of complex organic compounds.

The following procedure for the conversion of 2-methylcyclohexanone to 2-methyl-6-nerylcyclohexanone is representative. Bis(trimethylsilyl)amine (3.87 g, 24 mmol) is added to a suspension of KH[4] (0.88 g, 22 mmol) in dry THF (15 mL) at 25 °C. After the evolution of hydrogen is complete (<30 min), the reaction mixture is cooled to −78 °C, and 2-methylcyclohexanone (2.24 g, 20 mmol) in 10 mL of THF is added dropwise, followed by addition of 27 mL (27 mmol) of a 1 M solution of triethylborane in THF. After the resultant mixture is warmed to 25 °C, it is added to a mixture of neryl acetate (3.92 g, 20 mmol), $Pd(PPh_3)_4$[13] (1.15 g, 1 mmol), and 10 mL of THF. The reaction mixture is stirred for 24 h and is treated with 10 mL each of 3 M NaOH and 30% H_2O_2 for 1 h at 0 °C to oxidize triethylborane. The organic layer is separated, and the aqueous layer is extracted with ether. The combined organic layer is sequentially treated with 3 N HCl, aqueous $NaHCO_3$, and water, dried over $MgSO_4$, concentrated, and passed through a short Florisil (100–200 mesh) column (10% ether–hexane) to remove any palladium-containing compounds.[14] After evaporation of the solvents, distillation gives 3.62 g (73% yield) of **13**: bp 145–149 °C (0.5 mm); IR (neat) 1710 (s) cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.95–1.15 (m with peaks at 0.95, 1.03 and 1.10, 3 H), 1.5–2.5 (m with peaks at 1.61 and 1.68, 23 H), 4.9–5.2 (m, 2 H). The ^1H NMR spectrum of **13** taken at 470 MHz shows two sets of doublets for the cis- and trans-2,6 isomers at 1.05 and 0.99 ppm (J = 6.6 Hz) along with a partially resolved singlet at 1.03 ppm for the regioisomer. This and the ^{13}C NMR spectrum of **13** indicate that the regioselectivity of the reaction is ca. 95%.

Finally, we briefly examined the possibility of using other countercations by reacting various metal cyclohexenolates with geranyl acetate in THF at room temperature in the presence of 5 mol % of $Pd(PPh_3)_4$. Although the metal enolates containing Li,[10,11,15] Me_3Si,[11] and $ClZr(\eta^5\text{-}C_5H_5)_2$ did not produce any detectable amount of **6** in 24 h, those obtained by treating lithium cyclohexenolate with $MgCl_2$, $ZnCl_2$, and $AlEt_3$ gave **6** in 15%, 70%, and 65% yields, respectively. Efforts are being made to clarify the relative merits and demerits of these enolates as well as of potassium enoxyborates.

Acknowledgment. We thank the National Science Foundation and the National Institutes of Health for support. The high-field NMR study was supported by the Purdue University Biochemical Magnetic Resonance Laboratory (Grant NIH RR 01077). H.M. was on leave from the Japan Tobacco and Salt Public Corp. (Jan 1980–Dec 1981) on funds partially provided by that corporation. S.C. was recipient of a National Scholarship awarded by the Ministry of Education, Government of India.

Registry No. 2, 82167-44-0; **3**, 17392-07-3; **6**, 74016-20-9; **7**, 82167-42-8; **8**, 74016-21-0; **9**, 82167-45-1; **10**, 82167-46-2; **11** (isomer 1), 82167-43-9; **11** (isomer 2), 82189-53-5; **12**, 76524-73-7; **13** (isomer 1), 82189-52-4; **13** (isomer 2), 82189-54-6; $Pd(PPh_3)_4$, 14221-02-4; *isoprenyl chloride*, 503-60-6; *2,3-dichloropropene*, 78-88-6; *isoprenylated cyclohexanone*, 704-99-4; 2-methylcyclohexanone, 583-60-8; geranyl acetate, 105-87-3; neryl acetate, 141-12-8.

Ei-ichi Negishi,* Hajime Matsushita
Sugata Chatterjee, Robert A. John
Department of Chemistry
Purdue University
West Lafayette, Indiana 47907

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[13] The Pd catalyst was prepared according to the literature procedure (Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121) and used within a few weeks. This catalyst slowly decomposes on standing. It is not known how long it can be stored at room temperature.

[14] This short-path column chromatography has been used in our laboratories as a precautionary measure. In this case, its need has not been rigorously established. No isomeric separation is achieved in this step.

[15] The reason for the striking difference between our results with lithium enolates and those reported by Fiaud and Malleron[10] is not clear, although it may be suspected to be due to the difference in catalysts. It is clear to us, however, that, in our reaction, metal enolates containing ZnCl and $AlEt_3Li$ are far more reactive than the corresponding lithium enolates under the same reaction conditions.

Alkoxide-Accelerated Sigmatropic Rearrangements. A Novel Entry to the Bicyclo[5.3.1]undec-7-ene System of the Taxane Diterpenes

Summary: An anionic oxy-Cope rearrangement serves as the key step in a novel route to the bicyclo[5.3.1]undec-7-ene ring system, which is an important structural element of the taxane diterpenes.

Sir: One of the principal challenges in designing a synthetic approach to the taxane class of diterpenes,[1] which includes taxusin (**1**),[2] is the development of a general and efficient technique for the construction of suitably substituted bicyclo[5.3.1]undec-7-enes such as **2**.[3] It occurred to us that one eminently attractive entry to the bicyclo[5.3.1]undecene **2** would involve the skeletal reorganization of the bicyclo[2.2.2]octane **3** via an anionic oxy-Cope rearrangement, a reaction which was originally investigated by Evans[4–6] and subsequently exploited in numerous synthetic applications.[3i,j,6,7] We herein report that this expectation has now been realized in practice (Scheme I).

In order to test the feasibility of employing an anionic oxy-Cope rearrangement for the construction of bicyclo[5.3.1]undec-7-enes, it was necessary to prepare simple

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[1] For a leading reference, see Miller, R. W. *J. Nat. Prod.* **1980**, *43*, 425–437.

[2] Della Casa de Marcano, D. P.; Halsall, T. G. *J. Chem. Soc., Chem. Commun.* **1969**, 1282–1283.

[3] For approaches to substituted bicyclo[5.3.1]undecenes, see: (a) Prelog, V.; Barman, P.; Zimmerman, M. *Helv. Chim. Acta* **1949**, *32*, 1284–1296. (b) Marshall, J. A.; Scanio, C. J. V. *J. Org. Chem.* **1965**, *30*, 3019–3023. (c) Warnhoff, E. W.; Wong, C. M.; Tai, W. T. *Ibid.* **1967**, *32*, 2664–2669. (d) Buchanan, G. L.; Jamieson, G. *Tetrahedron* **1972**, *28*, 1129–1135. (e) Dauben, W. G.; Ipaktschi, J. *J. Am. Chem. Soc.* **1973**, *95*, 5088–5089. (f) Roth, W. R.; Erker, G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 503–504. (g) Masamune, S.; Brooks, D. W. *Tetrahedron Lett.* **1977**, 3239–3240. (h) Shea, K. J. *Tetrahedron* **1980**, *36*, 1683–1715. (i) Kahn, M. *Tetrahedron Lett.* **1980, 21**, 4547–4548. (j) Levine, S. G.; McDaniel, R. L., Jr. *J. Org. Chem.* **1981**, *46*, 2199–2200. (k) Trost, B. M.; Hiemstra, H. *J. Am. Chem. Soc.* **1982**, *104*, 886–887.

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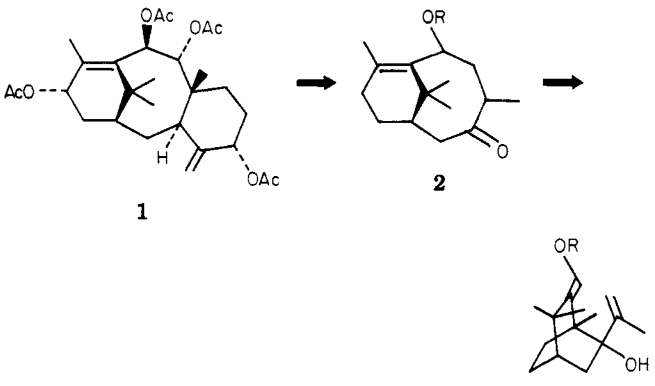
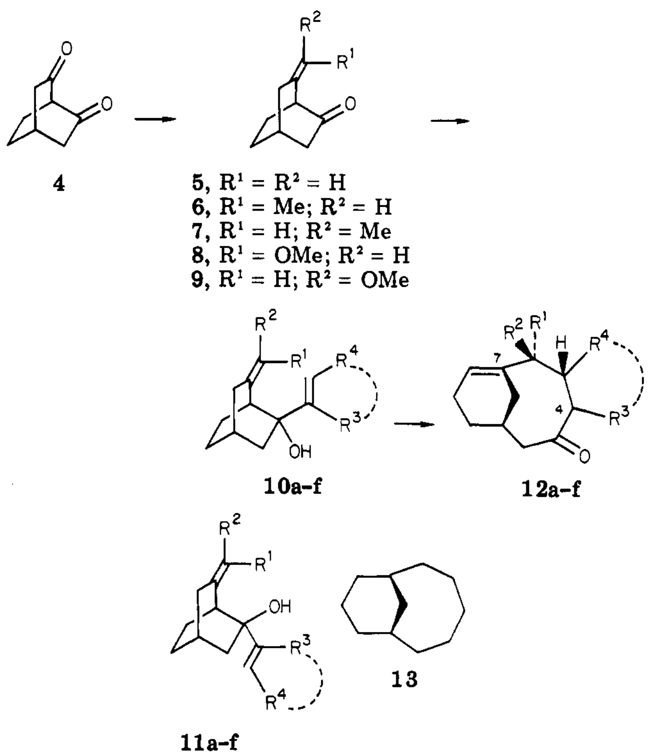


1 **2** **3**

bicyclic dienols related to **3**, and initial model studies were directed toward the synthesis of the bicyclo[2.2.2]octadienol **10a**. Thus, reaction of the readily available dione **4**[8] with methylenetriphenylphosphorane (1.1 equiv, −78 → 25 °C) under salt-free conditions[9] afforded the enone **5** in 80% yield.[10] The addition of vinylmagnesium bromide to **5** (THF, −35 → 25 °C, 1 h) proceeded smoothly to give a 1.6:1 mixture of the diastereomeric alcohols **10a** and **11a** (81%), which were readily separated by HPLC.[11] Several attempts to improve the yield of **10a** by changing the reaction conditions or altering the organometallic reagent were of no avail. Indeed, reaction of **5** with $CH_2{=}CHLi$, $(CH_2{=}CH)_3CuLi_2$, and $(CH_2{=}CH)_2CuCNLi_2$ provided **11a** as the major product. When **10a** was deprotonated with potassium hydride (THF, 25 °C, 10 h), it underwent a remarkably facile anionic oxy-Cope rearrangement to give the desired bicyclo[5.3.1]undec-7-en-3-one (**12a**) in 83% yield. The rearrangement proceeded more rapidly in the presence of 18-crown-6 (1 equiv) or by using hexamethylphosphoramide as a cosolvent, but the yields were slightly lower (75–80%). In accordance with previous observations,[4,6b] it was not surprising that the epimeric alcohol **11a** was recovered unchanged when subjected to the same conditions. The structure of the rearranged product **12a** was easily confirmed by its conversion to the fully saturated hydrocarbon **13** via a straightforward sequence of reactions [(1) H_2 (1 atm)/(5%) Pd–C/EtOH; (2) $HSCH_2CH_2SH/BF_3{\cdot}Et_2O$; (3) Raney nickel (W-2)/$EtOH/\Delta$]. The symmetry of **13** was apparent upon examination of its proton-decoupled ^{13}C NMR spectrum, which exhibited the expected seven lines.[12]

Having thus ascertained that **10a** underwent a facile, alkoxide-accelerated [3,3] sigmatropic rearrangement to give **12a**, we then turned to an examination of the skeletal reorganization of the more highly substituted dienols **10b–f**, which were readily prepared from the dione **4** via the keto olefins **6**, **8**, and **9**.[11,13] For example, upon deprotonation with potassium hydride at room temperature in tetrahydrofuran, each of the dienols **10b–d** were smoothly transformed into the corresponding bicyclo[5.3.1]undec-7-en-3-ones **12b–d** in 70–85% yields.[16] It may be noted that compound **12c** possesses the basic tricyclic framework that is characteristic of the taxane diterpenes. Although the potassium salts derived from an inseparable mixture (3:1) of the geometric isomers **10e** and **10f** failed to undergo rearrangement at room temperature, rearrangement of these salts did occur upon heating in re-

Scheme I



4

5, $R^1 = R^2 = H$
6, $R^1 = Me$; $R^2 = H$
7, $R^1 = H$; $R^2 = Me$
8, $R^1 = OMe$; $R^2 = H$
9, $R^1 = H$; $R^2 = OMe$

10a–f **12a–f**

11a–f **13**

a, $R^1 = R^2 = R^3 = R^4 = H$
b, $R^1 = R^2 = R^4 = H$; $R^3 = Me$
c, $R^1 = R^2 = H$; R^3, $R^4 = -(CH_2)_4-$
d, $R^1 = Me$; $R^2 = R^3 = R^4 = H$
e, $R^1 = OMe$; $R^2 = R^3 = R^4 = H$
f, $R^1 = R^3 = R^4 = H$; $R^2 = OMe$

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(8) Gerlach, H.; Müller, W. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 1030–1031.

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(10) The structure assigned to each compound was in accord with its spectral (^1H, ^{13}C NMR, IR, mass) characteristics. Analytical samples of all new compounds were obtained by chromatography (HPLC) and gave satisfactory combustion analysis (C, H) and/or parent ion identification by high-resolution mass spectrometry. All yields are based upon isolated materials which were >95% pure.

(11) The stereochemical assignments of the diastereomers **10a–f** and **11a–f** rest primarily upon which isomer undergoes [3,3] sigmatropic rearrangement. This assignment is supported by the observation that the vinyl protons at the terminus of the allylic alcohol moiety of **10a–f** appear at higher field (0.1–0.2 ppm) than the corresponding protons of **11a–f**, presumably as a consequence of diamagnetic shielding of these protons by the exocyclic double bond.

(12) ^{13}C NMR ($CDCl_3$) δ 32.8, 31.7, 31.6, 31.3, 28.2, 25.5, 16.0.

(13) The dienols **10b–f** were prepared by standard reactions. Thus, addition of 2-propenylmagnesium bromide to **5** (THF, −35 → 25 °C, 1 h) afforded a mixture (1:1.2; 80%) of the epimeric alcohols **10b** and **11b**, whereas the reaction of **5** with 1-cyclohexenyllithium (THF, 0 °C, 1 h) produced a mixture (1:2; 72%) of **10c** and **11c**. Olefination of **4** with ethylidenetriphenylphosphorane under salt-free conditions[9] gave a mixture (>15:1; 58%) of the isomeric keto olefins **6** and **7**.[14] When this mixture was treated with vinylmagnesium bromide, the dienols **10d** and **11d** (1.7:1; 73%) were obtained as the only isolable products. Treatment of the dione **4** with (methoxymethylene)triphenylphosphorane under salt-free conditions[9] produced an inseparable mixture (3:1; 55%) of methoxymethylene ketones, whose structures have been tentatively assigned as **8** and **9**, respectively. Subsequent addition of vinyl magnesium bromide to this mixture of **8** and **9** provided the epimeric vinyl carbinols **10e,f** and **11e,f** (1:1.2; 68%), each as an inseparable pair (3:1) of geometric isomers. The dienols **10b–f** were readily separated from the diastereomeric alcohols **11b–f** by preparative HPLC.

(14) The stereochemistry about the carbon–carbon double bond of the major geometric isomer **6** was assigned as *Z* on the basis of a comparison of the ^{13}C NMR spectra of **4** and **6** in which all the carbons except the bridgehead carbon at C(1) appear at approximately the same chemical shift. In **6** the C(1) resonance is 6.4 ppm upfield from the corresponding resonance in **4** as a result of the syn relationship of the vinyl methyl with the bridgehead carbon.[15]

(15) Stothers, J. B. In "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972; p 80.

(16) Compound **12b** was obtained as a 1.5:1 mixture of methyl ketones epimeric at C(4). On the other hand, **12c** was produced as a single substance, but the relative stereochemistry at C(4) has not been determined.

fluxing glyme (10 h) to provide a mixture (3:1) of **12e** and **12f** (72%). Once again, the diastereomeric alcohols **11b–f** exhibited no tendency toward either an anionic [3,3] or [1,3][17] rearrangement under the conditions identical with those required for the transformation of **10b–f** → **12b–f**.

Thus, we have unveiled a useful variant of the anionic oxy-Cope rearrangement which allows ready access to the bicyclo[5.3.1]undec-7-ene ring system. The application of this process to the total synthesis of the taxane diterpenes via intermediates related to **2** and **3** is the subject of present investigations and will be reported in due course.

Acknowledgment. We thank the Robert A. Welch Foundation and the National Cancer Institute (CA 21860) for their generous support of this research.

Registry No. 4, 38231-60-6; **5**, 66921-89-9; **6**, 82281-04-7; **7**, 82281-05-8; **8**, 82281-06-9; **9**, 82281-07-0; **10a**, 82281-08-1; **10b**, 82281-09-2; **10c**, 82281-10-5; **10d**, 82281-11-6; **10e**, 82281-12-7; **10f**, 82335-17-9; **11a**, 82335-18-0; **11b**, 82335-19-1; **11c**, 82335-20-4; **11d**, 82335-21-5; **11e**, 82335-22-6; **11f**, 82335-23-7; **12a**, 82281-13-8; **12b**, 82281-14-9; **12c**, 82281-15-0; **12d**, 82281-16-1; **12e**, 82281-17-2; **12f**, 82281-18-3; **13**, 82281-19-4; 2-propenyl bromide, 106-95-6; 1-cyclohexenyllithium, 37609-34-0; ethylidenetriphenylphosphorane, 1754-88-7; (methoxymethylene)triphenylphosphorane, 20763-19-3; methylenetriphenylphosphorane, 3487-44-3.

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[17] For example, see: (a) Franzus, B.; Scheinbaum, M. L.; Waters, D. L.; Bowlin, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 1241–1247. (b) Thies, R. W.; Seitz, E. P. *J. Chem. Soc., Chem. Commun.* **1976**, 846–847. (c) Wilson, S. R.; Mao, D. T. *J. Chem. Soc., Chem. Commun.* **1978**, 479–480. (d) Danheiser, R. L.; Martinez-Davila, C.; Auchus, R. J.; Kadonaga, J. T. *J. Am. Chem. Soc.* **1981**, *103*, 2443–2446. (e) Danheiser, R. L.; Martinez-Davila, C.; Sard, H. *Tetrahedron* **1981**, *37*, 3943–3950. (f) Zoeckler, M. T.; Carpenter, B. K. *J. Am. Chem. Soc.* **1981**, *103*, 7661–7663.

[18] Recipient of National Institutes of Health (National Cancer Institute) Research Career Development Award (1980–1985).

Stephen F. Martin,*[18] James B. White, Rolf Wagner
Department of Chemistry
University of Texas at Austin
Austin, Texas 78712

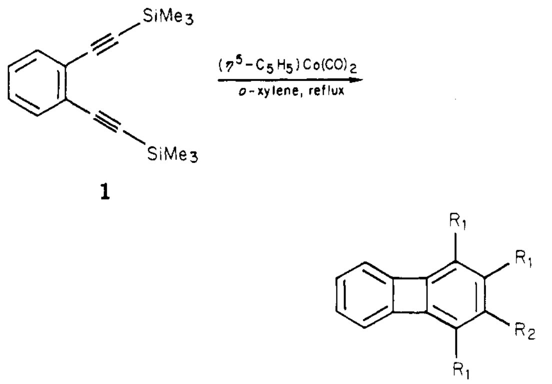
Received April 13, 1982

A New Route to Biphenylene via "Vollhardt Cyclization" from *o*-Bis[(trimethylsilyl)ethynyl]benzene

Summary: Reaction of *o*-bis[(trimethylsilyl)ethynyl)]-benzene with cyclopentadienyldicarbonylcobalt as catalyst and reagent is described, yielding biphenylene derivatives and cobalt complexes bearing novel organic ligands, respectively.

Sir: In the last decade, cobalt-catalyzed intra- and intermolecular acetylene and olefin cooligomerizations have been investigated intensively,[1,2] yielding a number of natural products[3] and species of theoretical interest.[4] 3-Hexene-1,5-diyne derivatives, however, have not played a role, hitherto, although interesting strained molecules might be synthesized.

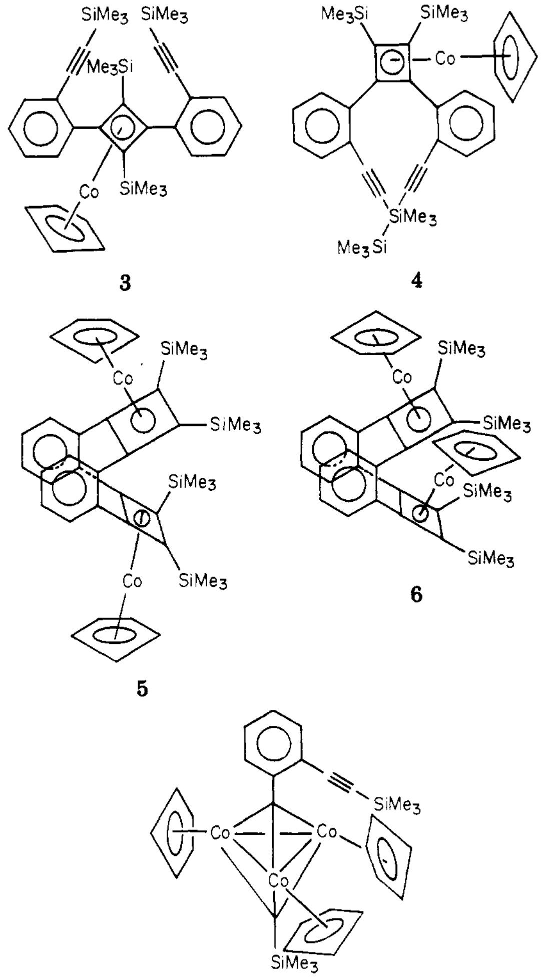
Scheme I



1

2, R_1 = $SiMe_3$; R_2 = $(o\text{-}Me_3SiC{\equiv}C)C_6H_4$

Chart I



3 4 5 6 7

With use of syringe–pump techniques 1,2-bis[(trimethylsilyl)ethynyl]benzene (**1**)[5] dimerizes in refluxing *o*-xylene in the presence of catalytic amounts of (η^5-cyclopentadienyl)dicarbonylcobalt to yield biphenylene derivative **2** in 72% (Scheme I).[6,7]

Under the same reaction conditions in a cobalt-mediated cyclization (ratio of **1** and $CpCo(CO)_2$ = 1:1) **2** was obtained in 8% yield in addition to a variety of cobalt complexes

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[1] (a) Vollhardt, K. P. C. *Acc. Chem. Res.* **1977**, *10*, 1. (b) Gesing, E. R. F.; Sinclair, J. A.; Vollhardt, K. P. C. *J. Chem. Soc., Chem. Commun.* **1980**, 286.

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[3] Funk, R. L.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1980**, *102*, 5253 and references therein.

[4] (a) Saward, C. J.; Vollhardt, K. P. C. *Tetrahedron Lett.* **1975**, 4539. (b) Duclos, R. I., Jr.; Vollhardt, K. P. C.; Yee, L. S. *J. Organomet. Chem.* **1979**, *174*, 109.

[5] Gesing, E. R. F. *J. Chem. Soc., Chem. Commun.*, **1982**, 426.

[6] Mass spectrum, m/e 540 (M^+, 12); ^1H NMR (90 MHz, acetone-d_6) δ 7.50–7.17 (m, 4 H), 6.83 (s, 4 H), 0.47 (s, 9 H), 0.07 (s, 9 H), −0.10 (s, 18 H); ^1H NMR (90 MHz, CCl_4) δ 7.43–7.10 (m, 4 H), 6.67 (s, 4 H), 0.40 (s, 9 H), 0.03 (s, 9 H), −0.17 (s, 9 H), −0.18 (s, 9 H); IR (CH_2Cl_2) 2960 (s), 2900 (s), 2160 (s), 1240 (s) cm^{-1}.

[7] All new compounds gave satisfactory analytical data and/or high-resolution mass spectral data.

0022-3263/82/1947-3192$01.25/0