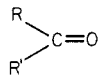
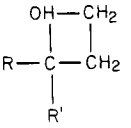
Table II. Preparation of Oxetanes from Carbonyl Compounds[a]





compd	R	R'	compd	yield, %	bp, °C (mmHg)
5a	H	C_6H_5	2a	93	37-38 (0.016)
5b	C_6H_5	C_6H_5	2b	97	111-115 (0.013)
5c	H	p-ClC_6H_4	2c	90	60-64 (0.018)
5d	CH_3	C_6H_5	2d	90	31-35 (0.009)
5e	cyclohexanone		2e	88	31-33 (0.013)
5f	H	p-$CH_3C_6H_4$	2f	80	44-47 (0.007)
5g	C_2H_5	C_6H_5	2g	96	44-48 (0.022)
5h	4-methylcyclohexanone		2h	80	24-26 (0.072)
5i	4-*tert*-butyl cyclohexanone		2i	87	63-65 (0.040)

[a] Reactions carried out at 50 °C for 3 days.

NMR spectra were measured with a JEOL PMX-60 spectrometer or a JEOL FX-200 spectrometer. Mass spectra were recorded of a JEOL DX-300 mass spectrometer.

Methylene-Transfer Reaction. Oxetane 2a from Epoxide 3a. To a solution of 4.40 g (20 mmol) of trimethyloxosulfonium iodide in 40 mL of *t*-BuOH was added a solution of 2.24 g (20 mmol) of *t*-BuOK in 25 mL of *t*-BuOH at 50 °C. After 30 min of stirring, 1.20 g (10 mmol) of **3a** (freshly distilled) in 20 mL of *t*-BuOH was added dropwise to this solution. After 3 days of stirring, the resulting suspension was evaporated, washed with water, and extracted three times with *n*-hexane. The combined extract was dried over $MgSO_4$ and evaporated to give oxetane **2a** (1.26 g, 9.4 mmol) in 94% yield. Without further purification, resulting **2a** was spectroscopically pure: ^1H NMR ($CDCl_3$) δ 2.33-3.43 (m, 2 H), 4.20-5.20 (m, 2 H), 5.73 (t, 1 H, J = 7.2 Hz), 7.30 (s, 5 H); HRMS, m/e 134.0731 ($C_9H_{10}O$ requires 134.0721).

2b-e were prepared in a similar manner from 10 mmol of epoxide; yields are shown in Table I. **2b**: mp 41-43 °C; ^1H NMR ($CDCl_3$) δ 3.17 (t, 2 H, J = 8.0 Hz), 4.63 (t, 2 H, J = 8.0 Hz), 7.07-7.63 (m, 10 H); HRMS, m/e 210.1044 ($C_{15}H_{14}O$ requires 210.1045). Anal. Calcd for $C_{15}H_{14}O$: C, 85.71; H, 6.67. Found: C, 85.73; H, 6.61. **2c**: ^1H NMR ($CDCl_3$) δ 2.33-3.23 (m, 2 H), 4.40-5.06 (m, 2 H), 5.70 (t, 1 H, J = 8.0 Hz), 7.07-7.63 (m, 10 H); HRMS, m/e 168.0342, 170.0312 (C_9H_9OCl requires 168.0342, 170.0312). **2d**: ^1H NMR ($CDCl_3$) δ 1.73 (s, 3 H), 2.75 (t, 2 H, J = 7.8 Hz), 4.55 (dt, 2 H, J = 1.8, 8.0 Hz), 7.35 (s, 5 H); HRMS, m/e 148.0888 ($C_{10}H_{12}O$ requires 148.0888). **2e**: ^1H NMR δ 1.0-2.0 (m, 10 H), 2.27 (t, 2 H, J = 7.8 Hz), 4.43 (t, 2 H, J = 7.8 Hz); HRMS, m/e 124.1043 ($C_8H_{14}O$ requires 126.1045).

Double Methylene-Transfer Reaction. Oxetane 2b from 5b. To a solution of 8.80 g (40 mmol) of trimethyloxosulfonium idodide in 80 mL of *t*-BuOH was added a solution of 4.48 g (40 mmol) of *t*-BuOK in 50 mL of *t*-BuOH at 50 °C. After 30 min of stirring, 1.82 g (10 mmol) of benzophenone (**5b**) in 20 mL of *t*-BuOH was added dropwise. After 3 days of stirring, the resulting suspension was evaporated, washed with water, and extracted three times with *n*-hexane. The combined extract was dried over $MgSO_4$ and evaporated to give oxetane **2b** (2.04 g, 9.7 mmol) in 97% yield. Without further purification, **2b** was spectroscopically pure: mp 41-43 °C.

2a,c-i were prepared in a similar manner from 10 mmol of ketone; yields are shown in Table II **2f**: ^1H NMR ($CDCl_3$) δ 2.32 (s, 3 H), 2.40-3.33 (m, 2 H), 4.37-4.93 (m, 2 H), 5.72 (t, 1 H, J = 7.8 Hz), 7.17 (s, 4 H); HRMS, m/e 148.0888 ($C_{10}H_{12}O$ requires 148.0888). **2g**: ^1H NMR ($CDCl_3$) δ 0.82 (t, 3 H, J = 7.3 Hz), 1.63-2.23 (m, 2 H), 2.73 (dt, 2 H, J = 3, 8 Hz), 4.52 (t, 2 H, J = 7.7 Hz), 7.28 (s, 5 H); HRMS, m/e 162.1045 ($C_{11}H_{14}O$ requires 162.1045). **2h**: ^1H NMR ($CDCl_3$) δ 0.57-2.03 (m, 11 H), 1.80-2.53 (m, 1 H), 2.28 (t, 2 H, J = 7.8 Hz), 4.43 (t, 2 H, J = 7.8 Hz); HRMS, m/e 140.1183 ($C_9H_{16}O$ requires 140.1201). **2i**: ^1H NMR ($CDCl_3$) δ 0.85 (s, 9 H), 1.00-1.83 (m, 8 H), 2.00-2.40 (m, 1 H), 2.28 (t, 2 H, J = 8.0 Hz), 4.42 (t, 2 H, J = 8.0 Hz); HRMS, m/e 182.1691 ($C_{12}H_{22}O$ requires 182.1671).

Acknowledgment. This work was partly supported by a grant from the Central Research Institute of Fukuoka University. We are grateful to Dr. H. Kikuchi and Y. Matsuzaki at Tsumura Research Institute of Pharmacology for the high-resolution mass spectroscopic analysis.

Registry No. 1, 5367-24-8; **2a**, 4436-23-1; **2b**, 884-73-1; **2c**, 17492-23-8; **2d**, 19352-10-4; **2e**, 185-18-2; **2f**, 5583-71-1; **2g**, 87597-07-7; **2h**, 87597-08-8; **2i**, 87597-09-9; **3a**, 96-09-3; **3b**, 882-59-7; **3c**, 2788-86-5; **3d**, 2085-88-3; **3e**, 185-70-6; **5a**, 100-52-7; **5b**, 119-61-9; **5c**, 104-88-1; **5d**, 98-86-2; **5e**, 108-94-1; **5f**, 104-87-0; **5g**, 93-55-0; **5h**, 589-92-4; **5i**, 98-53-3.

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Synthesis of a Conjugated Nitrile from a Benzylic Ketone via a Cyanotrimethylsilane Adduct: 3,4-Dihydro-6-methoxynaphthalene-1-carbonitrile

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Received June 10, 1983

6-Methoxynaphthalene-1-carbonitrile (**4**) and its 3,4-dihydro derivative **3** are useful intermediates for the synthesis of steroids and the oxidized metabolites of carcinogenic hydrocarbons.[1-4] The fully aromatic nitrile **4** is commonly prepared from 6-methoxy-1-aminonaphthalene via diazotization and the Sandmeyer reaction.[1] However, preparation of the starting compound entails a multistep synthesis and affords relatively poor overall yields. The 3,4-dihydro compound **3** is presently available through addition of diethylaluminum cyanide to 6-methoxy-1-tetralone followed by dehydration.[5] Since diethylaluminum cyanide is a relatively expensive and hazardous reagent, and large solvent volumes are required, this method is impractical for larger scale preparations.

We now report a convenient one-pot synthesis of **3** from 6-methoxytetralone (**1**) and dehydrogenation of **3** directly to **4** (Scheme I). Boron trifluoride-catalyzed addition of cyanotrimethylsilane[6] to **1** yields the adduct **2** which on

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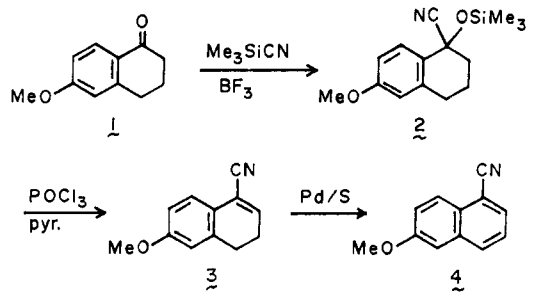
Scheme I



treatment with $POCl_3$ in pyridine undergoes elimination of trimethylsilanol to afford **3**. Dehydrogenation of **3** was most efficiently accomplished by heating with sulfur and a 10% palladium–charcoal catalyst in refluxing triglyme. This reagent combination was more effective than palladium in the absence of sulfur or chemical oxidants such as 2,3-dichloro-5,6-dicyano-1,4-benzoquinone or *o*-chloranil, which furnished substantial amounts of secondary products. The utility of the combination of sulfur and palladium for dehydrogenation has been documented previously.[7,8]

While no attempt has been made to extend this synthetic approach to other conjugated nitriles, the method appears potentially quite general.[9]

Experimental Section

3,4-Dihydro-6-methoxynaphthalene-1-carbonitrile (3). 6-Methoxy-1-tetralone[10] (17.6 g, 100 mmol) is placed in a 250-mL Erlenmeyer flask, and cyanotrimethylsilane (10.9 g, 110 mmol) is added with stirring, followed by 2 or 3 drops of BF_3 etherate. The mixture is warmed on a hotplate at 60 °C for 2 h, the temperature is raised to 100 °C to prevent solidification, and heating is continued for an additional 2 h.[11] Then pyridine[12] (75 mL) and $POCl_3$ (15 mL) are added along with a few carborundum boiling chips. A simple distillation head is attached, and the solution is gently boiled for 2 h while a mixture of chlorotrimethylsilane and pyridine distills over. The reaction mixture is then poured into 500 mL of crushed ice, and the product is extracted into ether. The ether layer is washed with water, dilute hydrochloric acid, and water and evaporated to dryness under vacuum. The gummy product is dissolved in a small volume of benzene (25–30 mL), diluted with three times the same volume of hexane, and decolorized by passage through a short column (20 g) of neutral alumina. Concentration of the solution to approximately half volume by partial evaporation of the solvent with a stream of nitrogen followed by cooling precipitates 14.7 g (79%) of **3** as a pale tan, somewhat sticky solid, which was twice recrystallized from methanol: mp 50–51.5 °C (lit.[5] mp 50.5–51.5 °C); NMR ($CDCl_3$) δ 2.3–3.1 (m, 4, CH_2), 3.8 (s, 3 CH_3), 6.6–7.5 (m, 4, vinylic and aromatic). Compound **3** may be dehydrogenated directly without recrystallization or further purification.

6-Methoxynaphthalene-1-carbonitrile (4). Since H_2S is generated as a side product, it is advisable to conduct this reaction in a hood. The unrecrystallized nitrile **3** (30 g, 162 mmol) is combined with 6 g of sulfur, 1.5 g of 10% Pd on charcoal, and 200 mL of triglyme in a 500-mL flask fitted with an air-cooled condenser. The stirred mixture is heated at reflux for 2 h, cooled, and filtered, and the residue is rinsed with ether (100 mL). The ether washings and filtrate are combined in a 2-L separatory funnel. Additional ether (500 mL) is added, and the ether solution is washed with water (500 mL), 10% aqueous NaOH (2 × 100 mL), and water (2 × 100 mL) and dried (Na_2SO_4). The solvent was removed in vacuo to give a viscous oil, which was induced to crystallize by chilling in a dry ice bath. Recrystallization of the crude product from methanol gives 25 g (84%) of **4** [mp 77–78 °C (lit.[1,3] mp 79, 78–79 °C)] and a second crop of 2.7 g (mp 76–78 °C), giving a total yield of the nitrile of 27.7 g (93%).

Acknowledgment. This research was supported by Grants CA 09183 and CA 14599 from the National Cancer Institute, National Institutes of Health, and Grant BC 132 from the American Cancer Society.

Registry No. 1, 1078-19-9; 2, 80859-07-0; 3, 6398-50-1; 4, 77029-01-7.

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(11) If it is desired to isolate the cyanohydrin trimethylsilyl ether intermediate, triethylamine may be added at this point to neutralize the BF_3, and the cyanohydrin derivative may be obtained by vacuum distillation, employing an air condenser to avoid solidification.
(12) Purification of the pyridine by distillation from *p*-toluenesulfonyl chloride is advisable to prevent tar formation.

A Convenient Synthesis of 4-Ethynylphthalic Anhydride via 2-Methyl-3-butyn-2-ol

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Received May 31, 1983

Arylacetylenes are important in organic syntheses, judging by the increasing number of publication appearing in recent years.[1–6] Important classical methods for their synthesis include halogenation/dehydrohalogenation of ketones,[7] or olefinic derivatives,[8] displacement of halogens with cupric acetylides,[9,10] and the use of Vilsmeier reagent ($DMF–POCl_3$) with acetophenones.[11,12] While the yields vary from fair to excellent, the procedures are often unreliable, they require isolation and/or purification of intermediates, and are either cumbersome, costly, or unsafe to perform on a preparative scale. Some catalytic method, therefore, is needed for the preparation of arylacetylenes in a cost-effective manner.

In 1975, three papers appeared in the literature describing the palladium-catalyzed reaction of aryl and vinyl halides with acetylenes.[13–15] The order of reactivity for halogens followed the sequence I > Br > Cl.[14–16] Attempts

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