

Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.61; H, 9.08.

Ethyl 5-oxocycloundecane-1-carboxylate (12d) was isolated by column chromatography on silica gel as a colorless oil: R_f 0.33 (AcOEt-hexane, 1:5); IR (neat) 1735, 1700 cm^{-1} ; 1H NMR (CCl_4) δ 1.22 (t, 3 H, $J = 7$ Hz), 1.36-2.69 (m, 19 H), 3.96 (q, 2 H, $J = 7$ Hz); ^{13}C NMR ($CDCl_3$) 13.80 (q), 22.44 (t), 24.33 (t), 25.01 (t), 25.22 (t), 26.96 (t), 31.43 (t), 32.32 (t), 33.83 (t), 41.79 (t), 49.94 (d), 60.00 (t), 173.49 (s), 220.36 (s) ppm; exact mass calcd for $C_{14}H_{24}O_3$ 240.1726, found 240.1697. Anal. Calcd for $C_{14}H_{24}O_3$: C, 69.96; H, 10.07. Found: C, 69.68; H, 10.36.

Ethyl 5-oxocyclotetradecane-1-carboxylate (12e) was isolated by column chromatography on silica gel as a colorless oil: R_f 0.55 (AcOEt-hexane, 1:5); IR (neat) 1730, 1700 cm^{-1} ; 1H NMR (CCl_4) δ 1.22 (t, 3 H, $J = 7$ Hz), 1.25-2.88 (m, 27 H), 3.96 (q, 2 H, $J = 7$ Hz); ^{13}C NMR ($CDCl_3$) 13.92 (q), 21.53 (t), 21.87 (t), 22.15 (t), 22.68 (t), 22.98 (t), 23.34 (t), 23.72 (t), 25.50 (t), 25.85 (t), 29.21 (t), 30.19 (t), 33.94 (t), 36.67 (t), 51.77 (t), 60.15 (t), 176.60 (s), 214.91 (s) ppm; exact mass calcd for $C_{18}H_{32}O_3$ 296.2353, found 296.2335. Anal. Calcd for $C_{18}H_{32}O_3$: C, 72.93; H, 10.88. Found: C, 72.93; H, 10.97.

Ethyl 2-methyl-6-oxoheptanoate (12f) was isolated by column chromatography on silica gel as a colorless oil: R_f 0.33 (AcOEt-hexane, 1:5); IR (neat) 1720 cm^{-1} ; 1H NMR (CCl_4) δ 1.15

(d, 3 H, $J = 7$ Hz), 1.24 (t, 3 H, $J = 7$ Hz), 1.38-2.70 (m, 7 H), 2.05 (s, 3 H), 4.04 (q, 2 H, $J = 7$ Hz); ^{13}C NMR ($CDCl_3$) 14.00 (q), 16.86 (q), 21.19 (t), 29.71 (q), 32.88 (t), 39.21 (d), 43.29 (t), 60.14 (t), 176.80 (s), 209.07 (s) ppm; exact mass calcd for $C_{10}H_{18}O_3$ 186.1256, found 186.1242. Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74. Found: C, 64.53; H, 9.81.

cis-1-Hydroxy-5-phenylbicyclo[4.3.0]nonane (cis-14c) was isolated by column chromatography on silica gel as a colorless oil: R_f 0.50 (AcOEt-hexane, 1:5); IR (neat) 3580, 3460, 1600, 1500 cm^{-1} ; 1H NMR (CCl_4) δ 1.00-2.35 (m, 14 H), 6.74-7.50 (m, 5 H); ^{13}C NMR ($CDCl_3$) 18.45 (t), 21.41 (t), 23.30 (t), 34.84 (t), 36.15 (t), 36.89 (t), 38.06 (t), 52.30 (s), 81.10 (s), 125.76 (d), 127.97 (d, 2C), 128.33 (d, 2C), 145.78 (s) ppm; exact mass calcd for $C_{15}H_{20}O$ 216.1515, found 216.1508. Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.15; H, 9.26.

Conversion of trans-10f to 12. To a solution of sodium ethoxide (0.2 mmol) in ethanol (5 mL) was added *trans*-10f (2 mmol) at room temperature, and the mixture was stirred for 3 h. After usual workup, the product 12 was isolated by column chromatography on silica gel.

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Photochemical Reaction of Phenyliodonium Ylides of β -Dicarbonyl Compounds with Terminal Alkynes

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The photochemical reaction of phenyliodonium ylides of acyclic β -dicarbonyl compounds bearing at least one benzoyl group with terminal alkynes leads to the formation of 4-substituted-2-acyl-1-naphthol derivatives, probably through iodanes and ethynylated derivatives 6. A hydroxy benzothiophene derivative, 15, was also isolated from the reaction of ylide 14 with (trimethylsilyl)acetylene.

Introduction

Phenyliodonium ylides constitute an interesting class of hypervalent iodine compounds, for which the chemistry up to 1982 has been reviewed.¹ There are various types of these ylides, depending on the ylidic carbon moiety, but the best known are those derived from β -dicarbonyl compounds. Among the reactions of these species, perhaps the most interesting are those leading to C-C bond formation: phenyliodonium dimedonide undergoes cycloaddition reactions with unsaturated compounds (dipolarophiles) such as diphenylketene,² carbon disulfide,³ and alkenes,⁴ whereas phenyliodonio 1,2,4-trioxo-1,2,3,4-tetrahydro-naphthalenide reacts with both alkenes and alkynes.⁵ Some reactions of iodonium ylides of acyclic β -dicarbonyl compounds leading to C-C bond formation have also been reported: phenyliodonium dibenzoylmethylide gives 1,3-

oxathiole-2-thione³ with carbon disulfide and gives dihydrofurans⁶ with alkenes, while phenyliodonium dimethylmalonate reacts with various olefins in the presence of Lewis acids and lithium perchlorate⁷ to afford 3-carbomethoxy δ -lactones. Recently, Moriarty reported the intramolecular cyclopropanation of iodonium ylides of β -dicarbonyl compounds in the presence of CuCl as catalyst.⁸

Results and Discussion

In our continuing exploration of the reactions of iodonium ylides and iodonium zwitterions with various dipolarophiles,^{3,5,6,9} we have studied the reactivity of phenyliodonium dibenzoylmethylide (1), a typical iodonium ylide derived from an acyclic β -diketone, with alkynes.

No reaction between the ylide and alkynes (terminal or internal) was observed in acetonitrile at room temperature

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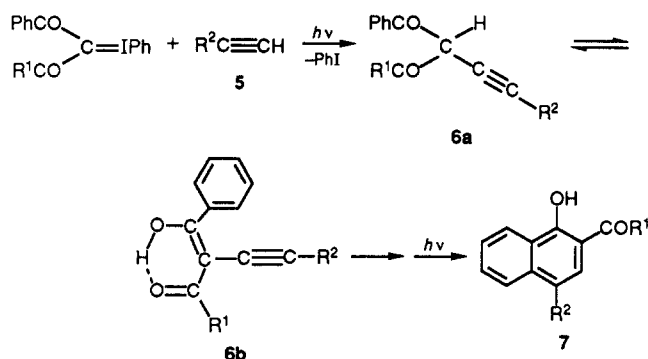
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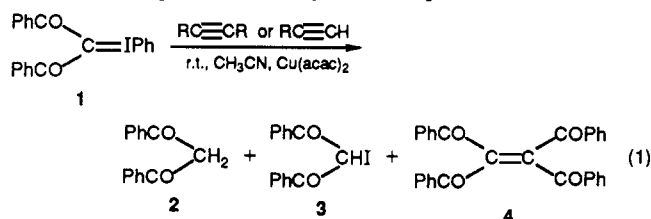
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Table I. Photochemical Reaction of Phenyliodonium Ylides with Terminal Alkynes

| | | yield, % |
|--|--|---------------|
| 1, R ¹ = Ph | 7a, R ² = C ₄ H ₉ | 28 |
| | 7b, R ² = Ph | 32 |
| | 7c, R ² = SiMe ₃ | 30 |
| | 7d, R ² = CMe ₂ OH | 19 |
| | 7e, R ² = COOMe | traces by NMR |
| 8, R ¹ = Me | 7f, R ² = Ph | 28 |
| | 7g, R ² = SiMe ₃ | 30 |
| 9, R ¹ = OCH ₂ CH ₃ | 7h, R ² = Ph | 21 |

in the presence of a catalytic amount of copper acetylacetonate (eq 1). The only isolable products were those

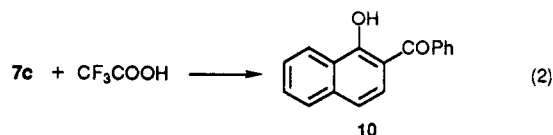


derived from the decomposition of the ylide: dibenzoylmethane (2) (25–35%), iododibenzoylmethane (3) (10–15%), and tetrabenzoyl ethylene (4) (8–10%). Compounds 2 and 3 were also produced from the reaction of 1 with terminal alkynes under photolytic conditions.

However, when a suspension of 1 in acetonitrile or dichloromethane solution was irradiated in the presence of an excess of different terminal alkynes, a new type of product was isolated, the side products again being 2 and 3. Other iodonium ylides, namely, 8 and 9, gave the same reaction (Table I).

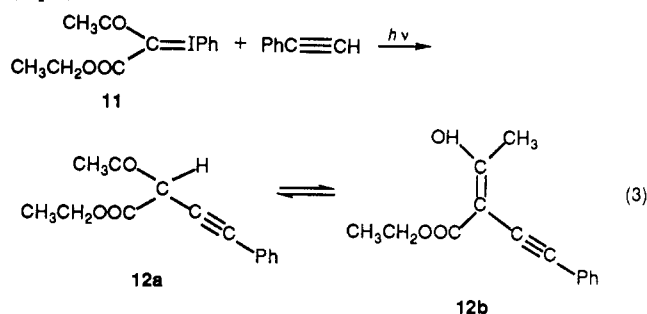
Initially it was thought that the isolated compounds were the ethynylated β -dicarbonyl derivatives 6, since elemental analyses and MS and ¹H NMR spectra were in agreement with the enolic form of these compounds. However, the lack of C≡C absorptions in their IR spectra, along with an intense yellow color, suggested the possibility of naphthalene ring formation arising from the cyclization of the enolic form of the ethynylated compounds 6b. This reaction could be photochemical and is favored by the cis configuration of the benzene ring and the triple bond. It must be noted that analogous photochemical cyclizations involving double bonds have been reported in the literature for the formation of dihydroindoles,¹⁰ dihydrobenzofurans,¹¹ and benzothiophenes,¹² the latter proceeding in the presence of an oxidizing agent like iodine. Also, the cyclization of alkynyl amidines to 2-amino quinolines provides a related example, although it is mediated¹³ by polyphosphoric acid.

The trimethylsilyl group in 7c was removed by treatment with acid in order to prove the structure of these new compounds (eq 2).



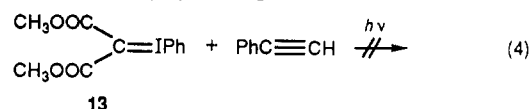
The resulting compound 10 was identical with 2-benzoyl- α -naphthol prepared by another method (Fries rearrangement of α -(benzoyloxy)naphthalene¹⁴).

The intermediacy of the ethynylated compounds 6 is strongly supported by the fact that such a compound was isolated from the photoreaction of the phenyliodonium ylide of ethyl acetoacetate (11) with phenylacetylene in 14% yield; in this case, no further cyclization is possible (eq 3).



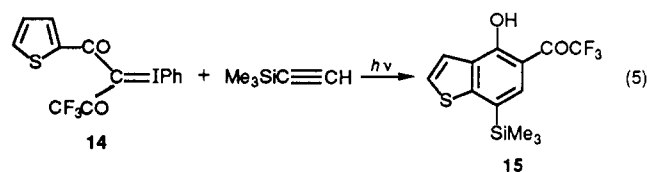
The two forms, keto (12a) and enolic (12b), exist in solution in a ratio of ca. 1:1 as indicated by ¹H NMR spectroscopy. This finding supports the assumption that the final cyclization to the α -naphthol ring proceeds through the enolic form 6b, since this form does exist and is the predominant form in compounds 6.

In contrast, the phenyliodonium ylide of diethyl malonate (13) failed to react with phenylacetylene under the same conditions (eq 4), possibly indicating that the potential enolization of the β -dicarbonyl compound plays some important role for either the reaction itself or for the stabilization of the ethynylated product 6.



The same ylide 13 has been reported to react with cyclohexene to yield the *gem*-dicarbomethoxycyclopropane derivative¹⁵ in a thermal reaction.

The reaction also proceeds when the phenyl group in the β -dicarbonyl compound is replaced by a heteroaromatic ring. Indeed, the phenyliodonium ylide of 2-thenoyltrifluoroacetone (14) reacts with (trimethylsilyl)acetylene to afford the hydroxybenzothiophene derivative 15 in 24% yield (eq 5).



From the reaction of 1 with 2-methyl-3-butyn-2-ol (5d), the ether derivative 16 was also isolated in 25% yield, while 17 was the product of the photoreaction of 1 with 2,2-dimethylpropanol (65% yield). Other nontertiary alcohols

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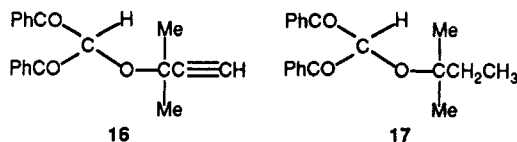
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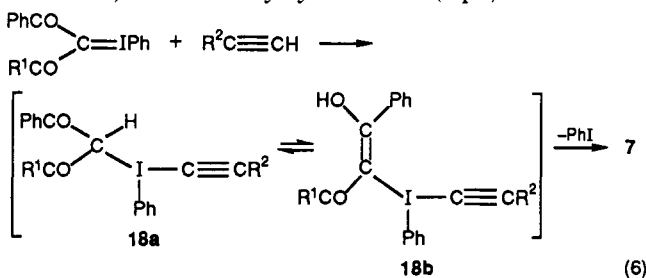
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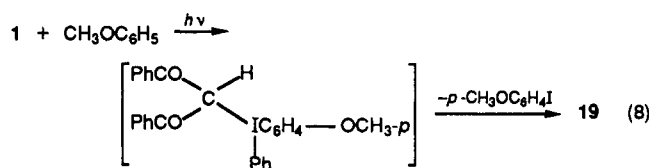
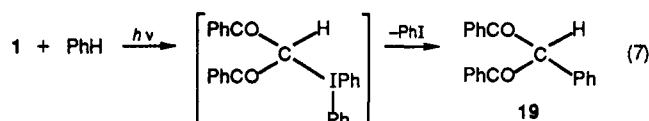
primarily gave oxidation products of the alcohol.

With regard to the first steps of the reaction with alkynes, it has been proposed in the literature^{3,5,8} that C-C bond formation via iodonium ylides proceeds through the intermediacy of iodanes, compounds with three I-C bonds, although the role of the copper catalysts (or of the light, in this case) is not very clear.

Iodanes 18, as is the case for almost all iodanes, are unstable under photolytic conditions and easily decompose with the expulsion of iodobenzene to form 6. It is also possible that iodanes 18 are more stable in their enolic form 18b, which finally cyclizes to 7 (eq 6).

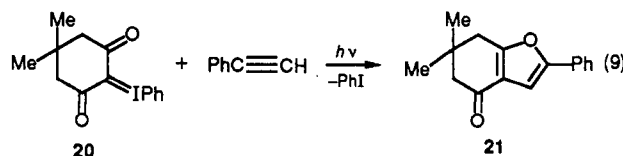


The intermediacy of iodane 18 is supported by the fact that irradiation of 1 in benzene or anisole gave the same product, dibenzoylphenylmethane (19), in 25 and 23% yield, respectively (eqs 7 and 8). In the case of anisole,



p-iodoanisole was detected among the products of the reaction. The reaction with aromatic compounds offers an alternative route for the arylation of β -dicarbonyl compounds.

The photochemical reaction, as well as the copper-catalyzed thermal reaction of terminal alkynes, was also attempted with phenyliodonium ylides of cyclic β -dicarbonyl compounds such as dimedone, 2,4-quinolinediol, 2,2-dimethyl-1,3-dioxane-4,6-dione, and 2-hydroxycoumarin but with no success. In only one case, the photoreaction of phenyliodonium dimedonide (20) with phenylacetylene, was a cyclization product, the furan 21, isolated in 14% yield (eq 9).



The same compound 21 was isolated from the reaction of the corresponding bismuthonium ylide with phenylacetylene in the presence of a catalytic amount of CuCl.¹⁶ This difference in reactivity between ylides of cyclic and acyclic β -dicarbonyl compounds is possibly due to the

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different conformations of these two classes. This discrepancy has also been observed in other classes, e.g., upon heating there is a migration of the phenyl group from iodine to oxygen in ylides of cyclic β -diketones, but never in ylides of acyclic ones.¹

Conclusion

In summary, we have presented a new type of reaction between phenyliodonium ylides of acyclic β -dicarbonyl compounds and terminal alkynes. The reaction leads to substituted α -naphthols through ethynylated β -dicarbonyl derivatives. The latter can be isolated in the case of β -dicarbonyl compounds with aliphatic substituents. It is envisioned that this reaction will find application in the synthesis of substituted benzoheterocyclic derivatives analogous to 15. The results of such a study will be reported in due course.

Experimental Section

General Methods and Materials. Melting points (uncorrected), Kofler hotstage; IR, Perkin-Elmer 1370 spectrophotometer; UV, Shimadzu UV 210A spectrophotometer; ¹H NMR (CDCl₃ solvent, TMS internal standard), Bruker AW 80; ¹³C NMR (CDCl₃, TMS), Varian VRX 300; MS (70 eV), Hitachi/Perkin-Elmer RMU-6L single focusing spectrometer. Irradiations were performed with a low pressure Hg lamp (400 W, Pyrex vessel).

Ylides 1, 8, 9, 11, 13, and 20 were prepared by the action of PhI(OAc)₂ and KOH on the corresponding β -dicarbonyl compounds,¹⁷ while ylide 14 was prepared by a transylidation reaction using (tosylimino)iodobenzene and the proper β -diketone.¹⁸

Thermal Reaction of 1 with Terminal and Internal Alkynes. A suspension of 1 (1 mmol) in acetonitrile (or solution in dichloromethane) (15 mL), the alkyne (10 mmol), and copper acetylacetonate (2–3 mg) were stirred at room temperature until the complete decomposition of the ylide was accomplished (30–60 min). The resulting solution was chromatographed on a column (silica gel, CH₂Cl₂-hexane 1:1) to afford iodobenzene (80%), dibenzoylmethane (2) (25–35%), iododibenzoylmethane (3), mp 105 °C [lit.¹⁹ mp 104–105 °C] (10–15%), and tetrabenzoyl ethylene (4), mp 183–185 °C [lit.²⁰ mp 184–186 °C] (8–10%).

Photochemical Reaction of 1 with Internal Alkynes. A suspension of 1 (1 mmol) in acetonitrile or dichloromethane solution (10 mL) and the proper alkyne (10 mmol) was irradiated for 15–20 min. Column chromatography gave iodobenzene, 2, and 3 as the only products.

General Procedure for the Photoreaction of Ylides 1, 8, 9, 11, 13, and 14 with Terminal Alkynes. A suspension of the proper ylide (1 mmol) in acetonitrile (10 mL) and the proper alkyne (10 mmol) was irradiated for 15–30 min. The resulting yellow solution was chromatographed on a column (silica gel, hexane-CH₂Cl₂, 60–40%). Compounds 7 were eluted immediately after iodobenzene and their solutions exhibited distinct yellow color. Compounds 2 and 3 were side products in each of these reactions.

Reaction of 1 with 1-Hexyne. 2-Benzoyl-4-butylnaphthol-1 (7a) was isolated in 28% yield: mp 59–61 °C (from hexane); UV (EtOH) λ_{\max} (log ϵ) 392 (3.58), 306 (3.51); IR (Nujol) 3020, 1615, 1565 cm⁻¹; ¹H NMR δ 13.72 (s, 1 H), 8.57 (d, 1 H), 7.37–8.01 (m, 9 H), 2.87 (t, 2 H), 1.22–1.68 (m, 4 H), 0.83 (t, 3 H); MS, *m/z* (rel intensity) 304 (M⁺, 71) 261 (96), 183 (100), 155 (20), 127 (53), 105 (40), 77 (64). Anal. Calcd for C₂₁H₂₀O₂: C, 82.86; H, 6.62. Found: C, 82.38; H, 6.39.

Reaction of 1 with Phenylacetylene. 2-Benzoyl-4-phenylnaphthol-1 (7b) was isolated in 32% yield: mp 156–157 °C (from hexane); UV (EtOH) λ_{\max} (log ϵ) 392 (3.94), 304 (3.63); IR (Nujol) 3020, 1620, 1595, 1565, 1440 cm⁻¹; ¹H NMR δ 13.93

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(s, 1 H), 8.59 (m, 1 H), 7.49–7.78 (m, 9 H), 7.38 (s, 5 H); MS, m/z (rel intensity) 324 (M^+ , 100), 323 (20), 246 (51), 189 (62), 165 (25), 105 (28), 77 (69). Anal. Calcd for $C_{23}H_{16}O_2$: C, 85.16; H, 4.94. Found: C, 85.33; H, 4.84.

Reaction of 1 with (Trimethylsilyl)acetylene. 2-Benzoyl-4-(trimethylsilyl)naphthol-1 (7c) was isolated in 30% yield: mp 92–92 °C (from hexane); UV (EtOH) λ_{max} (log ϵ) 384 (3.63), 313 (3.38), 303 (3.55); IR (Nujol) 3020, 1595, 1565, 1500, 1440, 1330, 1260 cm^{-1} ; 1H NMR δ 14.01 (s, 1 H), 8.57 (m, 1 H), 7.90–8.10 (m, 2 H), 7.40–7.77 (m, 7 H), 0.35 (s, 9 H); MS, m/z (rel intensity) 320 (M^+ , 68), 305 (100), 152 (11), 105 (16), 77 (21). Anal. Calcd for $C_{20}H_{20}O_2Si$: C, 74.96; H, 6.74. Found: C, 75.04; H, 6.78.

Reaction of 1 with 2-Methyl-3-butyn-2-ol. 2-Benzoyl-4-(2'-hydroxy-2'-methyl-ethyl)naphthol-1 (7d) was isolated in 19% yield: mp 147–149 °C (hexane); UV (EtOH) λ_{max} (log ϵ) 387 (3.88), 302 (3.93); IR (Nujol) 3550, 1620, 1595, 1570, 1500, 1330 cm^{-1} ; 1H NMR δ 13.87 (s, 1 H), 8.43–8.80 (m, 2 H), 7.25–7.84 (m, 8 H), 1.90 (s, br, 1 H), 1.70 (s, 6 H); MS, m/z (rel intensity) 306 (M^+ , 13), 291 (8), 218 (10), 105 (100), 77 (38). Anal. Calcd for $C_{20}H_{18}O_3$: C, 78.41; H, 5.92. Found: C, 78.39; H, 6.11.

From the same reaction 2-[(1',1'-dimethylbut-2'-ynyl)-oxy]-1,3-diphenylpropanedione (16) was isolated in 25% yield: mp 95–96 °C (hexane), IR (Nujol) 3280, 3020, 2090, 1750, 1670, 1580, 1500, 1225 cm^{-1} ; 1H NMR δ 7.83–8.04 (m, 2 H), 7.30–7.45 (m, 8 H), 5.56 (s, 1 H), 2.46 (s, 1 H), 1.64 (s, 6 H); MS m/z (rel intensity) 306 (M^+ , 3), 165 (16), 118 (100), 105 (62), 90 (18), 77 (51). Anal. Calcd for $C_{20}H_{18}O_3$: C, 78.41; H, 5.92. Found: C, 78.64; H, 6.01.

Reaction of 1 with Methyl Propiolate. The desired product 2-benzoyl-4-(methoxycarbonyl)naphthol-1 (7e) was formed in traces and was detected in the crude reaction mixture by 1H NMR from the characteristic peaks at δ 13.95 (enolic hydrogen) and δ 8.52 (8-hydrogen).

Reaction of 8 with Phenylacetylene. 2-Acetyl-4-phenyl-naphthol-1 (7f) was isolated in 28% yield: mp 178–180 °C (hexane); UV (EtOH) λ_{max} (log ϵ) 363 (3.75); IR (Nujol) 3020, 1640, 1570 cm^{-1} ; 1H NMR δ 13.96 (s, 1 H), 8.51 (m, 1 H), 7.53–7.70 (m, 4 H), 7.43 (s, 5 H), 2.64 (s, 3 H); MS, m/z (rel intensity) 262 (M^+ , 100), 247 (52), 244 (22), 215 (20), 191 (41), 189 (50), 165 (24), 105 (10), 96 (17). Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.28; H, 5.22.

Reaction of 8 with (Trimethylsilyl)acetylene. 2-Acetyl-4-(trimethylsilyl)naphthol-1 (7g) was isolated in 30% yield: mp 102–105 °C (hexane); UV (EtOH) λ_{max} (log ϵ) 368 (3.84); IR (Nujol) 3020, 1645, 1590 cm^{-1} ; 1H NMR δ 14.01 (s, 1 H), 8.51 (m, 1 H), 7.55–8.01 (m, 4, H), 2.67 (s, 3 H), 0.41 (s, 9 H); MS, m/z (rel intensity) 258 (M^+ , 75), 243 (100), 114 (41). Anal. Calcd for $C_{15}H_{18}O_2Si$: C, 69.72; H, 7.02. Found: C, 69.89; H, 6.88.

Reaction of 9 with Phenylacetylene. 2-(Ethoxycarbonyl)-4-phenyl-naphthol-1 (7h) was isolated in 21% yield: mp 105–107 °C (hexane); UV (EtOH) λ_{max} (log ϵ) 362 (3.74), 348 (3.76), 308 (3.62); IR (Nujol) 3020, 1660, 1630, 1600, 1405, 1255 cm^{-1} ; 1H NMR δ 12.03 (s, 1 H), 8.45 (m, 1 H), 7.45–7.72 (m, 4 H), 7.43 (s, 5 H), 4.44 (q, 2 H, $J = 9$ Hz), 1.38 (t, 3 H, $J = 9$ Hz); MS, m/z (rel intensity) 292 (M^+ , 40), 246 (100), 218 (9), 189 (14). Anal. Calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.51. Found: C, 78.19; H, 5.66.

Reaction of 11 with Phenylacetylene. Ethyl 2-(phenylethynyl)acetoacetate (12) was isolated as an oil in 14% yield: UV (EtOH) λ_{max} (log ϵ) 293 (4.23); IR (neat) 3020, 2980, 1715, 1610, 1580, 1225 cm^{-1} ; 1H NMR δ 7.98 (br, 1 H, OH), 7.25–7.64 (m, 1 OH), 6.76 (s, 1 H), 4.34 (q, 2 H, $J = 9$ Hz), 4.31 (q, 2 H, $J = 9$ Hz), 2.63 (s, 3 H), 2.27 (s, 3 H), 1.35 (t, 3 H, $J = 9$ Hz), 1.32 (t, 3 H, $J = 9$ Hz); MS, m/z rel intensity 230 (M^+ , 10), 229 (59), 201 (90), 142 (25), 115 (27), 105 (100), 77 (85). Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 72.61; H, 5.87.

Reaction of 14 with (Trimethylsilyl)acetylene. 4-(Trimethylsilyl)-6-(trifluoroacetyl)-7-hydroxybenzo[*b*]-thiophene (15) was isolated in 24% yield: mp 88–90 °C (hexane); (EtOH) λ_{max} (log ϵ) 378 (3.20), 306 (3.60); IR (Nujol) 1635, 1605, 1530, 1245 cm^{-1} ; 1H NMR δ 12.11 (s, 1 H), 7.87 (d, 1 H, $J = 8$ Hz), 7.82 (s, 1 H), 7.54 (d, 1 H, $J = 8$ Hz), 0.38 (s, 9 H); MS, m/z (rel intensity) 318 (M^+ , 100), 304 (41), 253 (42), 191 (13), 118 (12). Anal. Calcd for $C_{13}H_{13}F_3O_2SSi$: C, 49.04; H, 4.11. Found: C, 48.82; H, 3.88.

Desilylation of 7c. 7c (160 mg) was dissolved in dichloromethane (10 mL), trifluoroacetic acid (1 mL) was added, and the solution remained for 2 h at room temperature. After water workup and evaporation of the solvent 2-benzoylnaphthol-1 (10) was isolated (120 mg, 97%): mp 71–73 °C (hexane); lit.¹⁴ mp 74–76 °C; UV (EtOH) λ_{max} (log ϵ) 383 (3.67), 310 (3.35), 300 (3.52); IR (Nujol) 3020, 1630, 1600, 1570 cm^{-1} ; 1H NMR δ 13.92 (s, 1 H), 8.54 (m, 1 H), 7.42–7.79 (m, 10 H); ^{13}C NMR 201.4, 163.9, 138.2, 137.3, 131.6, 130.3, 129.1, 128.3, 127.4, 125.9, 125.8, 124.5, 117.9, 112.5; MS, m/z (rel intensity) 248 (M^+ , 100), 247 (32), 170 (51), 105 (38), 77 (85). Anal. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.84. Found: C, 82.41; H, 5.26.

Reaction of 1 with 2-Methylbutanol-2. The reaction was performed under the same conditions as the reaction with alkynes. The ether 17 was isolated in 65% yield: mp 45–47 °C (from hexane at –20 °C); IR (Nujol) 3020, 1735, 1670, 1600, 1320 cm^{-1} ; 1H NMR δ 7.96 (m, 4 H), 7.39 (m, 6 H), 5.50 (s, 1 H), 1.69 (q, 2 H, $J = 9$ Hz), 1.37 (s, 6 H), 0.74 (t, 3 H, $J = 9$ Hz); MS, m/z (rel intensity) 310 (M^+ , traces), 240 (5), 223, 222 (4), 196 (9), 165 (6), 118 (92), 105 (100), 90 (12), 77 (29), 71 (26). Anal. Calcd for $C_{20}H_{22}O_3$: C, 77.39; H, 7.14. Found: C, 77.33; H, 7.05.

Reaction of 1 with Benzene and Anisole. 1 (1 mmol) in benzene (15 mL) or anisole (7 mL) was irradiated for 30 min. After removal of volatiles and column chromatography 2-phenyl-1,3-diphenylpropanedione-1,3 (19) was isolated in 25 and 23% yield, respectively: mp 148–149 °C; lit.²¹ mp 151 °C; 1H NMR δ 7.80–8.07 (m, 4 H), 7.30–7.52 (m, 11 H), 5.80 (s, 1 H). From the reaction with anisole, *p*-iodoanisole is eluted with iodobenzene and detected by 1H NMR.

Reaction of Phenyliodonium Dimedonide (20) with Phenylacetylene. The reaction was performed under the same conditions as the reactions of the other ylides. The only isolable product was 6,6-dimethyl-4-oxo-2-phenyl-4,5,6,7-tetrahydrobenzo[*b*]furan (21) in 14% yield: mp 100–101 °C; lit.¹⁵ mp 101–102 °C; 1H NMR identical with that reported in the literature.¹⁵