(73%) the trisubstituted pyrrolidine **9**, $[\alpha]^{25}_{D}$ −72.04 °C (c 0.98, $CHCl_3$), as a single stereoisomer.[12] All syn stereochemistry of the product is confirmed by nuclear Overhauser effect difference spectroscopy (NOEDS) (500 MHz) of **9** which shows distinct enhancements in the 2-H, 4-H, and 7-H signals when the 3-H is irradiated.[13] Although there are four possible diastereomers which could have been produced from the azomethine ylide intermediate, it is noteworthy that only one of these with all syn stereochemistry (**9**) is produced in the cycloaddition. The extremely high diastereofacial selectivity for the cycloaddition of **7** is best in accord with the *anti*-azomethine ylide[14] **8** as the reactive conformer in which the bulky benzyloxymethyl group takes the most stable spatial arrangement to give the all syn product **9**.

Upon sequential double debenzylation, *N*-protection, glycol cleavage, esterification,[15] and *N*-reprotection, the adduct **9** yields (26% overall)[16] the dimethyl ester **10**, $[\alpha]^{24}_{D}$ −9.28° (c 0.97, $CHCl_3$). Treatment of **10** with sodium hydride in the presence of DBU allows smooth epimerization[17] (94%) to afford the trans 2/3 compound **11**, $[\alpha]^{24}_{D}$ +1.11° (c 0.72, $CHCl_3$), as a single product. Oxidation[18] of **11**, followed by esterification of the resulting acid furnishes (64%) the known triester[4,19] **12**, $[\alpha]^{28}_{D}$ +12.23° (c 0.77, $CHCl_3$) [lit.[4] +6.5° (c 0.73, $CHCl_3$)], with 2*S*,3*R*,4*S* configuration. Oxidation of **12** with peracid gives (72%) the *N*-oxide **13**, $[\alpha]^{22}_{D}$ +19.04° (c 1.22, $CHCl_3$), which is treated with trifluoroacetic anhydride[20] to give (64%) the pyridone[4,5,19] **14**, $[\alpha]^{26}_{D}$ −127.48° (c 1.02, $CHCl_3$) [lit.[4] −114.3° (c 0.74, $CHCl_3$)]. Conversion of **14** into natural acromelic acid A (**1**) has already been done in a satisfactory yield.[4]

Synthesis of acromelic acid B (**2**) from (*S*)-*O*-benzylglycidol (**3**) employing the same methodology is currently under investigation.

Acknowledgment. We thank Professor Haruhisa Shirahama, Faculty of Science, Hokkaido University, for providing spectra of synthetic intermediates.

Registry No. 1, 86630-09-3; **3**, 16495-13-9; **4**, 109552-75-2; **5**, 109552-76-3; **7**, 109552-77-4; **9**, 109552-78-5; **10**, 109552-79-6; **11**, 109552-80-9; **12**, 103314-35-8; **13**, 103314-36-9; **14**, 103335-11-1; $BrCH_2CHBrCOCl$, 18791-02-1; $PhCH_2NH_2$, 100-46-9; lithium 2-(2′-methyl-5′-pyridyl)acetylide, 109552-81-0.

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(11) Xylene[7] in place of *o*-dichlorobenzene may be used; however, more vigorous conditions (sealed tube, 300 °C, 7 min) were required to obtain **9** in 68% yield.

(12) ^1H NMR ($CDCl_3$, 500 MHz) δ 0.93 (1 H, 6 lines, C_6-$H(\alpha)$), 1.75 (1 H, 8 lines, C_6-$H(\beta)$), 2.51 (3 H, s, py_2Me), 2.86 (1 H, dd, J = 7.5 and 10 Hz, C_5-$H(\alpha)$), 3.05 (1 H, dd, J = 2 and 10 Hz), C_5-$H(\beta)$), 3.08 (1 H, 9 lines, C_3-H), 3.32 (1 H, br t, J = 7.5 Hz, C_4-H), 3.39 (1 H, dd, J = 10 and 5 Hz, C_8-H), 3.48 (1 H, d, J = 11.25 Hz, C_2-H), 3.55 (1 H, dd, J = 10 and 6.25 Hz, C_8-H), 3.60 (1 H, d, J = 12.5 Hz, -N-benzyl-H), 4.38 (1 H, 10 lines, C_7-H), 4.48 (1 H, d, J = 15 Hz, -O-benzyl-H), 4.51 (1 H, d, J = 15 Hz, -O-benzyl-H), 4.56 (1 H, d, J = 12.5 Hz, -N-benzyl-H), 7.10 (1 H, d, J = 8.6 Hz, py_3-H), 7.15–7.5 (10 H, m, 2 × C_6H_5), 7.75 (1 H, dd, J = 2.8 and 8.6 Hz, py_4-H), 8.2 (1 H, d, J = 2.8 Hz, py_6-H). No other diastereomeric adducts are detected from the reaction mixture. Enantiomeric homogenity of the adduct **9** is ascertained by examination of the ^1H NMR spectra (500 MHz) of (*R*)- and (*S*)-MTPA esters derived from the primary alcohol (**9**: -OBn = -OH) which is obtained from **9** by selective *O*-debenzylation (BBr_3, −90 °C in CH_2Cl_2, 10 min).

(13) DeShong, P.; Dicken, C. M.; Staib, R. R.; Freyer, A. J.; Weinreb, S. M. *J. Org. Chem.* **1982**, *47*, 4397.

(14) The generation of a pyrrolidine with all syn stereochemisry via an *anti*-azomethine ylide such as **8** is not unexpected in light of DeShong's results with related systems.[7]

(15) The carbamate bond is also cleft under these conditions.

(16) This sequence of reactions is carried out without purifying each intermediate.

(17) The 2,3-stereochemistry of the kainoids has shown to be readily distinguishable by ^1H NMR spectrum comparison.[1a] Generally, C_2–H of trans isomers resonates at higher field (ca. 0.5 ppm) than that of cis isomers; for example **10** exhibits at δ 4.05, while **11** exhibits at δ 4.50.

(18) Cf.: Jerchel, D.; Heider, J.; Wagner, H. *Justus Liebigs Ann. Chem.* **1958**, *613*, 153.

(19) The compound shows the same spectra (IR and ^1H NMR (500 MHz)) as those of an authentic material[4] though there is discrepancy in optical rotations.

(20) Konno, K.; Hashimoto, K.; Shirahama, H.; Matsumoto, T. *Heterocycles* **1986**, *24*, 2169.

Synthesis of 10-Selenatricyclo[3.3.3.0^{3,7}]undec-3(7)-ene. X-ray Structure of an Alkene Containing a Pyramidalized Double Bond

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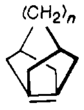
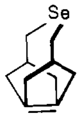
Received April 27, 1987

Recently we have reported the preparation of the n = 1[2] and n = 2[3] members of a homologous series of pyramidalized alkenes **1**, the spectroscopic characterization of the n = 2 olefin in matrix isolation,[4] and the reverse vinylcyclopropane rearrangement that these alkenes undergo on pyrolysis or on photolysis.[5] In this communication we describe the synthesis of the 10-selena derivative **2** of the n = 3 olefin.



1



2

A previous attempt to synthesize the n = 3 hydrocarbon **1** involved preparation of the diol precursor by transannular reductive ring closure[6] of bicyclo[3.3.3]undecane-3,7-dione. Unfortunately, Demjanov–Tiffeneau ring expansion of bicyclo[3.2.2]nonane-2,5-dione led, instead, to the 2,6-isomer of the desired 3,7-diketone.[7] Consequently, we turned our attention to a different route (Scheme I), involving expansion of the bridge between C-1 and C-5 in diol **3**, which had previously served as a precursor of the 9,10-benzo derivative of the n = 2 alkene.[8]

After protection of the diol as the acetonide, the benzene ring in **4** could be oxidatively cleaved, either with RuO_4[9] or O_3/H_2O_2,[10] to afford diacid **5**[11] in 60–80% yield. The diacid was reduced with $LiAlH_4$ to diol **6**,[11] which was converted to dimesylate **7**[11] and thence to diiodide **8**.[11] The diiodide was treated with 1 equiv of KSeCN[12] in acetone, and the crystalline monoselenacyanate **9**[11] was purified by flash chromatography and recrystallization. Ring closure was effected by slowly adding **9** to a 1:9 ethanol–THF solution of $NaBH_4$[12] under high dilution conditions, and **10**,[11] mp 120–121 °C, was isolated in 70% yield after chromatography and sublimation. The acetonide protecting group was removed by acid hydrolysis, and tricyclic diol **11**,[11] mp 267–269 °C, was converted to dimesylate **12**, which was reduced with sodium naphthalane in THF.[13] From this reaction alkene **2**[11] was isolated in 90% yield

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(1) (a) University of Washington. (b) National Science Foundation Small College Faculty Summer Research Fellow. (c) Cornell University.

(2) Renzoni, G. E.; Yin, T.-K.; Borden, W. T. *J. Am. Chem. Soc.* **1986**, *108*, 7121.

(3) Renzoni, G. E.; Yin, T.-K.; Miyake, F.; Borden, W. T. *Tetrahedron* **1986**, *42*, 1581.

(4) Radziszewski, J. G.; Yin, T.-K.; Miyake, F.; Renzoni, G. E.; Borden, W. T.; Michl, J. *J. Am. Chem. Soc.* **1986**, *108*, 3544.

(5) Yin, T.-K.; Radziszewski, J. G.; Renzoni, G. E.; Downing, J. W.; Michl, J.; Borden, W. T. *J. Am. Chem. Soc.* **1986**, *109*, 820.

(6) Borden, W. T.; Ravindranathan, T. *J. Org. Chem.* **1971**, *36*, 4125.

(7) Greenhouse, R.; Borden, W. T.; Ravindranathan, T.; Hirotsu, K.; Clardy, J. *J. Am. Chem. Soc.* **1977**, *99*, 6955.

(8) Greenhouse, R.; Borden, W. T.; Hirotsu, K.; Clardy, J. *J. Am. Chem. Soc.* **1977**, *99*, 1664.

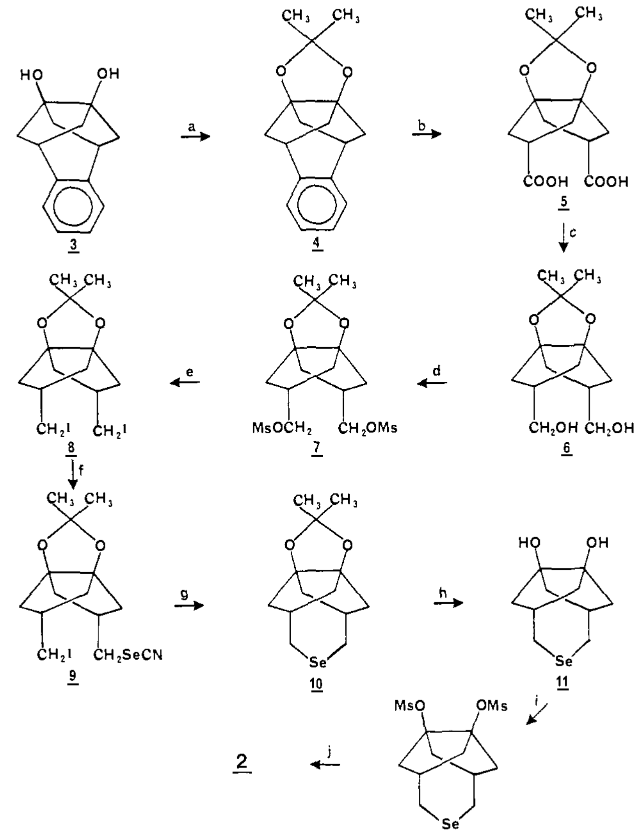
(9) Carlsen, P. H. J.; Katsuki, T.; Martin, V. S.; Sharpless, K. B. *J. Org. Chem.* **1981**, *46*, 3936.

(10) Berson, J. A.; Pedersen, L. D.; Carpenter, B. K. *J. Am. Chem. Soc.* **1976**, *98*, 122.

(11) This compound gave spectral and analytical data consistent with the structure assigned.

(12) Otsubo, T.; Ogura, F.; Yamaguchi, H.; Higuchi, H.; Misumi, S. *Synth. Commun.* **1980**, *10*, 595. We are indebted to Professor Reg Mitchell for calling our attention to this method.

Scheme I[a]



[a](a) Acetone/HCl, reflux, 22 h, 98%. (b) $RuO_2/NaIO_4-H_2O/CH_3CN/CCl_4$ (3:2:2), 24 h, 80%. (c) $LiAlH_4$-THF, reflux, 24 h, 87%. (d) MsCl-Et_3N/CH_2Cl_2, -10 °C, 30 m, 76%. (e) NaI-acetone, reflux, 96 h, 95%. (f) KSeCN-acetone, reflux, 2 h, 60%. (g) $NaBH_4$-THF/EtOH (9:1), 40 °C, 65 h, 70%. (h) 20% aqueous HOAc, reflux, 24 h, 94%. (i) MsCl-Et_3N/CH_2Cl, -10 °C, 30 m, 70%. (j) Na/naphthalene-THF, -50 °C, 90%.

after purification by chromatography and sublimation.

The alkene was characterized by ^{1}H NMR [($CDCl_3$) δ 2.07 (d, 4 H, J = 12.9 Hz), 2.57 (d of d, 4 H, J = 12.9 and 2.5 Hz), 2.80 (m, 2 H), and 2.85 (d, 4 H, J = 3.4 Hz)] and by ^{13}C NMR [($CDCl_3$) δ 35.54, 38.24, 49.24, and 150.74]. These spectra indicate that at room temperature the selenium bridge is flipping rapidly enough to confer on **2** effective C_{2v} symmetry on the NMR time scale.

The chemical shift of the doubly bonded carbons in **2** does not seem exceptional, since in bicyclo[3.3.0]oct-1(5)-ene these carbons are reported to be at δ 146.0.[14] However, the double bond stretch at 1625 cm^{-1} in **2** is well below that (1685 cm^{-1})[15] in the unbridged bicyclic alkene. Moreover, whereas the double bond stretch in bicyclo[3.3.0]oct-1(5)-ene can only be observed in the Raman spectrum, that in **2** is both IR and Raman active. As is the case in **1**, n = 2,[4] pyramidalization of the doubly bonded carbons in **2** probably causes the double bond stretching mode to have a transition dipole, which is oriented perpendicular to the C–C bond.

Presumably, pyramidalization of these carbons is also responsible for the fact that attempted purification of **2** by preparative thin-layer chromatography led to the isolation of the epoxide of **2**.[11] Epoxide formation on exposure to O_2 appears to be a characteristic reaction of strained alkenes.[16]

Although **2** is a solid, all our attempts to obtain crystals met with failure. Taking advantage of the nucleophilicity of selenium, we prepared the methylselenonium triflate salt[11] by reaction of **2** with methyl triflate. This salt gave crystals, mp 120–122 °C, which were suitable for an X-ray structure determination.[17]

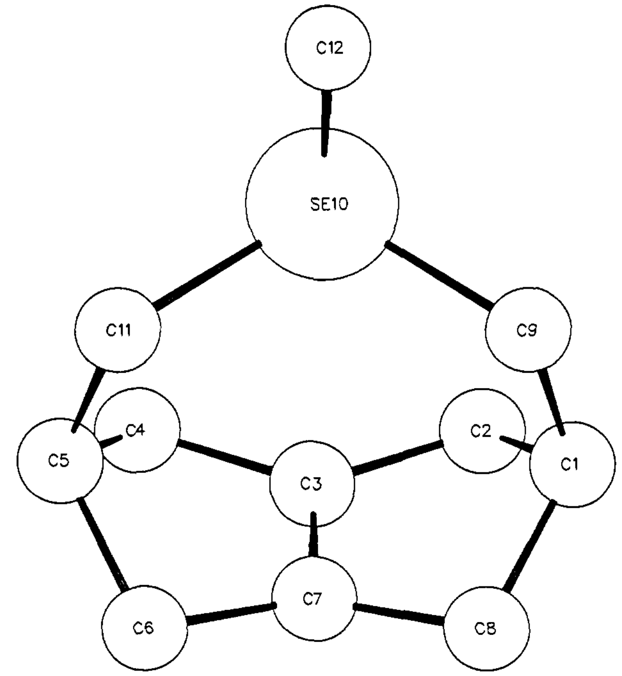


Figure 1. X-ray structure of the methylselenonium salt of **2**.

The structure of the methylselonium ion is shown in Figure 1. The structural parameters[18] reveal how the bicyclo[3.3.0]octene moiety accommodates itself to the three-atom bridge between C-1 and C-5. The five-membered rings pucker strongly, giving intraring bond angles of about 100° at the four allylic carbons and just over 100° at C-1 and C-5. The C–C–Se bond angles in the three-atom bridge are also distorted from the tetrahedral value, but they are opened to about 115° to help the bridge span the distance between C-1 and C-5. However, the C–Se–C bond angle of 111.4° in the bridge appears to be the most highly distorted in the molecule, since this angle is more than 12° larger than either of the two CH_3–Se–CH_2 bond angles. In addition, both CH_2–Se bond lengths are more than 0.05 Å longer than the CH_3–Se bond length.

Despite these accommodations between the bicyclo[3.3.0]octene moiety and the three-atom bridge, there is still appreciable pyramidalization at the doubly bonded carbon atoms. As shown in Figure 1, the carbon anti to the selenium atom is the more highly pyramidalized. The bisector of the bond angle between C-7 and the two allylic carbons attached to it makes an angle of 20.3° with the extension of the bond between C-3 and C-7, whereas the analogously defined pyramidalization angle at C-3 is only 12.3°. The pyramidalization angle at C-7 is comparable to that found in 9,9′,10,10′-tetradehydrodianthracene[19] but slightly smaller than that observed in the closely related tricyclo[4.2.2.2^{2,5}]dodeca-1,5-diene.[20]

Molecular mechanics calculations using MM2[21] predict structural features for **1**, n = 3, that are qualitatively similar to those found experimentally in the salt of **2**. These include a pyramidalization angle at the doubly bonded carbon, anti to the three-atom bridge, which is larger than that at the syn carbon. However, the fact that C–C bond lengths of 1.55 Å, which are predicted for the three-atom bridge in **1**, n = 3, are considerably

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(13) Carnahan, J. C.; Closson, W. D. *Tetrahedron Lett.* **1972**, 3447.

(14) Becker, K. B. *Helv. Chim. Acta* **1977**, *60*, 68.

(15) Warner et al. (Warner, P.; LaRose, R.; Schleis, T. *Tetrahedron Lett.* **1974**, 1409.) have reported 1675 cm^{-1}.

(16) Wiberg, K. B.; Matturro, M.; Okarma, P. J.; Jason, M. E. *J. Am. Chem. Soc.* **1984**, *106*, 2194 and references cited therein.

(17) The crystals belonged to the space group *Pbca* with a = 7.754 (1), b = 16.459 (2), and c = 22.933 (3) Å. The final R factor was 0.066 for the 1370 observed reflections.

(18) A complete listing is available as Supplementary Material.

(19) Viavattene, R. L.; Greene, F. D.; Cheung, L. D.; Majeste, R.; Trefonas, L. M. *J. Am. Chem. Soc.* **1974**, *96*, 4342.

(20) Wiberg, K. B.; Adams, R. D.; Okarma, P. J.; Matturro, M.; Segmuller, B. *J. Am. Chem. Soc.* **1984**, *106*, 2200.

(21) Allinger, N. J. *J. Am. Chem. Soc.* **1977**, *99*, 8127.

shorter than the C–Se bond lengths of 1.97 Å found in the salt of **2**, causes the distortions in **1**, $n = 3$, to be quantitatively larger. For example the pyramidalization angles at the double-bonded carbons are predicted to be 30° and 33° in **1**, $n = 3$.[22] Therefore, the finding that **2** is an isolable molecule, stable at room temperature, makes the hydrocarbon (**1**, $n = 3$) an especially attractive target for synthesis and study.

Acknowledgment. We thank the National Science Foundation for support of this work.

Supplementary Material Available: Crystallographic data for the methylselenonium triflate salt of **2**—crystal data and summary of data collection and refinement, fractional coordinates and thermal parameters, anisotropic thermal parameters, interatomic distances, and interatomic angles (5 pages). Ordering information is given on any current masthead page.

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[22] There is some evidence that MM2 may tend to overestimate the amount of pyramidalization in **1**, $n = 3$.[4]

Preparation and Characterization of Molecule-Based Transistors with a 50-nm Source-Drain Separation with use of Shadow Deposition Techniques: Toward Faster, More Sensitive Molecule-Based Devices

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We report preparation and characterization of the molecule-based transistor in Figure 1a having a significantly smaller ($\sim$50 nm vs. 1.5 μm) source-drain separation and smaller (10^{-14} vs. 10^{-12} mol) amount of redox polymer comprising the channel compared to previously reported[1] devices like that in Figure 1b. The new microstructure with 50-nm source-drain spacing can be prepared by shadow deposition techniques[2] avoiding the need for X-ray[3] or e$^-$ beam[4] lithography. The 50-nm spacing for the open-faced sandwich structure rivals the smallest spacing achievable with conventional sandwich arrangements of electrode/polymer/electrode used to demonstrate the first "bilayer" assemblies.[5]

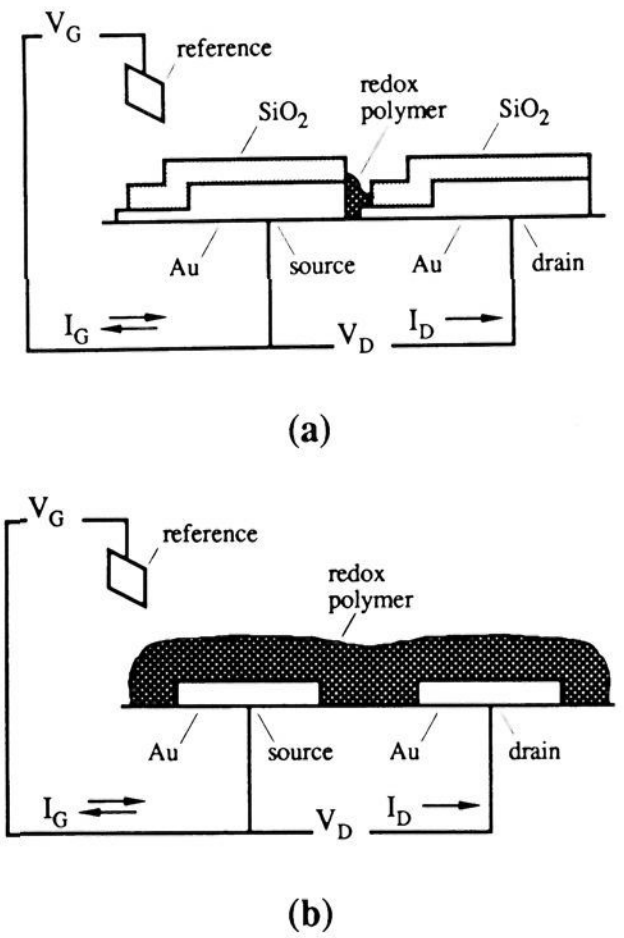
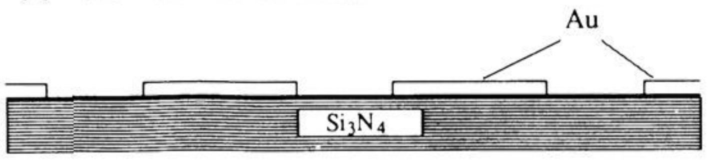
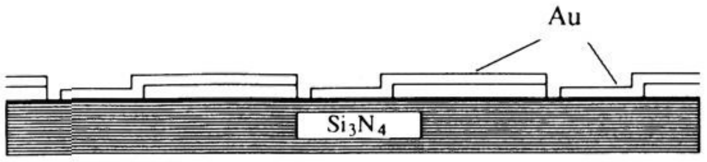


Figure 1. (a) Device structure reported here and (b) previously.[1d]

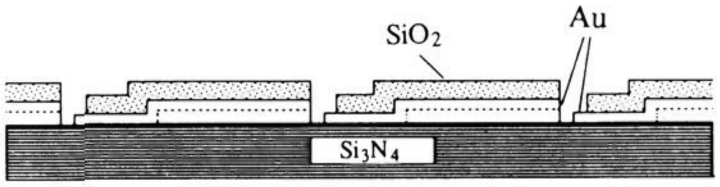
(a) AS FABRICATED



(b) **Au SHADOWED**



(c) **SiO$_2$ SHADOWED**



(d) **POLYMER MODIFIED**

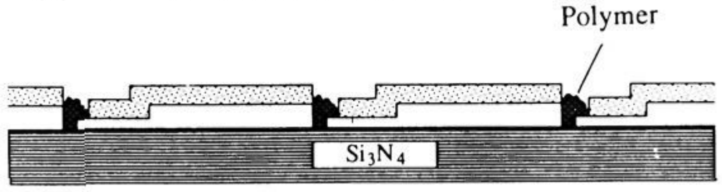


Figure 2. Fabrication sequence for a 50-nm device.

Figure 2 shows the sequence used to prepare the new microstructure in Figure 1a. The procedure begins with a Si_3N_4-coated Si wafer of microelectrode arrays previously described.[1a] Each chip on the wafer consists of eight, individually addressable Au microelectrodes each $\sim$50 μm long × 2.5 μm wide × 0.1 μm thick with spacings between microelectrodes of $\sim$1.5 μm. The first step involves a line of sight e$^-$ beam deposition of 50 nm of Au onto the wafer at an angle $\propto$ as illustrated in Figure 3. Generally, prior to Au deposition 5 nm of Cr is deposited as an adhesion layer. The line of sight deposition of Au results in a larger ($\sim$4 μm wide) microelectrode than the original (2.5 μm wide), but the spacing can be closed to 50–100 nm as established by scanning electron microscopy (SEM), Figure 4. Variation of $\propto$ gives rise to variation in the spacing in a manner consistent with the length of the expected shadow. From SEM it is evident that imperfections on the edges of the original microelectrodes give rise to uneven

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[1] (a) Kittlesen, G. P.; White, H. S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 7389. (b) Paul, E. W.; Ricco, A. J.; Wrighton, M. S. *J. Phys. Chem.* **1985**, *89*, 1441. (c) Thackeray, J. W.; White, H. S.; Wrighton, M. S. *J. Phys. Chem.* **1985**, *89*, 5133. (d) Lofton, E. P.; Thackeray, J. W.; Wrighton, M. S. *J. Phys. Chem.* **1986**, *90*, 6080.

[2] (a) Dean, R. H.; Matarese, R. J. *IEEE Trans. Electron Devices* **1975**, *ED-22*, 358. (b) Dolan, G. J. *Appl. Phys. Lett.* **1977**, *31*, 337. (c) Speidell, J. L. *J. Vac. Sci. Technol.* **1981**, *19*, 693. (d) Holdeman, L. B.; Barber, R. C.; Abita, J. L. *J. Vac. Sci. Technol.* **1985**, *B3*, 956.

[3] (a) Flanders, D. C. *Appl. Phys. Lett.* **1980**, *36*, 93. (b) Chou, S. Y.; Smith, H. I.; Antoniadis, D. A. *J. Vac. Sci. Technol.* **1985**, *B3*, 1587. (c) Smith, H. I. *J. Vac. Sci. Technol.* **1986**, *B4*, 148.

[4] (a) Crewe, A. V. *J. Vac. Sci. Technol.* **1979**, *16*, 255. (b) Howard, R. E.; Hu, E. L.; Jackel, L. D.; Grabbe, P.; Tennant, D. M. *Appl. Phys. Lett.* **1980**, *36*, 592. (c) Dix, C.; Flavin, P. G.; Hendy, P.; Jones, M. E. *J. Vac. Sci. Technol.* **1985**, *B3*, 131. (d) Emoto, F.; Gamo, K.; Namba, S.; Samoto, N.; Shimizu, R. *Jpn. J. Appl. Phys.* **1985**, *24*, L809.

[5] (a) Pickup, P. G.; Murray, R. W. *J. Am. Chem. Soc.* **1983**, *105*, 4510. (b) Pickup, P. G.; Leidner, C. R.; Denisevich, P.; Murray, R. W. *J. Electroanal. Chem.* **1984**, *164*, 39. (c) Pickup, P. G.; Kutner, W.; Leidner, C. R.; Murray, R. W. *J. Am. Chem. Soc.* **1984**, *106*, 1991. (d) Morishima, Y.; Fukushima, Y.; Nozakura, S. *J. Chem. Soc., Chem. Commun.* **1985**, *13*, 912. (e) Elliott, C. M.; Redepenning, J. G.; Balk, E. M. *J. Electroanal. Chem.* **1986**, *213(2)*, 203. (f) Chidsey, C. E. D.; Murray, R. W. *Science (Washington, DC)* **1986**, *231*, 25.

0002-7863/87/1509-5526$01.50/0