254 (40); 179 (25); 178 (35); 164 (45). Anal. Calcd for $C_{19}H_{23}NO_2$: C, 76.76; H, 7.74; N, 4.71. Found: C, 76.71; H, 7.73; N, 4.70. Hydrochloride mp 204-205 °C.

2-Methyl-1-phthalidyl-1,2,3,4-tetrahydroisoquinoline (15a). Reaction of **1b** with iminium compound **8a** by procedure A afforded *threo*-**15a** (14%), mp 130-131 °C (lit.[15] mp 132-133 °C), and *erythro*-**15a** (43%), mp 100-101 °C (lit.[15] mp 100-102 °C). ^{1}H NMR of both isomers corresponded with literature data.[15] These could also be secured through reaction of 3-silylphthalide **17a** with **8a**.

6,7-Dimethoxy-2-methyl-1-phthalidyl-1,2,3,4-tetrahydroisoquinoline (15b). Reaction of **1b** with iminium compound **8b** by procedure A afforded *threo*-**15b** (12%), mp 156-157 °C (lit.[17] mp 159 °C), and *erythro*-**15b** as an oil (40%). ^{1}H NMR of both isomers corresponded with literature values.[17] These could also be secured through reaction of 3-silylphthalide **17a** with **8b**.

3-(Trimethylsilyl)phthalide (17a). Into a flame-dried 100-mL two-necked round-bottom flask equipped with a stir bar and a septum cap was introduced THF (10 mL) and diisopropylamine (0.84 mL, 6 mmol). It was cooled to -78 °C, and a 2.8 M solution of BuLi in hexane (2.14 mL, 6 mmol) was added via a syringe. After 15 min, a solution of phthalide **16a**[30] (0.536 g, 4 mmol) in THF (5 mL) was added. The resulting orange-red solution was further stirred for 30 min at -78 °C and the reaction quenched with trimethylsilyl chloride (0.76 mL, 6 mmol). The reaction mixture was gradually allowed to come to room temperature, poured into water (30 mL), and extracted with ether (100 mL × 3). The combined organic extract was washed with water and dried. The solvent was removed under reduced pressure to afford the silylphthalide **17a** as a yellow oil, giving a single spot on TLC (0.772 g, 93.6%). ^{1}H NMR (CCl_4): δ 0.00 (s, 9 H, $SiMe_3$), 5.15 (s, 1 H, ArCH); 7.28-7.85 (m, 4 H, ArH). Its attempted chromatographic purification led to decomposition.

3-(Trimethylsilyl)-6,7-dimethoxyphthalide (17b). Reaction of 6,7-dimethoxyphthalide (**16b**,[31] 0.194 g, 1 mmol) with LDA (1.5 mmol) in THF (10 mL) followed by addition of trimethylsilyl chloride (0.19 mL, 1.5 mmol), as in the previous text, afforded **17b** as a light yellow solid (0.256 g, 96%), mp 110-112 °C. ^{1}H NMR ($CDCl_3$): δ 0.00 (s, 9 H, $SiMe_3$); 3.82 (s, 3 H, OMe); 4.04 (s, 3 H, OMe); 5.1 (s, 1 H, ArCH); 6.90 (d, 1 H, J = 9 Hz, ArH); 7.26 (d, 1 H, J = 9 Hz, ArH).

General Procedure for Reaction of Silylphthalides 17 with Dihydroisoquinoline Methiodides 8. These reactions were carried out according to procedure A using 2 equiv of CsF and stirring at room temperature for 15 h.

(±)-Cordrastine (15c). The alkaloid **15c** was obtained in 76% yield by reaction of the phthalide **17b** (266 mg) with isoquinolinium salt **8b** (400 mg).

***threo*-15c**: 184 mg, 46%, mp 155-156 °C (lit.[15] mp 156-157 °C). R_f: 0.66 (silica gel, benzene:methanol = 9:1). ^{1}H NMR ($CDCl_3$): δ 2.53 (m, 4 H, C_3 and C_4 H's); 2.7 (s, 3 H, NMe); 3.78, 3.85, 3.95 (3 s, 12 H, 4×OMe); 4.15 (d, 1 H, J = 3.2 Hz, C_1H); 5.68 (d, 1 H, J = 3.2 Hz, C_9H); 6.46 (s, 1 H, ArH); 6.81 (s, 1 H, ArH); 7.14 (d, 1 H, J = 8 Hz, ArH); 7.41 (d, 1 H, J = 8 Hz, ArH).

***erythro*-15c**: 120 mg, 30%, mp 107-108 °C (lit.[15] mp 110-114 °C) R_f: 0.55 (silica gel, benzene:methanol = 9:1). ^{1}H NMR ($CDCl_3$): δ 2.3-3.2 (m, 4 H, C_3 and C_4 H's); 2.63 (s, 3 H, NMe); 3.74 (s, 3 H, OMe); 3.96 (s, 3 H, OMe); 3.98 (s, 3 H, OMe); 4.12 (s, 3 H, OMe); 4.14 (d, 1 H, J = 3.3 Hz, C_1H); 5.69 (d, 1 H, J = 3.3 Hz, C_9H); 6.47 (s, 1 H, ArH); 6.7 (d, 1 H, J = 8 Hz, ArH); 6.73 (s, 1 H, ArH); 7.28 (d, 1 H, J = 8 Hz, ArH).

(±)-Hydrastine (15d). Reaction of the phthalide **17b** (266 mg) with isoquinolinium salt **8c**[14c] (381 mg) afforded the alkaloid **15d** in 74% yield.

***threo*-15d**: 158 mg, 41%, mp 149-151 °C (lit.[14c] mp 150-154 °C). R_f: 0.68 (silica gel, benzene:methanol = 9:1). ^{1}H NMR ($CDCl_3$): δ 2.35-3.3 (m, 4 H, C_3 and C_4 H's); 2.55 (s, 3 H, NMe); 3.95 (s, 3 H, OMe); 4.1 (s, 3 H, OMe); 4.15 (d, 1 H, J = 3 Hz, C_1H); 5.67 (d, 1 H, J = 3 Hz, C_9H); 5.92 (s, 2 H, OCH_2O); 6.48 (s, 1 H, ArH); 6.86 (s, 1 H, ArH); 7.23 (d, 1 H, J = 8 Hz, ArH); 7.41 (d, 1 H, J = 8 Hz, ArH).

***erythro*-15d**: 126 mg, 33%, mp 136-137 °C (lit.[14c] mp 136-140 °C). R_f: 0.49 (silica gel, benzene:methanol = 9:1). ^{1}H NMR ($CDCl_3$): δ 2.2-3.1 (m, 4 H, C_3 and C_4 H's); 2.55 (s, 3 H, NMe); 3.92 (s, 3 H, OMe); 4.1 (s, 3 H, OMe); 3.98 (d, 1 H, J = 3.6 Hz, C_1H); 5.52 (d, 1 H, J = 3.6 Hz, C_9H); 5.93 (s, 2 H, OCH_2O); 6.34 (s, 1 H, ArH); 6.6 (s and d overlapping, 2 H, ArH); 7.18 (d, 1 H, J = 8 Hz, ArH).

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Synthesis of Alkynyl(phenyl)iodonium Triflates and Their Reaction with Diethyl 2-Aminomalonate

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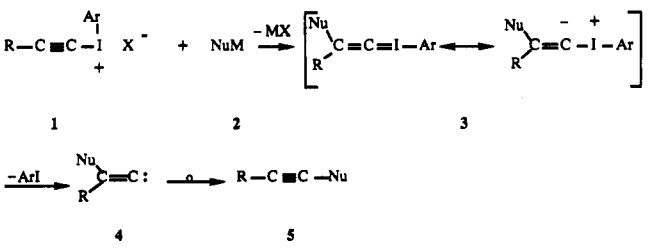
Alkynyl(phenyl)iodonium triflates **9** react with the Li (or K) salt of diethyl 2-[(diphenylmethylene)amino]malonate (**10**) (M = Li or K) to give the corresponding diethyl 2-alkynyl-2-[(diphenylmethylene)amino]malonate (**11**) in 30-95% yield.

The reaction between alkynyl(aryl)iodonium salts **1** and various nucleophiles has been the subject of numerous recent publications.[1,2] Of particular interest are reactions in which the aryliodonium functionality in **1** is formally substituted by the nucleophilic group Nu to give alkynes **5** (Scheme I).[2] It has been postulated[2b-e] that the mechanism of these reactions involves the addition of the nucleophile to the β-position of the polarized triple bond to give an alkylidenecarbene–iodonium ylide **3**. Elimination

Scheme I



of aryl iodide generates the free alkylidene carbene **4**, which rearranges to the alkyne **5**.[3] This course of events

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0022-3263/91/1956-3912$02.50/0

Scheme II

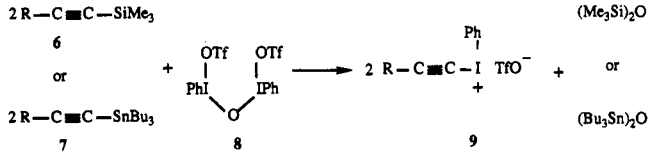


Table I. Reactions of Alkynyl(phenyl)iodonium Triflates 9 with M Salts of Enolate 10

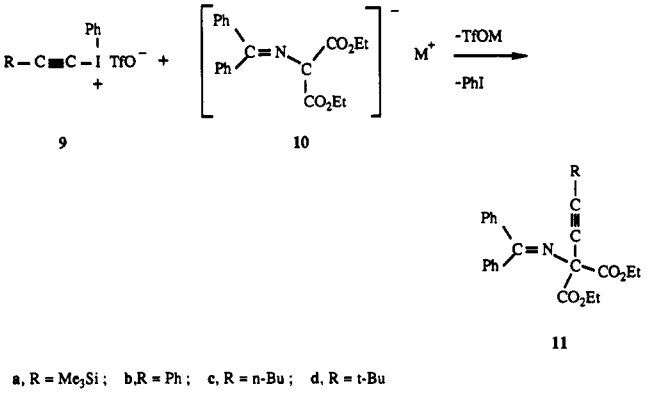
entry	iodonium triflate 9	R	M (addition mode)[a]	temp, °C	product 11	yield, %
1	a	Me_3Si	Li (a)	−78	a	95
2	a	Me_3Si	Li (b)	0	a	71
3	b	Ph	Li (a)	0	b	33
4	b	Ph	Li (b)	0	b	33
5	c	*n*-Bu	Li (a)	0	c	40
6	c	*n*-Bu	Li (b)	0	c	30
7	d	*t*-Bu	Li (a)	0	d	95
8	d	*t*-Bu	Li (b)	0	d	95
9	d	*t*-Bu	K (c)	0	d	58

[a] Addition mode: (a) Li enolate added to triflate; (b) triflate added to Li enolate; (c) triflate added to K enolate.

is highly dependent on the reaction conditions, on the alkyne's substituent R, and on the nature of the nucleophile. Indeed reactions engaging other sites of the alkynyl(aryl)iodonium salts 1,[1a,c] or that involve other transformations of the intermediate 3,[1d,e] or the cyclization of the carbene 4,[1d,2b] were observed. It seems that the reaction path shown in Scheme I prevails over the other aforementioned transformations when at least one of two requirements is fulfilled: (a) the group R in the starting materials 1 exhibits high migratory aptitute in 1,2-carbene rearrangements[4,5] as in the cases in which R = H,[2e] Ph,[2b] or Me_3Si;[2e] (b) heteroatom nucleophiles like $RCOO^-$, manifesting a similarly high migratory aptitude, were used.[2c,d] In order to assess the synthetic potential of this type of reaction, additional alkynyl(aryl)iodonium salts and nucleophilic reagents should be investigated. We now report on the employment of the Li (or K) enolate of diethyl 2-[(diphenylmethylene)amino]malonate (**10**, M = Li or K) as a carbon nucleophile which is efficiently alkynylated by the alkynyl(phenyl)iodonium triflates **9**.

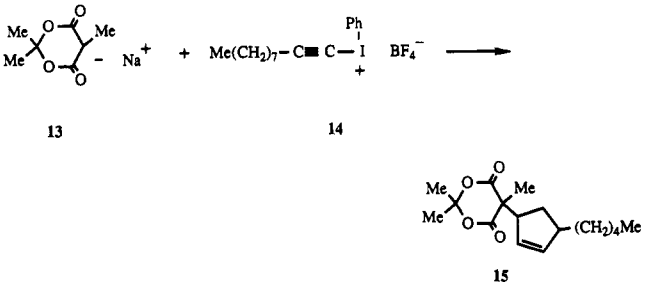
The alkynyl(phenyl)iodonium triflates **9** were obtained by interaction of the appropriate alkynyltrimethylsilane **6**, or alkynyltributylstannane **7**, with Zefirov's reagent **8**,[6] prepared[7] in situ from iodosobenzene and triflic anhydride

Scheme III



a, R = Me_3Si; b, R = Ph; c, R = n-Bu; d, R = t-Bu

Scheme IV



(Scheme II). This simple procedure was recently applied to the preparation of the parent ethynyl(phenyl)iodonium triflate **9** (R = H),[8] which could not be directly obtained by methods previously employed for the preparation of substituted alkynyl(phenyl)iodonium species.[9-11] Alkynyl(phenyl)iodonium triflates **9** are stable microcrystalline solids and are characterized by IR, multinuclear NMR, and analytical methods, as detailed in the Experimental Section. Diethyl 2-[(diphenylmethylene)amino]malonate was prepared by condensation of diethyl 2-aminomalonate hydrochloride and benzophenone imine.[12]

Treatment of the lithium enolate of diethyl 2-[(diphenylmethylene)amino]malonate (**10**, M = Li) with the alkynyl(phenyl)iodonium triflates **9** in THF at or below 0 °C afforded the corresponding diethyl 2-alkynyl-2-[(diphenylmethylene)amino]malonate **11** in 30–95% yield, as described in Scheme III and in Table I. These reactions probably followed the mechanism displayed in Scheme I. In the reactions described in entries 1–4 involving the alkynyl(phenyl)iodonium triflates **9a** or **9b**, the trimethylsilyl or the phenyl groups may be responsible for the 1,2-carbene rearrangement [**4** → **5**] as in Scheme I. However, in the reactions described in entries 5–9 involving the *n*-hexynyl(phenyl)iodonium triflate **9c** or the (3,3-dimethylbutynyl)(phenyl)iodonium triflate **9d** the migratory group in this rearrangement is most probably the diethyl 2-[(diphenylmethylene)amino]malonate anion. The most common mode of 1,2-rearrangement of carbenes seems to

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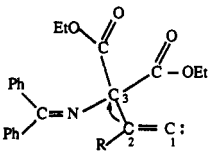
involve a migratory group which carries its electrons into the vacant orbital of a singlet state carbene.[4] High delocalization of the negative charge in the migrating diethyl 2-[(diphenylmethylene)amino]malonate anion should strongly facilitate its formation through the heterolysis of the C-2 to C-3 bond in the intermediate 12. The con-



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tribution of the (diphenylmethylene)amino group to the migratory aptitude is of primary importance. It was reported that sodium enolates of the similar 1,3-diesters 13, in which the (diphenylmethylene)amino group is substituted by a methyl group, were not alkynylated by decynyliodonium tetrafluoroborate 14, but the intermediate carbene 4 (R = n-C_8H_{17}, Nu = 13) underwent 1,5 carbon–hydrogen insertion, affording the cyclopentene 15.[2b] Similar reactions occurred with a series of other 1,3-dicarbonyl compounds[2b] but were not observed in the present study.

In summary, the reaction between alkynyl(phenyl)iodonium triflates 9 and the Li (or K) salt of diethyl 2-[(diphenylmethylene)amino]malonate (10, M = Li or K) constitutes a synthetically useful process for the preparation of α-alkynyl-α-amino carboxylic acid derivatives. Esters of 2-alkynyl-2-aminomalonic acids derived from N-deprotection of diphenylmethylenamines 11 have been conceived as starting materials in a planned synthesis of new bicyclic β-lactams.[13]

Experimental Section

Melting points were measured using a capillary melting point apparatus and are uncorrected. IR spectra were recorded on a Mattson Cygnus 25 FT-IR or a Mattson Polaris FT-IR spectrometer. NMR spectra were determined on a Varian FT-80A, a Bruker WH-270, or a Varian XL-300 spectrometer. High-resolution mass spectra were obtained on a Varian MAT-731 (double focusing) spectrometer. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl. All reactions were carried out under an atmosphere of argon, in dry glassware. Flash chromatography was carried out using Merck silica gel 60 (230–400 mesh).

[(Trimethylsilyl)ethynyl](phenyl)iodonium Triflate (9a). A mixture of iodosobenzene[14] (13.2 g, 60.0 mmol) and trifluoromethanesulfonic anhydride (5.05 mL, 30.0 mmol) in dichloromethane (60 mL) was stirred at 0 °C for 10 min (until the suspension became a clear, homogeneous yellow solution). To the resulting Zefirov reagent 8, bis(trimethylsilyl)acetylene (10.2 g, 60.0 mmol) in dichloromethane (60 mL) was added, and the solution was stirred at 0 °C for an additional 30 min.

Evaporation of the solvent under reduced pressure gave a yellow oil. Trituration of the oil in diethyl ether precipitated 23.8 g (88%) of **9a** as a white powder: mp 138–139 °C dec; IR (KBr) 3064, 2969, 2124 (C≡C), 1291, 1256, 1231, 1176, 1048, 1024, 987, 852, 763, 745, 713, 686, 655, 638 cm^{-1}; ^{1}H NMR (CD_3NO_2) δ 8.22 (d, 2 H), 7.81 (t, 1 H), 7.68 (t, 2 H), 0.25 (s, 9 H); ^{19}F NMR (CD_3NO_2) δ −76.0; ^{13}C NMR (CD_3NO_2) δ 136.1, 134.8, 134.0, 122 (q, J = 318 Hz), 121.2, 118.0 (β-C), 42.9 (α-C), −0.03. Anal. Calcd for $C_{12}H_{14}O_3SF_3SiI$: C, 32.01; H, 3.13; S, 7.12. Found: C, 31.92, H, 3.15; S, 7.03.

(Phenylethynyl)(phenyl)iodonium Triflate (9b). Phenyl(trimethylsilyl)acetylene (7.87 mL, 40.0 mmol) in dichloromethane (40 mL) was added to a stirred solution of iodosobenzene (8.80 g, 40.0 mmol) and trifluoromethanesulfonic anhydride (3.37 mL, 20.0 mmol) in dichloromethane (40 mL) at 0 °C. The reaction was complete in 30 min, and concentration of the solution followed by addition of diethyl ether precipitated the crude product. Recrystallization from chloroform–pentane (5:1) afforded 12.2 g (67%) of **9b** as a white microcrystalline solid: mp 83 °C dec; IR (KBr) 3047, 2121 (C≡C), 1289, 1282, 1274, 1263, 1255, 1179, 1034, 997, 990, 756, 732, 690, 650 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.12 (d, 2 H), 7.65 (t, 1 H), 7.55–7.35 (m, 7 H), ^{19}F NMR ($CDCl_3$) δ −78.3; ^{13}C NMR ($CDCl_3$) δ 134.0, 133.7, 133.0, 132.8, 131.9, 128.9, 120.0 (q, J = 319 Hz), 119.8, 117.6, 108.0 (β-C), 32.2 (α-C). Anal. Calcd for $C_{15}H_{10}O_3SF_3I$: C, 39.67; H, 2.22; S, 7.06. Found: C, 39.66; H, 2.23; S, 6.98.

1-Hexynyl(phenyl)iodonium Triflate (9c). 1-Hexynyltributylstannane (14.85 g, 40.0 mmol) in dichloromethane (40 mL) was added to a stirred solution of iodosobenzene (8.80 g, 40.0 mmol) and trifluoromethanesulfonic anhydride (3.37 mL, 20.0 mmol) in dichloromethane (40 mL) at 0 °C. The reaction was complete in 30 min. Removal of the solvent followed by washing with pentane precipitated the crude product. Recrystallization from dichloromethane–pentane (3:1) afforded 7.83 g (45%) of **9c** as off-white needles: mp 67–68 °C; IR (KBr) 3085, 2955, 2933, 2873, 2188 (C≡C), 1471, 1448, 1430, 1260, 1231, 1218, 1172, 1026, 987, 736, 676, 650, 636 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.05 (d, 2 H), 7.62 (t, 1 H), 7.48 (t, 2 H), 2.55 (t, 2 H), 1.56–1.42 (m, 2 H), 1.40–1.26 (m, 2 H), 0.86 (t, 3 H); ^{19}F NMR ($CDCl_3$) δ −78.4; ^{13}C NMR ($CDCl_3$) δ 133.8, 132.4, 132.2, 119.7 (q, J = 319 Hz), 116.1, 111.4 (β-C), 29.5, 21.7, 21.0 (α-C), 20.2, 13.2. Anal. Calcd for $C_{13}H_{14}O_3SF_3I$: C, 35.96; H, 3.25; S, 7.38. Found: C, 35.82; H, 3.68; S, 7.42.

(3,3-Dimethyl-1-butynyl)(phenyl)iodonium Triflate (9d). (3,3-Dimethyl-1-butynyl)trimethylsilane (6.17 g, 40.0 mmol) in dichloromethane (40 mL) was added to a stirred solution of iodosobenzene (8.80 g, 40.0 mmol) and trifluoromethanesulfonic anhydride (3.37 mL, 20.0 mmol) in dichloromethane (40 mL) at 0 °C. The reaction was complete in 30 min. Removal of the solvent followed by addition of diethyl ether precipitated 13.2 g (76%) of **9d** as a white powder: mp 130–131 °C dec (lit.[11b] mp 125–135 °C). The IR, ^{1}H NMR, ^{19}F NMR, and ^{13}C NMR spectral data agreed with literature data.[11b] Anal. Calcd for $C_{13}H_{14}O_3SF_3I$: C, 35.96; H, 3.25; S, 7.38. Found: C, 35.83; H, 3.22; S, 7.26.

Diethyl 2-[(Diphenylmethylene)amino]malonate. The title compound was prepared (92% yield) from diethyl aminomalonate hydrochloride and benzophenone imine by the method of O'Donnell and Polt:[12] mp 39 °C; ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.26 (6 H, t, J = 7.1 Hz, 2 CH_2CH_3), 4.22 (4 H, q, J = 7.1 Hz, 2 CH_2CH_3), 4.83 (1 H, s, NCH), 7.18–7.67 (m, PhH); IR (CH_2Cl_2) 1753, 1735 (C=O), 1624 (C=N) cm^{-1}; MS m/z M$^+$ 339.1558 (calcd for $C_{20}H_{21}NO_4$ 339.1465), 266.1203 (M$^+$ − CO_2Et). Anal. Calcd for $C_{20}H_{21}NO_4$: C, 70.76; H, 6.24; N, 4.13. Found: C, 70.77; H, 6.50; N, 4.09.

General Procedure for the Reaction of Alkynyl(phenyl)iodonium Triflates 9 with the Li (or K) Salt of Diethyl 2-[(Diphenylmethylene)amino]malonate (10) (M = Li or K).

A. To a stirred solution of diethyl 2-[(diphenylmethylene)amino]malonate (4.5 mmol) in THF (60 mL) at 0 °C was added n-BuLi (1 equiv, 1.4 M in hexane). After 20 min at 0 °C, the dark red reaction mixture was added dropwise (30 min) to a cold (−78 to 0 °C) stirred solution of an alkynyl(phenyl)iodonium triflate **9a–d** (4.5 mmol) in THF (20 mL). The reaction mixture, which turned light yellow, was allowed to warm to room temperature and evaporated. The residue was taken up in dichloromethane (60 mL), washed with water (20 mL), dried (Na_2SO_4), and evaporated. Chromatography (EtOAc/Hex, 1:4) of the residue afforded the corresponding diethyl 2-alkynyl-2-[(diphenylmethylene)amino]malonates **11a–d**.

B. n-BuLi (1 equiv, 1.4 M in hexane) was added to a stirred solution of diethyl 2-[(diphenylmethylene)amino]malonate (4.5 mmol) in THF (60 mL) at 0 °C. After 20 min at 0 °C, a solution of alkynyl(phenyl)iodonium triflates **9a–d** (4.5 mmol) in THF (20 mL) was added dropwise (30 min). The reaction mixture was allowed to warm to room temperature and worked up as described in procedure A.

C. The same as procedure B, but t-BuOK was used instead of n-BuLi.

(13) For general strategy see: Bachi, M. D. In *Recent Advances in the Chemistry of β-Lactam Antibiotics*; Bentley, P. H., Southgate, R., Eds.; The Royal Society of Chemistry: London, 1989; p 91.

(14) Saltzman, H.; Sharefkin, J. G. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, p 658.

Diethyl 2-[(diphenylmethylene)amino]-2-[(trimethylsilyl)ethynyl]malonate (11a): oil; IR (neat) 2170 (C≡C), 1756 (C=O), 1627 (C=N) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.10 (9 H, s, $Si(CH_3)_3$, 1.24 (6 H, t, J = 7.1 Hz, 2 CH_2CH_3), 4.15 and 4.16 (4 H, two q, J = 7.0 and 7.1 Hz, 2 OCH_2CH_3), 7.30–7.60 (m, C_6H_5); ^{13}C NMR (270 MHz, $CDCl_3$) δ 0.48 ($SiCH_3$), 13.7 (CH_2CH_3), 62.47 (OCH_2CH_3), 70.05, 93.50, and 98.87 (C≡C), 127.45, 127.88, 128.98, 129.14, 129.30 and 130.72 (C_6H_5), 136.14 and 140.41 (NC and Ph_2C), 166.82 and 172.65 (CO_2); MS ($M^+ - CO_2Et$) m/z 362.1498 (calcd for $C_{22}H_{24}NO_2Si$ 362.1570). Anal. Calcd for $C_{25}H_{29}NO_4Si$: C, 68.9; H, 6.72; N, 3.22. Found: C, 69.21; H, 6.78; N, 2.93.

Diethyl 2-[(diphenylmethylene)amino]-2-(phenylethynyl)malonate (11b): light yellow powder; mp 92 °C (from hexane); IR (film) 2236 (C≡C), 1750 (C=O), 1627 (C=N) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.29 (6 H, t, J = 7.1 Hz, 2 CH_2CH_3), 4.23 (4 H, q, J = 7.1 Hz, 2 OCH_2CH_3), 7.32–7.41 (m, C_6H_5); ^{13}C NMR (270 MHz, $CDCl_3$) δ 13.84 (CH_2CH_3), 62.66 (OCH_2CH_3), 83.97 and 88.19 (C≡C), 127.32, 127.64, 127.96, 128.49, 128.89, 128.97, 129.32, 130.80, and 131.84 (C_6H_5), 136.33 and 140.36 (NC and Ph_2C), 167.01 and 172.92 (CO_2); MS M^+ m/z 439.1744 (calcd for $C_{28}H_{25}NO_4$ 439.1777), ($M^+ - CO_2Et$) 366.1537 (calcd for $C_{25}H_{20}NO_2$ 366.1494). Anal. Calcd for $C_{28}H_{25}NO_4$: C, 76.50; H, 5.74; N, 3.19. Found: C, 76.48; H, 5.68; N, 3.26.

Diethyl 2-[(diphenylmethylene)amino]-2-*n*-hexynylmalonate (11c): oil; IR (neat) 2244 (C≡C), 1748 (C=O), 1629 (C≡N) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.86 (t, J = 6.9 Hz, CH_3), 1.25 (t, J = 7.1 Hz, 2 CH_2CH_3), 1.34 (m, 2 CH_2), 2.06 (t, J = 6.9 Hz, CH_2), 4.17 (q, J = 7.1 Hz, 2 OCH_2CH_3), 7.27–7.82 (m, C_6H_5); ^{13}C NMR (270 MHz, $CDCl_3$) δ 13.53 (CH_3), 13.84 (CH_3), 18.69 (CH_2), 21.83 (CH_2), 30.08 (C≡CCH_2), 62.45 (OCH_2CH_3), 76.57 and 89.61 (C≡C), 127.45, 127.90, 128.27, 128.87, 128.95, 129.33, 130.01, 130.64 and 132.35 (C_6H_5), 136.50 and 140.60 (NC and Ph_2C), 164.41 and 172.13 (CO_2). Anal. Calcd for $C_{28}H_{29}NO_4$: C, 74.43; H, 6.97; N, 3.34. Found: C, 74.15; H, 6.82; N, 3.27.

Diethyl 2-[(diphenylmethylene)amino]-2-(3,3-dimethyl-1-butynyl)malonate (11d): white powder; mp 77 °C (from hexane); IR (film) 2245 (C≡C), 1746 (C=O), 1629 (C=N) cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 1.11 (9 H, s, $C(CH_3)_3$), 1.23 (6 H, J = 7.2 Hz, 2 CH_2CH_3), 4.17 (4 H, br q, J = 7.2 Hz, 2 OCH_2CH_3), 7.35, 7.58 (10 H, m, C_6H_5); ^1H NMR (270 MHz, 325 K, CD_3Br) δ 1.52 (9 H, s, $C(CH_3)_3$), 1.69 and 1.70 (6 H, 2 t, J = 6.9 and 7.1 Hz, 2 CH_2CH_3), 4.56 and 4.57 (4 H, 2 q, J = 6.9 and 7.1 Hz, 2 OCH_2CH_3), 7.80–9.10 (m, C_6H_5); ^1H NMR (270 MHz, 383 K, CD_3Br) δ 1.51 (9 H, s, $C(CH_3)_3$), 1.68 (6 H, t, J = 7.1 Hz, 2 CH_2CH_3), 4.57 (4 H, q, J = 7.1 Hz, 2 CH_2CH_3), 7.80–9.10 (m, C_6H_5); ^{13}C NMR (270 MHz $CDCl_3$) δ 13.8 (CH_2CH_3), 27.5 ($C(CH_3)_3$), 30.3 ($C(CH_3)_3$), 62.28 (OCH_2CH_3), 73.8 and 96.6 (C≡C), 127.4, 127.5, 127.8, 128.0, 128.6, 128.9, 129.3 and 130.6 (C_6H_5), 136.5 and 140.7 (NC and Ph_2C), 167.5 and 172.2 (CO_2); MS ($M^+ - CO_2Et$) m/z 346.1773 (calcd for $C_{23}H_{24}NO_2$ 346.1801). Anal. Calcd for $C_{26}H_{29}NO_4$: C, 74.43; H, 6.97; N, 3.34. Found: C, 74.25; H, 6.84; N, 3.53.

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Supplementary Material Available: Carbon and proton NMR spectra of compound **11a** and **11c** (4 pages). Ordering information is given on any current masthead page.

Perhalodioxins and Perhalodihydrodioxins†

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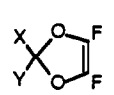
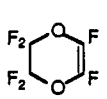
Two perhalo-1,4-dioxins, representatives of a previously unknown class of compounds, have been synthesized and shown to exhibit unusual reactivity. In particular, reaction with oxygen is spontaneous and exothermic, and radical-catalyzed homopolymerization will proceed through a fluorinated double bond. Representatives of the perhalo-2,3-dihydro-1,4-dioxin class have also been prepared and found to have reactivity in general intermediate to that of the perhalodioxoles and acyclic trifluorovinyl ethers. Computational studies of the two systems established that introduction of the first double bond raises the energy substantially, while the second double bond results in a near-planar ring with dramatically increased energy content.

Introduction

The effectiveness with which *F*-alkyl trifluorovinyl ethers copolymerize with monomers such as tetrafluoroethylene is well known,[1] but no reports have appeared describing radical-catalyzed homopolymerization of such trifluorovinyl ethers under commonly used pressures. In contrast, *F*-1,3-dioxoles **1** homopolymerize with extraordinary ease.[2] This difference in reactivity may reasonably be ascribed to minimization of steric constraints and/or to the presence of ring strain in the dioxoles **1**, raising the question of whether or not the related six-membered vinylene diethers **2** and **3** would exhibit similar high reactivity.



1, X,Y = F or CF_3



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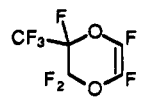
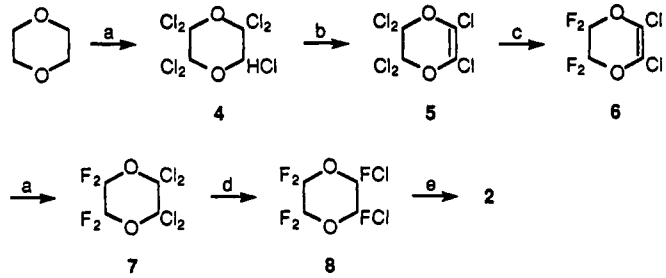


3

F-2,3-Dihydro-1,4-dioxin (**2**) has already been obtained by Coe, Dodman, and Tatlow[3] by dehydrofluorination of *F*-2*H*-1,4-dioxane, itself one of many products formed during partial fluorination of 1,4-dioxane. The low yields

Scheme I[a]



[a] (a) Cl_2; (b) $NaOH/CH_3OH$; (c) $SbF_3/SbCl_5$/100 °C; (d) $SbF_3/SbCl_5$/reflux; (e) Zn + DMF.

† Contribution No. 5649.

(1) Cf.: "*Fluorocarbon and Related Chemistry*;" Banks, R. E., Barlow, M. G., Eds.; The Chemical Society: London, 1976; Vol. 3, pp 280–281.
(2) (a) Polymer Preprints, Vol. 31, No. 1, April 1990, presented at the 199th National ACS Meeting, Boston, MA, by P. R. Resnick. (b) Resnick, P. R. U.S. Patent 3,978,030 (1976). (c) Squire, E. N. U.S. Patent 4,399,264 (1983).

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