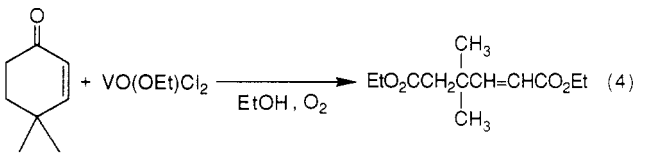
a 4-proton, was not aromatized under the same conditions. The reaction under oxygen gave the ring-opened oxygenation product diethyl 4,4-dimethyl-2-hexene-1,6-dioate (**5m**), resulting from bond cleavage between C_1 and C_6 (eq 4).



1m 5m, 35% (4)

A one-electron-transfer mechanism seems to be operative in the oxovanadium-induced oxidations.[1] One plausible reaction course would involve the intermediacy of the dienolate followed by dehydrogenative elimination. $VO(OR)Cl_2$ can be considered to be a Lewis acid that induces further oxidative transformations of carbonyl compounds.

Experimental Section

IR spectra were measured with a Hitachi 270-30 spectrometer. ^1H NMR spectra were measured on JEOL JNM-FX90Q or JNM-GSX270 spectrometers. Mass spectra were determined by the electron impact method on a JEOL JMS-DX303 (Faculty of Engineering, Osaka University).

$VO(OR)Cl_2$ was prepared by dropwise addition of an alcohol to an equimolar amount of commercially available $VOCl_3$ in hexane while bubbling nitrogen into the reaction mixture at room temperature and was distilled under the reduced pressure (e.g., bp $VO(OEt)Cl_2$, 52–54 °C/2 mmHg; $VO(OPr\text{-}i)Cl_2$, 68–70 °C/4 mmHg). $VO(OEt)_3$ was obtained from Shinko Chemical Co., Ltd.

Representative Procedure for $VO(OR)Cl_2$-Induced Aromatization Reactions. A mixture of 2-cyclohexen-1-one (**1a**, 0.192 g, 2.0 mmol) in ethanol (2 mL) was treated with $VO(OEt)Cl_2$ (0.732 g, 4.0 mmol) under oxygen. The resulting solution was refluxed for 0.5 h. Small amounts of concentrated HCl and saturated aqueous NaCl were added to the mixture, which was extracted with ether (3 × 40 mL). The combined organic layers were washed with water, dried over Na_2SO_4, and concentrated. The residue was an almost pure product **2a** by ^1H NMR, which was purified by silica gel column chromatography if required.

The other reactions were carried out in the same manner, and the conditions are shown in Scheme I, eq 2 and 3, and Table I. Yields were determined by GLC (10% PEG 20M 2.1-m column, 180 °C) based on **1**. The products **2** were identified by comparison of spectral data with those of authentic compounds reported or prepared by alkylation of the corresponding phenols.[5]

Oxidative Ring-Opening of 4,4-Dimethyl-2-cyclohexen-1-one (1m). The ketone **1m** (0.248 g, 2.0 mmol) was treated with $VO(OEt)Cl_2$ (1.098 g, 6.0 mmol) in ethanol (2 mL) under oxygen at 80 °C for 2 h. Workup was carried out as above. GLC analysis showed that **5m** was produced in 35% yield. **5m**: IR (neat) 2980, 1732, 1642, 1422, 1182, 1034, 964, 940, 828 cm^{-1}; ^1H NMR ($CDCl_3$ with TMS, 90 MHz) δ 1.24 (t, 3 H, J = 6.9 Hz), 1.29 (s, 6 H), 1.30 (t, 3 H, J = 6.9 Hz), 2.73 (s, 2 H), 4.10 (q, 2 H, J = 6.9 Hz), 4.17 (q, 2 H, J = 6.9 Hz), 5.71 (d, 1 H, J = 13.3 Hz), 6.18 (d, 1 H, J = 13.3 Hz); MS, m/z 228 (M^+).

Acknowledgment. This study was partly supported by a Grant-in-Aid for Special Project Research from the Ministry of Education, Science and Culture, Japan.

Registry No. **1a**, 930-68-7; **1f**, 1193-18-6; **1g**, 1123-09-7; **1h**, 99-49-0; **1i**, 5323-87-5; **1l**, 78-59-1; **1m**, 1073-13-8; **2a**, 103-73-1; **2b**, 100-66-3; **2c**, 2741-16-4; **2d**, 2206-38-4; **2e**, 1746-13-0; **2f**, 621-32-9; **2g**, 18102-49-3; **2h**, 123507-46-0; **2i**, 2049-73-2; **2j**, 79128-08-8; **2k**, 123507-48-2; **2l**, 123507-47-1; **3a**, 13619-73-3; **4**, 504-02-9; **5m**, 123507-45-9; $VO(OEt)Cl_2$, 1801-77-0; $VO(OEt)_3$, 1686-22-2; $VO(CH_3CO\text{-}CHCOCH_3)_2$, 3153-26-2; $VO(OSiPh)_3$, 18822-50-9; $VO(OPr\text{-}i)Cl_2$, 1636-01-7; $VO(OPr\text{-}i)_2$, 119254-23-8; cyclohexanol, 108-93-0; 2-propen-1-ol, 107-18-6.

Supplementary Material Available: Listing of spectral data (IR, ^1H NMR, and MS) of the products reported (2 pages). Ordering information is given on any current masthead page.

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Chemistry of Oxaziridines. 12.[1] Oxidation of Alkylidenetriphenylphosphoranes with *N*-Sulfonyloxaziridines

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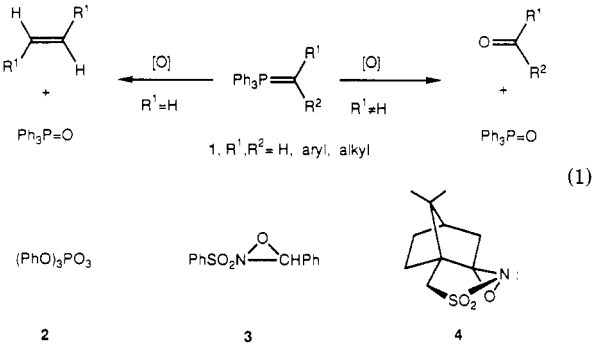
The oxidation of alkylidenephosphoranes (ylides) to alkenes and ketones has been explored by Bestmann and co-workers.[2] Ylides of type **1** (R^1 = H) gave alkenes while



(1)

bis(ylides) afforded cycloalkenes. Two molecules of vitamin A were oxidized to β-carotene by using this methodology.[3] Ketones are formed on oxidation of **1** ($R^1 \neq H$) making possible the synthesis of acylsilanes from silyl ylides (R^1 = aryl, R^2 = $SiMe_3$).[2b,4] Triphenyl phosphite–ozone (**2**) was generally used in these oxidations because of its aprotic nature. Although this reagent is readily prepared by treatment of triphenyl phosphite with O_3 at −78 °C, it is inconvenient to use because above −35 °C it decomposes to $^1O_2$ and triphenyl phosphate.[5] Symmetrical carotenoids have been prepared by oxidation of resonance-stabilized ylides using 50% hydrogen peroxide.[6] More recently Wassmerman and co-workers reported useful methodology for the preparation 1,2,3-tricarbonyl compounds via oxidation of phosphorane keto ylide carboxylates with ozone or singlet oxygen.[7]

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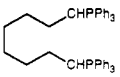
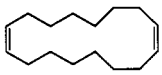
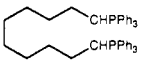
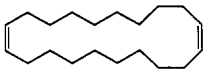
Table I. Oxidation of Alkylidenetriphenylphosphoranes 1 with *N*-Sulfonyloxaziridines 3 and 4 at 25 °C

entry	$Ph_3P=CR^1R^2$ R^1	R^2	conditions oxaziridine (equiv) solvt	product	% yield[a] (E/Z ratio)[b] [% yield][c]
1	MeO_2C	H	3 (1.1) $CHCl_3$	$MeCO_2CH=CHCO_2Me$	99 (91/9) [83]
2			4 (1.1) $CHCl_3$		93 (96/4)
3	PhCO	H	3 (1.1) CH_2Cl_2	PhC(O)CH=CH(O)CPh	97 (100/0)[d] [62]
4			4 (1.1) CH_2Cl_2		98 (100/0)[d]
5	MeCO	H	3 (1.1) CH_2Cl_2	MeC(O)CH=CH(O)Me	90 (100/0) [87]
6			4 (1.1) CH_2Cl_2		99 (95/5)
7	Ph	H	3 (1.1) THF	PhCH=CHPh	88 (77/23) [89]
8			3 (1.1) THF −78 to 25 °C		96 (37/63)
9			3 (1.1) PhMe		73 (96/4)
10			3 (1.1) PhMe −78 to 25 °C		78 (95/5)
11			4 (1.1) THF		95 (46/34)
12			4 (1.1) PhMe		85 (83/17)
13			4 (1.1) PhMe −78 to 25 °C		89 (91/9)
14			4 (2.0) PhMe −78 to 25 °C		86 (91/9)
15	$CH_3(CH_2)_{10}$	H	4 (1.1) THF	$CH_3(CH_2)_{10}CH=CH(CH_2)_{10}CH_3$	63 (100/0) [61]
16			4 (1.1) PhMe		84 (100/0)
17			4 (2.0) THF		23 (25:75)[e] [12]
18			4 (2.5) THF		31 (25:75)[e]
19			4 (2.5) THF		43 [14]
20	PhCO	Ph	3 (2.0) CH_2Cl_2	PhC(O)(O)CPh	76 [62]
21			4 (2.0) CH_2Cl_2		71
22	EtO_2C	Me	3 (2.0) $CHCl_3$	$EtCO_2CC(O)Me$	100[f]
23			4 (2.0) $CHCl_3$		100[f]
24			4 (1.0) $CHCl_3$	$EtCO_2CC(O)Me$	(50)[f]
				$EtO_2C(Me)=C(Me)CO_2Et$	(50)[f]

[a] Isolated yields unless otherwise noted. Yields calculated based on the alkene and/or ketone. [b] Determined by NMR. [c] Yields reported by Bestmann et al.; see ref 2. [d] Determined by GLC. [e] GLC indicates a 25:75 mixture of alkenes. [f] Yields determined by proton NMR,

N-Sulfonyloxaziridines, such as **3** and **4**, developed in our laboratories, are useful aprotic oxidizing reagents for the hydroxylation of lithium and Grignard reagents to alcohols and phenols[8] and for the oxidation of enolates to α-hydroxy carbonyl compounds.[9,10] Not only are these reagents readily prepared[1,11] and storable, but (camphorylsulfonyl)oxaziridine (**4**) is now commercially available.[12] In connection with our interest in developing new applications of *N*-sulfonyloxaziridines for organic synthesis, we investigated the oxidation of alkylidenephosphoranes **1**. These studies show that **3** and **4** are the reagents of choice for the oxidation of **1**, not only being more convenient to use but also affording higher yields than **2** (Table I).

Ylides of type **1** (R^1 = H) were typically (1.0 mmol) oxidized to alkenes by addition of a slight excess (1.1 equiv) of **3** or **4** to the ylide at −78 or 25 °C. On addition of the oxidant, the solution became colorless, indicating that oxidation was immediate, which was also confirmed by TLC. Oxidation of the bis(ylides) to the cycloalkenes and **1** ($R^1 \neq$ H) to ketones required 2 equiv of **4**. The alkenes and ketones were isolated by preparative TLC and identified by comparison of their spectral properties with authentic samples or with values reported in the literature. The two cycloalkenes (entries 17–19), isolated as oils, exhibited M^+ ions at 220 and 276, respectively. Capillary gas chromatography of 1,9-cyclohexadecadiene (entries 17 and 18) indicated the presence of two isomeric dienes (75:25) of unknown cis, trans composition, while 1,11-cycloeicosadiene (entry 19) was obtained as a single isomer.

Although only 0.5 equiv of **3** or **4** is required to oxidize the ylides to the alkenes, excess oxidant is used to oxidize the triphenylphosphine byproduct to triphenylphosphine oxide. Product isolation proved to be more difficult when triphenylphosphine was present.

In general yields of alkenes, ketones, and diketones using **3** or **4** are better than previously reported by using **2**. This is particularly true for the oxidation of the bis(ylides) to the cycloalkenes (entries 17–19). Although *N*-sulfonyloxaziridines **3** and **4** gave similar yields in these oxidations (Table I), (camphorylsulfonyl)oxaziridine (**4**) was more convenient to use because isolation of the products was easier. On silica gel the sulfonimine reduction product corresponding to **3**, i.e., $PhSO_2N{=}CHPh$, decomposes to benzaldehyde and benzenesulfonamide, complicating workup.[11] Under similar conditions sulfonimine **5** is stable and can be isolated in 85–90% yield.

In 1983 Bestmann et al., reported; a useful two-step procedure for the synthesis of unsymmetrical 1,2-diketones.[13] Phosphorus ylides were reacted with an acid chloride followed by oxidation of the isolated acyl ylide **6** with **2**. Overall yields for the two-step procedure were modest. Using **4**, we have developed a simple "one-pot" variation of this procedure (eq 2). Triphenylethylphosphonium bromide was treated with an equivalent of sodium bis(trimethylsilyl)amide (NHMDS) followed ad-

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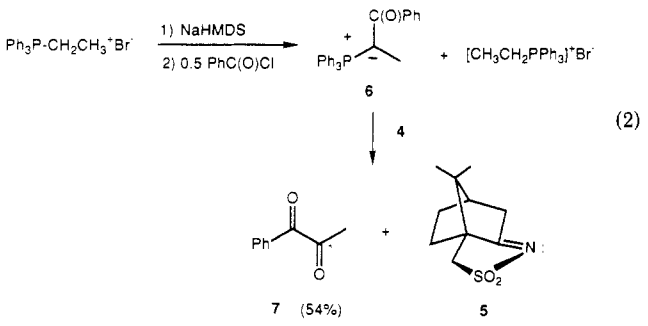
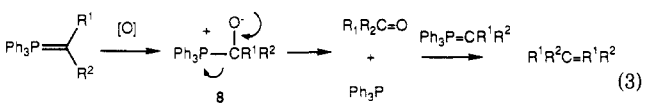


(2)

dition of 0.5 equiv of benzoyl chloride. After 4 h the intermediate benzoyl ylide **6** was oxidized by addition of **4**, affording 1-phenyl-1,2-propanedione (**7**) in 54% isolated yield.

As previously discussed by Bestmann, the formation of alkenes on oxidation of **1** presumably involves initial oxidation of the ylide to give **8**, which rearranges to the aldehyde and triphenylphosphine.[2b] The ylide then reacts with the aldehyde to give the alkene. This requires that the Wittig reaction be faster than oxidation of the ylide to **8** (eq 3). Although we were unable to detect aldehydes



(3)

in these oxidations, (carbethoxyethylidene)triphenylphosphorane with 1.1 equiv of **4** gave both the alkene and the α-keto ester (entry 24). Oxaphospetanes have been detected in oxidation of **1** by **2** by using ^{31}P NMR spectroscopy.[2b] Furthermore, the results summarized in the table are typical of the Wittig reaction.[14] For example, resonance-stabilized ylides **1** (R^1 = MeO_2C, PhC(O), entries 1–6) give predominantly the (*E*)-alkene and salt-free ylides afford higher proportions of the (*E*)-alkenes (compare entries 8 and 11 with 9 and 11).

In summary, oxidation of ylides to alkenes (cycloalkenes) and ketones using *N*-sulfonyloxaziridines **3** and **4** is a useful alternative to triphenyl phosphite–ozone (**2**), not only being more convenient to use but also resulting in higher yields.

Experimental Section

Melting points were determined on a Mel-Temp apparatus and are uncorrected. ^1H and ^{13}C-NMR spectra were obtained on a Bruker 250 (250 MHz) NMR spectrometer using Me_4Si as the internal reference. IR spectra were taken on a Perkin-Elmer 467 spectrometer. Gas–liquid partition chromatography (GLC) was performed on a Perkin-Elmer 8310 gas chromatographer using 3% OV-17 80/100 Supelcoport column and on a Varian 3700 gas chromatograph equipped with an FID and connected to a Varian CDS 111 Integrator using a Supelco SPB-20 wide-bore borosilicate glass column (30 M; 0.75-mm i.d.; 1-μm film thickness). GC/MS data were obtained on a Finnigan 4000 GC/MS instrument using a 6 ft × 1.4 in. 3% OV-17 column on 80/100 Supelcoport glass column. Preparative thin-layer chromatography was performed on a silica gel plate (GF 20 × 20 cm, 1000 μm). THF was distilled from sodium benzophenone under nitrogen, and toluene was distilled from CaH_2 under Ar prior to use.

Stable ylides methyl (triphenylphosphoranylidene)acetate, 1-triphenylphosphoranylidene-2-propanone, and (carbethoxyethylidene)triphenylphosphorane and phosphonium halides phenacyltriphenylphosphonium bromide, benzyltriphenylphosphonium chloride, and ethyltriphenylphosphonium bromide were purchased from Aldrich Chemical Co. α-Benzoylbenzylidenetriphenylphosphorane[15] and benzoylmethylenetriphenylphosphorane[16] were prepared according to literature procedures. Dodecyltriphenylphosphonium bromide was prepared by reaction of triphenylphosphine and neat *n*-dodecyl bromide as described by Ivashchenko et al.[17] The crude phosphonium bromide required repeated washing with anhydrous ethyl ether for solidification. The bis(triphenylphosphonium bromides) were prepared by heating the neat dibromides with triphenylphosphine as described in a patent.[18]

General Procedure for Oxidation of Stable Ylides. In a 25-mL single-necked round-bottom flask equipped with a magnetic stirring bar were placed 1.0 mmol of the stable ylide and 1.1 equiv of *N*-sulfonyloxaziridine **3** or **4**. To the solid reaction mixture was added 10 mL of methylene chloride or chloroform. After the reaction mixture stirred for 0.5 h, the solvent was removed on the rotatory evaporator, and the products isolated by preparative TLC eluting with ether–*n*-pentane. The products were identified by comparison of their IR and NMR spectra with authentic samples.[19]

General Procedure for Oxidation of Unstable Ylides. In a 25-mL two-necked round-bottom flask equipped with a magnetic stirring bar, argon inlet, and rubber septa was placed 1.0 mmol of benzyltriphenylphosphonium chloride or dodecyltriphenylphosphonium bromide in 10 mL of dry THF followed by addition of 0.4 mL of *n*-butyllithium (1.1 mmol). The resulting red solution was stirred for 0.5 h, at which time 1.1 mmol of oxaziridine **3** or **4** was added all at once at the specified temperature (Table I). After the reaction mixture stirred for 0.5 h at the indicated temperature, the reaction mixture was quenched by addition of 5 mL of saturated NH_4Cl solution followed by addition of 5 mL of water. The solution was transferred to a 125-mL separatory funnel, extracted with methylene chloride (3 × 10 mL), and dried over anhydrous $MgSO_4$. After removal of the solvent, the alkenes were isolated by preparative TLC.

12-Tetracosene[2a] had the following properties: oil; IR (neat) 3005, 2921, 2855, 1585, 1465 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, *J* = 3 Hz, 6 H), 1.26 (m, 36 H), 2.01 (m, 4 H), 5.34 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.21, 22.81, 27.31, 29.42, 29.69, 29.79, 29.89 (m), 32.04, 129.8.

Oxidation of Salt-Free Ylides. Benzylidene- and dodecylenetriphenylphosphorane were prepared as described above except that diethyl ether was used in the place of THF. After the red solution stirred for 0.5 h, the solvent was removed by using a stream of dry argon, and 5 mL of dry toluene was added. The toluene solution was transferred under argon pressure via a flex-needle assembly (12 gauge, 36 in.) to a 15-mL sintered glass funnel connected to a 25-mL two-necked round-bottom flask equipped with argon inlet and magnetic stirring bar. A second 5 mL of dry toluene was used to rinse the original reaction flask. The salt-free ylides in toluene were oxidized and the products isolated as described above.

Oxidation of Bis(ylides). In a 50-mL two-necked round-bottom flask equipped with a magnetic stirring bar, argon inlet, and rubber septa were placed 1.0 mmol of octamethylene-1,8-bis(triphenylphosphonium bromide) or decamethylene-1,10-bis(triphenylphosphonium bromide) and 20 mL of dry THF followed by addtion of 0.9 mL of *n*-butyllithium (2.2 mmol). The resulting red solution was stirred for 0.5 h, at which time the appropriate amount of **4** was added all at once (Table I). After the reaction mixture stirred for 0.5 h, it was quenched by addition of 10 mL of saturated NH_4Cl solution followed by addition of 10 mL of water. The solution was transferred to a 125-mL separatory funnel and extracted with methylene chloride (3 × 15 mL). After removal of the solvent, the alkenes were isolated by preparative TLC.

1,9-Cyclohexadecadiene[2a] had the following properties: oil; IR (neat) 3005, 2922, 2860, 1590, 1465 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.32 (m, 16 H), 2.05 (m, 8 H), 5.40 (m, 4 H); ^{13}C NMR ($CDCL_3$) δ 26.70,

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25.16, 29.25, 129.83; MS, *m/e* (rel intensity) 220 (M^+), 176 (1), 149 (12), 96 (18), 95 (24), 94 (21), 83 (10), 82 (25), 68 (27), 67 (53), 66 (8), 55 (42), 54 (32), 44 (17), 43 (13).

1,11-Cycloeicosadiene[2a] had the following properties: oil; IR (neat) 3005, 2925, 2895, 1590, 1465 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.28 (m, 20 H), 2.02 (m, 8 H), 5.38 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 26.81, 28.92, 29.07, 29.43, 129.77; MS, *m/e* (rel intensity) 276 (M^+), 135 (12), 122 (7), 121 (14), 110 (9), 109 (16), 108 (12), 107 (14), 96 (38), 95 (43), 94 (49) 93 (21), 83 (24), 82 (45), 81 (68), 80 (96), 79 (22), 69 (38), 68 (35), 67 (74), 55 (93), 54 (43), 53 (15).

Synthesis of 1-Phenyl-1,2-propanedione (7). In a 25-mL two-necked round-bottom flask equipped with a magnetic stirring bar, argon inlet, and rubber septa was placed 0.74 g (2.0 mmol) of ethyltriphenylphosphonium bromide in 20 mL of THF followed by addition of 2.2 mL (2.2 mmol) of sodium bis(trimethylsilyl)-amide via syringe. After the red solution stirred for 3 h, 1.2 mL (1.0 mmol) of benzoyl chloride was added, immediately discharging the color of the solution and producing a white precipitate. Stirring was continues for an additional 4 h, at which time 0.5 g (2.2 mmol) of oxaziridine **4** was added all at once. The reaction mixture was quenched after 0.5 h by addition of 10 mL of saturated NH_4Cl solution and 10 mL of water. The solution was transferred to a 125-mL separatory funnel, extracted with methylene chloride (3 × 10 m), and dried over anhydrous $MgSO_4$. After removal of solvent, the product was isolated by preparative TLC eluting with 20% ether–*n*-pentane to afford 0.8 g (54%) as a yellow oil identical in all respects with an authentic sample of 1-phenyl-1,2-propanedione (**7**).[19]

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Registry No. 1 (R^1 = MeO_2C, R^2 = H), 2605-67-6; 1 (R^1 = PhCO, R^2 = H), 859-65-4; 1 (R^1 = MeCO, R^2 = H), 1439-36-7; 1 (R^1 = Ph, R^2 = H), 16721-45-2; 1 (R^1 = $CH_3(CH_2)_{10}$, R^2 = H), 54208-04-7; 1 (R^1 = PhCO, R^2 = Me), 1450-07-3; 1 (R^1 = EtO_2C, R^2 = Me), 5717-37-3; **3**, 63160-13-4; **4**, 104322-63-6; **7**, 579-07-7; $Ph_3P{=}CH(CH_2)_6CH{=}PPh_3$, 38451-22-8; $Ph_3P{=}CH(CH_2)_8CH{=}PPh_3$, 38451-25-1; (*E*)-$MeO_2CCH{=}CHCO_2Me$, 624-49-7; (*Z*)-$MeO_2CCH{=}CHCO_2Me$, 624-48-6; (*E*)-PhCOCH=CHCOPh, 959-28-4; (*E*)-$CH_3COCH{=}CHCOCH_3$, 820-69-9; (*Z*)-$CH_3COCH{=}CHCOCH_3$, 17559-81-8; (*E*)-PhCH=CHPh, 103-30-0; (*Z*)-PhCH=CHPh, 645-49-8; (*E*)-$CH_3(CH_2)_{10}CH{=}CH(CH_2)_{10}CH_3$, 76665-54-8; $PhCOCOPh$, 134-81-6; EtO_2CCOCH_3, 617-35-6; (*E*)-$EtO_2CC(CH_3){=}C(CH_3)CO_2Et$, 1587-30-0; $Ph_3PEt^+Br^-$, 1530-32-1; PhCOCl, 98-88-4; $PhCH_2(Ph)_3P^+Cl^-$, 1100-88-5; $CH_3(CH_2)_{11}P(Ph)_3^+Cl^-$, 15510-55-1; (*E,E*)-1,9-cyclohexadecadiene, 7433-62-7; (*Z,Z*)-1,9-cyclohexadecadiene, 7431-74-5; (*E,E*)-1,11-cyclocosadiene, 6568-71-4; octamethylene-1,8-bis(triphenylphosphonium bromide), 23739-64-2; decamethylene-1,10-bis(triphenylphosphonium bromide), 917-20-4.

Improved Synthesis of Symmetrical and Unsymmetrical 5,11-Methanodibenzo[*b,f*][1,5]diazocines. Readily Available Nanoscale Structural Units[1]

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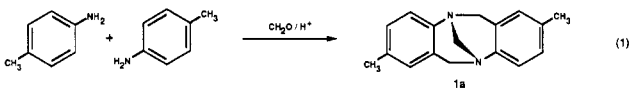
Enzymes and biogenic receptors are impressive examples of nanoscale devices. The development of nanoscale (10–500 Å) functional devices and the growth of a nanotechnological capability will require methods to prepare and characterize larger molecules or molecular aggregates than have heretofore been prepared.[3] A goal in our lab has been to develop general synthetic methods for preparing large and relatively rigid molecules of unambiguous shape.[4] These molecules are of interest as components of synthetic receptors and orderly functional group arrays.

Symmetrical 5,11-methanodibenzo[*b,f*][1,5]diazocines have been shown to be conveniently available chiral structural units for preparing such devices.[4b,f] We report here a process which makes available for the first time unsymmetrical 5,11-methanodibenzo[*b,f*][1,5]diazocines and illustrate the use of this new process by preparing some simple examples of such molecules.

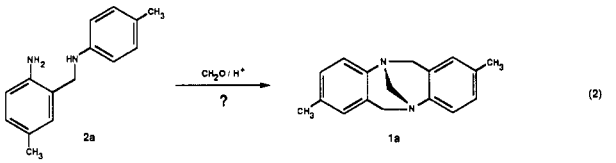
The preparation of 2,8-dimethyl-6*H*,12*H*-5,11-methanodibenzo[*b,f*][1,5]diazocine (**1a**, eq 1) was described by Tröger in 1887.[5] Since that time several additional



(1)

1a

examples of the reaction of aniline derivatives with formaldehyde have been reported.[4a-d,f,h-j,6] These reactions afford symmetrical, chiral dibenzodiazocines. Consideration of the possible mechanisms for formation of **1a** led to the hypothesis (eq 2) that (2-aminobenzyl)amine **2a** might, in the presence of formaldehyde and acid, afford a diazocine product.



(2)

2a 1a

To explore this idea, benzylamine **2a** was prepared (Scheme I) by two-step reduction (83%) of the 2-nitrobenzamide **3a** obtained through dicyclohexylcarbodiimide-mediated condensation (94%) of toluidine and 5-methyl-2-nitrobenzoic acid.[7,8] In the crucial test, treatment of diamine **2a** with formaldehyde and HCl afforded a 97% yield of Tröger's base, the symmetrical dibenzodiazocine **1a**.

The success of this simple experiment provides for the first time a way of preparing unsymmetrical 5,11-methanodibenzo[*b,f*][1,5]diazocines that bear *electron-withdrawing* substituents. Prior experiments had indicated that such molecules (not previously reported) are not available by the classical method described by Tröger.[4f,6] It was reasoned that the present method circumvents the need for electrophilic aromatic substitution at one of the

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