3 H); ^{13}C NMR δ 148.5 (s), 141.3 (s), 132.9 (s), 127.1 (d), 125.3 (d), 124.3 (d), 123.1 (s), 121.5 (s), 120.8 (d), 118.7 (d), 28.1 (t), 26.2 (t), 23.1 (t), 15.2 (q), 14.4 (q); HRMS calcd for $C_{15}H_{18}O$ 214.1358, found 214.1371.

2-Methyl-3-propylinden-1-one (22a): IR 1700, 1600, 1450, 710 cm^{-1}; MS 186 (M^+, 100), 171 (76); ^{1}H NMR δ 7.36 (d, J = 7.0 Hz, 1 H), 7.28 (t, J = 7.0 Hz, 1 H), 7.01 (d, J = 7.0 Hz, 1 H), 7.13 (t, J = 7.3 Hz, 1 H), 2.52 (t, J = 7.3 Hz, 2 H), 1.82 (s, 3 H), 1.65 (tq, J = 7.3, 7.3 Hz, 2 H), 1.01 (t, J = 7.3 Hz, 3 H); ^{13}C NMR δ 198.5 (s), 157.5 (s), 145.8 (s), 133.2 (d), 131.2 (s), 130.7 (s), 127.8 (d), 121.7 (d), 118.8 (d), 28.1 (t), 20.8 (t), 14.2 (q), 7.6 (q); HRMS calcd for $C_{13}H_{14}O$ 186.1045, found 186.1038.

2,3-Dipropylinden-1-one (22b): IR 1700, 1600, 1460, 760, 720 cm^{-1}; MS 214 (M^+, 52), 185 (100), 143 (64); ^{1}H NMR δ 7.35 (d, J = 7.3 Hz, 1 H), 7.29 (td, J = 7.3, 1.0 Hz, 1 H), 7.12 (t, J = 6.8 Hz, 1 H), 7.01 (d, J = 6.8 Hz, 1 H), 2.51 (t, J = 7.8 Hz, 2 H), 2.24 (t, J = 7.8 Hz, 2 H), 1.64 (qt, J = 7.8, 7.3 Hz, 2 H), 1.50 (qt, J = 7.8, 7.3 Hz, 2 H), 1.03 (t, J = 7.3 Hz, 3 H), 0.93 (t, J = 7.3 Hz, 3 H); ^{13}C NMR δ 198.5 (s), 157.6 (s), 145.7 (s), 134.8 (s), 133.2 (d), 131.2 (s), 127.9 (d), 121.7 (d), 119.0 (d), 28.3 (t), 25.2 (t), 22.5 (t), 21.3 (t), 14.4 (q), 14.2 (q); HRMS calcd for $C_{15}H_{18}O$ 214.1358, found 214.1355.

5-Ethyl-1,7-dimethyl-3,4-benzobicyclo[4.1.0]hept-3-en-2-one (23a): IR 1660, 1600, 1450, 1350, 880, 750 cm^{-1}; MS 214 (M^+, 19), 185 (100); ^{1}H NMR δ 7.85 (dd, J = 7.5, 1.5 Hz, 1 H), 7.43 (td, J = 7.7, 1.5 Hz, 1 H), 7.29 (td, J = 7.7, 1.5 Hz, 1 H), 7.12 (d, J = 7.3 Hz, 1 H), 3.19 (br t, J = 5.9 Hz, 1 H), 1.65 (qd, J = 7.7, 6.2 Hz, 2 H), 1.40 (s, 3 H), 1.34 (m, 1 H), 1.14 (m, 1 H), 1.16 (br s, 3 H), 0.80 (t, J = 7.7 Hz, 3 H); ^{13}C NMR δ 200.1 (s), 143.3 (s), 132.3 (d), 131.4 (s), 128.7 (d), 127.0 (d), 126.9 (d), 40.3 (d), 34.9 (d), 33.3 (s), 32.9 (t), 26.0 (d), 13.3 (q), 13.1 (q), 10.3 (q). Anal. Calcd for $C_{15}H_{18}O$: C, 84.00; H, 8.47. Found: C, 84.24; H, 8.50.

5-Ethyl-7-methyl-1-propyl-3,4-benzobicyclo[4.1.0]hept-3-en-2-one (23b): IR 1660, 1500, 1450, 1190, 970, 760 cm^{-1}; MS 242 (M^+, 52), 213 (100), 199 (51), 171 (65), 157 (35); ^{1}H NMR δ 7.86 (dd, J = 7.8, 1.5 Hz, 1 H), 7.42 (td, J = 7.8, 1.5 Hz, 1 H), 7.28 (td, J = 7.3, 1.0 Hz, 1 H), 7.11 (d, J = 7.3 Hz, 1 H), 3.07 (br t, J = 6.5 Hz, 1 H), 2.25 (ddd, J = 14.2, 11.7, 4.3 Hz, 1 H), 1.7–1.3 (m, 5 H), 1.2–1.15 (m, 4 H, containing s at 1.17), 1.13 (ddd, J = 13.7, 11.7, 4.9 Hz, 1 H), 0.99 (t, J = 7.3 Hz, 3 H), 0.92 (t, J = 7.3 Hz, 3 H); ^{13}C NMR δ 199.1 (s), 143.4 (s), 132.2 (d), 131.2 (s), 128.8 (d), 127.2 (d), 126.9 (d), 40.6 (d), 38.2 (s), 33.3 (t), 33.0 (d), 29.4 (t), 27.2 (d), 21.1 (t), 14.7 (q), 13.5 (q), 11.4 (q); HRMS calcd for $C_{17}H_{22}O$ 242.1670, found 242.1677.

3-Ethyl-2-methyl-1,4-naphthoquinone (24): mp 65–69 °C; IR (KBr) 1660, 1620, 1595, 1335, 1305, 720 cm^{-1}; MS 200 (M^+, 100); ^{1}H NMR δ 8.08 (m, 2 H), 7.69 (m, 2 H), 2.66 (q, J = 7.7 Hz, 2 H), 2.19 (s, 3 H), 1.13 (t, J = 7.7 Hz, 3 H); ^{13}C NMR δ 185.4 (s), 184.5 (s), 148.5 (s), 142.8 (s), 133.3 (s), 133.2 (s), 132.2 (d), 132.1 (d), 126.2 (d), 126.1 (d), 20.3 (t), 12.9 (q), 12.3 (q). Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 77.71; H, 6.09.

(2S*,3S*)-3-(Bromomethyl)-2-propylindan-1-one (25b): IR 1700, 1600, 1460, 1320, 1280, 1220, 740 cm^{-1}; MS 226 (M^+ – 40, 16), 224 (M^+ – 42, 16), 145 (100); ^{1}H NMR δ 7.76 (d, J = 7.6 Hz, 1 H), 7.65 (t, J = 7.4 Hz, 1 H), 7.58 (d, J = 7.8 Hz, 1 H), 7.45 (t, J = 7.5 Hz, 1 H), 3.80 (dd, J = 10.4, 4.4 Hz, 1 H), 3.67 (dd, J = 10.4, 6.5 Hz, 1 H), 3.50 (m, 1 H), 2.64 (ddd, J = 8.3, 5.2, 3.1 Hz, 1 H), 1.87 (m, 1 H), 1.63 (m, 1 H), 1.49 (m, 2 H), 0.96 (t, J = 7.2 Hz, 3 H); ^{13}C NMR δ 206.9 (s), 153.5 (s), 136.8 (s), 134.9 (d), 128.6 (d), 125.4 (d), 123.9 (d), 52.8 (d), 46.3 (d), 36.6 (t), 33.5 (t), 20.3 (t), 14.1 (q).

5-Methoxy-3-propylinden-1-one (30): IR 1700, 1600, 1570, 1460, 1220, 800 cm^{-1}; MS 202 (M^+, 57), 174 (100); ^{1}H NMR δ 7.36 (d, J = 8.1 Hz, 1 H), 6.67 (d, J = 2.2 Hz, 1 H), 6.62 (dd, J = 8.1, 2.2 Hz, 1 H), 5.86 (s, 1 H), 3.85 (s, 3 H), 2.49 (t, J = 7.3 Hz, 2 H), 1.71 (qt, J = 7.3, 7.3 Hz, 2 H), 1.04 (t, J = 7.3 Hz, 3 H); ^{13}C NMR δ 196.8 (s), 164.3 (s), 164.2 (s), 148.1 (s), 124.5 (s), 124.0 (d), 123.6 (d), 110.1 (d), 108.1 (d), 55.7 (q), 30.2 (t), 20.3 (t), 14.0 (q). Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.36; H, 7.28.

3-Ethyl-6-methoxy-1-naphthol (32): IR 3600–3100, 1640, 1600, 1580, 1390, 1220, 1015, 820 cm^{-1}; MS 202 (M^+, 100), 187 (56); ^{1}H NMR δ 8.02 (d, J = 8.4 Hz, 1 H), 7.12 (s, 1 H), 7.06 (d, J = 8.4 Hz, 1 H), 7.05 (s, 1 H), 6.53 (s, 1 H), 5.56 (s, 1 H), 3.90 (s, 3 H), 2.69 (q, J = 7.7 Hz, 2 H), 1.27 (t, J = 7.7 Hz, 3 H); ^{13}C NMR δ 158.2 (s), 151.6 (s), 143.2 (s), 136.4 (s), 123.2 (d), 118.2 (s), 117.4 (d), 116.8 (d), 107.8 (d), 105.6 (d), 55.3 (q), 29.1 (t), 15.4 (q).

Photoreaction of 2-Naphthol (2a) with Allene in the Presence of $AlCl_3$. A mixture of 800 mg (5.55 mmol) of **2a**, 3.69 g of $AlCl_3$ (27.8 mmol), and ca. 10 mL of allene in 80 mL of CH_2Cl_2 was irradiated at −78 °C for 2 h as described above. Workup gave **13** (431 mg, 35%), **14** (185 mg, 18%), and **15a** (88 mg, 9%).

13: mp 66–68 °C; IR (KBr) 1700, 1500, 1140, 1060, 860, 780, 740 cm^{-1}; MS 222 (M^+ + 2, 1), 220 (M^+, 4), 144 (100), 116 (54); ^{1}H NMR (CCl_4) δ 7.3–6.9 (m, 4 H), 3.96 (d, J = 8 Hz, 1 H), 3.66 (ABq, J = 18 Hz, $\Delta\nu$ = 26 Hz, 2 H), 3.2–2.6 (m, 3 H), 1.82 (s, 3 H); ^{13}C NMR δ 208.5 (s), 134.8 (s), 132.7 (s), 128.7 (d), 128.2 (d), 127.6 (d), 126.6 (d), 73.1 (s), 54.1 (d), 42.3 (t), 41.5 (t), 39.5 (d), 32.0 (q). Anal. Calcd for $C_{13}H_{13}ClO$: C, 70.75; H, 5.94. Found: C, 70.71; H, 5.93.

14: IR 3050, 1700, 1660, 870, 740 cm^{-1}; MS 184 (M^+, 84), 156 (42), 141 (100), 128 (65), 116 (64); ^{1}H NMR (CCl_4) δ 7.4–6.9 (m, 4 H), 4.87 (m, 2 H), 4.42 (m, 1 H), 3.59 (ABq, J = 18 Hz, $\Delta\nu$ = 24 Hz, 2 H), 3.4–2.6 (m, 3 H).

15a: IR 3600–3100, 3050, 1610, 1580, 1180, 800, 740 cm^{-1}; MS 184 (M^+, 78), 169 (100); ^{1}H NMR (CCl_4) δ 7.8–7.0 (m, 6 H), 5.60 (m, 1 H), 5.4–5.1 (m, 2 H), 2.11 (s, 3 H).

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Supplementary Material Available: Copies of ^{1}H and ^{13}C NMR spectra of **7d**, **7e**, **8d**, **8e**, **14**, **15a**, **17b**, **17c**, **22a**, **22b**, **23b**, **25b**, and **32**, and 2D ^{13}C-INADEQUATE spectrum of **23a** (22 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from ACS; see any current masthead page for ordering information.