The Reaction of 1,3,5-Trinitrobenzene with Methoxide and Hypochlorite Ions†

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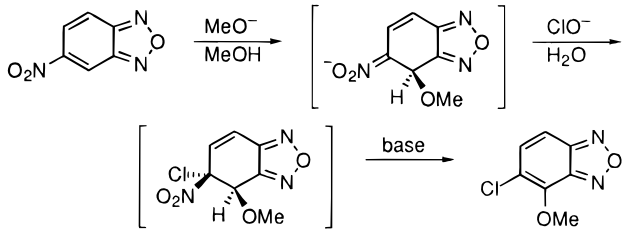
Some years ago we reported a novel reaction involving various heterocyclic systems in which an aromatic nitro substituent and an adjacent ring hydrogen are replaced by chloro and methoxy substituents, respectively, through the action of a combination of methoxide and hypochlorite ions in aqueous methanol solution.[1] In Scheme 1 we show a representative example of this so-called chloromethoxy reaction along with our hypothesis about its three-step mechanism: nucleophilic addition of methoxide ion, electrophilic chlorination by attack of hypochlorite ion trans to the methoxy group, and base-induced E2 elimination. All of the examples of this reaction in our original work[1] and also in subsequent work[2] involved heterocycles. In order to test our view that there is no special role of the heterocycle in these systems other than to provide electron-withdrawing stabilization for the initial Meisenheimer-like intermediate we decided to determine whether 1,3,5-trinitrobenzene (**1**), a nonheterocyclic system that readily forms a Meisenheimer adduct, would undergo the chloromethoxy reaction.

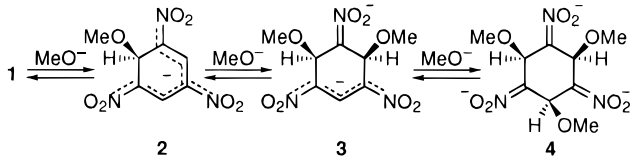
It was first reported more than a century ago[3] that a bright red color is produced when a methanol solution of 1,3,5-trinitrobenzene (**1**) is treated with methoxide ion (generated by dissolving potassium hydroxide in the solution). This phenomenon has been studied extensively in the ensuing years. It is now understood,[4] as illustrated in Scheme 2, that with 1 equiv of methoxide ion these red solutions contain predominantly the simple monoanionic Meisenheimer adduct **2**, and that with an excess of methoxide ion the dianionic adduct **3** is produced. Although the trianionic adduct **4** seems not to have been reported specifically for **1** and methoxide ion, analogous triple adducts of **1** are known for other nucleophiles.[4a]

We now report that treatment of these red methanolic solutions with aqueous sodium hypochlorite gives 3,5-dichloro-2,4,6-trimethoxynitrobenzene (**5**) as the major isolated product and 1,3,5-trichloro-2,4,6-trimethoxybenzene (**6**) as a minor isolated product (Scheme 3).[5] Although products **5** and **6** are easily isolated the yields are only 14% and 1%, respectively; the dominant reaction

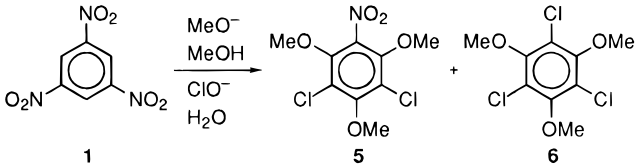
Scheme 1



Scheme 2



Scheme 3



of **1** under our reaction conditions is the well-precedented total degradation of the aromatic ring by reaction with hypochlorite ion to generate chloropicrin, Cl_3CNO_2, and carbon dioxide.[6] This type of degradative reaction apparently is not a major competing pathway in the previously reported heterocyclic examples of the chloromethoxy reaction, which give yields in the 40−90% range.[1,2] The isolation of products **5** and **6** from the reaction of **1** suggests that chemistry analogous to that illustrated in Scheme 1 can indeed take place in a nonheterocyclic system.

As depicted in Scheme 4 the structure of product **5** was established by reducing it to amine **7**, converting **7** to 1,3-dichloro-2,4,6-trimethoxybenzene (**8**) by treatment with nitrous acid and hypophosphorous acid, and comparing this material to an authentic sample of **8** prepared by the known reaction[7] of 1,3,5-trimethoxybenzene (**9**) with phosphorus pentachloride. The spectral properties and elemental analysis of product **5** provide additional support for the assigned structure. Product **6** is a previously known compound.[8] The mp and spectral properties of our sample of **6** are consistent with the assigned structure. We also confirmed the identity of this product by comparing it to an authentic sample of **6** prepared by a Sandmeyer reaction of amine **7** as shown in Scheme 4.

The transformation of 1,3,5-trinitrobenzene (**1**) to a mixture of **5** and **6** obviously involves a multistep pathway that is very complicated mechanistically. At one mechanistic extreme one might imagine that products **5** and **6** each are formed by three consecutive chloromethoxy-type reactions. In this context (Scheme 5) the mecha-

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(1) (a) Mallory, F. B.; Varimbi, S. P. *J. Org. Chem.* **1963**, *28*, 1656. (b) Mallory, F. B.; Wood, C. S.; Hurwitz, B. M. *J. Org. Chem.* **1964**, *29*, 2605.

(2) Eckroth, D. R.; Cochran, T. G.; Taylor, E. C. *J. Org. Chem.* **1966**, *31*, 1303.

(3) (a) Hepp, P. *Liebigs Ann. Chem.* **1882**, *215*, 345. (b) Lobry de Bruyn, C. A.; Van Leent, F. H. *Recl. Trav. Chim. Pays-Bas* **1895**, *14*, 150.

(4) (a) Strauss, M. J. *Chem. Rev.* **1970**, *70*, 667. (b) Servis, K. L. *J. Am. Chem. Soc.* **1967**, *89*, 1508. (c) Bernasconi, C. F.; Bergstrom, R. G. *J. Am. Chem. Soc.* **1974**, *96*, 2397.

(5) A small amount (3% yield) of 3,5-dinitroanisole also is obtained under these reaction conditions. This compound is the major product from the reaction of 1,3,5-trinitrobenzene (**1**) with methoxide ion in methanol solution in the absence of hypochlorite ion. (a) Lobry de Bruyn, C. A. *Recl. Trav. Chim. Pays-Bas* **1890**, *9*, 208. (b) Reverdin, F. *Organic Syntheses*; Wiley: New York, 1932; Collect. Vol. I, p 219. (c) Gold, V.; Rochester, C. H. *J. Chem. Soc.* **1964**, 1692.

(6) Butler, A. R.; Wallace, H. F. *J. Chem. Soc. (B)* **1970**, 1758.

(7) Lloyd, G.; Whalley, W. B. *J. Chem. Soc.* **1956**, 3209.

(8) Strating, J.; Thijs, L.; Zwanenburg, B. *Recl. Trav. Chim. Pays-Bas* **1966**, *85*, 291.

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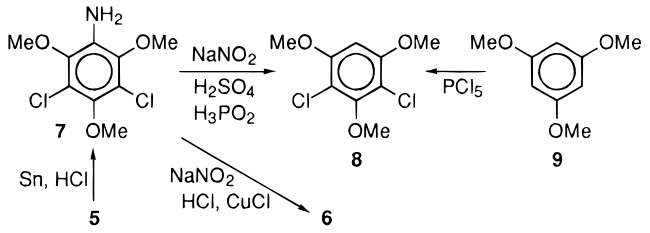
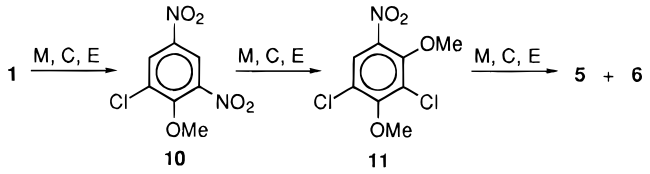
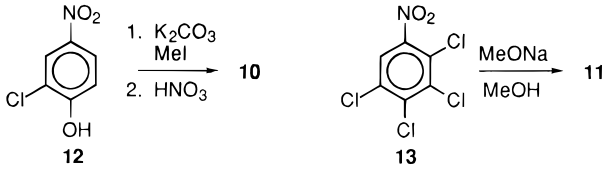
Scheme 4



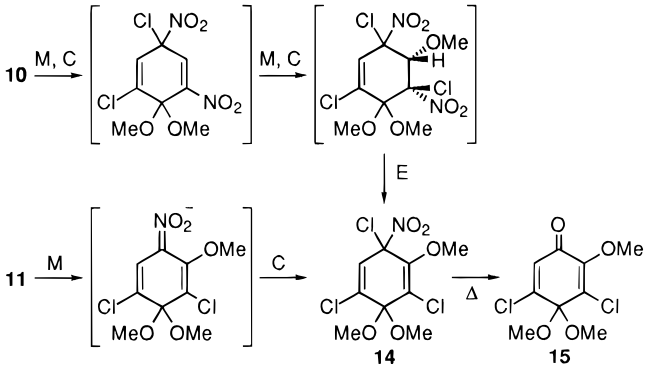
Scheme 5



Scheme 6



Scheme 7

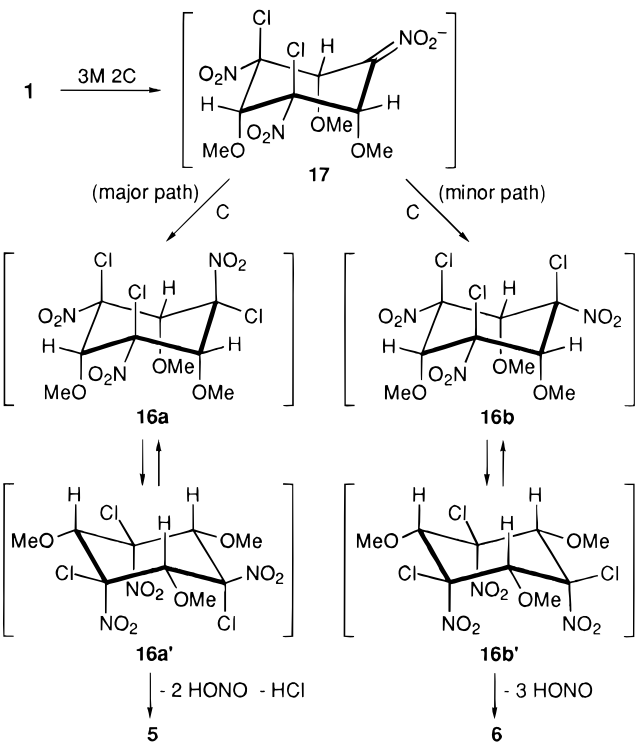


nistic pathways each would involve methoxide addition (M), chlorination (C), and elimination (E) steps in the sequence M-C-E-M-C-E-M-C-E, and compounds **10** and **11** would be formed as intermediates. To test the validity of this idea we synthesized the putative intermediates **10** and **11** by the reactions shown in Scheme 6. By demonstrating that these independently synthesized samples of compounds **10** and **11** fail to undergo conversion to products **5** and **6** under the reaction conditions employed for the formation of these two products from **1**, we ruled out the mechanistic pathway shown in Scheme 5. We did find, however, that under these reaction conditions compounds **10** and **11** each are transformed to the substituted cyclohexadiene **14**. A mechanistic rationalization for these unusual transformations is offered in Scheme 7. The structure of **14** was proved by its spectral properties and its elemental analysis, and also by the spectral properties and elemental analysis of ketone **15**, which is obtained from the thermal decomposition of **14** in chloroform solution.[9]

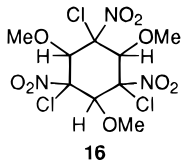
Although we do not have enough information to make a well-founded mechanistic proposal regarding the con-

(9) The conversion of **14** to **15** has a close parallel in the reported formation of 1,2-naphthoquinone from 1-chloro-1-nitro-2-keto-1,2-dihydronaphthalene in chloroform solution by the thermally induced loss of nitrosyl chloride. Perrin, C. L. *J. Org. Chem.* **1971**, *36*, 420.

Scheme 8



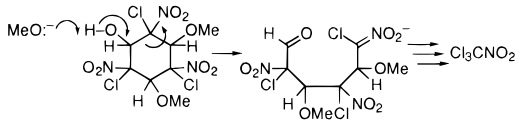
version of **1** to the mixture of **5** and **6**, we feel obliged to present at least a plausible rationalization. In that spirit we offer as a working hypothesis the pathway shown in Scheme 8 in which we imagine, at another mechanistic extreme, that the three M steps and the three C steps all are complete[10] before any E step takes place. This pathway would involve a cyclohexane of type **16** as a key intermediate.[11] One might think that the six-step transformation of **1** to **16** could be very complicated stereo-



chemically because many different stereoisomers are possible for **16**. On the basis of steric and stereoelectronic considerations, however, we suggest that the three M steps and the first two C steps may lead preferentially to a single species, anion **17**. From consideration of molecular models it appears that the trans pathway for the chlorination of anion **17**, which would generate stereoisomer **16b**, would be disfavored by steric interactions between the incoming hypochlorite ion and the two axial chlorine atoms in **17**. As a consequence we suggest that for this final C step the normal preference for overall

(10) Five permutations are conceivable for the sequence of these six steps: M-C-M-C-M-C, M-C-M-M-C-C, M-M-C-C-M-C, M-M-C-M-C-C, and M-M-M-C-C-C.

(11) We speculate further that intermediates related to **16**, especially those formed from hydroxide addition rather than methoxide addition, might be involved in the formation of the dominant product chloropicrin[6] by way of base-induced ring-opening followed by a series of chlorination and fragmentation reactions.



trans addition of the chloro and methoxy groups might be skewed, by default, in favor of overall cis addition to give mostly stereoisomer **16a**. For simplicity we assume that all of the subsequent base-induced elimination reactions of **16a** and **16b** are of the E2 type, with *anti* conformations strongly preferred in the transition structures. Thus **16a** and **16b** would undergo aromatization only after conformational isomerization to **16a′** and **16b′**, respectively. By a sequence of three consecutive E2 eliminations stereoisomer **16a′** would give the major isolated product **5**, and similarly stereoisomer **16b′** would give the minor isolated product **6**.

Experimental Section

Melting points were measured in an oil-bath apparatus and are uncorrected. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. Unless specified otherwise ^{1}H NMR spectra were measured in $CDCl_3$ solution at 300.1 MHz. Sublimations at reduced pressure were carried out as described previously.[12]

3,5-Dichloro-2,4,6-trimethoxynitrobenzene (5) and 1,3,5-Trichloro-2,4,6-trimethoxybenzene (6) from 1,3,5-Trinitrobenzene (1). Samples of 4.26 g (20 mmol) of 1,3,5-trinitrobenzene (**1**) and 11.2 g (170 mmol) of 85% KOH were dissolved in 300 mL of methanol to give a red solution. This color gradually changed to yellow as 250 mL (176 mmol) of 5.25% aqueous NaOCl (Clorox) was added over 3 h at 25−28 °C. After 48 h at room temperature some inorganic salts were filtered off and the filtrate was chilled to 0 °C. The resulting precipitate was collected, washed with cold water, and air-dried to give 1.0 g of white crystalline material that was shown by gas chromatography (GC) to consist of an approximately 80:15:5 mixture of three components.

The crude product mixture was chromatographed on alumina with a 1:4 mixture of benzene and hexane as the eluent to yield 0.8 g (14%) of **5**: mp 81.8−82.8 °C; ^{1}H NMR δ 3.98 (s, 6 H), 3.95 (s, 3 H). Anal. Calcd for $C_9H_9Cl_2NO_5$: C, 38.32; H, 3.22; N, 4.97. Found: C, 38.49; H, 3.33; N, 4.88.

This same chromatographic separation also yielded 0.05 g (1%) of **6**: mp 125−128 °C (lit.[8] mp 130−131 °C); ^{1}H NMR δ 3.90 (s, 9 H). The identity of this compound was confirmed by comparisons (infrared spectrum and GC retention time) with an authentic sample of **6** synthesized as described below.

The relative yield of the other minor product increased at higher reaction temperatures, rising from about 15% at 28 °C to about 60% at 70 °C. Recrystallization of the crude product mixture from a reaction at 70 °C gave, in addition to 0.3 g of **5** and a trace of **6**, 0.4 g (10%) of 3,5-dinitroanisole: mp 105.0−106.5 °C (lit.[5b] mp 105.5−106.5 °C). The identity of this material was confirmed by comparisons (mixed mp 105.0−106.5 °C, infrared spectrum, and GC retention time) with an authentic sample prepared as described previously.[5b]

1,3,5-Trichloro-2,4,6-trimethoxybenzene (6) via Amine 7. A previously reported method[13] (Scheme 4) was used to convert 1.0 g (3.5 mmol) of **5** to 0.45 g (51%) of 3,5-dichloro-2,4,6-trimethoxyaniline (**7**): mp 62.6−64.0 °C; ^{1}H NMR δ 3.90 (s, 2 H), 3.85 (s, 6 H), 3.83 (s, 3 H); IR (CCl_4) 3500, 3400 cm^{-1}.

Amine **7** (0.10 g, 0.4 mmol) was diazotized at 0−5 °C in 10 mL of 8 M HCl by adding 0.17 g (2.5 mmol) of $NaNO_2$ dissolved in 4 mL of water. The resulting solution was added slowly to a solution of 1.0 g (10 mmol) of cuprous chloride in 4 mL of 6 M HCl at 8−10 °C. This mixture was heated at 70 °C for 30 min and then filtered. The filtrate was chilled in an ice bath, and the resulting precipitate was collected and recrystallized from aqueous ethanol to yield **6**: mp 128.0−129.5 °C (lit.[8] mp 130−131 °C); ^{1}H NMR δ 3.90 (s, 9 H).

1,3-Dichloro-2,4,6-trimethoxybenzene (8). Amine **7** (0.50 g, 2.0 mmol) was diazotized at 0−5 °C in 9 mL of glacial acetic acid by adding 0.17 g (2.5 mmol) of $NaNO_2$ dissolved in 2 mL of concd H_2SO_4. Then 5 mL (36 mmol) of 50% aqueous H_3PO_2 was added, and the resulting mixture was stirred for 1 h at 0−5 °C and then for 24 h at room temperature. The mixture was diluted with 40 mL of water, and the resulting precipitate was collected and washed with 20% aqueous NaOH and water. The crude product was recrystallized twice from hexane to yield 0.25 g (53%) of **8**: mp 125.3−126.8 °C (lit.[7] mp 129 °C); mixed mp with authentic sample (see below) 125.6−127.0 °C; ^{1}H NMR δ 6.38 (s, 1 H), 3.92 (s, 6 H), 3.89 (s, 3 H).

Chlorination of 1.0 g (6 mmol) of 1,3,5-trimethoxybenzene by a previously reported method[7] (Scheme 4) gave, after recrystallization of the crude product from hexane, 1.2 g (75%) of an authentic sample of **8**: mp 126.7−127.4 °C (lit.[7] mp 129 °C).

5-Chloro-4-methoxy-1,3-dinitrobenzene (10). 2-Chloro-4-nitrophenol (**12**) (4.35 g, 25 mmol) was treated with anhydrous K_2CO_3 (12.5 g, 93 mmol) and methyl iodide (10 mL, 160 mmol) in refluxing acetone for 3 h. The residue after evaporation of the solvent was washed with 150 mL of water and collected. Sublimation of the crude product (60 °C, 0.05 Torr) yielded 4.40 g (93%) of 2-chloro-4-nitroanisole: mp 93.0−95.0 °C (lit.[14] mp 96 °C).

A previously reported method[15] (Scheme 6) was used to convert 4.0 g (21 mmol) of 2-chloro-4-nitroanisole to 4.0 g (83%) of **10**: mp 34.8−35.2 °C (lit.[15] mp 36 °C); ^{1}H NMR δ 8.66 and 8.60 (ABq, 2H, J = 2.2 Hz), 4.20 (s, 3 H).

3,5-Dichloro-2,4-dimethoxynitrobenzene (11). A powdered sample of 1.65 g (6.3 mmol) of 2,3,4,5-tetrachloronitrobenzene (**13**) was added to a stirred solution prepared previously by the reaction of 1.5 g (65 mmol) of sodium with 65 mL of methanol. This mixture was heated under reflux for 1 h and then was poured over 60 g of crushed ice. The resulting precipitate was collected and recrystallized twice from aqueous methanol to yield 1.0 g (63%) of **11**: mp 72.8−73.6 °C; ^{1}H NMR δ 7.89 (s, 1 H), 4.03 (s, 3 H), and 3.99 (s, 3 H); GC/MS m/z 251, 253, 255; IR (KBr) 1525, 1345, 1210, 1071 cm^{-1}. Anal. Calcd for $C_8H_7Cl_2NO_4$: C, 38.12; H, 2.80. Found: C, 38.22; H, 2.97.

1,3,5-Trichloro-2,4,4-trimethoxy-1-nitro-2,5-cyclohexadiene (14) and 3,5-Dichloro-2,4,4-trimethoxy-2,5-cyclohexadienone (15). Samples of 1.0 g (4.0 mmol) of **11** and 2.8 g (42 mmol) of 85% KOH were dissolved in 200 mL of methanol to give a yellow solution to which 80 mL (56 mmol) of 5.25% aqueous NaOCl (Clorox) was added dropwise over 15 min at 25−31 °C. After two days at room temperature the reaction mixture was diluted with 1 L of water and placed in a freezer for 12 h. The resulting precipitate was collected, washed with water, and air-dried to yield 0.5 g (39%) of **14**: mp 90.0−91.0 °C; ^{1}H NMR δ 6.56 (s, 1 H), 4.13 (s, 3 H), 3.35 (s, 3 H), 3.25 (s, 3 H); IR (KBr) 1645, 1570, 1345, 1100 cm^{-1}; UV (ethanol) no peaks above 205 nm. Anal. Calcd for $C_9H_{10}Cl_3NO_5$: C, 33.94; H, 3.16; Cl, 33.39. Found: C, 33.25; H, 2.97; Cl, 33.48.

Samples of 0.32 g (1.4 mmol) of 5-chloro-4-methoxy-1,3-dinitrobenzene (**10**) and 1.4 g (21 mmol) of 85% KOH were dissolved in 35 mL of methanol to give a red solution. The color gradually changed to yellow as 40 mL (28 mmol) of 5.25% aqueous NaOCl (Clorox) was added dropwise over 1 h at 15−18 °C. After two days at room temperature the reaction mixture was placed in a freezer for 3 h. The resulting precipitate was collected, washed with water, and air-dried to yield 0.1 g (22%) of material identified as **14** by ^{1}H NMR and GC comparisons with the sample of **14** produced from **11** as described above.

A sample of **14** was found to undergo slow decomposition in $CDCl_3$ solution at 40−50 °C. After this reaction was substantially complete, as monitored by ^{1}H NMR, the solvent was evaporated and the residue was dissolved in diethyl ether. The ether solution was cooled to about -35 °C to give crystalline (**15**): mp 41.2−42.0 °C; ^{1}H NMR δ 6.66 (s, 1 H), 3.96 (s, 3 H), 3.24 (s, 6 H); GC/MS m/z 256, 254, 252; IR (KBr) 1600, 1665 cm^{-1}; UV (ethanol) 242.5 nm (ϵ = 26000), 298 nm. In confirmation of this structural assignment for **15**, the increases in δ values that were observed[16] to accompany the addition of tris-(dipivalomethanato)europium to a CCl_4 solution of **15** were

(12) Mallory, F. B. *J. Chem. Educ.* **1962**, *39*, 261.

(13) Oliverio, A.; Castelfranchi, G.; Borra, G. *Gazz. Chim. Ital.* **1952**, *82*, 115.

(14) Schouten, A. E. *Recl. Trav. Chim. Pays-Bas* **1937**, *56*, 541.

(15) (a) Reverdin, F.; Philipp, K. *Chem. Ber.* **1905**, *38*, 3774. (b) Holleman, A. F.; de Mooy, W. J.; Terweel, J. *Recl. Trav. Chim. Pays-Bas* **1916,** *35*, 1. (c) Terrier, F.; Hallé, J.-C.; Simonnin, M.-P. *Org. Magn. Reson.* **1971**, *3*, 361. (d) Terrier, F.; Millot, F.; Schaal, R. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1192.

(16) We thank Professor David R. Dalton of Temple University for these measurements.

largest for the aryl signal at 6.66 ppm, 75% as large for the methoxy signal at 3.96 ppm, and 31% as large for the methoxy signal at 3.24 ppm. Anal. Calcd for $C_9H_{10}Cl_2O_4$: C, 42.71; H, 3.98; Cl, 28.08. Found: C, 42.78; H, 4.21; Cl, 27.57.

Acknowledgment. We thank the W. M. Keck Foundation, Merck & Co., Inc., the Camille and Henry Dreyfus Foundation, and PQ Corporation for contributions to Bryn Mawr College that enabled the purchase of an NMR spectrometer and a GC/MS system. A Research Corporation grant to F.B.M. also is gratefully acknowledged.

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Additions and Corrections

Vol. 60, 1995

Kazuhiro Kondo, Mikiko Sodeoka, and Masakatsu Shibasaki*. Regioselective Olefin Insertion in Asymmetric Heck Reaction. Catalytic Asymmetric Synthesis of a Versatile Intermediate for Diterpene Syntheses.

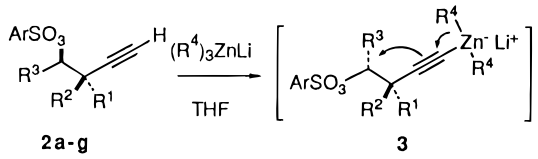
Page 4323, Scheme 3 should include the following legend:

(a) $LiAlH_4$, Et_2O, 23 °C; (b) HMPA, 224 °C (81%, 2 steps); (c) TBDMSCl, imidazole, DMF (98%); (d) LDA, THF, −78 °C, then Tf_2NPh, 0 °C (65%); (e) **12**, 9-BBN, THF, 23 °C, then H_2O; **14**, $Pd(PPh_3)_4$ (cat.), K_3PO_4, 60 °C (72%); (f) TBAF, THF; (g) Tf_2O, NEt_3, −78 °C (63%, 2 steps); (h) $Pd(OAc)_2$ (9 mol %), (*R*)-BINAP (18 mol %), K_2CO_3 (3 molar equiv), toluene, 50 °C, 96 h; naphthalene·$Cr(CO)_3$ (20 mol %), THF, 50 °C (62%, 2 steps); (i) OsO_4, *t*-BuOH−H_2O, then $NaHSO_3$, pyridine (76%); (j) TBDMSCl, DMAP, CH_2Cl_2 (94%); (k) SO_3·Py, NEt_3, DMSO (90%); (l) HF, MeCN−H_2O (70%); (m) PhOC(=S)Cl, DMAP, MeCN; (n) Bu_3SnH, AIBN, benzene, 90 °C (43%, 2 steps).

JO954033M

Toshiro Harada,* Hiroki Wada, and Akiro Oku*. Preparation of (1-Cyclopropylidenealkyl)zinc Reagents by the Reaction of Homopropargylic Sulfonates with Triorganozincates.

Page 5370, Scheme 1. The correct drawings for homopropargylic sulfonates **2a**−**g** and intermediate **3** are shown below.



JO954030+

Douglass F. Taber,* Rama S. Bhamidipati, and Larry Yet. Phenyldimethylsilyl as an Alcohol Surrogate in Intramolecular Diels−Alder Cycloaddition: Synthesis of α-Dictyopterol.

Page 5537. We neglected to cite prior work on the intramolecular Diels−Alder cycloaddition of silyl-substituted acrylates:

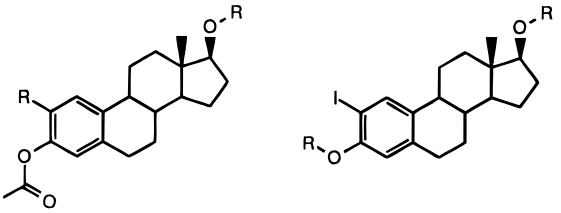
Kolb, H. C.; Ley, S. V.; Slawin, A. M. Z.; Williams, D. J. *J. Chem. Soc., Perkin Trans. 1* **1992**, 2735.

Kolb, H. C.; Ley, S. V.; Sheppard, R. N.; Slawin, A. M. Z.; Smith, S. C.; Williams, D. J.; Wood, A. *J. Chem. Soc., Perkin Trans. 1* **1992**, 2763.

JO954029A

Hu-Ming He, Phillip E. Fanwick, Karl Wood, and Mark Cushman*. A Novel 1,3 O → C Silyl Shift and Deacylation Reaction Mediated by Tetra-*n*-butylammonium Fluoride in an Aromatic System.

Page 5905. Structures **4**, **5**, and **20** were misassigned and should be corrected as shown below. Consequently, the reported 1,3-silyl migration occurs in the anions generated on treatment of **3** and **19** with *n*-butyllithium, and compounds **4**, **5**, and **20** deacylate in the presence of tetra-*n*-butylammonium fluoride in THF. We are grateful to Professor Scott Rychnovsky, University of California, Irvine, for bringing this error to our attention.



JO9540357

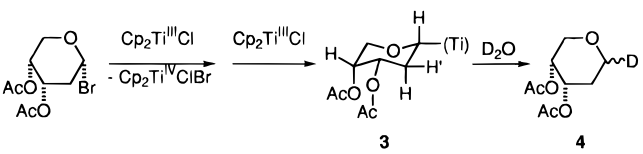
Stephen R. Wilson* and Qing Lu. 1,3-Dipolar Cycloaddition of *N*-Methylazomethine Ylide to C_{70}.

Page 6497, column 2, last line, and page 6498, column 1, first line. With respect to the sentence "To our knowledge, the structure proposed for **1c** is the first reported product of addition across the 22,23-bond in C_{70}.", we regret our failure to cite an earlier study in which the first adduct across the 22,23-bond in C_{70} was described: Herrmann, A.; Diederich, F.; Thilgen, C.; ter Meer, H.-U.; Müller, W. H. *Helv. Chim. Acta* **1994**, *77*, 1689.

JO954036Z

Cullen L. Cavallaro and Jeffrey Schwartz*. A Rapid Synthesis of Pyranoid Glycals from Glycosyl Bromides.

Page 7056, column 2. Corrected Scheme 3 is shown below:



JO954028I