using a mixed solvent (C_6H_6/hexane/AcOEt, 47/47/5) as an eluent to give 1.04 g (88%) of **11** as a colorless oil: IR (CCl_4) 1743 (C=O), 1720 (C=O) cm^{-1}; NMR (CCl_4) δ 1.3–2.4 (m, 11 H), 3.62 (s, 3 H, H_3CO).

Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.58; H, 8.36.

***trans*-2-(*cis*-2-Pentenyl)-3-[(methoxycarbonyl)(trimethylsilyl)methyl]cyclopentan-1-one (12a).** Analytically pure **12a** (1.08 g, 94%) was obtained as a colorless oil by an analogous reaction of **9** (1.31 g, 5.99 mmol) with **6a** (0.583 g, 3.89 mmol) activated by titanium tetrachloride (0.83 g, 4.35 mmol) in 20 mL of dichloromethane: bp 120 °C (0.1 mm) (Kugelrohr distillation); IR (CCl_4) 1744 (C=O), 1723 (C=O), 1252 (SiC_3) cm^{-1}; NMR (CCl_4) δ 0.12 (s, 9 H, H_3CSi), 0.95 (t, J = 7.7 Hz, 3 H, H_3CC), 1.8–2.3 (m, 11 H), 3.59 (s, 3 H, H_3CO), 5.29 (m, 2 H, vinyl protons).

Anal. Calcd for $C_{16}H_{28}O_3Si$: C, 64.82; H, 9.52. Found: C, 64.57; H, 9.66.

Protodesilylation of **12a** (0.585 g, 1.98 mmol) in a 20% aqueous methanol solution (20 mL) of potassium fluoride (0.255 g, 4.39 mmol) gave 0.398 g (90%) of methyl jasmonate (**13a**) as a colorless oil by a procedure analogous to that for **10**. For **13a**: IR (CCl_4) 1744 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 0.96 (t, J = 7.2 Hz, 3 H, H_3CC), 1.8–3.0 (m, 12 H), 3.70 (s, 3 H, H_3CO), 5.38 (m, 2 H, vinyl protons).

Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.93; H, 9.21.

***trans*-2-Pentyl-3-[(methoxycarbonyl)(trimethylsilyl)methyl]cyclopentan-1-one (12b).** Analytically pure **12b** (0.746 g, 95%) was obtained as a colorless oil by an analogous reaction of **9** (0.807 g, 3.69 mmol) with **6b** (0.402 g, 2.64 mmol) activated by titanium tetrachloride (0.52 g, 2.74 mmol) in 15 mL of dichloromethane: bp 120 °C (0.1 mm) (Kugelrohr distillation); IR (CCl_4) 1743 (C=O), 1722 (C=O), 1252 (SiC_3) cm^{-1}; NMR (CCl_4) δ 0.14 (s, 9 H, H_3CSi), 0.89 (t, J = 5.3 Hz, 3 H, H_3CC), 1.2–2.8 (m, 15 H), 3.62 (s, 3 H, H_3CO).

Anal. Calcd for $C_{16}H_{30}O_3Si$: C, 64.38; H, 10.13. Found: C, 64.31; H, 10.06.

Protodesilylation of **12b** (0.287 g, 0.961 mmol) in 20% aqueous methanol solution (15 mL) of potassium fluoride (0.26 g, 4.47 mmol) gave 0.193 g (89%) of methyl dihydrojasmonate (**13b**) as a colorless oil by a procedure analogous to that for **10**.

When **12b** was immediately desilylated without purification, **13b** was obtained in quantitative yield: IR (CCl_4) 1744 (C=O) cm^{-1}; NMR (CCl_4) δ 0.86 (t, J = 4.5 Hz, 3 H, H_3CC), 1.1–2.5 (m, 16 H), 3.58 (s, 3 H, H_3CO).

Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 69.28; H, 10.07.

Acknowledgment. The authors thank the Ministry of Education, Japan, for Grant-in-Aid No. 375469 and Shinetsu Chemical Co. for the supply of chlorotrimethylsilane and *cis*-3-hexen-1-ol.

Registry No. **1**, 72049-81-1; **2**, 66408-81-9; **3**, 72049-82-2; **4a**, 72049-83-3; **4d**, 72049-84-4; **5a**, 41031-87-2; **5b**, 43160-78-7; **5c**, 5312-86-7; **5d**, 72049-85-5; **5e**, 6126-53-0; **6a**, 41031-88-3; **6b**, 25564-22-1; **6c**, 3569-36-6; **6e**, 39163-29-6; **7**, 72049-86-6; **8**, 63095-33-0; **9**, 32583-40-7; **10**, 72049-87-7; **11**, 2808-12-0; **12a**, 72049-88-8; **12b**, 72049-89-9; **13a**, 1211-29-6; **13b**, 29852-02-6; *cis*-1-bromo-3-hexene, 5009-31-4; acetonitrile, 75-05-8; chlorotrimethylsilane, 75-77-4; ethylene oxide, 75-21-8; cyclohexene oxide, 286-20-4; methyl (trimethylsilyl)acetate, 2916-76-9; methyl bromoacetate, 96-32-2; 4-chlorobutyl bromide, 6940-78-9; lithium diisopropylamide, 4111-54-0; 2-cyclohexen-1-one, 930-68-7.

Arynic Condensations of Ketone Enolates. 15.[1] New Synthetic Applications of the Condensation of α,β-Unsaturated Ketone Enolates on Benzyne

Munir Essiz, Gérald Guillaumet, Jean-Jacques Brunet, and Paul Caubere*

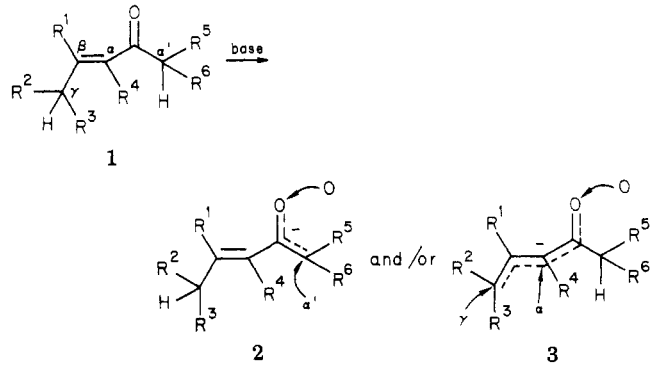
Laboratoire de Chimie Organique I, ERA CNRS No. 476, Université de Nancy I, Case Officielle 140, 54037 Nancy Cédex, France

Received June 15, 1979

Arynic condensations of both cyclic and acyclic α,β-unsaturated ketone enolates are studied. First, condensation of substituted cyclohexenone enolates with benzyne leads to a new class of cyclobutanic alcohols **6**. Ring opening of **6** under basic conditions is described as a good means of synthesizing benzocyclooctadienones **10** and **19**, and, in appropriate cases, benzocyclooctenediones of type **12**. Thermal dehydration of **6** affords 1,3-disubstituted naphthalenes in good yields. Second, condensations of a few acyclic α,β-unsaturated ketone enolates with benzyne are shown to be of synthetic usefulness; depending on the substituents on both sides of the carbonyl group, these condensations may lead either to substituted naphthalenes or to phenyl ketones or tetralones.

$S_{RN}1$[2] and arynic[3] condensations of saturated ketone enolates on aryl halides have attracted much interest in view of their synthetic usefulness. Thus, numerous phenyl ketones,[2,4] benzocycloenones,[5] and benzocyclobutenols[6] may be easily obtained from inexpensive starting materials.

Scheme I



As far as arynic condensations are concerned, α,β-unsaturated ketone enolates have been much less studied than saturated ones. Of course, much more complex re-

(1) For part 14, see M. Essiz, G. Guillaumet, and P. Caubere, *Tetrahedron*, **35**, 1167 (1979). Parts 14 and 15 together with ref 11 and 12 represent part of the research work of M.E. for his Ph.D. Thesis.

(2) J. F. Bunnett, *Acc. Chem. Res.*, 413 (1978); J. A. Zoltewicz, *Top. Curr. Chem.*, **59**, 33 (1975).

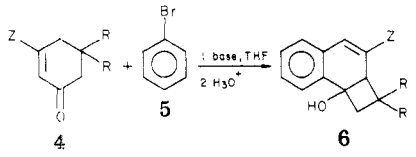
(3) P. Caubere, *Top. Curr. Chem.*, **73**, 50 (1978), and references cited therein.

(4) (a) P. Caubere, M. S. Mourad, and G. Guillaumet, *Tetrahedron*, **29**, 1843 (1973); (b) R. G. Scamehorn and J. F. Bunnett, *J. Org. Chem.*, **42**, 1457 (1977).

(5) (a) P. Caubere, G. Guillaumet, and M. S. Mourad, *Tetrahedron*, **29**, 1851 (1973); (b) P. Caubere, G. Guillaumet, and M. S. Mourad, *Bull. Soc. Chim. Fr.*, 3493 (1973); M. C. Carre, M. L. Viriot-Villaume, and P. Caubere, *Synthesis*, 48 (1977).

(6) P. Caubere and M. S. Mourad, *Bull. Soc. Chim. Fr.*, 1415 (1974), and ref 5a.

Table I. Condensation of Cyclohexenone Enolates with Benzyne in THF[a]



4 5 6

compd	Z	R	base	t, h	yield of 6,[f] %
a	CH_3	CH_3	cb[b]	4	30
b	i-C_3H_7	CH_3	cb	2.5	65
c	C_6H_5	CH_3	cb	4	45
d	C_2H_5O	H	$NaNH_2$[c]	3	37
e	C_2H_5O	CH_3	$NaNH_2$	3	50
f	C_6H_5O	CH_3	cb	2	45
g	p-$CH_3OC_6H_4O$	CH_3	$NaNH_2$	3	55
h	p-FC_6H_4O	CH_3	$NaNH_2$	3	55
i	C_2H_5S	CH_3	cb	12	20[d]
j	C_6H_5S	CH_3	$NaNH_2$	3	45
k	p-$CH_3OC_6H_4S$	CH_3	$NaNH_2$	4	55

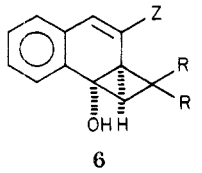
[a] 60 mL. [b] $NaNH_2$/t-BuONa/enolate/C_6H_5Br = 50/25/25/12.5 in mmol. [c] $NaNH_2$/enolate/C_6H_5Br = 50/25/12.5 in mmol. Enolates were prepared at 45–50 °C for **2b** (except for **4h**, 30 °C). Temperature of condensation 50 °C (except for **4h**, 30 °C). [d] 50% recovered C_6H_5Br. [e] For the determination of the structure of alcohols **6**, see Experimental Section. [f] Yield of isolated alcohol **6** with respect to C_6H_5Br.

sults should be expected as these substrates may be attacked by electrophiles at several sites (Scheme I).[7]

Note that O reactions are generally not observed during arynic condensations.[8] Moreover, if C condensations were regioselective, versatile synthetic applications would result.

Illustrations of these possibilities have been previously described by Sammes[9,10] and ourselves.[1,11] Thus, it was reported that arynic condensations of α,β-unsaturated ketone enolates are a good way of preparing naphthalene derivatives[9,10] as well as tetralones and indanones.[1,11]

Continuing our works in this field, we found that a new class of alcohols, i.e., dihydronaphthocyclobutanols **6**, might be obtained from bromobenzene and cyclohexenone enolates.



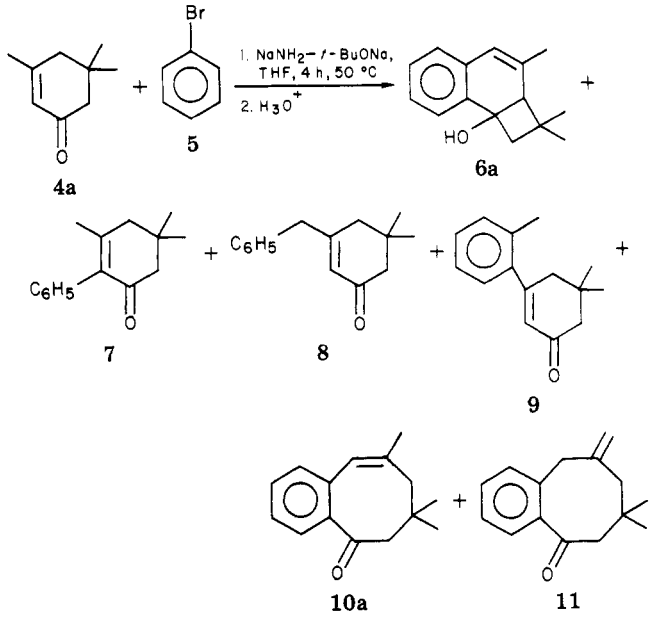
6

A few examples have been briefly described in a preliminary paper.[12] We now report much more complete results on this unexpected reaction and present a few synthetic applications of arynic condensation of acyclic α,β-unsaturated ketones.

Results and Discussion

It is now well-known[3] that arynic condensations of ketone enolates may be conveniently performed, in an aprotic solvent, by suitable generation of benzyne from bromobenzene and sodamide. Generally, with $NaNH_2$, saturated ketone enolates give a complex base[3] capable of generating benzyne. However, preliminary experiments showed that arynic condensations of α,β-unsaturated ketone enolates sometimes needed the use of the complex base $NaNH_2$–t-BuONa.

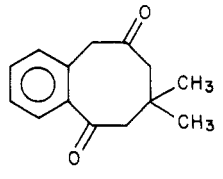
Scheme II



4a 5 6a 7 8 9 10a 11

Condensation of Cyclohexenone Enolates. With the object of developing the synthesis of alcohols **6**, condensations of various cyclohexenone enolates were performed (Table I).

Thus, arynic condensation of cyclohexenone enolates appears as a general method for the synthesis of alcohols **6**. However, when the β substituent, Z, of the starting enone (R = CH_3) was an amino group (*N*-piperidino or *N*-morpholino), the expected alcohols were too unstable to be isolated. They were rapidly hydrolyzed during workup and purification to give benzocyclooctenedione **12** (40 and 50% yield, respectively).



12

Besides the easily separated alcohols **6**, complex mixtures of ketonic compounds were formed. However, we succeeded in the separation and determination of structures of these ketones by a more complete study of the condensation of the easily available isophorone. Thus, the more general reaction we observed in this case is pictured in Scheme II.

In order to improve the selectivity of this reaction to allow a more easy separation and identification of the ketonic derivatives **7–11**, solvent effects were briefly studied. The more important observations were the following: (i) better overall yields were obtained in THF (82%), 1,2-dimethoxyethane (DME, 72%), HMPA (64%), and benzene (46%); (ii) phenyl ketones **7**, **8**, and **9** were the only compounds formed in HMPA; (iii) the best yields of ketones **10a** were obtained in DME; (iv) benzene favored the formation of ketones **10a** and **11**; (v) THF was the best solvent for the formation of **6a**.

(7) J. D'Angelo, *Tetrahedron*, **32**, 2979 (1976), and references cited therein.
(8) R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes", Verlag Chemie, Weinheim/Bergstr., Germany, 1967.
(9) P. G. Sammes and T. W. Wallace, *J. Chem. Soc., Perkin Trans. 1*, 1377 (1975).
(10) P. G. Sammes and T. W. Wallace, *Chem. Commun.*, 524 (1973).
(11) J. J. Brunet, M. Essiz, and P. Caubere, *Tetrahedron Lett.*, 871 (1974).
(12) M. Essiz, G. Guillaumet, J. J. Brunet, and P. Caubere, *Chem. Commun.*, 276 (1979).

Scheme III

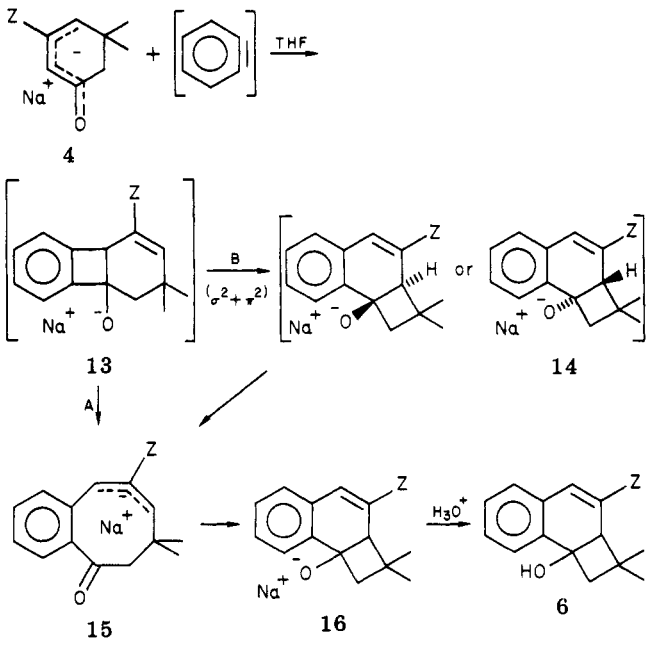
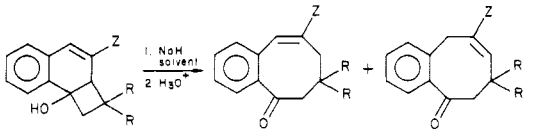


Table II. Ring Opening of Alcohols 6 in Basic Conditions[a]



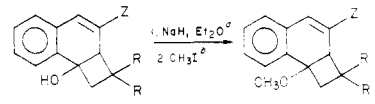
alcohol	solvent	t, h	isolated compd (rel percent) 10	19	overall yield, %
6a	HMPA	6	100		85
6b	DME	6			*b*
6c	DME	24			*c*
6d	HMPA	1.25	100		75
6e	HMPA	3	100		80
6f	DME	3	35	65[d]	90
6g	DME	3	100	*d*	80
6h	DME	4	100	*d*	55[e]
6i	HMPA	4	100		85
6j	DME	3	83	17[d]	85
6k	DME	5	85	15[d]	75

[a] NaH, 1 equiv; 6, 1 mmol in 20 mL of solvent at room temperature. [b] The starting alcohol was quantitatively recovered; in HMPA with $NaNH_2$ as base; formation of numerous unidentified products was registered. [c] Several unidentified products were formed. [d] Ratios 10/19 depend upon hydrolysis conditions. [e] Unidentified byproducts were formed.

Reaction Mechanism. For clarity, we shall now briefly comment on the reaction mechanism. The formation of ketonic side products such as 7–11 has previously been rationalized.[9,11] Concerning the formation of alcohols 6, the observed reactions are obviously due to type 3 dienolates (Scheme I). It is tentatively proposed that the reaction proceeds according to Scheme III. We feel that pathway A would be more probable in view of (i) the large ring strain that the intermediate alkoxides 14 would exhibit and (ii) the possible delocalization of the negative charge in 15.

The contradictory fact that type 6 compounds when treated with NaH in HMPA rearrange to benzocyclooctadienones (vide infra, Table II) though type 6 compounds are formed in our reaction under basic conditions cannot presently be explained satisfactorily.

Table III



alcohol	t, h	yield of 20, %
6c	5	90
6e	12	90
6j	3	85

[a] NaH/6 = 2/1 (mmol) in 20 mL of refluxing diethyl ether. [b] A threefold excess of CH_3I was used.

Some Chemical Properties of Alcohols 6. Behavior in Basic Media. It is noteworthy that, like the benzocyclobutenols obtained from saturated cyclanone enolates,[6] alcohols 6 were opened when added to a basic medium. The main results are reported in Table II.

Thus, ring opening of alcohols 6 is a good means of obtaining benzocyclooctadienone derivatives 10 and 19 which, in appropriate cases, may be further hydrolyzed, in acidic media, to benzocyclooctenediones of type 12. This was exemplified by the synthesis of 12 from 10e (Z = OEt) in 80% yield (see Experimental Section).

On the contrary, alcohols 6 were stable in the presence of NaH in weakly polar solvents such as diethyl ether, as demonstrated by alkylation of three representative alcohols. As may be seen from Table III, methylations may be achieved in very good yields.

Compared to the results obtained in HMPA, it appears that during the reaction of 6 with the insoluble sodium hydride in diethyl ether, the cation must remain near the oxygen, thus preventing liberation of the electrons which should lead to ring opening.

Dehydration of Alcohols 6. Of course, we were interested by the possible dehydration of alcohols 6. However, in the presence of *p*-toluenesulfonic acid, preliminary experiments indicated the formation of mixtures of hydrocarbons and alcohols. Thus, the softer dehydrating system Ph_3P–Br_2–DMF[13] was tested. With this reagent, alcohol 6e led to a mixture of naphthalene derivatives 21e and 22e in 90% yield.

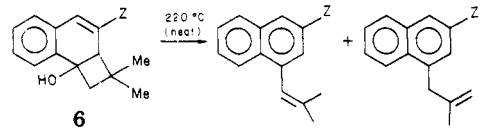
However, this dehydration was not general, and we found that simple thermolysis led to more general results. Thus, the thermal dehydration of alcohols 6 was performed. When warmed to 220 °C (neat), alcohols 6 dehydrate to yield isomeric mixtures of naphthalene derivatives 21 and 22 in good yield (Table IV).[14]

Catalytic hydrogenation of these isomeric mixtures may be a good means of synthesizing naphthalene derivatives. This was exemplified in the case of 21e and 22e which led quantitatively to 1-isobutyl-3-ethoxynaphthalene (43) (see Experimental Section).

Condensations of Acyclic α,β-Unsaturated Ketone Enolates. Previous results from Sammes and Wallace[9] and ourselves[11] indicate that the arynic condensation of mesityl oxide enolate led to several products among which are naphthalene derivatives. However, Sammes and Wallace were obliged to use rather complicated basic reagents and experimental procedures.[9] Moreover, the naphthalene yields were rather low when they used un-

(13) P. Caubere and M. S. Mourad, *Tetrahedron*, 30, 3439 (1974).
(14) The thermal dehydration of 6d (R = H, Z = OEt) did not yield the expected naphthalene derivative but a complex mixture from which ketone 10d could be isolated in 25% yield.

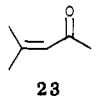
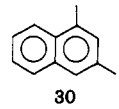
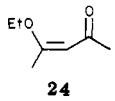
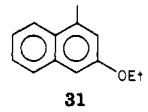
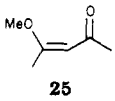
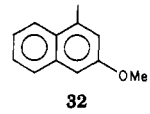
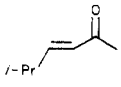
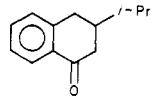
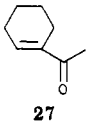
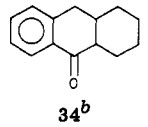
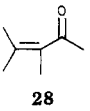
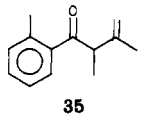
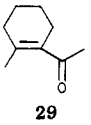
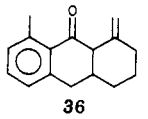
Table IV. Thermal Dehydration of Alcohols 6



alcohol	t, min	isolated compd[a] (rel percent) 21	22	overall yield, %[b]
6a	90	40	60	60
6b	120	40	60	80
6c	20	40	60	85
6e	60	50	50	70
6f	15	80	20	80
6g	20	40	60	85
6h	120	55	45	85
6i	60	55	45	80
6j	15	40	60	90
6k	15	30	70	95

[a] The relative percentages of 21 and 22 were determined by NMR. [b] Isolated yields after purification by column chromatography.

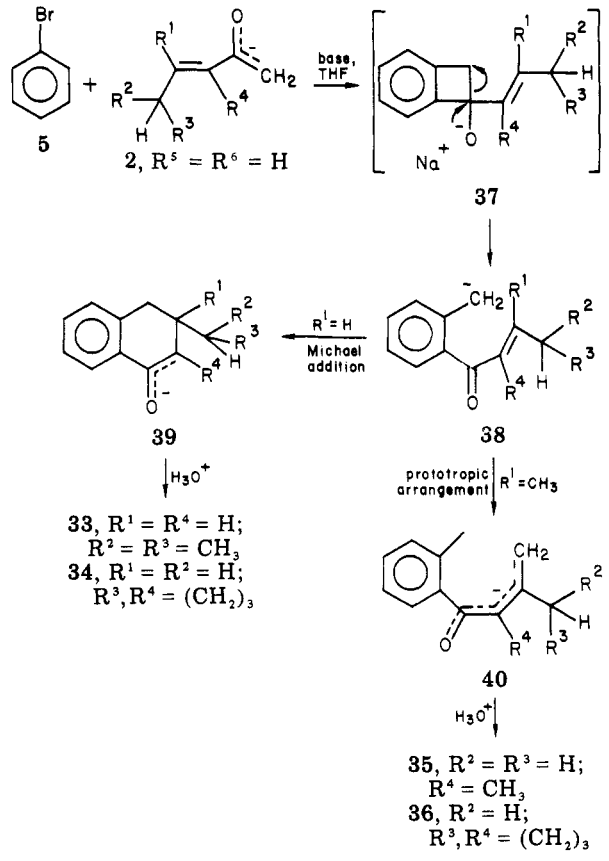
Table V. Arynic Condensations of Methyl Alkenyl Ketone Enolates in THF[a]

enone	condensation site	T, °C	t, h	isolated compd	overall yield, %[c,e]
 23	α and/or γ	45	4	 30	10[d]
 24	α and/or γ	50	7	 31	50
 25	α and/or γ	55	6	 32	40
 26	α′	45	4	 33	60
 27	α′	45	3.5	 34[b]	60
 28	α′	30	4	 35	40
 29	α′	45	3	 36	55

[a] $NaNH_2$/t-BuONa/enolate/C_6H_5Br = 50/25/25/12.5 (in mmol) in 60 mL of THF. Enolates of 23–25 and 26–29 were prepared at 45 °C for 2 h and 15 min at 30 °C, respectively. [b] Isomeric mixture trans–cis (65:35). [c] In all cases, mixtures of side products were formed. [d] From ref 11. [e] With respect to C_6H_5Br.

substituted bromobenzene. Taking into account our present results, it might be conjectured that our experimental conditions were more favorable for the cyclization

Scheme IV



to naphthalene derivatives. With the intent of synthesizing some naphthalene derivatives and also of enhancing the field of application of this kind of reaction, it was decided to examine some representative acyclic enones.

As may be seen from Table V our results compare favorably with those of Sammes in the cases where naphthalenes were formed from bromobenzene. On the other hand, enones **26–29**, which reacted at the α′ site, provided ketones **33–36** in good yields. Thus it appears that the major products of these reactions strongly depend upon the substituents on the double bond.

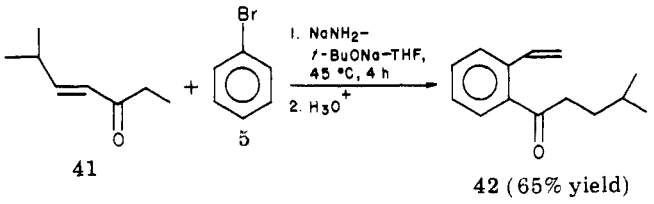
As far as the presently studied enones are concerned, the following observations can be made. (i) Enones **27**, **28**, and **29**, bearing an alkyl substituent at the α position, furnish derivatives arising from condensation at the α′ site (see Scheme IV). (ii) Enone **26**, unsubstituted in the α position but having only a tertiary hydrogen in the γ position, also reacts at the α′ position. (iii) Enones **23**, **24**, and **25**, unsubstituted at the α position but exhibiting a methyl group in the γ position, lead to naphthalene derivatives arising from α and/or γ condensation.[9] In the case of **23**, it has been previously reported[11] that the main products (80% overall yield) were ketones which arose from condensation at the α site.

The formation of naphthalenes **30**, **31**, and **32** has been previously rationalized.[9,11] The formation of ketones **33–36** may be explained by the mechanism pictured in Scheme IV.

With ketones **33–36**, the first step of the condensation leads to **37** which transposes to **38**. With ketone **28** and **29** ($R^1 = CH_3$), the double bond in **38** is too hindered to allow the Michael cyclization to **39**.[1]

It should be underlined that the present results were obtained with methyl alkenyl ketones **1** ($R^5 = R^6 = H$, Scheme I). The arynic condensation may take another pathway when one hydrogen of the methyl group is replaced by an alkyl 1 (R^5 or $R^6 \neq H$, Scheme I) as exem-

Scheme V



41 42 (65% yield)

plified by the condensation of benzyne on **41** (Scheme V).

The formation of ketones of the type **42** has been previously rationalized by an oxido-reduction mechanism.[1]

Conclusion

The present work shows that arynic condensations of α,β-unsaturated ketones constitute a very simple and versatile synthetic method leading to numerous varied structures and enhances the application field previously developed with saturated ketones.

Experimental Section

Materials. Fluka broken sodamide was used after being washed several times and ground in a mortar under solvent. Fluka sodium hydride (55–60% in oil) was used after being washed several times with the desired solvent. Badische Anilin reagent grade THF was distilled from sodium and stored over sodium wire. *tert*-Butyl alcohol was distilled from sodium before use. Enones **4f**, **4g**, and **4h** were prepared according to the following procedure. A mixture of 3-chloro-5,5-dimethylcyclohex-2-en-1-one[15] (60 mmol), Bu_4NCl (500 mg), and the corresponding sodium phenoxide [prepared from the phenol (65 mmol), NaOH (65 mmol), and water (30 mL)] was refluxed in benzene for 24–36 h. The disappearance of the chlorocyclohexenone was monitored by TLC. Water was then added and the mixture extracted with benzene, washed with water, and dried over K_2CO_3. After evaporation of solvent, recrystallization yielded ketones **4f**, **4g**, and **4h**.

4f: $C_{14}H_{16}O_2$; yield 60%; mp (petroleum ether) 80 °C (lit.[16] mp 80–82 °C).

4g: $C_{14}H_{15}O_3$; yield 60%; mp (petroleum ether/benzene) 85 °C; NMR (CCl_4) δ 1.10 (s, 6 H, CH_3), 2.07 (s, 2 H, CH_2), 2.41 (br s, CH_2), 3.73 (s, 3 H, OCH_3), 4.92 (m, 1 H, CH=C), 6.85 (s, 4 H, Ar H).

4h: $C_{14}H_{15}O_2F$; yield 80%; mp (petroleum ether/benzene) 73 °C; NMR (CCl_4) δ 1.10 (s, 6 H, CH_3), 2.08 (s, 2 H, CH_2), 2.42 (br s, 2 H, CH_2), 4.92 (m, 1 H, CH=C), 6.96–7.16 (2 s, 4 H, Ar H).

Enones **4j** and **4k** were prepared by the procedure described in the literature for the synthesis of **4i**[17] but by using $NaNH_2$ instead of CH_3ONa.

4j: $C_{14}H_{16}OS$; yield 90%; mp (petroleum ether) 51–52 °C (lit.[18] mp 50–51 °C).

4k: $C_{15}H_{18}O_2S$; yield 70%; mp (ether/petroleum ether) 78 °C; NMR (CCl_4) δ 1.04 (s, 6 H, CH_3), 2.10 (s, 2 H, CH_2), 2.30 (br s, 2 H, CH_2), 3.80 (s, 3 H, OCH_3), 5.34 (m, 1 H, CH=C), 6.87–7.58 (m, 4 H, Ar H).

All other enones either were commercial (Fluka or Aldrich) or were prepared by classical procedures.

All reactions were performed under nitrogen (R). Silica column chromatography was performed by using Kieselgel (Merck, 0.063–0.200 mm).

General Methods. All melting points (Kofler) reported are uncorrected. NMR spectra were recorded on a Perkin-Elmer R 12 B or Cameca (250 MHz) spectrometer using Me_4Si as internal standard. Infrared spectra were recorded with a Perkin-Elmer 457 instrument. UV spectra were recorded with a Beckman DK 2A spectrometer using EtOH as solvent. Satisfactory analytical data (±0.4%) were reported for all new compounds prepared in this work.

General Procedure for Arynic Condensation of α,β-Unsaturated Ketones (Tables I and V). Reactions Carried Out in the Presence of the Complex Base $NaNH_2$-*t*-BuONa. A solution of *t*-BuOH (25 mmol) in THF (10 mL) was added dropwise to a suspension of $NaNH_2$ (100 mmol) in THF (20 mL). The mixture was then heated for 2 h and 40–45 °C. After the mixture cooled, the enone (25 mmol) in THF (20 mL) was added dropwise at 25–30 °C and the mixture stirred at temperatures and for durations indicated in the tables. Bromobenzene (12.5 mmol) in THF (10 mL) was then added, and stirring was continued for the times indicated in the tables. After cooling to room temperature, the mixture was poured into ice (and acidified with 0.2 N HCl for enones **23–29**) and then extracted with diethyl ether. After removal of solvents under reduced pressure, the residual oil was shaken in acetone (20 mL) and HCl (1 mL). The mixture was then extracted with diethyl ether, dried over $MgSO_4$ or K_2CO_3, evaporated, and chromatographed.

Reactions Carried Out in the Presence of $NaNH_2$. The enone (25 mmol) in THF (20 mL) was added dropwise to a suspension of $NaNH_2$ (75 mmol) in THF (30 mL) at 25–30 °C. After the mixture had stirred for 2 h at 45–50 °C (30 °C for **4h**), bromobenzene (12.5 mmol) in THF (10 mL) was added. After the times indicated in the tables, the reaction mixture was treated as above.

Arynic Condensation of Cyclohexenone Enolates (Table I). Classical workup and purification yielded alcohols **6**.[19,20] Alcohol **6a** has been previously described.[12]

6b: $C_{17}H_{22}O$; mp 50–52 °C; NMR (CCl_4) δ 0.66 (s, 3 H, CH_3), 1.02–1.25 [m, 6 H, superposition of 2 d at 1.07 (J = 7 Hz) and at 1.18 (J = 7 Hz), CH_3], 1.27 (s, 3 H, CH_3), 1.90–2.58 (m, 4 H, CH_2, isopropylic H, OH), 2.90 (s, 1 H, allylic H), 6.23 (br s, 1 H, C=CH), 6.83–7.56 (m, 4 H, Ar H); IR (film) 3320–3380 (OH), 1640 cm^{-1} (C=C); UV λ_{max} nm (log ε) 305 (sh, 3.25), 293 (sh, 3.49), 278 (sh, 4.00), 268 (4.06), 260 (sh, 3.96).

6c: $C_{20}H_{20}O$; NMR (CCl_4) δ 0.63 (s, 3 H, CH_3), 1.23 (s, 3 H, CH_3), 2.06–2.59 (AB, J = 12 Hz, 2 H, CH_2), 2.56 (s, 1 H, OH), 3.42 (s, 1 H, allylic H), 6.74 (s, 1 H, C=CH), 6.94–7.62 (m, 9 H, Ar H); IR (film) 3320–3350 (OH), 1605 (C=C) cm^{-1}; UV λ_{max} nm (log ε) 335 (sh, 3.95), 318 (4.22), 300 (sh, 4.23), 307 (4.26).

6d: $C_{14}H_{16}O_2$; NMR (CCl_4) δ 1.30 (t, J = 7 Hz, 3 H, CH_3), 1.50–2.63 (m, 5 H, CH_2CH_2, OH), 2.98 (m, 1 H, allylic H), 3.78 (q, J = 7 Hz, OCH_2), 5.27 (s, 1 H, C=CH), 6.66–7.48 (m, 4 H, Ar H); IR (film) 3340–3380 (OH), 1645 cm^{-1} (C=C); UV λ_{max} nm (log ε) 300 (sh, 3.54), 280 (sh, 4.05), 272 (4.10).

6e: $C_{16}H_{20}O_2$; NMR (CCl_4) δ 0.75 (s, 3 H, CH_3), 1.16–1.54 [m, 6 H, superposition of 1 s at 1.26 (CH_3) and 1 t (J = 7 Hz) at 1.31 (CH_3)], 1.96–2.47 (m, 3 H, cyclic CH_2, OH), 2.80 (s, 1 H, allylic H), 3.81 (q, J = 7 Hz, 2 H, OCH_2), 5.35 (s, 1 H, C=CH), 6.62–7.40 (m, 4 H, Ar H); IR (film) 3360–3420 (OH), 1645 cm^{-1} (C=C); UV λ_{max} nm (log ε) 303 (3.52), 280 (4.07), 272 (4.11).

6f: $C_{20}H_{20}O_2$; NMR (CCl_4) δ 0.93 (s, 3 H, CH_3), 1.25 (s, 3 H, CH_3), 2.03–2.55 (m, 2 H, CH_2), 3.05 (s, 1 H, allylic H), 3.16 (br s, 1 H, OH), 5.39 (s, 1 H, C=CH), 6.55–7.50 (m, 9 H, Ar H); IR (film) 3360–3410 (OH), 1650 cm^{-1} (C=C); UV λ_{max} nm (log ε) 310 (sh, 3.47), 298 (sh, 3.64), 280 (sh, 4.09), 273 (4.12), 230 (4.24), 224 (4.30).

6g: $C_{21}H_{22}O_3$; mp 82 °C; NMR (CCl_4) δ 0.93 (s, 3 H, CH_3), 1.31 (s, 3 H, CH_3), 2.09–2.60 (m, 3 H, CH_2, OH), 3.05 (s, 1 H, allylic H), 3.71 (s, 3 H, OCH_3), 5.27 (s, 1 H, C=CH), 6.51–7.40 (m, 8 H, Ar H); IR (KBr) 3340–3400 (OH), 1645 cm^{-1} (C=C); UV λ_{max} nm (log ε) 310 (sh, 3.52), 300 (sh, 3.71), 282 (sh, 4.17), 276 (4.18), 229 (sh, 4.31), 224 (4.37).

(15) R. D. Clark and C. H. Heathcock, *J. Org. Chem.*, **41**, 636 (1976).
(16) O. Neilands, G. Vanags, and E. Gudriniece, *Chem. Abstr.*, **52**, 19988*d* (1958).
(17) L. Bateman and F. W. Shipley, *J. Chem. Soc.*, 1966 (1955).
(18) E. E. Campeigne and J. R. Leal, *J. Am. Chem. Soc.*, **76**, 1272 (1954).

(19) When the isolated alcohols **6** were still contaminated by ketonic impurities, they were treated with $LiAlH_4$ (excess) in diethyl ether for 1 h at room temperature. After purification by column chromatography pure alcohols **6** were obtained.
(20) The UV spectra of alcohols **6** were quite different from the previously reported UV spectra of benzocyclobutenols (see ref 4a) and exhibited characteristic absorptions of β-alkyl-substituted dihydronaphthalenes: J. Shabtai, L. H. Klemm, and D. R. Taylor, *J. Org. Chem.*, **33**, 1489 (1968). The structure of alcohol **6a** was further confirmed by recording the NMR spectrum in the presence of increasing amounts of the shift reagent $Eu(fod)_3$ which allowed the determination of the stereochemistry of this alcohol.

6h: $C_{20}H_{19}OF$; mp 140 °C; NMR ($CDCl_3$) δ 0.95 (s, 3 H, CH_3), 1.32 (s, 3 H, CH_3), 2.17–2.68 (m, 3 H, CH_2, OH), 3.13 (s, 1 H, allylic H), 5.39 (s, 1 H, C=CH), 6.65–7.50 (m, 4 H, Ar H); IR (KBr) 3310–3350 (OH), 1645 cm^{-1} (C=C); UV λ_{max} nm (log ε) 310 (sh, 3.46), 299 (sh, 3.65), 280 (sh, 4.13), 273 (4.17), 230 (sh, 4.26), 224 (4.33).

6i: $C_{16}H_{20}OS$; NMR (CCl_4) δ 0.72 (s, 3 H, CH_3), 1.15–1.50 [m, 6 H, superposition of 1 s at 1.23 (CH_3) and 1 t (J = 7.3 Hz) at 1.32 (CH_3)], 2.02–2.48 (m, 2 H, cyclic CH_2), 2.45–2.99 [m, 4 H, superposition of 1 br s at 2.70 (OH), 1 s at 2.75 (allylic H) and 1 q (J = 7.3 Hz) at 2.78 (SCH_2)], 5.98 (s, 1 H, vinylic H), 6.65–7.38 (m, 4 H, Ar H); IR (film) 3330–3360 (OH), 1620 cm^{-1} (C=C); UV λ_{max} nm (log ε) 321 (sh, 3.95), 307 (sh, 4.05), 288 (sh, 4.19), 297 (4.24).

6j: $C_{20}H_{20}OS$; mp 75 °C; NMR (CCl_4) δ 0.78 (s, 3 H, CH_3), 1.14 (s, 3 H, CH_3), 2.00–2.47 (m, 2 H, CH_2), 2.62 (s, 1 H, OH), 2.85 (s, 1 H, allylic H), 6.11 (s, 1 H, vinylic H), 6.60–7.60 (m, 9 H, Ar H); IR (KBr) 3360–3440 (OH), 1620 cm^{-1} (C=C); UV λ_{max} nm (log ε) 320 (sh, 4.03), 309 (sh, 4.09), 304 (sh, 4.10), 297 (4.11), 290 (sh, 4.08), 237 (sh, 4.19), 232 (4.21).

6k: $C_{21}H_{22}O_2S$; NMR (CCl_4) δ 0.77 (s, 3 H, CH_3), 1.15 (s, 3 H, CH_3), 1.96–2.43 (m, 2 H, CH_2), 2.58 (s, 1 H, OH), 2.77 (s, 1 H, allylic H), 3.64 (s, 3 H, OCH_3), 5.79 (br s, 1 H, C=CH), 6.42–7.41 (m, 8 H, Ar H); IR (film) 3360–3440 (OH), 1610 cm^{-1} (C=C); UV λ_{max} nm (log ε) 320 (sh, 4.06), 310 (sh, 4.12), 298 (4.18), 288 (sh, 4.14), 232 (4.42).

Arynic Condensation of Isophorone (4a, Scheme II). The general procedure was used in THF, HMPA, DME, or benzene (see text) to allow separation and identification of the ketonic compounds 7–11. **7** and **8** were identified by comparison of their physical and spectroscopic properties with those described in the literature.[21,22] **9** was identified by comparison with an authentic sample prepared according to ref 22.

9: $C_{15}H_{18}O$; NMR (CCl_4) δ 1.15 (s, 6 H, CH_3), 2.14 (s, 2 H, $COCH_2$), 2.30 (s, 3 H, Ar CH_3), 2.43 (d, J = 2 Hz, 2 H, allylic CH_2), 5.84 (m, 1 H, vinylic H), 6.98–7.28 (m, 4 H, Ar H); IR (CCl_4) 1675 cm^{-1} (C=O).

10a will be described later (vide infra).

11: $C_{15}H_{18}O$; mp 63 °C; NMR (CCl_4) δ 0.98 (s, 6 H, CH_3), 1.91 (m, 2 H, vinylic CH_2), 2.81 (s, 2 H, CH_2),[23] 3.84 (m, 2 H, Ar CH_2), 4.72 (m, 1 H, vinylic H), 4.92 (m, 1 H, vinylic H), 6.97–7.40 (m, 3 H, Ar H), 7.91–8.12 (m, 1 H, Ar H); IR (CCl_4) 1670 (C=O), 1635 cm^{-1} (C=C).

Arynic Condensation of Acyclic Ketones 23–29 (Table V). The general procedure and classical workup and purification yielded derivatives **30–36**; **30**,[24] **32**,[9] **33**,[25] and **34**[26] were identified by comparison of their physical and spectroscopic properties with those described in the literature.

31: $C_{13}H_{14}O$; mp 63 °C; NMR (CCl_4) δ 1.40 (t, J = 7 Hz, 3 H, CH_3), 2.57 (s, 3 H, CH_3), 4.00 (q, J = 7 Hz, 2 H, CH_2), 6.61–6.93 (m, 2 H, Ar H), 7.02–7.88 (m, 4 H, Ar H).

31 (0.5 g) heated (neat) in the presence of pyridine hydrochloride[27] (1 g) for 2 h yielded 4-methyl-2-naphtol in 86% yield, mp 80 °C (lit.[28] mp 81–82 °C).

35: $C_{13}H_{16}O$; NMR (CCl_4) δ 1.22 (d, J = 7 Hz, 3 H, CH_3), 1.65 (br s, 3 H, vinylic CH_3), 2.37 (s, 3 H, Ar CH_3), 3.88 (q, J = 7 Hz, 1 H, tertiary H), 4.76 (m, 2 H, vinylic H), 6.88–7.33 (m, 3 H, Ar H), 7.42–7.67 (m, 1 H, Ar H); IR (film) 1685 cm^{-1} (C=O).

36: $C_{15}H_{18}O$; NMR (CCl_4) δ 1.30–2.35 (m, 8 H, cyclic CH_2), 2.42 (s, 3 H, CH_3), 3.82 (m, 1 H, tertiary H), 4.53 (m, 1 H, vinylic H), 4.77 (m, 1 H, vinylic H), 6.91–7.33 (m, 3 H, Ar H), 7.43–7.70 (m, 1 H, Ar H); IR (film) 1685 cm^{-1} (C=O).

Arynic Condensation of 41 (Scheme V). The general procedure and classical workup and purifications yielded **42** in 65% yield: $C_{14}H_{18}O$; NMR (CCl_4) δ 0.80–1.05 (m, 6 H, CH_3), 1.35–1.80 (m, 3 H, CH_2, tertiary H), 2.61–2.96 (m, 2 H, $COCH_2$), 5.10–5.75 (m, 2 H, $C=CH_2$), 6.83–7.62 (m, 5 H, Ar H, CH=C); IR (film) 1690 (C=O), 990 and 920 (C=C), 775 cm^{-1} (aromatic); UV λ_{max} nm (log ε) 298 (3.19), 249 (sh, 4.00).

General Procedure for the Ring Opening of 6 (Table II). **6** (1 mmol) in 10 mL of solvent was added to a suspension of NaH (2 mmol) in 10 mL of solvent at room temperature. The mixture was stirred for the durations indicated in the table. Classical workup and column chromatography yielded ketones **10** and **19**.

10a: $C_{15}H_{18}O$; NMR (CCl_4) δ 1.11 (s, 6 H, CH_3), 1.91 (s, 2 H, allylic CH_2), 2.07 (d, J = 1.5 Hz, 3 H, CH_3), 2.59 (s, 2 H, CH_2),[23] 6.62 (m, 1 H, vinylic H), 6.98–7.43 (m, 3 H, Ar H), 7.92–8.15 (m, 1 H, Ar H); IR (film) 1665 cm^{-1} (br signal, C=O and C=C); UV λ_{max} nm (log ε) 320 (3.58), 262 (3.80), 234 (4.28).

10d: $C_{14}H_{16}O_2$; mp 86–87 °C; NMR (CCl_4) δ 1.36 (t, J = 7 Hz, 3 H, CH_3), 1.89–2.41 (m, 4 H, CH_2), 2.63–3.00 (m, 2 H, CH_2), 3.91 (q, J = 7 Hz, 2 H, OCH_2), 5.80 (s, 1 H, C=CH), 6.94–7.51 (m, 3 H, Ar H), 7.84–8.13 (m, 1 H, Ar H); IR (CCl_4) 1670 (C=O), 1640 cm^{-1} (C=C); UV λ_{max} nm (log ε) 336 (3.63), 272 (3.90), 243 (4.37).

10e: $C_{16}H_{20}O_2$; mp 51–52 °C; NMR ($CDCl_3$) δ 1.09 (s, 6 H, CH_3), 1.34 (t, J = 7 Hz, 3 H, CH_3), 1.98 (s, 2 H, CH_2), 2.64 (s, 2 H, CH_2), 3.88 (q, J = 7 Hz, 2 H, OCH_2), 5.79 (s, 1 H, C=CH), 6.94–7.49 (m, 3 H, Ar H), 7.94–8.18 (m, 1 H, Ar H); IR (film) 1670 (C=O), 1640 cm^{-1} (C=C); UV λ_{max} nm (log ε) 339 (3.72), 273 (3.96), 245 (4.46).

Hydrolysis of **10e** (5 mmol) for 7.5 h at 40–45 °C in acidic media [Me_2CO (20 mL), H_2O (12 mL), HCl (a few drops)] led to diketone **12** in 80% yield: $C_{14}H_{16}O_2$; mp 81–82 °C; NMR (CCl_4) δ 1.00 (s, 6 H, CH_3), 2.23 (s, 2 H, CH_2), 2.86 (s, 2 H, CH_2), 3.92 (s, 2 H, CH_2), 7.03–7.65 (m, 3 H, Ar H), 8.00–8.25 (m, 1 H, Ar H); IR (CCl_4) 1710 and 245 cm^{-1} (C=O); UV λ_{max} nm (log ε) 295 (3.33), 253 (3.92).

12 refluxed for 12 h with Na and D_2O yielded the corresponding hexadeuterated diketone: NMR (CCl_4) δ 1.00 (s, 6 H, CH_3), 7.03–7.65 (m, 3 H, Ar H), 8.00–8.25 (m, 1 H, Ar H); IR (CCl_4) 1710 and 1675 cm^{-1} (C=O).

10f: $C_{20}H_{20}O_2$; mp 85 °C; NMR (CCl_4) δ 1.22 (s, 6 H, CH_3), 2.20 (s, 2 H, CH_2), 2.74 (s, 2 H, CH_2), 6.04 (s, 1 H, C=CH), 6.89–7.62 (m, 8 H, Ar H), 8.00–8.22 (m, 1 H, Ar H); IR (KBr) 1660 (C=O), 1640 cm^{-1} (C=C); UV λ_{max} nm (log ε) 332 (3.70), 272 (3.98), 242 (4.37).

19f: $C_{20}H_{20}O_2$; mp 100 °C; NMR (CCl_4) δ 1.24 (s, 6 H, CH_3), 2.92 (s, 2 H, CH_2), 3.84 (s, 2 H, CH_2), 4.69 (s, 1 H, C=CH), 6.52–7.45 (m, 8 H, Ar H), 7.63–7.91 (m, 1 H, Ar H); IR (KBr) 1670 cm^{-1} (C=O); UV λ_{max} nm (log ε) 241 (4.13).

10g: $C_{21}H_{22}O_3$; mp 114 °C; NMR (CCl_4) δ 1.21 (s, 6 H, CH_3), 2.18 (s, 2 H, CH_2), 2.71 (s, 2 H, CH_2), 3.78 (s, 3 H, OCH_3), 5.83 (s, 1 H, C=CH), 6.72–7.40 (m, 7 H, Ar H), 7.95–8.15 (m, 1 H, Ar H); IR (KBr) 1660 (C=O), 1640 cm^{-1} (C=C); UV λ_{max} nm (log ε) 334 (3.77), 273 (4.04), 242 (4.39).

10h: $C_{20}H_{19}OF$; mp 115 °C; NMR (CCl_4) δ 1.18 (s, 6 H, CH_3), 2.14 (s, 2 H, CH_2), 2.69 (s, 2 H, CH_2), 5.90 (br s, 1 H, C=CH), 6.80–7.44 (m, 7 H, Ar H), 7.91–8.14 (m, 1 H, Ar H); IR (KBr) 1660 (C=O), 1645 cm^{-1} (C=C); UV λ_{max} nm (log ε) 330 (3.73), 272 (4.02), 242 (4.41).

10i: $C_{16}H_{20}OS$; NMR (CCl_4) δ 1.11 (s, 6 H, CH_3), 1.37 (t, J = 7 Hz, 3 H, CH_3), 2.03 (s, 2 H, CH_2), 2.60 (s, 2 H, CH_2), 2.89 (q, J = 7 Hz, 2 H, SCH_2), 6.40 (s, 1 H, C=CH), 6.97–7.55 (m, 3 H, Ar H), 7.95–8.20 (m, 1 H, Ar H); IR (film) 1670 (C=O), 1610 cm^{-1} (C=C); UV λ_{max} nm (log ε) 347 (3.84), 288 (3.96), 258 (4.22).

10j: $C_{20}H_{20}OS$; NMR (CCl_4) δ 1.20 (s, 6 H, CH_3), 2.12 (s, 2 H, CH_2), 2.63 (s, 2 H, CH_2), 6.49 (s, 1 H, C=CH), 6.82–7.55 (m, 8 H, Ar H), 7.93–8.15 (m, 1 H, Ar H); IR (film) 1665 (C=O), 1610 cm^{-1} (C=C); UV λ_{max} nm (log ε) 345 (3.91), 280 (3.92), 257 (4.29).

19j: $C_{20}H_{20}OS$; mp 110 °C; NMR (CCl_4) δ 1.30 (s, 6 H, CH_3), 2.95 (s, 2 H, CH_2), 3.82 (s, 2 H, CH_2), 5.74 (br s, 1 H, C=CH), 6.75–7.47 (m, 8 H, Ar H), 7.62–7.84 (m, 1 H, Ar H); IR (KBr) 1675 cm^{-1} (C=O); UV λ_{max} nm (log ε) 249 (4.22).

10k: $C_{21}H_{22}O_2S$; NMR (CCl_4) δ 1.17 (s, 6 H, CH_3), 2.03 (s, 2 H, CH_2), 2.56 (s, 2 H, CH_2), 3.73 (s, 3 H, OCH_3), 6.11 (s, 1 H, C=CH), 6.60–7.49 (m, 7 H, Ar H), 7.80–8.04 (m, 1 H, Ar H); IR (film) 1665 (C=O), 1610 cm^{-1} (C=C); UV λ_{max} nm (log ε) 349 (3.91), 284 (3.97), 257 (4.27), 235 (4.40).

(21) G. Stork and A. A. Ponaras, *J. Org. Chem.*, 41, 2937 (1976).
(22) N. F. Firrell and P. W. Hickmott, *J. Chem. Soc. C*, 716 (1970).
(23) This signal disappeared on deuteration with Na–D_2O.
(24) W. Reppe, *Justus Liebigs Ann. Chem.*, **596**, 80 (1955).
(25) A. Card, B. Gautheron, and J. Besancon, *Bull. Soc. Chim. Fr.*, 1607 (1974).
(26) J. W. Cook, C. L. Hewett, and C. A. Lawrence, *J. Chem. Soc.*, 71 (1936).
(27) R. Royer, P. Demerseman, J. P. Lechartier, A. M. Laval-Jeantet, and A. Cheutin, *Bull. Soc. Chim. Fr.*, 315 (1964).
(28) Z. Vasely and S. Stursa, *Collect. Czech. Chem. Commun.*, 1, 493 (1929).

19k: $C_{21}H_{22}O_2S$; NMR (CCl_4) δ 1.27 (s, 6 H, CH_3), 2.92 (s, 2 H, CH_2), 3.69–3.88 (m, 5 H, Ar CH_2, OCH_3), 5.52 (s, 1 H, C=CH), 6.57–7.84 (m, 8 H, Ar H); IR (film) 1670 cm^{-1} (C=O); UV λ_{max} nm (log ϵ) 237 (4.30).

Methylation of Alcohols 6 (Table III). A solution of **6** (1 mmol) in diethyl ether (10 mL) was added to a suspension of NaH (2 mmol) in diethyl ether (10 mL). After the mixture stirred for 15 min at room temperature, CH_3I (3 mmol) was added and the mixture refluxed for the durations indicated in Table III. Classical workup and chromatography yielded ethers **20**.

20c: $C_{21}H_{22}O$; NMR (CCl_4) δ 0.71 (s, 3 H, CH_3), 1.31 (s, 3 H, CH_3), 2.09–2.69 (m, 2 H, CH_2), 2.82 (s, 3 H, OCH_3), 3.41 (s, 1 H, allylic H), 6.87 (s, 1 H, vinylic H), 7.00–7.71 (m, 9 H, Ar H).

20e: $C_{17}H_{22}O_2$; NMR (CCl_4) δ 0.80 (s, 3 H, CH_3), 1.20–1.52 [m, 6 H, superposition of 1 s at 1.26 (CH_3) and 1 t (J = 7 Hz) centered at 1.32 (CH_3)], 1.97–2.51 (m, 2 H, cyclic CH_2), 2.73–2.88 (br s, 4 H, OCH_3, allylic H), 3.85 (q, J = 7 Hz, 2 H, OCH_2), 5.41 (s, 1 H, vinylic H), 6.69–7.35 (m, 4 H, Ar H); IR (film) 1645 cm^{-1} (C=C).

20j: $C_{21}H_{22}OS$; NMR (CCl_4) δ 0.84 (s, 3 H, CH_3), 1.19 (s, 3 H, CH_3), 2.00–2.53 (nm, 2 H, CH_2), 2.77 (br s, 4 H, OCH_3, allylic H), 6.21 (s, 1 H, vinylic H), 6.72–7.70 (m, 9 H, Ar H); IR (film) 1625 cm^{-1} (C=C).

General Procedure for the Thermal Dehydration of 6 (Table IV). **6** (2 mmol) in a 10-mL flask, equipped with a reflux condenser, was warmed to 220 °C with a metallic bath for the durations indicated in Table IV. Classical workup and purification yielded isomeric mixtures of **21** and **22**.

21a and 22a: $C_{15}H_{16}$; NMR (CCl_4) δ 1.60–1.74 (m, 3 H (**21**), 3 H (**22**), vinylic CH_3), 1.92 (m, 3 H (**21**), vinylic CH_3), 2.38 (s, 3 H (**21**), 3 H (**22**), Ar CH_3), 3.60 (br s, 2 H (**22**), Ar CH_2), 4.50–4.85 (2 m, 2 H (**22**), C=CH_2), 6.45–6.62 (m, 1 H (**21**), Ar CH=C), 6.97–8.05 (m, 6 H (**21**), 6 H (**22**), Ar H); IR (film) 1615 and 1640 cm^{-1} (C=C).

21b and 22b: $C_{17}H_{20}$; NMR (CCl_4) δ 1.31 (d, J = 7 Hz, 6 H (**21**), 6 H (**22**), isopropylic CH_3), 1.62–1.81 (m, 3 H (**21**), 3 H (**22**), vinylic CH_3), 1.98 (m, 3 H (**21**), vinylic CH_3), 2.98 (septet, J = 7 Hz, 1 H (**21**), 1 H (**22**), isopropylic H), 3.69 (br s, 2 H (**22**), Ar CH_2), 4.54–4.89 (2 m, 2 H (**22**), C=CH_2), 6.60 (br s, 1 H (**21**), Ar CH=C), 7.08–8.03 (m, 6 H (**21**), 6 H (**22**), Ar H); IR (film) 1645 and 1625 cm^{-1} (C=C).

21c and 22c: $C_{20}H_{18}$; NMR (CCl_4) δ 1.60–1.80 (m, 3 H (**21**), 3 H (**22**), vinylic CH_3), 1.99 (m, 3 H (**21**), vinylic CH_3), 3.74 (br s, 2 H (**22**), Ar CH_2), 4.58–4.86 (2 m, 2 H (**22**), C=CH_2), 6.62 (br s, 1 H (**21**), Ar CH=C), 7.12–8.04 (m, 11 H (**21**), 11 H (**22**), Ar H).

21e and 22e: $C_{16}H_{18}O$; NMR (CCl_4) δ 1.34 (t, J = 7 Hz, 3 H (**21**), 3 H (**22**), CH_3), 1.61–1.78 (m, 3 H (**21**), 3 H (**22**), vinylic CH_3), 1.96 (m, 3 H (**21**), vinylic CH_3), 3.63 (br s, 2 H (**22**), Ar CH_2), 3.99 (q, J = 7 Hz, 2 H (**21**), 2 H (**22**), OCH_2), 4.58–4.86 (2 m, 2 H (**22**), C=CH_2), 6.53 (m, 1 H (**21**), Ar CH=C), 6.84 (m, 2 H (**21**), 2 H (**22**), Ar H), 6.98–7.93 (m, 4 H (**21**), 4 H (**22**), Ar H); IR (film) 1610 and 1625 cm^{-1} (C=C).

A mixture of **21e** and **22e** (3 mmol) hydrogenated at atmospheric pressure in the presence of Pd/C (5%) in AcOEt (30 mL) gave quantitatively 3-ethoxy-1-isobutylnaphthalene (**43**): $C_{16}H_{20}O$; NMR (CCl_4) δ 0.98 (d, J = 6.4 Hz, 6 H, isopropylic CH_3), 1.42 (t, J = 7 Hz, 3 H, CH_3), 1.64–2.41 (m, 1 H, tertiary H), 2.81 (d, J = 7 Hz, 2 H, Ar CH_2), 4.04 (q, J = 7 Hz, 2 H, OCH_2), 6.83 (br s, 2 H, Ar H), 7.12–7.96 (m, 4 H, Ar H).

43 (0.4 g) was heated at 230 °C in the presence of pyridine hydrochloride (1 g) for 1.5 h. Chromatography furnished 4-isobutyl-2-naphthol, $C_{14}H_{16}O$, in 70% yield: mp 99–100 °C; NMR (CCl_4) δ 0.95 (d, J = 6.7 Hz, 6 H, CH_3), 1.64–2.33 (m, 1 H, tertiary H), 2.82 (d, J = 7 Hz, 2 H, Ar CH_2), 4.73 (br s, 1 H, OH), 6.84 (m, 2 H, Ar H), 7.05–8.00 (m, 4 H, Ar H); IR (CCl_4) 3620 cm^{-1} (OH); UV λ_{max} nm (log ϵ) 335 (3.37), 324 (3.30).

21f and 22f: $C_{20}H_{18}O$; NMR (CCl_4) δ 1.65–1.75 (m, 3 H (**21**), 3 H (**22**), vinylic CH_3), 1.95 (m, 3 H (**21**), vinylic CH_3), 3.65 (br s, 2 H (**22**), Ar CH_2), 4.57–4.88 (2 m, 2 H (**22**), C=CH_2), 6.50–6.67 (m, 1 H (**21**), Ar CH=C), 6.80–8.00 (m, 11 H (**21**), 11 H (**22**) Ar H); IR (film) 1620 cm^{-1} (C=C).

21g and 22g: $C_{21}H_{20}O_2$; NMR (CCl_4) δ 1.67–1.82 (m, 3 H (**21**), 3 H (**22**), vinylic CH_3), 1.99 (m, 3 H (**21**), vinylic CH_3), 3.66–3.82 (m, 3 H (**21**), 5 H (**22**), OCH_3, Ar CH_2), 4.61–4.98 (2 m, 2 H (**22**), C=CH_2), 6.55–8.11 (m, 11 H (**21**), 10 H (**22**), Ar CH=C and Ar H); IR (film) 1625 cm^{-1} (C=C).

21h and 22h: $C_{20}H_{17}OF$; NMR (CCl_4) δ 1.63–1.80 (m, 3 H (**21**), 3 H (**22**), vinylic CH_3), 1.94 (m, 3 H (**21**), vinylic CH_3), 3.63 (br s, 2 H (**22**), Ar CH_2), 4.53–4.88 (2 m, 2 H (**22**), C=CH_2), 6.42–6.61 (m, 1 H (**21**), CH=C), 6.75–7.98 (m, 10 H (**21**), 10 H (**22**), Ar H); IR (film) 1620 cm^{-1} (C=C).

21i and 22i: $C_{16}H_{18}S$; NMR (CCl_4) δ 1.31 (t, J = 7.3 Hz, 3 H (**21**), 3 H (**22**), CH_3), 1.64–1.81 (m, 3 H (**21**), 3 H (**22**), vinylic CH_3), 1.98 (m, 3 H (**21**), vinylic CH_3), 2.94 (q, J = 7.3 Hz, 2 H (**21**), 2 H (**22**), SCH_2), 3.65 (br s, 2 H (**22**), Ar CH_2), 4.55–4.87 (m, 2 H (**22**), C=CH), 6.56 (m, 1 H (**21**), Ar CH=C), 7.12–8.03 (m, 6 H (**21**), 6 H (**22**), Ar H).

21j and 22j: $C_{20}H_{18}S$; NMR (CCl_4) δ 1.58–1.78 (m, 3 H (**21**), 3 H (**22**), vinylic CH_3), 1.94 (m, 3 H (**21**), vinylic CH_3), 3.62 (br s, 2 H (**22**), Ar CH_2), 4.52–4.85 (2 m, 2 H (**22**), C=CH_2), 6.50 (m, 1 H (**21**), Ar CH=C), 7.00–7.95 (m, 11 H (**21**), 11 H (**22**), Ar H); IR (film) 1650 and 1620 cm^{-1} (C=C).

21k and 22k: $C_{21}H_{20}OS$; NMR (CCl_4) δ 1.56–1.73 (m, 3 H (**21**), 3 H (**22**), vinylic CH_3), 1.93 (m, 3 H (**21**), vinylic CH_3), 3.61 (br s, 2 H (**22**), Ar CH_2), 3.71 (s, 3 H (**21**), 3 H (**22**), OCH_3), 4.51–4.84 (2 m, 2 H (**22**), C=CH_2), 6.42–6.61 (m, 1 H (**21**), Ar CH=C), 6.64–7.98 (m, 10 H (**21**), 10 H (**22**), Ar H).

Acknowledgment. We are grateful to M. Dorme (Laboratoire de Microanalyse, Paris VI) for the microanalyses. J.J.B. gratefully acknowledges the Centre National de la Recherche Scientifique, France, for financial aid.

Registry No. **4a**, 78-59-1; **4b**, 28017-79-0; **4c**, 36047-17-3; **4d**, 5323-87-5; **4e**, 6267-39-6; **4f**, 72035-56-4; **4g**, 72035-57-5; **4h**, 72035-58-6; **4i**, 52735-49-6; **4j**, 52735-51-0; **4k**, 72035-59-7; **5**, 108-86-1; **6a**, 71736-01-1; **6b**, 72035-60-0; **6c**, 72035-61-1; **6d**, 71736-02-2; **6e**, 71736-03-3; **6f**, 72035-62-2; **6g**, 72059-89-3; **6h**, 72035-63-3; **6i**, 71736-04-4; **6j**, 72035-64-4; **6k**, 72035-65-5; **9**, 72035-66-6; **10a**, 71736-05-5; **10d**, 71736-06-6; **10e**, 71736-07-7; **10f**, 72035-67-7; **10g**, 72035-68-8; **10h**, 72035-69-9; **10i**, 71736-08-8; **10j**, 72035-70-2; **10k**, 72035-71-3; **11**, 72035-72-4; **12**, 72035-73-5; **12**, hexadeuterated, 72035-74-6; **19f**, 72035-75-7; **19j**, 72035-76-8; **19k**, 72035-77-9; **20c**, 72035-78-0; **20e**, 72035-79-1; **20j**, 72035-80-4; **21a**, 72035-81-5; **21b**, 72035-82-6; **21c**, 72035-83-7; **21e**, 72035-84-8; **21f**, 72035-85-9; **21g**, 72035-86-0; **21h**, 72035-87-1; **21i**, 72035-88-2; **21j**, 72035-89-3; **21k**, 72035-90-6; **22a**, 72035-91-7; **22b**, 72035-92-8; **22c**, 72035-93-9; **22e**, 72035-94-0; **22f**, 72035-95-1; **22g**, 72035-96-2; **22h**, 72035-97-3; **22i**, 72035-98-4; **22j**, 72035-99-5; **22k**, 72036-00-1; **23**, 141-79-7; **24**, 1540-24-5; **25**, 2845-83-2; **26**, 5166-53-0; **27**, 932-66-1; **28**, 684-94-6; **29**, 15564-32-6; **30**, 575-41-7; **31**, 72036-01-2; **32**, 57404-87-2; **33**, 41816-69-7; *cis*-**34**, 72036-02-3; *trans*-**34**, 3586-86-5; **35**, 72036-03-4; **36**, 72036-04-5; **41**, 3132-12-5; **42**, 72036-06-7; **43**, 72036-05-6; 3-chloro-5,5-dimethylcyclohex-2-en-1-one, 17530-69-7; sodium phenoxide, 139-02-6; sodium *p*-methoxyphenoxide, 1122-95-8; sodium *p*-fluorophenoxide, 371-35-7; 4-methyl-2-naphthalenol, 26207-06-7; 4-isobutyl-2-naphthol, 52096-47-6.