The resulting solution was stirred 20 min, and then a solution of chlorotrimethylsilane (5.82 g, 53.6 mmol) in THF (20 mL) was added dropwise. After being stirred an additional 20 min, the solution was warmed to room temperature and then distilled to afford 5.00 g (85%) of **5** as a pale yellow oil: bp 85 °C (0.25 mmHg); ^{1}H NMR (60 MHz, $CDCl_3$) δ 0.20 (9 H, s), 1.27 (6 H, t, J = 8 Hz), 2.75 (4 H, q, J = 8 Hz), 7.07 (3 H, m).

Pinacol [(2,6-Diethylphenyl)(trimethylsilyl)amino]-methaneboronate (6). BuLi in hexane (13.2 mL, 22.4 mmol) was added dropwise to an ice-water cooled, stirred solution of 2,6-diethyl-*N*-(trimethylsilyl)aniline (**5**, 4.98 g, 22.6 mmol) in THF (20 mL), maintaining an internal reaction temperature <5 °C. The resulting reaction mixture was stirred an additional 20 min with cooling, then a solution of pinacol iodomethaneboronate (**3**, 6.29 g, 23.5 mmol) in THF (10 mL) was added dropwise. After 20 min of additional stirring, the solution was warmed to room temperature, then distilled to afford 5.88 g (73%) of **6** as a pale yellow oil: bp 140 °C (0.25 mmHg); ^{1}H NMR (60 MHz, $CDCl_3$) δ 0.33 (9 H, s), 1.33 (12 H, s), 1.53 (6 H, t, J = 8 Hz), 3.00 (4 H, m), 3.13 (2 H, s), 7.33 (3 H, s).

Acylation of 6 (General Procedure to 7-9). The acyl halide (17.0 mmol) was added in a single portion to an ice-water cooled solution of pinacol [(2,6-diethylphenyl)(trimethylsilyl)amino]-methaneboronate (**6**, 5.86 g, 16.2 mmol) in THF (20 mL). The solution was warmed to room temperature and stirred for 1 h and then concentrated to afford pure **7-9** as solids, though each was also recrystallized from hexane. Data for **7**: mp 45.0-46.8 °C; ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.23 (6 H, t, J = 7.5 Hz), 1.27 (12 H, s), 2.60 (4 H, q, J = 7.5 Hz), 2.77 (2 H, s), 3.73 (2 H, s), 7.23 (3 H, m); MS, m/e 365 (M^+). Anal. Calcd for $C_{19}H_{29}BClNO_3$: C, 62.40; H, 7.99; B, 2.96; Cl, 9.69; N, 3.83. Found: C, 62.60; H, 8.11; B, 2.80; Cl, 9.90; N, 3.92. Data for **8**: mp 54.6-56.0 °C; ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.23 (6 H, t, J = 8 Hz), 1.27 (12 H, s), 2.60 (4 H, q, J = 8 Hz), 2.73 (2 H, s), 3.57 (2 H, s), 7.23 (3 H, m); MS, m/e 409 (M^+). Anal. Calcd for $C_{19}H_{29}BBrNO_3$: C, 55.64; H, 7.13; B, 2.64; Br, 19.48; N, 3.41. Found: C, 55.80; H, 7.11; B, 2.70; Br, 19.31; N, 3.39. Data for **9**: mp 52.0-54.8 °C; ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.23 (6 H, t, J = 8 Hz), 1.30 (12 H, s), 2.67 (4 H, q, J = 8 Hz), 2.90 (2 H, s), 5.68 (1 H, s), 7.23 (3 H, m); MS, m/e 399 (M^+). Anal. Calcd for $C_{19}H_{28}BCl_2NO_3$: C, 57.03; H, 7.05; B, 2.70; Cl, 17.72; N, 3.50. Found: C, 56.87; H, 6.98; B, 3.00; Cl, 17.97; N, 3.36.

Registry No. **2**, 100899-92-1; **3**, 70557-99-2; **4**, 579-66-8; **5**, 100899-93-2; **6**, 100899-94-3; **7**, 100899-95-4; **8**, 100899-96-5; **9**, 100899-97-6; CH_3SCH_3, 75-18-3; $(MeO)_3B$, 121-43-7; pinacol, 76-09-5.

Regiocontrol in Opening of 2*H*-Cyclopenta[*b*]furanones with Organocopper Reagents

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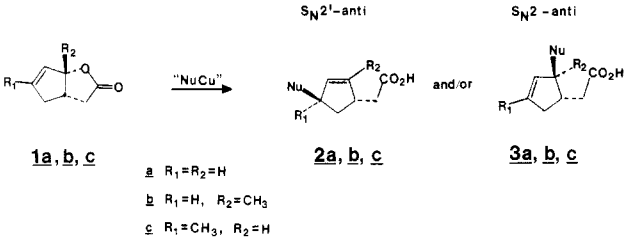
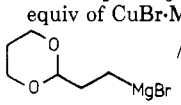
Received November 13, 1985

Recently, we had need of a general method for the synthesis of *trans*-3,5-disubstituted-cyclopentenes **2**. These compounds serve as versatile precursors for tandem radical cyclizations to produce linear condensed cyclopentanoids such as hirsutene[1] and $\Delta^{9(12)}$-capnellene.[2] We envisioned organocopper-promoted S_N2' anti opening of readily available substituted vinyl lactones **1** as a direct method which would control both regio- and stereochemistry.[3,4] A variety of related vinyl lactones have been opened in the past with contrasting results.[5,6] While the products of anti opening are usually observed, regioselectivity has varied from complete S_N2' to complete S_N2 depending on the substituents on the vinyl lactone and the nature of the organocopper reagent.[7] We have investigated the opening of 2*H*-cyclopenta[*b*]furan-2-one (**1a**) and its 6- and 8-methyl derivatives (**1c**, **1b**) and we now report a method for selective S_N2' anti opening of these vinyl lactones.

Table I. Oganocopper-Promoted Opening of 2*H*-Cyclopenta[*b*]furanones



entry	lactone	reagent[a]	2/3	yield,[b] %
1	**1a**	MeMgBr/1 equiv of $CuBr\cdot Me_2S$	>98/2	97
2	**1a**	$LiMe_2Cu$	62/38	91
3	**1a**	$LiMe_2Cu(Et_2O)$	54/46	90
4	**1a**	$CH_2{=}CHCH_2CH_2MgBr$/1 equiv of $CuBr\cdot Me_2S$	>98/2	94
5	**1a**	$CH_2{=}CHCH_2CH_2MgBr$/0.1 equiv of $CuBr\cdot Me_2S$	50/50	96
6	**1a**	MeLi/1 equiv of $CuBr\cdot Me_2S$	86/14	91
7	**1a**	MeLi/1 equiv of CuI	76/24	90
8	**1a**	MeLi/1 equiv of CuCN	75/25	60
9	**1b**	$LiMe_2Cu$	>98/2	92
10	**1b**	$THPOCH_2C(CH_3)_2CH_2Li$/1 equiv of $CuBr\cdot Me_2S$	>98/2	50
11	**1b**	 /1 equiv of $CuBr\cdot Me_2S$	>98/2	83
12	**1c**	$LiMe_2Cu$	7/93	61
13	**1c**	MeMgBr/1 equiv of $CuBr\cdot Me_2S$	95/5	73
14	**1c**	$MeLi/CuI/BF_3\cdot Et_2O$	98/2	45
15	**1c**	4/1 equiv of $CuBr\cdot Me_2S$	92/8	90

[a] All reactions were run in THF at -20 °C unless otherwise indicated (see Experimental Section). In general, an excess of organocopper reagent (1.2-2.0 equiv) was employed. [b] Yields represent yields of crude acid after isolation by base extraction. All acids were characterized by diazomethane esterification. Yields of purified methyl esters were generally good.

(1) Curran, D. P.; Rakiewicz, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 1448. Curran, D. P.; Rakiewicz, D. M. *Tetrahedron* **1985**, *41*, 3943.
(2) Curran, D. P.; Chen, M.-H. *Tetrahedron Lett.* **1985**, *26*, 4991.
(3) Magid, R. M. *Tetrahedron* **1980**, *36*, 1901.
(4) (a) For mechanistic studies on the alkylation of allylic derivatives with organocopper reagents, see: Goering, H. L.; Kanter, S. S. *J. Org. Chem.* **1984**, *49*, 422 and references therein. (b) For a stereoelectronic rational for the anti preference observed in these reactions, see: Corey, E. J.; Boaz, N. W. *Tetrahedron Lett.* **1984**, *25*, 3063.
(5) (a) Corey, E. J.; Mann, J. *J. Am. Chem. Soc.* **1973**, *95*, 6832. (b) Grieco, P. A.; Srinivasan, C. V. *J. Org. Chem.* **1981**, *46*, 2591. (c) Ali, S. M.; Chapleo, C. B.; Finch, M. A. W.; Roberts, S. M.; Woolley, G. T.; Cave, R. J.; Newton, R. F. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2093. Chapleo, C. B.; Finch, M. A. W.; Roberts, S. M.; Woolley, G. T.; Newton, R. F.; Selby, D. W. *Ibid.* **1980**, 1847.
(6) For some other relevant vinyl lactone openings, see: Beale, M. H. *J. Chem. Soc., Perkin Trans. 1* **1985**, 1151. Trost, B. M.; Klun, T. *J. Org. Chem.* **1980**, *45*, 4256. Fujisawa, J.; Sato, T.; Kawashima, M.; Naruse, K.; Tamai, K. *Tetrahedron Lett.* **1982**, *23*, 3583.
(7) For example, in the opening of similar unbiased vinyl lactones, Corey observed exclusive S_N2 selectivity with a divinylcuprate (ref 5a) while Grieco observed exclusive S_N2' selectivity with lithium dimethylcuprate (ref 5b).

0022-3263/86/1951-1612$01.50/0

The results of the opening of vinyl lactones **1a–c** with a variety of organo-copper reagents are collected in Table I. In general, a maximum of two products (**2a–c, 3a–c**) were observed. These result from anti S_N2' and/or anti S_N2 opening, respectively. The regiochemistry was readily ascertained from ^1H NMR analysis of the product or (in some cases) of the derived iodo lactone. The stereochemistry of all the S_N2 products was assumed to be anti since there is little precedent for S_N2 syn substitution.[4] The stereochemistry of the S_N2' adducts was implied by ^1H NMR coupling constants in the derived iodolactones (see Experimental Section) and rigorously confirmed by subsequent synthetic transformations for the products of entries 1, 4, 10, and 15.[1,2] Note that from the standpoint of substitution, lactone **1a** is unbiased (both sites are secondary) while lactone **1b** is biased toward S_N2' substitution and lactone **1c** is biased toward S_N2 substitution.

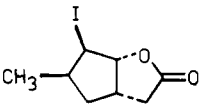
Based on the results presented in Table I, at least two generalizations can be advanced for allylic alkylation of these cyclic vinyl lactones. First, opening with lithium dimethyl cuprate is controlled largely by substitution.[8] While a slight preference for S_N2' substitution is observed for **1a** (entry 3), reaction with **1b** and **1c** occurs mainly or exclusively at the less substituted site (entries 9 and 12). A variety of other commonly employed reagents exhibit moderate S_N2' selectively with lactone **1a** (entries 6, 7, and 8). Second, the reagent derived from addition of an alkylmagnesium bromide to *one full equivalent* of copper bromide/dimethyl sulfide complex exhibits good to excellent S_N2' selectivity regardless of the inherent substituent bias. The reagent, formulated as "RCu"/$MgBr_2$,[9] shows complete selectivity in unbiased or favorably biased lactones **1a** and **1b** (entries 1, 4, 10, 11). Note that regioselectivity was completely destroyed when a *catalytic* amount of CuBr/Me_2S was used under otherwise identical conditions (entry 5). Significantly, useful selectivity was observed with the unfavorably biased vinyl lactone **1c** (entries 13, 15). This reagent combination is reminiscent of the Yamamoto reagent (RCu/BF_3/LiX) which shows very high S_N2' selectivity in the displacement of acyclic allylic acetates and halides.[10] Indeed, the Yamamoto reagent exhibits marginally increased regioselectivity in the opening of **1c** (entry 14). However, the availability and stability of the Stowell Grignard reagent **4**[11] prompted us to use this method in our recent synthesis of capnellene.[2]

In conclusion, opening of vinyl lactones **1** by lithium dialkyl cuprates is controlled largely by substituent location. In contrast, reaction with "RCu"/$MgBr_2$ provides an operationally simple method to open vinyl lactones **1a–c** with good to excellent regioselectivity. The products have already been shown to be versatile precursors for synthesis of linear condensed cyclopentanoid natural products.[1,2]

Experimental Section[12]

Methyl *trans*-4-Methyl-2-cyclopentene-1-acetic Acid. Methyl Ester of Acid 2a (Nu = CH_3). General Procedure for Lactone Opening with RCu/$MgBr_2$. To a solution of CuBr·Me_2S (71.0 g, 0.35 mol) in Me_2S (300 mL) and THF (700 mL) at −20 °C was added CH_3MgBr (125 mL, 2.85 M in THF, 0.35 mol). After stirring 1 h at −20 °C, lactone **1a** (21.5 g, 0.18 mol) in THF (200 mL) was added dropwise via an addition funnel. The mixture was stirred for 5 h at −20 °C, poured into 1 N NaOH, and stirred for 2 h. The organic layer was separated and the aqueous layer was acidified to pH ~2 with 1 N HCl. After extraction with ether, the organic phase was washed with water and brine, dried over $MgSO_4$, and concentrated in vacuo to provide acid **2a** (Nu = CH_3) (23.65 g, 97.6%) as a yellow oil. This was characterized as the methyl ester (prepared by standard diazomethane treatment); ^1H NMR δ 5.65 (2 H, m), 3.65 (3 H, s), 3.14 (1 H, br m), 2.80 (1 H, br m), 2.30 (2 H, AB portion of ABX), 1.67 (2 H, m), 0.97 (3 H, d); IR ($CHCl_3$), 1730 cm^{-1}. Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.01, H, 9.19.

Iodo Lactone i. To a mixture of the above acid (22.8 g, 0.163 mol) in THF (1.5 L) and saturated aqueous $NaHCO_3$ (290 mL) was added a solution of iodine (83.3 g, 0.33 mol) and KI (163.6 g, 0.98 mol) in water (700 mL). The mixture was stirred in the dark for 24 h and quenched by shaking with saturated $Na_2S_2O_3$. After extraction with ether, the combined extracts were washed with $NaHSO_4$, water, and brine, dried over $MgSO_4$, and concentrated in vacuo to afford i as a yellow solid (36.4 g, 84%); an analytical sample was prepared by recrystallization from EtOH, mp 73–75 °C; ^1H NMR δ 5.30 (1 H, d, J = 6 Hz), 4.53 (1 H, d, J = 4 Hz) 3.18 (1 H, m), 2.90 (1 H, dd, J = 18 Hz, 10 Hz), 2.37 (1 H, dd, J = 18 Hz, 2 Hz), 1.94 (1 H, m), 1.50 (2 H, m), 1.06 (3 H, d); IR ($CHCl_3$) 1775 cm^{-1}; MS, m/e calcd for $C_8H_{11}O_2I$ 265.9804, found 265.9813. Anal. Calcd for $C_8H_{11}O_2I$; C, 36.11, H, 4.17. Found: C, 35.95, H, 4.28.



i

Methyl *trans*-2-Methyl-3-cyclopentene-1-acetic Acid. Methyl ester from acid 3a (Nu = CH_3): ^1H NMR δ 5.56 (2 H, m), 3.66 (3 H, s), 2.63 (1 H, m), 2.48 (1 H, dd), 2.33 (2 H, m overlapping dd), 2.02 (1 H, m), 1.03 (3 H, d); IR ($CHCl_3$) 1730 cm^{-1}.

6-Methyl-2*H*-cyclopenta[*b*]furan-2-one (1c). DBU (22.0 mL, 0.15 mol) was added slowly to a solution of crude iodo lactone i (36.0 g, 0.14 mol) in THF (200 mL) at 0 °C. After being stirred for 3 h at 0 °C, the reaction was poured into saturated $NaHSO_4$ and extracted with ether. The organic extract was washed with $NaHSO_4$, $NaHCO_3$, water, and brine and dried over $MgSO_4$. Concentration in vacuo and short-path distillation (bp 63–65 °C, 0.25 mm) gave **1c** as a clear oil (15.0 g, 80%): ^1N NMR δ 5.51 (1 H, s), 5.46 (1 H, d, J = 8 Hz), 3.14 (1 H, m), 2.82 (1 H, dd, J = 18 Hz, 10 Hz), 2.67 (1 H, dd, J = 17 Hz, 8.5 Hz), 2.34 (1 H, dd, J = 18 Hz, 5 Hz), 2.19 (1 H, d, J = 17 Hz), 1.80 (3 H, br s); IR ($CHCl_3$) 3030, 2945, 2910, 2845, 1760, 1175, 995 cm^{-1}; MS, m/e 138, 95, 94, 93, 92, 79, calcd for $C_8H_{10}O_2$ 138.0681, found 138.0681. Anal. Calcd for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.92; H, 7.62.

Methyl *trans*-2,4-Dimethyl-2-cyclopentene-1-acetic Acid. Methyl ester from acid 2b (Nu = CH_3): ^1H NMR δ 5.28 (1 H, s), 3.68 (3 H, s), 2.93 (1 H, m), 2.69 (1 H, m), 2.51 (1 H, dd), 2.13

(8) Liu, H. J.; Ho, L. K. *Can. J. Chem.* **1983**, *61*, 632.

(9) The formulation simply indicates the stoichiometry of the reactants. The actual reacting species is unknown. The structure of the CH_3MgBr/CuBr reagent has been extensively investigated by Ashby et al. and consists of a variety of magnesium methylcuprates [$Mg_xCu_y(Me_{x+y})$]. The composition varies with temperature, time, and stoichiometry, and the reactivity of the various cuprates differs widely. Interestingly, the presence of free $MgBr_2$ has been shown to be beneficial in addition of these species to phenylacetylene. See: Ashby, E. C.; Goel, A. B.; Smith, R. S. *J. Organomet. Chem.* **1981**, *212*, C47; **1981**, *215*, Cl; *J. Org. Chem.* **1981**, *46*, 5133; **1983**, *48*, 2125. For structural studies of lithium methylcuprates, see: Lipshutz, B. H.; Kozlowski, J. A.; Breneman, C. M. *J. Am. Chem. Soc.* **1985**, *107*, 3197.

(10) Yamamoto, Y.; Yamamoto, S.; Yatagai, H.; Maruyama, K. *J. Am. Chem. Soc.* **1980**, *102*, 2318.

(11) Stowell, J. C. *J. Org. Chem.* **1976**, *41*, 560. Stowell, J. C.; Keith, D. R.; King, B. T. *Org. Synth.* **1984**, *62*, 140.

(12) General: All reactions were run under nitrogen atmosphere unless otherwise indicated. THF and ether were distilled from sodium/benzophenone. Dimethyl sulfide was distilled from CaH_2. Copper bromide/dimethyl sulfide was prepared by the method of Townsend [Townsend, C. A.; Thies, A. B. *Synth. Commun.* **1981**, *11*, 157]. Other copper reactions were conducted by standard literature procedures [Posner, G. *Introduction to Synthesis Using Organocopper Reagents*"; Wiley: New York, 1980]. All NMR spectra were recorded in $CDCl_3$ on a Brucker WH-300 MHz unless otherwise indicated. Vinyl lactones **1a** and **1b** were prepared as described in ref 1. Characterization of the products from entries 4 and 9 is also provided in ref 1 while entry 14 is contained in ref 2.

(1 H, dd), 1.9–1.6 (2 H, m), 1.65 (3 H, br s), 0.97 (3 H, d); IR ($CHCl_3$) 1725 cm^{-1}; MS, m/e calcd for $C_{10}H_{16}O_2$ 168.1151, found 168.1156.

Methyl *trans*-2,4-Dimethyl-3-cyclopentene-1-acetic Acid. Methyl ester from acid 3c (Nu = CH_3): ^1H NMR δ 5.15 (1 H, m), 3.67 (3 H, s), 2.46 (2 H, m), 2.33 (2 H, m), 2.16 (1 H, m), 1.97 (1 H, m), 1.68 (3 H, br s), 1.00 (3 H, d); IR ($CHCl_3$) 1730 cm^{-1}. Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.37; H, 9.30.

Methyl 4,4-Dimethyl-2-cyclopentene-1-acetic Acid. Methyl ester of acid 2c (Nu = CH_3): ^1H NMR δ 5.51 (2 H, m), 3.67 (3 H, s), 2.38 (1 H, m), 2.43 (1 H, dd, J = 7 Hz, 15 Hz), 2.31 (1 H, dd, J = 7 Hz, 15 Hz), 1.96 (1 H, dd, J = 8 Hz, 13 Hz), 1.27 (1 H, dd, J = 7 Hz, 13 Hz), 1.09 (3 H, s), 1.03 (3 H, s); IR ($CHCl_3$) 1730 cm^{-1}. Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.20; H, 9.34.

Acknowledgment. We thank the National Institutes of Health (GM 33372) for funding this work. D.P.C. also thanks the Dreyfus Foundation, the Alfred P. Sloan Foundation, and Eli Lilly for Fellowships.

Registry No. **1a**, 38110-76-8; **1b**, 100948-63-8; **1c**, 100948-64-9; **2a** (Nu = Me), 100948-65-0; **2a** (Nu = $(CH_2)_2CH{=}CH_2$), 100948-66-1; **2b** (Nu = Me), 100948-67-2; **2b** (Nu = Me, methyl ester), 100948-75-2; **2b** (Nu = $THPOCH_2C(CH_3)_2CH_2$), 94957-76-3; **2b** (Nu = 2-ethyl-1,3-dioxane), 100948-68-3; **2c** (Nu = Me), 100948-69-4; **2** (Nu = Me, methyl ester), 100948-77-4; **2c** (Nu = 2-ethyl-1,3-dioxane), 100948-70-7; **3a** (Nu = Me), 100948-71-8; **3a** (Nu = Me, methyl ester), 100948-74-1; **3a** (Nu = $(CH_2)_2CH{=}CH_2$), 100948-72-9; **3c** (Nu = Me), 100948-73-0; **3c** (Nu = Me, methyl ester), 100948-76-3; **i**, 100948-78-5.

Synthesis of 2,6,2′,6′-Tetramethylazobenzene and the Azodioxy and Azoxy Compounds

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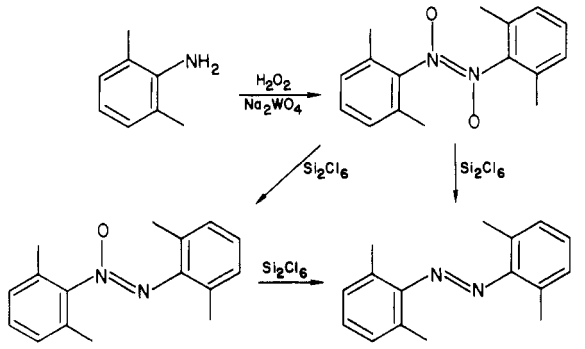
Received November 19, 1985

The method of choice for detection of traces of blood involves the use of 2,6,2′,6′-tetramethylbenzidine which gives a blue color with hydrogen peroxide in the presence of blood peroxidase.[1] This benzidine is made in low overall yield from 2,6-dimethylaniline.[2] The yield loss is in the first step, the oxidation of the aniline to the title azo compound. The ancient[3] oxidation with potassium ferricyanide gives only a 14.7% yield.[1,2] The use of silver(II) oxide[4] or silver carbonate[5] gave 33% and 35% yields. The azo compound has also been prepared by lithium aluminum hydride reduction of 2,6-dimethylnitrobenzene, but again the yield was only 13%.[6]

In unhindered aryl cases the N–N bond formation may occur at several levels of oxidation, but the 2,6-dimethyl groups lessen these possibilities.[7] The exception is at the nitroso level where ortho substituents interfere with coplanarity and conjugation in the monomer, favoring the azodioxy compound. In solution nitrosobenzene is essentially all monomer under conditions where nitrosomesitylene and 1,3-dimethyl-2-nitrosobenzene are mostly dimer.[8]

Scheme I



We have found that the title azo compound can be prepared in 92% overall yield by first oxidizing the aniline to the azodioxide and then reducing it to the azo level (Scheme I). Sodium tungstate catalyzed[9] oxidation of 2,6-dimethylaniline with hydrogen peroxide gives the crystalline, colorless azo dioxide in 98% yield. Heating this with 2.5 mol/mol of hexachlorodisilane in chloroform gives the dark red azo compound in 97% yield. With 1.1 mol/mol of hexachlorodisilane, the azoxy compound may be made in 94% yield.

Earlier workers[10] employed Caro's acid (potassium persulfate in sulfuric acid) to oxidize 2,6-dimethylaniline to the azo dioxide in 20% to 60% yield. The azoxy compound was made previously by oxidation of the azo compound.[6]

Hexachlorodisilane has been used to deoxygenate alkyl amine oxides[11] nitrones,[12] and a few cyclic cis azo dioxides[13,14] and azoxy compounds.[15]

Experimental Section

The NMR spectra were run on a Varian EM-360 spectrometer with tetramethylsilane as an internal standard.

2,6,2′,6′-Tetramethylazobenzene *N,N′*-Dioxide. 2,6-Dimethylaniline (47.2 g, 0.390 mol), 60 mL of water, 8.0 g of sodium tungstate, and 100 mL of ether were placed in a 500-mL Erlenmeyer flask and cooled in an ice bath. Hydrogen peroxide (132 mL of 30%, 1.17 mol) was added dropwise to the mixture with stirring over a 40-min period. The resulting mixture was left at room temperature overnight. The pale yellow product was separated by filtration and washed with 50 mL of ice-cold ether to afford 51.8 g (97%) of white crystalline solid, mp 134.5–135 °C (lit.[8] mp 133.5–134 °C): IR (mineral oil) 1215 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.47 (s, 12 H), 7.12 (s, 6 H).

2,6,2′,6′-Tetramethylazoxybenzene. Hexachlorodisilane (3.0 g, 0.011 mol) was added dropwise to a solution of 2,6,2′,6′-tetramethylazobenzene *N,N′*-dioxide (2.7 g, 0.010 mol) in 50 mL of dry chloroform under a nitrogen atmosphere. After the initial exothermic reaction, the solution was heated at reflux overnight. Cold 1 M aqueous sodium hydroxide was added until the water layer was basic. The chloroform layer was separated and the water layer was extracted with three 50-mL portions of ether. The combined chloroform and ether solution was dried with sodium sulfate and rotary evaporated to leave an orange-red solid. This

(1) Holland, V. R.; Saunders, B. C.; Rose, F. L.; Walpole, A. L. *Tetrahedron* **1974**, *30*, 3299.
(2) Pinkus, J. L.; Goldman, L. S. *J. Chem. Educ.* **1977**, *54*, 380.
(3) Schultz, G. *Chem. Ber.* **1884**, *17*, 476. Haselbach, E. *Helv. Chim. Acta* **1970**, *53*, 1526.
(4) Ortiz, B.; Villaneuva, P.; Walls, F. *J. Org. Chem.* **1972**, *37*, 2748.
(5) Hedayatullah, M.; Dechatre, J. P.; Denivelle, L. *Tetrahedron Lett.* **1975**, 2039.
(6) Goon, D. J. W.; Murray, N. G.; Schoch, J.-P.; Bunce, N. J. *Can. J. Chem.* **1973**, *51*, 3827.
(7) Bamberger, E. *Chem. Ber.* **1926**, *59*, 418.
(8) Holmes, R. R. *J. Org. Chem.* **1964**, *29*, 3076. Azoulay, M.; Lippman, R.; Wettermark, G. *J. Chem. Soc., Perkin Trans. 2* **1981**, 256.
(9) Stowell, J. C. *J. Org. Chem.* **1971**, *36*, 3055.
(10) Mijs, W. J.; Hoekstra, S. E.; Ulmann, R. M.; Havinga, E. *Recl. Trav. Chim. Pays-Bos* **1958**, *77*, 746.
(11) Barton, D. H. R.; Beugelmans, R.; Young, R. N. *Nouv. J. Chim.* **1978**, *2*, 363.
(12) Hortmann, A. G.; Koo, J.; Yu, C.-C. *J. Org. Chem.* **1978**, *43*, 2289.
(13) Snyder, J. P.; Heyman, M. L.; Suciu, E. N. *J. Org. Chem.* **1975**, *40*, 1395.
(14) Greene, F. D.; Gilbert, K. E. *J. Org. Chem.* **1975**, *40*, 1409.
(15) Olsen, H.; Snyder, J. P. *J. Am. Chem. Soc.* **1977**, *99*, 1524.

0022-3263/86/1951-1614$01.50/0