Synthesis and Reactivity of Phenyliodonium Ylides of Benz[*b*]oxepine-3,5(2*H*,4*H*)-diones

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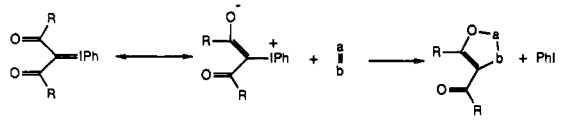
The reactions of phenyliodonium ylides of cyclic 7-membered β-diketones bearing two different carbonyl groups with alkynes and nitriles under mild conditions lead to cyclization products and exhibit remarkable regioselectivity. A possible reaction pathway is proposed in order to explain this reactivity.

Introduction

Zwitterionic iodonium compounds (ZIC), a major class of polyvalent iodine compounds, are attractive and versatile reagents in organic synthesis. Koser has reviewed the early chemistry of this class,[1] and Varvoglis[2] has thoroughly reviewed the chemistry of ZIC up to 1991.

ZIC react with both electrophiles and nucleophiles, give rise to carbenes, afford transylidation and rearrangement products, and have oxidative properties.

One of the most interesting modes of ZIC reactivity, which is characteristic of polyvalent iodine compounds generally,[3] is that leading to carbon–carbon bond formation. We are particularly interested in the reactions of phenyliodonium ylides of β-dicarbonyl compounds and phenyliodonium phenolates with unsaturated compounds (dipolarophiles). These reactions afford cyclization products according to the general scheme:



The success of this type of reaction is strongly dependent on the β-dicarbonyl moiety. The phenyliodonium ylide of dimedone yields a variety of heterocyclic products with diphenyl ketene,[4] carbon disulfide,[5] and alkenes,[6] but no cyclization products were isolated with alkynes and nitriles.[7] In contrast, phenyliodonio 1,2,4-trioxo-1,2,3,4-tetrahydronaphthalenide reacts with both alkenes and alkynes[8] to afford the corresponding cyclization products.

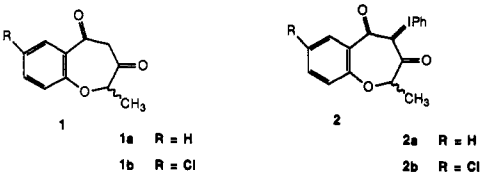
Phenyliodonium ylides of acyclic β-diketones react with alkynes under photolytic conditions and, through the intermediacy of ethynylated β-dicarbonyl derivatives, give substituted α-naphthols.[9] A different kind of reactivity was reported by Moriarty[10] for iodonium ylides of β-dicarbonyl compounds: in the presence of CuCl as catalyst, an intramolecular cyclopropanation of an appropriate precursor is observed, possibly through the intermediacy of a carbene.

Finally, phenyliodonium phenolates, upon irradiation with alkenes and alkynes, afford terahydrofurans and furans, respectively,[11] but no cyclization products were isolated with nitriles under the same conditions.

Results and Discussion

The diversity in the reactivity of ZIC with dipolarophiles prompted us to investigte this type of reaction more thoroughly, with some emphasis on the regioselectivity of the reaction when the cyclic β-diketone has two different carbonyl groups.

Benzo[*b*]oxepin-3,5(2*H*,4*H*)-diones **1**, easily accessible by means of the reaction of *o*-hydroxyacetophenones with ethyl 2-bromopropionate and subsequent cyclization with sodium ethoxide,[12] were selected as suitable systems for this study. Phenyliodonium ylides of β-diketones with a



seven-membered ring have not been prepared so far; indeed, most ylides of this type have a six-membered ring (the "dimedone" type), and only a few have a five-membered ring.

Phenyliodonium ylides **2** were prepared by the reaction of **1** with $PhI(OAc)_2$ and KOH according to the standard procedure of Schank.[13]

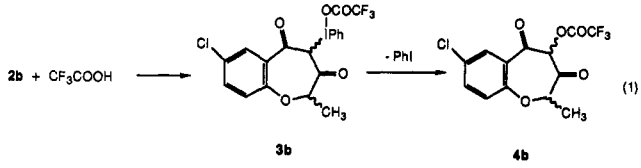
Ylides **2** are fairly stable and can be stored in the refrigerator (at 5 °C) for long periods without decomposition. They have spectroscopic data consistent with their structure. In the IR spectrum there are two C=O stretching frequencies, at 1610 and 1590 cm^{-1} for **2a** and at 1650 and 1610 cm^{-1} for **2b**; in comparison, the C=O stretching frequencies occur at 1720 and 1670 cm^{-1} in the parent diketones. In the ^1H NMR the ylides lack the characteristic two doublet pattern for the diastereoisomeric protons of the methylenic group of the parent compounds and exhibit a downfield shift of 0.35 ppm for the quadruplet

(1) Koser, G. F. *The Chemistry of Functional Groups*; Wiley: New York, 1983; Supplement D, Chapter 18, pp 774–806.
(2) Varvoglis, A. *The Organic Chemistry of Polycoordinated Iodine*; VCH: New York, 1992.
(3) Moriarty, R. M.; Vaid, R. K. *Synthesis* **1990**, 431.
(4) Koser, G. F.; Yu, S. M. *J. Org. Chem.* **1975**, 40, 1166.
(5) Papadopoulou, M.; Spyroudis, S.; Varvoglis A. *J. Org. Chem.* **1985**, 50, 1509.
(6) Hadjiarapoglou, L. *Tetrahedron Lett.* **1987**, 28, 4449.
(7) Spyroudis, S.; Tarantili, P. Unpublished results.
(8) Hatjigrigoriou, E.; Spyroudis, S.; Varvoglis, A. *Liebigs Ann. Chem.* **1989**, 167.
(9) Kalogiannis, S.; Spyroudis, S. *J. Org. Chem.* **1990**, 55, 5041.
(10) Moriarty, R. M.; Prakash, O.; Vaid, R. K.; Zhao, L. *J. Am. Chem. Soc.* **1989**, 111, 6443.
(11) Spyroudis, S. *J. Org. Chem.* **1986**, 51, 3453.
(12) Gabriel, G.; Pickles, R.; Tyman, J. *J. Chem. Res., Miniprint* **1989**, 2713.
(13) Schank, K.; Lick, C. *Synthesis* **1983**, 392.

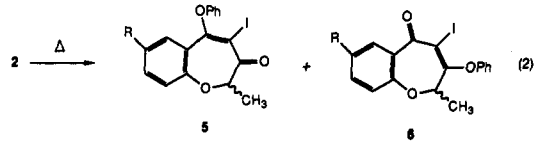
0022-3263/93/1958-4885$04.00/0

of the methinic proton. The molecular ion is of low intensity, the main fragment being iodobenzene.

Upon treatment with trifluoroacetic acid, **2b** is converted easily to phenyl iodonium salt **3b**, which is not isolable but decomposes to the corresponding trifluoroacetate **4b** with expulsion of iodobenzene, probably through a nucleophilic substitution pathway most commonly observed in the corresponding reactions of diaryl iodonium salts[14] (eq 1).



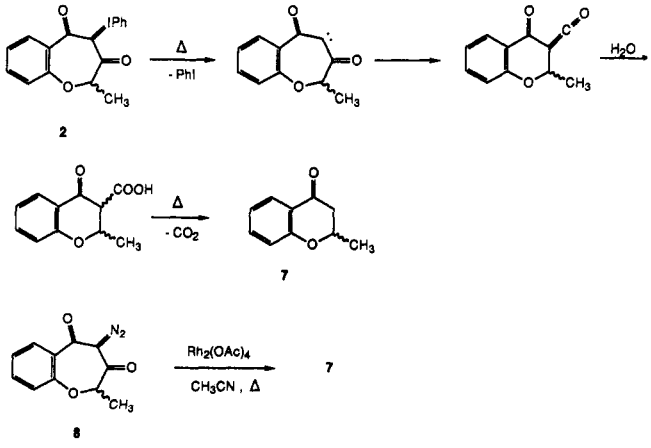
Upon heating, **2** are converted to an inseparable mixture of isomeric ethers **5** and **6** in a ratio of 3:1, the phenyl group migrating to the most enolizable of the two carbonyls (eq 2). The ratio is calculated from the ^{1}H-NMR spectrum



of the mixture; the methinic proton of **5** resonates at about 4.5 ppm and that of **6** at 5.20 ppm. The migration of the phenyl group takes place in refluxing CH_2Cl_2, CH_3CN, $CHCl_3$, and CCl_4 without significant change either in the yield or in the ratio of the regioisomers. Addition of Cu(acac)$_2$ accelerates the migration. These findings are in agreement with the generally accepted pathway for such rearrangements, involving an intermediary spiro–Meisenheimer complex.[15]

From the reaction in refluxing acetonitrile, a minor (10–15%) product is also isolated, especially when the solvent is not dry. This compound, dihydro chromanone **7**, probably results from carbene and Wolf rearrangement products according to Scheme I.

Scheme I

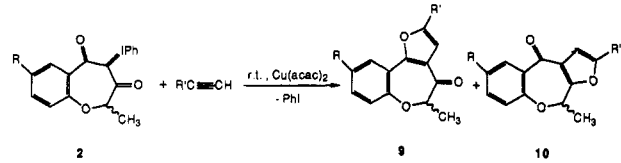


It is noteworthy that only **7**, one of the two possible regioisomers, is isolated, as usually happens with Wolf rearrangements of unsymmetrically substituted open-chain 2-diazo-1,3-dicarbonyl compounds.[16] Exclusive migration of the C_{Alk}-atom has also been observed during the Rh^{2+}-catalyzed decomposition of 2-diazo-4,4-dimethyl-1,3-tetralindione.[17] This exclusive migration was explained in terms of the *Z,Z* planar conformation of the dione compared to the twisted one of the noncyclic analogues.

In order to confirm the intermediacy of carbenes, 4-diazo-2-methyl-2,4*H*-benz[*b*]oxepine-3,5-dione (**8**) was prepared. A solution of **8** in refluxing acetonitrile and in the presence of a catalytic amount of $Rh_2(OAc)_4$ gave as the only isolable product dihydro chromanone **7**, thus proving the parallel decomposition pathway of ylide **2** and diazo compound **8**.

The reaction of ylides **2** with terminal alkynes proceeds smoothly at room temperature in CH_2Cl_2 in the presence of a catalytic amount of Cu(acac)$_2$ affording moderate yields of the corresponding furans **9** and **10**.

Table I. Reaction of Ylides 2 with Terminal Alkynes

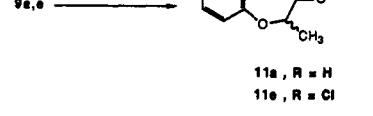


2a, R = H	9a R = H, R' = $SiMe_3$	43%
	9b R = H, R' = Ph	47%
	9c R = H, R' = $CH_3(CH_2)_3$	45%
	9d R = H, R' = CH_2Cl	30%
2b, R = Cl	9e R = Cl, R' = $SiMe_3$	48%
	9f, R = Cl, R' = Ph	52%

The reaction exhibits remarkable regioselectivity; only regioisomers **9** were isolated. Isomers **10** were detected in small amounts (5–7% of the yield of the product) in some cases by ^{1}H-NMR spectroscopy. The identification of **9** and **10** was based on comparison of the ^{1}H-NMR chemical shift of the quadruplet of the methinic proton with that of the parent ketone (4.25 for the ketone, 4.40 for **9** and 5.15 ppm for **10**) and on comparison of the shift of the aromatic hydrogen ortho to the carbonyl group with that of the ketone (8.15 for the ketone, 7.85 for **9**, and 8.10 ppm for **10**). In addition, in all cases, the isolated isomer **9** had the R′ substituent at the α-position of the furan ring.

No cyclization products were isolated when **2** was irradiated in the presence of alkynes; only complicated mixtures of unidentified products along with small amounts of PhI and mixtures of ethers **5** and **6** were obtained.

Treatment of compounds **9a** and **9e** with acid to remove the $SiMe_3$ group afforded quantitively unsubstituted furans **11a** and **11e** (eq 3).

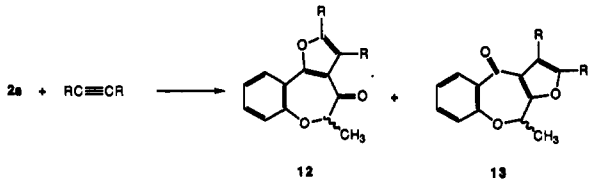


The reaction of **2a** with internal alkynes afforded mixtures of regioisomers **12** and **13** in different ratios as estimated by ^{1}H-NMR (Table II).

A plausible mechanism for the cyclizations with terminal alkynes involves the formation of either iodane **15** or a

(14) Grushin, V. V.; Demkina, I. I.; Tolstaya, T. P. *J. Chem. Soc., Perkin Trans. 2* **1992**, 505 and references cited therein.
(15) Reference 2, p 319.
(16) Meir, H.; Zeller, K. P. *Angew. Chem., Int. Ed. Engl.* **1975**, 14, 32.
(17) Nikolaev, V. A.; Popic, V. V. *Tetrahedron Lett.* **1992**, 31, 4483.

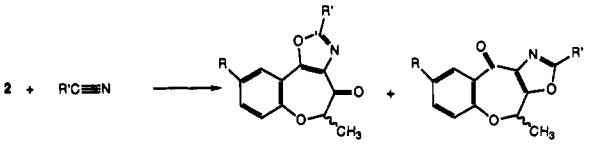
Table II. Reaction of Ylide 2a with Internal Alkynes



12a, R = Me : 13a, R = Me 4 : 1

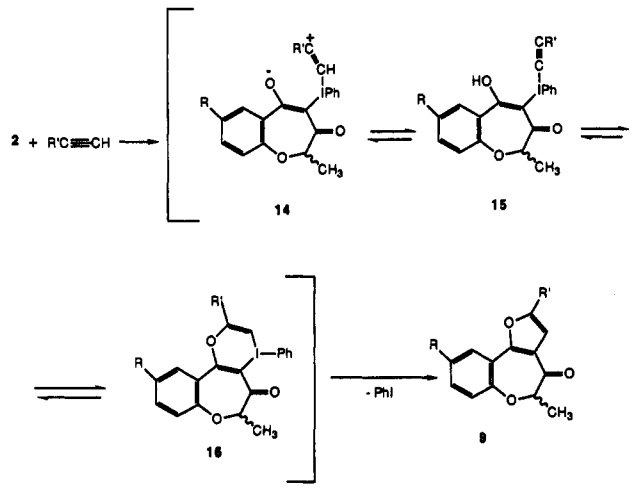
12b, R = $SiMe_3$: 13b, R = $SiMe_3$ 1 : 1

Table III. Reaction of Ylides 2 with Nitriles

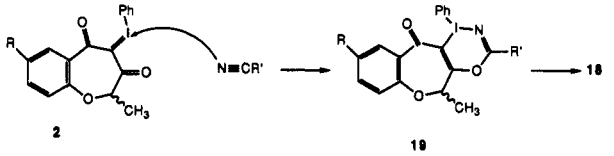


18a	R = H, R' = CH_3	60%
18b	R = H, R' = Ph	53%
18c	R = H, R' = $C(CH_3)_3$	49%
18d	R = Cl, R' = CH_3	54%

Scheme II



Scheme III



dipole of type 14 (Scheme II). Both 14 and 15 (and their cyclic equivalent 16) can be converted into furan derivative 9 by expulsion of PhI. Since the carbonyl group attached to the benzene ring is more enolizable than the other carbonyl, it is reasonable to assume that intermediates of type 14, 15, and 16 are favored; these intermediates lead predominantly to the formation of 4,5-fused furan derivatives. This reaction pathway also explains the regioselectivity in the substitution of the furan ring.

The reaction of **2a** with internal alkynes follows an analogous pathway, but it is obvious that steric hindrance plays an important role in the regioselectivity of the reaction. The ratio **12a:13a** is 4:1 for an alkyne with Me groups but 1:1 for **12b:13b** for an alkyne bearing the bulkier $SiMe_3$ groups. No cyclization products were isolated from the reaction of **2a** with diphenylacetylene and diethyl acetylenedicarboxylate.

The reactions of **2** with nitriles under the same conditions used for the reactions with alkynes (room temperature, $Cu(acac)_2$ catalyst) were slower (usually 24 h were needed for the completion of the reaction) and gave quite the opposite results (Table III). Oxazoles **18**, fused at 3,4 positions of the oxepine ring, were the main cyclization products. Regioisomers **17** were minor products detected by ^{1}H-NMR. The ratio 17:18 was usually 5:95. Again, structure elucidation of **17** and **18** was based on comparison of the shifts of the methinic proton and the aromatic proton at C9 with those of the parent diketone.

This high regioselectivity cannot be easily explained. It is possible that the first step of the reaction is the attack of nitrogen on the positive iodine leading to the formation of cyclic iodane **19**. Because the reaction is under kinetic control, it seems that the most favorable conformation in this case is that leading to **19** and finally to isomer **18** (Scheme III). In reactions with terminal alkynes, it is possible that the protonation of the most enolizable carbonyl leading to the formation of iodane **15** really takes place and regioisomers **9** are formed selectively.

Conclusion

The reactions of phenyliodonium ylides of cyclic 7-membered β-dicarbonyl compounds with alkynes and nitriles have been investigated. The reactions with alkynes afford furans in moderate yields in the presence of a catalytic amount of $Cu(acac)_2$ at room temperature. The regioselectivity of the reaction is very high: the carbonyl attached to the benzene ring cyclizes predominantly, and the corresponding α-substituted furans **9** are formed.

By contrast, the reactions with nitriles afford almost exclusively oxazoles from the cyclization of the other carbonyl group under the same mild conditions.

Finally, internal alkynes lead to the formation of both possible regioisomers in varying ratios.

This investigation of reactivity will be continued with iodonium ylides of other β-dicarbonyl systems in an effort to establish some rules for the reactivity pattern of this interesting class of polyvalent iodine compounds.

Experimental Section

Melting points are uncorrected. IR spectra were obtained in Nujol. ^{1}H-NMR, unless otherwise stated, were recorded with an 80-MHz instrument with $CDCl_3$ as solvent and $SiMe_4$ as an internal standard. MS spectra were obtained with an electron beam operating at 70 eV.

2-Methylbenz[*b*]oxepine-3,5(2*H*,4*H*)-dione (1a) and **7-chloro-2-methylben[*b*]oxepine-3,5(2*H*,4*H*)-dione (2a)** were prepared by the reaction of the corresponding *o*-hydroxyacetophenones with ethyl 2-bromopropionate and subsequent cyclization with sodium ethoxide.[12] Their phenyliodonium ylides (**2a** and **2b**) were obtained from the reaction of diketones with diacetoxyiodobenzene[13] and KOH.

Ylide 2a: yield 65%; mp 122–123 °C (from ether); IR 3040, 1610, 1590, 1100, 740 cm^{-1}; ^{1}H NMR δ 1.48 (d, 3H, J = 9 Hz), 4.63 (q, 1H, J = 9 Hz), 7.05–7.40 (m, 4H), 7.88–8.11 (m, 3H); MS m/z (relative intensity) 392 (M^+, 5), 204 (95), 127 (15), 77 (100). Anal. Calcd for $C_{17}H_{13}IO_3$: C, 52.06; H, 3.34. Found: C, 52.31; H, 3.30.

Ylide 2b: yield 60%; mp 85 °C (from ether); IR 3040, 1650, 1620, 1050, 750 cm^{-1}; ^{1}H NMR δ 1.55 (d 3H, J = 9 Hz), 4.52 (q, 1H, J = 9 Hz), 7.12 (d, 1H, J = 8 Hz), 7.67 (d, 1H, J = 8 Hz), 8.03 (s, 1H); MS m/z (relative intensity) 429, 427 (M^+, 15, 5), 204 (35), 155 (85), 77 (100). Anal. Calcd for $C_{17}H_{12}ClIO_3$: C, 47.86; H, 2.83. Found: C, 47.67; H, 2.75.

Reaction of 2b with Trifluoroacetic Acid. Ylide **2b** (1 mmol) was dissolved in CH_2Cl_2 (10 mL), and CF_3COOH (1 mL) was added. A precipitate, presumably **3b**, was formed but later redissolved. Upon addition of hexane, **6-(trifluoroacetoxy)-7-chloro-2-methylbenz[*b*]oxepine-3,5(2*H*,4*H*)-dione (4b)** crystallized: yield 60%; mp 60–65 °C; IR 1800, 1750, 1685, 1160 cm^{-1}; ^1H NMR δ 1.71 (d, 3H, J = 9 Hz), 4.45 (q, 1H, J = 9 Hz), 6.10 (s, 1H), 7–810 (m, 8H); MS m/z (relative intensity) 336 (M^+, 7), 240 (20), 184 (15), 155 (100), 154 (30), 69 (19). Anal. Calcd for $C_{13}H_8F_3ClO_5$: C, 46.39; H, 2.39. Found: C, 46.17; H, 2.51.

Rearrangement of Ylides 2a and 2b. A suspension or a solution of the ylide (1 mmol) in CH_2Cl_2, CH_3CN, or CCl_4 (10 mL) was refluxed for 2–4 h. After column chromatography (silica gel, CH_2Cl_2–hexane), inseparable mixtures of ethers **5a**, **6a**, and **5b**, **6b** were isolated in 70–90% yield. ^1H NMR for the nonaromatic protons of **4-iodo-5-phenoxy-2-methyl-2*H*-benz[*b*]oxepin-3-one (5a)**: δ 1.60 (d, 3H, J = 9 Hz), 4.61 (q, 3H, J = 9 Hz). For **4-iodo-3-phenoxy-2-methyl-2*H*-benz[*b*]oxepin-5-one (6a)**: δ 1.45 (d, 3H, J = 9 Hz), 5.07 (q, 1H, J = 9 Hz); the ortho aromatic proton resonated at 8.05 (d, 1H, J = 8 Hz). MS (for the mixture): m/z (rel intensity) 393 (M^+, 29), 299 (87), 266 (51), 145 (11), 115 (71), 77 (100).

^1H NMR data for the nonaromatic protons of **5b**: δ 1.57 (d, 3H, J = 9 Hz), 4.60 (q, 3H, J = 9 Hz). For **6b**: δ 1.38 (d, 3H, J = 9 Hz), 5.03 (q, 1H, J = 9 Hz); the ortho aromatic proton resonated at 7.99 (s, 1H). MS (for the mixture): m/z (rel intensity) 427, 425 (M^+, 7, 21), 333 (100), 305 (24), 299 (50), 195 (21), 115 (40), 94 (22), 77 (67).

When the reaction of **2a** was carried out in refluxing CH_3CN, a second compound was isolated. It proved to be **2-methyldihydrochromanone (7)**: mp 29–31 °C (lit.[18] mp 32 °C); IR 3040, 1680, 1260, 740 cm^{-1}; ^1H NMR δ 1.48 (d, 3H, J = 8 Hz), 2.64 (d, 2H, J = 9 Hz), 4.57 (m, 1H), 6.89–7.46 (m, 3H), 7.88 (d, 1H); MS m/z (rel intensity) 162 (M^+, 76), 147 (17), 121 (53), 120 (100), 92 (47).

Decomposition of 4-Diazo-2-methyl-2,4*H*-benz[*b*]oxepine-3,5-dione. 4-Diazo-2-methyl-2,4*H*-benz[*b*]oxepine-3,5-dione (**8**) was prepared from the parent ketone and TsN_3 in the presence of dibenzo-18-crown-6, according to the literature method,[19] in 70% yield: IR 2150, 2110, 1640, cm^{-1}; ^1H NMR δ 1.52 (d, 3H, J = 9 Hz), 4.53 (q, 1H, J = 9 Hz), 7.08–7.85 (m, 3H), 8.07 (d, 1H, J = 8 Hz). Compound **8** was used for the next step without further purification.

Diazo compound **8** (1 mmol) and $Rh_2(OAc)_4$ (2 mg) were added to acetonitrile (10 mL), and the mixture was refluxed for 2 h. After the usual workup and column chromatography, chromanone **7** was isolated in 70% yield.

Reaction of Ylides 2 with Terminal Alkynes. To a solution of **2** (1 mmol) in CH_2Cl_2 (5–10 mL, degassed with N_2) were added the alkyne (5–6 mmol) and a catalytic amount (2–3 mg) of Cu(acac)$_2$. After 15–20 min at rt, the solution was concentrated and chromatographed (silica gel, CH_2Cl_2–hexane). Compounds **9** were eluted after iodobenzene and excess alkyne. In some cases, regioisomer **10** was detected by ^1H NMR in small amounts, and it was removed by recrystallization of major regioisomer **9** from CH_2Cl_2–hexane.

2-(Trimethylsilyl)-5-methyl-5*H*-benzo[*b*]furo[2,3-*d*]oxepin-4-one (9a): yield 43%; mp 63–65 °C; IR 1670, 1605, 1250, 1100, 1080, 850 cm^{-1}; ^1H NMR δ 0.35 (s, 9H), 1.50 (d, 3H, J = 9 Hz), 4.44 (q, 1H, J = 9 Hz), 7.14–7.40 (m, 3H), 7.91 (m, 1H); MS m/z (rel intensity) 286 (M^+, 100), 271 (22), 256 (18), 242 (19), 169 (20), 73 (88). Anal. Calcd for $C_{16}H_{18}O_3Si$: C, 67.10; H, 6.33. Found: C, 67.19; H, 6.20.

2-Phenyl-5-methyl-5*H*-benzo[*b*]furo[2,3-*d*]oxepin-4-one (9b): yield 47%; mp 151–153 °C; IR 1670, 1600, 1250, 1100, 850 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.55 (d, 3H, J = 9 Hz), 4.47 (q, 1H, J = 9 Hz), 7.10–7.49 (m, 8H), 7.76 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.2, 81.9, 105.6, 113.0, 122.3, 124.4, 124.7, 124.9, 126.3, 128.9, 129.3, 131.4, 154.2, 155.3, 192,9; MS m/z (rel intensity) 290 (M^+, 100), 275 (16), 227 (32), 189 (31), 157 (25), 105 (96), 77 (74). Anal. Calcd for $C_{19}H_{14}O_3$: C, 78.61; H, 4.86. Found: C, 78.60; H, 4.88.

2-Butyl-5-methyl-5*H*-benzo[*b*]furo[2,3-*d*]oxepin-4-one (9c): yield 45%; mp 35 °C; IR (melt) 1665, 1580, 1230, 1140, 760 cm^{-1}; ^1H NMR δ 0.91 (t, 3H, J = 8 Hz), 1.43 (m, 4H), 1.51 (d, 3H, J = 9 Hz), 2.69 (t, 2H, J = 8 Hz), 4.42 (q, 1H, J = 9 Hz), 6.53 (s, 1H), 7.10–7.36 (m, 3H), 7.82 (m, 1H); MS m/z (rel intensity) 270 (M^+, 100), 227 (60), 219 (41), 185 (17), 131 (23), 69 (26). Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.68; H, 6.81.

2-(Chloromethyl)-5-methyl-5*H*-benzo[*b*]furo[2,3-*d*]oxepin-4-one (9d): yield 30%; mp 80 °C; IR 1665, 1600, 1250, 1160, 750 cm^{-1}; ^1H NMR 1.54 (d, 3H, J = 9 Hz), 4.51 (q, 1H, J = 9 Hz), 4.61 (s, 2H), 6.93 (s, 1H), 7.14–7.40 (m, 3H), 7.89 (m, 1H); MS m/z (rel intensity) 264, 262 (M^+, 29, 78), 227 (100), 219 (41), 189 (17), 157 (30), 128 (14). Anal. Calcd for $C_{14}H_{11}ClO_3$: C, 64.00; H, 4.22. Found: C, 63.46; H, 4.26.

9-Chloro-2-(trimethylsilyl)-5-methyl-5*H*-benzo[*b*]furo-[2,3-*d*]oxepin-4-one (9e): yield 48%; mp 78–80 °C; IR 1660, 1250, 1165, 840 cm^{-1}; ^1H NMR δ 0.37 (s, 9H), 1.51 (d, 3H, J = 9 Hz), 4.45 (q, 1H, J = 9 Hz), 7.19 (dd, 1H, J = 10, 2 Hz), 7.37 (dd, 1H, J = 10, 2 Hz), 7.87 (d, 1H J = 2 Hz); MS m/z (rel intensity) 320, 322 (M^+, 80, 33), 75 (26), 73 (100). Anal. Calcd for $C_{16}H_{17}ClO_3Si$: C, 63.03; H, 5.62. Found: C, 62.89; H, 5.48.

9-Chloro-2-phenyl-5-methyl-5*H*-benzo[*b*]furo[2,3-*d*]oxepin-4-one (9f): yield 52%; mp 160 °C; IR 1665, 1250, 1160, 710 cm^{-1}; ^1H NMR δ 1.53 (d, 3H, J = 9 Hz), 4.50 (q, 1H, J = 9 Hz), 7.05–7.43 (m, 5H), 7.69 (m, 2H), 7.88 (s, 1H); MS m/z (rel intensity) 326, 324 (M^+, 29, 69), 309 (15), 289 (11), 281 (23), 189 (15), 105 (100), 77 (53). Anal. Calcd for $C_{19}H_{13}O_3Cl$: C, 70.27; H, 4.03. Found: C, 70.48; H, 4.20.

Desilylation of Compounds 9a and 9e. Compound **9a** (30 mg) was dissolved in CH_2Cl_2 (10 mL), and CF_3COOH (1 mL) was added. After 2 h at rt, the solution was concentrated and filtered through silica gel to afford 20 mg (90%) of **5-methyl-5*H*-benzo-[*b*]furo[2,3-*d*]oxepin-4-one (11a)**: mp 56–58 °C (from CH_2Cl_2–hexane); IR 1660, 1250, 730 cm^{-1}; ^1H NMR δ 1.51 (d, 3H, J = 9 Hz), 4.46 (q, 1H, J = 9 Hz), 6.92 (d, 1H, J = 3 Hz), 7.13–7.24 (m, 3H), 7.44 (d, 1H, J = 3 Hz), 7.91 (m, 1H); MS m/z (rel intensity) 214 (M^+, 45), 149 (100). Anal. Calcd for $C_{13}H_{10}O_3$: C, 72.89; H, 4.70. Found: C, 72.85; H, 4.82.

In the same way, **9-chloro-5-methyl-5*H*-benzo[*b*]furo[2,3-*d*]-oxepin-4-one (11b)** was obtained in 92% yield: mp 59–62 °C (from CH_2Cl_2–hexane); IR 1665, 1260, 730 cm^{-1}; ^1H NMR δ 1.51 (d, 3H, J = 9 hz), 4.46 (q, 1H, J = 9 Hz), 6.94 (d, 1H, J = 3 Hz), 7.22–7.45 (m, 3H), 7.87 (m, 1H); MS m/z (rel intensity) 248, 250 (M^+, 25, 7), 213 (10), 205 (15), 149 (100), 121 (23), 77 (30). Anal. Calcd for $C_{13}H_9ClO_3$: C, 62.79; H, 3.65. Found: C, 62.77; H, 3.75.

Reaction of Ylide 2a with Internal Alkynes. The reaction was conducted under the same conditions reported above. From the reaction with 2-butyne, a 4:1 mixture of the two regioisomers, **2,3,5-trimethyl-5*H*-benzo[*b*]furo[2,3-*d*]oxepin-4-one (12a)** and **2,3,10-trimethyl-10*H*-benzo[*b*]furo[3,4-*e*]oxepin-4-one (13a)** was isolated, yield 54%. Upon recrystallization from hexane–CH_2Cl_2, pure **12a** was obtained: mp 70–71 °C; IR 1660, 1590, 1250, 710 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.47 (d, 3H, J = 9 Hz), 2.22 (s, 3H), 2.30 (s, 3H), 4.40 (q, 1H, J = 9 Hz), 7.07–7.32 (m, 3H), 7.84 (dd, 1H); MS m/z (rel intensity) 242 (M^+, 100), 227 (12), 199 (79), 171 (80), 128 (19), 115 (16). Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 74.44; H, 5.99.

Regioisomer **13a** had ν_{CO} at 1710 cm^{-1}. The ^1H NMR signals [δ 1.63 (d, 3H, J = 9 Hz), 2.20 (s, 3H), 2.26 (s, 3H), 5.15 (q, 1H, J = 9 Hz), and 8.06 (m, 1H)] were deduced by comparison of the spectra of the **12a** and that of the mixture **12a** and **13a**.

From the reaction of ylide **2a** with bis(trimethylsilyl)acetylene a 1:1 mixture of the two isomers, **2,3-bis(trimethylsilyl)-5-methyl-5*H*-benzo[*b*]furo[2,3-*d*]oxepin-4-one (12b)** and **2,3-bis(trimethylsilyl)-10-methyl-10*H*-benzo[*b*]furo[3,4-*e*]oxepin-4-one (13b)**, was isolated in 44% yield. The mixture was chromatographed again carefully, and pure **12b** was obtained as an oil: ^1H NMR δ 0.39 (s, 9H), 0.49 (s, 9H), 1.52 (d, 3H, J = 9 Hz), 4.66 (q, 1H, J = 9 Hz), 7.13–7.52 (m, 3H), 7.92 (m, 1H); MS m/z (rel intensity) 358 (M^+, 18), 343 (71), 315 (14), 221 (11), 193 (19), 73 (100). Anal. Calcd for $C_{19}H_{25}O_3Si_2$: C, 63.68; H, 7.26. Found: C, 63.38; H, 7.08.

The other isomer **13b** had: ^1H NMR δ 0.37 (s, 9H), 0.48 (s, 9H), 1.73 (d, 3H, J = 9 Hz), 5.26 (q, 1H, J = 9 Hz), 8.13 (m, 1H).

(18) Cavill, G. K.; Dean, F. M.; McGookin, A.; Marshall, B. M.; Robertson, A. *J. Chem. Soc.* **1954**, 4573.

(19) Popic, V. V.; Korneev, S. M.; Nikolaev, V. A.; Korobitsyna, I. K. *Synthesis* **1991**, 195.

Reaction of Ylide 2 with Nitriles. To a solution of ylide **2** (1mmol) in CH_2Cl_2 (5–10 mL, degassed with N_2) were added the nitrile (5–6 mmol) and a catalytic amount (2–3 mg) of $Cu(acac)_2$. The reaction was completed after 24 h at rt or after 30 min at reflux. Methanol 5–10% was added to CH_2Cl_2 in order to elute oxazoles **18** from the column (silica gel). Oxazoles **18** were recrystallized from hexane–CH_2Cl_2.

2,4-Dimethyl-4*H*-benz[2,3]oxepino[5,6-*d*]oxazol-10-one (18a): yield 60%; mp 162–164 °C; IR 1640, 1590, 1170, 770 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.70 (d, 3H, J = 9 Hz), 2.51 (s, 3H), 5.31 (q, 1H, J = 9 Hz), 7.15 (d, 1H, J = 4 Hz), 7.25 (m, 1H), 7.50 (m, 1H), 8.10 (d, 1H, J = 4 Hz); MS m/z (rel intensity) 229 (M^+, 85), 187 (100), 172 (32), 121 (90), 104 (31), 77 (20). Anal. Calcd for $C_{13}H_{11}NO_3$: C, 68.11; H, 4.84; N, 6.11. Found: C, 68.38; H, 4.98; N, 6.31.

2-Phenyl-4-methyl-4*H*-benz[2,3]oxepino[5,6-*d*]oxazol-10-one (18b): yield 53%; mp 102–105 °C; IR 1670, 1590, 730 cm^{-1}; ^1H NMR δ 1.79 (d, 3H, J = 10 Hz), 5.43 (q, 1H, J = 10 Hz), 7.20–7.50 (m, 6H), 8.02–8.21 (m, 3H); MS m/z (rel intensity) 291 (M^+, 10), 176 (95), 147 (31), 121 (100), 105 (77), 77 (65). Anal. Calcd for $C_{18}H_{13}NO_3$: C, 74.29; H, 4.49; N, 4.81. Found: C, 74.14; H, 4.32; N, 4.59.

2-*tert*-Butyl-4-methyl-4*H*-benz[2,3]oxepino[5,6-*d*]oxazol-10-one (18c): yield 49%; oil; IR 1650, 1590, 760 cm^{-1}; ^1H NMR δ 1.41 (s, 9H), 1.77 (d, 3H, J = 9 Hz), 5.45 (q, 1H, J = 9 Hz), 7.01–7.54 (m, 3H), 8.07 (dd, 1H); MS m/z (rel intensity) 271 (M^+, 32), 256 (8), 227 (8), 188 (29), 121 (33), 76 (14), 57 (100). Anal. Calcd for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.31; N, 5.17. Found: C, 71.04; H, 6.12; N, 5.14.

8-Chloro-2,4-dimethyl-4*H*-benz[2,3]oxepino[5,6-*d*]oxazol-10-one (18d): yield 54%; mp 145 °C; IR 1660, 1610, 1590, 1250, 1170 cm^{-1}; ^1H NMR δ 1.76 (d, 3H, J = 8 Hz), 2.41 (s, 3H), 5.34 (q, 1H, J = 8 Hz), 7.10 (d, 1H, J = 1 Hz), 7.45 (d, 1H, J = 1 Hz), 8.12 (s, 1H); MS m/z (rel intensity) 265, 263 (M^+, 26, 70), 223 (37), 221 (100), 157 (31), 76 (24), 43 (88). Anal. Calcd for $C_{13}H_{10}ClNO_3$: C, 59.21; H, 3.82; N, 5.31. Found: C, 59.15; H, 3.71; N, 5.36.