

**THE "TWO-FOLD REACTION" BENCHMARK
APPLIED TO THE COPPER CATALYZED ASSEMBLING OF
1, ω -DIFUNCTIONAL HYDROCARBON CHAINS**

Manfred SCHLOSSER * and Henri BOSSERT

Institut de Chimie organique de l'Université
Rue de la Barre 2, CH-1005 Lausanne, Switzerland

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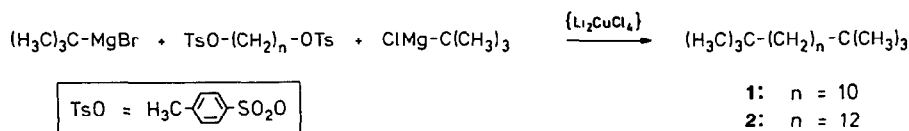
Summary : Long-chain hydrocarbons carrying vinyl groups, chlorine atoms or oxygen functions at the terminal positions can be prepared with excellent yields by copper mediated coupling of alkyl tosylates and Grignard reagents. No "breeding stage" is necessary if the cuprous complex dilithium trichlorocuprate rather than a cupric salt is employed as the catalyst.

How can one check on the reliability, efficiency and selectivity of a new synthetic method ? No other performance test is as simple and conclusive as a "double reaction", *i.e.*, employing a substrate endowed with two identical reaction centers. A little exercise in statistics may illustrate the argument (Table 1). Let us assume we have merely a 50% chance per reaction event to bring about the chemical transformation in the desired sense. If we perform the same reaction "two-fold", using a substrate disposing twice of the required functionality, we cannot expect to obtain more than 25% of the target compound. Its isolation and purification will be difficult since it will be accompanied by three times as much undesired materials. As a matter of fact, the yield per single step should exceed 70% or, better, 80%, if we want to be assured of getting a synthetically useful overall result.

Table 1. A comparison between single-step and two-fold reactions : ratios between desired product and "waste" (recovered starting material, by-products, decomposition residues etc.).

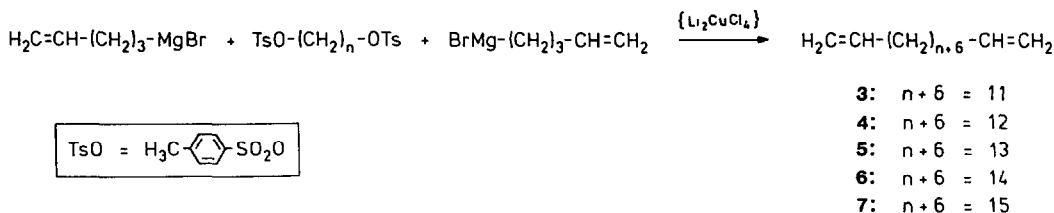
yield per single step	yield of two-fold reaction	by-products in two-fold reaction	product/"waste" ratio
90%	81%	19%	4.26
70%	49%	51%	0.96
50%	25%	75%	0.33
30%	9%	91%	0.10
10%	1%	99%	0.01

From the beginning we had submitted the copper catalyzed alkyl-alkyl coupling ^[1] to this test. When deca- and dodecamethylene *di-p*-toluenesulfonate were treated with a solution of *tert*-butylmagnesium chloride (2.0 equivalents) and dilithium tetrachlorocuprate (1 mol%) in tetrahydrofuran, 2,2,15,15-tetramethylhexadecane 2 ^[1] and 2,2,13,13-tetramethyltetradecane 1 ^[2] were formed and isolated in 85% (99% by gas chromatography) and 74% yield, respectively.



We now wanted to apply this method to the synthesis of straight-chain 1,(ω -1)-dienes, 1, ω -diols and 1, ω -dichloroalkanes. The dienes and their potential precursors deserve attention as starting materials for metathesis reactions ^[3, 4]. At the same time, our intention was to find out to what extent the copper catalytic cycle tolerates unsaturation and heterosubstituents.

First, a series of ditosylates was condensed with 4-pentenylmagnesium bromide, two molar equivalents of the Grignard reagent being used. The result was quite satisfactory in each individual case : 81% of 1,14-pentadecadiene (3), 78% of 1,15-hexadecadiene (4) ^[5], 85% of 1,16-heptadecadiene (5), 75% of 1,17-octadecadiene (6) and 88% of 1,18-nonadecadiene (7).



Next, we turned to Grignard reagents containing methoxymethoxy groups (m = 4, 6, 8). The yields of the resulting bisacetals 8 - 11, however, were very disappointing (see Table 2, first column). Eventually we realized what was needed to improve the outcome : either the dilithium *tetrachlorocuprate* catalyst had to be incubated with the organomagnesium solution for at least 2 h at -75 °C, or the cupric complex had to be replaced by the cuprous derivative dilithium *trichlorocuprate* ^[6, 7]. Applying either modification, we were rewarded with excellent yields (see Table 2, second column).

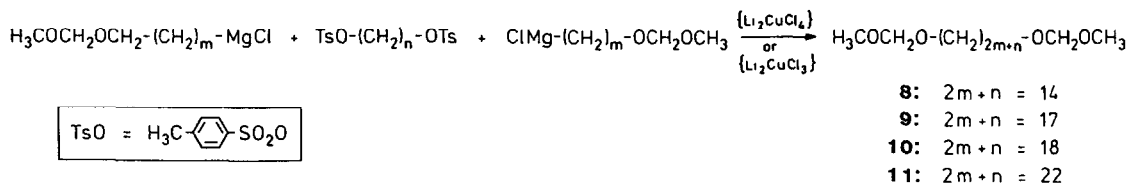
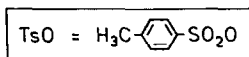
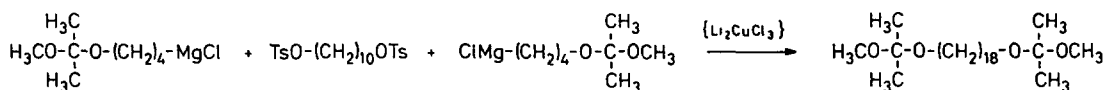


Table 2. Yields of 1,ω-di(methoxymethoxy)alkanes prepared by the copper catalyzed coupling of ω-(methoxymethoxy)alkylmagnesium bromides with hexa-, nona- or decamethylene di-*p*-toluenesulfonate under non-optimized ("A") and optimized ("B") conditions.

$\text{H}_3\text{COCH}_2\text{O}-(\text{CH}_2)_m-\text{MgBr}$	$\text{TsO}-(\text{CH}_2)_n-\text{OTs}$	product	A ^{a)}	B ^{b)}
m = 4	n = 6	8	50%	81%
m = 4	n = 9	9	23%	84%
m = 4	n = 10	10	32%	92%
m = 6	n = 6	10	73%	94%
m = 8	n = 6	11	11%	84%

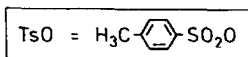
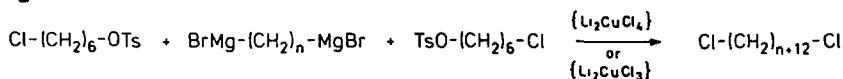
- a) Adding consecutively dilithium tetrachlorocuprate (in tetrahydrofuran) and the ditosylate to the Grignard reagent (in tetrahydrofuran) and allowing the mixture to reach 25 °C in the course of 2 h.
- b) Keeping a solution of the Grignard reagent and dilithium tetrachlorocuprate in tetrahydrofuran 2 h at -75 °C before adding the ditosylate or using dilithium trichlorocuprate rather than the cupric complex (see Experimental Part).

The same modification proved necessary when 4-(1-methoxy-1-methylethoxy)butylmagnesium bromide was employed as the organometallic component. Without incubation only a 50% yield of bisacetal 12 was obtained rather than the 71% under optimized conditions.



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Problems were also encountered when short-chain 1,ω-organodimagnesium compounds were coupled with tosylates. The yield of isolated 1,17-dichloroheptadecane (13) rose from 56% to 81% upon replacement of dilithium tetra- by trichlorocuprate in the reaction between 6-chlorohexyl *p*-toluenesulfonate and pentamethylenedi(magnesium bromide). On the other hand, hexa- and octamethylenedi(magnesium bromide) always reacted smoothly to afford the homologous 1,ω-dichloroalkanes 14 (76%) and 15 (88%), even without special precautions being taken.



13: n + 12 = 17
 14: n + 12 = 18
 15: n + 12 = 20

It became a standard joke to blame us for propagating voodoo witchcraft when, in our first publication on copper mediated carbon-carbon linking reactions ^[1], it was recommended to enhance the efficiency of the catalyst by allowing for a "breeding" (incubation) stage at -75 °C. On the basis of our new findings we can now offer a rational explanation. The active species could be a complex constructed from one organocopper and two or more organomagnesium moieties ^[8, 9]. Such a "higher-order cuprate" ^[10] could be directly formed using copper(I) iodide or any other cuprous salt. The commercially supplied Cu(I) compounds, however, frequently contain impurities ^[11] which later may trigger radical type side reactions. Therefore, it was found advantageous to use a pure cupric salt such as the dilithium tetrachlorocuprate ^[12] complex and to reduce it *in situ* to the Cu(I) species. As we recognize now, this process can be seriously hampered if chelating substituents or intramolecular aggregation stabilize the Grignard reagent to the point that it loses much of its reducing power. If this happens the cupric salt may be converted to an unstable diorganocopper derivative which rapidly undergoes reductive elimination, producing catalytically inactive zero-valent copper. The easiest way to avoid this sort of complication is to always use dilithium trichlorocuprate which has already the required lower oxidation state and which can be easily obtained free from troublesome contaminations. ^[6,7]

Incidentally, the catalyst, regardless of its nature, should be employed only in small amounts, for example 0.5%. Quantities bigger than 2% are often detrimental.

EXPERIMENTAL PART

1. General

For standard laboratory practice, techniques and abbreviations, see related articles, e.g. ref. ^[13].

2. Starting Materials and Reagents

a) *O*-(ω -Chloroalkyl)acetals : At 0 °C, chloromethyl methyl ether ^[14] (0.22 mol) was added dropwise and under stirring to a solution of the ω -chloroalkanol (0.20 mol) and *N*-ethyl-diisopropylamine (0.25 mol) in anhydrous dichloromethane. Then the solvent was stripped off and the residue extracted with hexane. Distillation afforded the acetal as a clear colorless liquid : 1-Chloro-4-(methoxymethoxy)butane ^[15] : 77%; bp 67 - 68 °C/11 mmHg; n_D^{20} 1.4282. - ¹H-NMR : 4.62 (2 H, s), 3.58 (2 H, t, *J* 6.5), 3.56 (2 H, t, *J* 6.0), 3.36 (3 H, s), 1.81 (4 H, symm. m); like 2 × 2 H, 2 × dqd, *J* ~ 8.5, 6.5, 1.5 at δ 1.86 and 1.75). - 1-Chloro-6-(methoxymethoxy)hexane : 92%; bp 97 - 98 °C/11 mmHg; n_D^{20} 1.4361. - ¹H-NMR : 4.62 (2 H, s), 3.54 (2 H, t, *J* 6.8), 3.53 (2 H, t, *J* 6.5), 3.36 (3 H, s), 1.79 (2 H, pent, *J* 6.5), 1.61 (2 H, pent, *J* 6.8) 1.4 (4 H, m). - Analysis : calc. for C₈H₁₇ClO₂ (180.68) C 53.18, H 9.48; found C 53.51, H 9.12%. - 1-Chloro-8-(methoxymethoxy)octane : 49%; bp 67 - 69 °C/0.5 mmHg; n_D^{20} 1.4420. - ¹H-NMR : 4.62 (2 H, s), 3.54 (2 H, t, *J* 6.8), 3.52 (2 H, t, *J* 6.5), 3.37 (3 H, s), 1.78 (2 H, pent, *J* 6.8), 1.59 (2 H, m, pent-like, *J* ~ 7), 1.4 (4 H, m), 1.3 (4 H, m, narrow). - Analysis : calc. for C₁₀H₂₁ClO₂ (208.73) C 57.54, H 10.14; found 57.74, H 9.91%. - 1-Chloro-4-(1-methoxy-1-methylethoxy)butane : 80% (isolated by elution with hexane from a Florisil column rather than by distillation); n_D^{20} 1.4450. - ¹H-NMR : 4.58 (2 H, td, *J* 6.5, 1.3), 4.43 (2 H, t, *J* 6.4), 4.19 (3 H, s), 1.9 (2 H, m), 1.7 (2 H, m), 1.34 (6 H, s). - Analysis : calc. for C₈H₁₇ClO₂ (180.68) C 53.18, H 9.48; found C 53.00, H 9.57%.

b) *Grignard reagents* : The *O*-(ω -chloroalkyl)acetals described in the preceding Section were converted into the corresponding organomagnesium compounds following a standard procedure ^[15]. Penta-^[16], hexa-^[16] and octa-^[16]methylenebis(magnesium bromide) (from the corresponding 1, ω -dibromides ^[17]) as well as 4-pentenyl-magnesium bromide ^[18] (from 4-pentenyl bromide ^[19]) have been prepared according to the literature.

c) *p*-Toluenesulfonates : Penta-^[20], hexa-^[21, 22], hepta-^[22], octa-^[23], nona-^[24] and deca-^[21]methylene di-*p*-toluenesulfonate are known compounds. The same holds for 6-chlorohexyl *p*-toluenesulfonate ^[25].

3. Coupling Products

a) *1,(\omega-1)*-Dienes : Solutions of the Grignard reagent (100 mmol, approx. 2 M in diethyl ether), the di-*p*-toluenesulfonate (50 mmol, 0.6 M in tetrahydrofuran) and dilithium tetrachlorocuprate ^[12] (0.05 mmol, 1 M in tetrahydrofuran) were combined at -75 °C. After the mixture had slowly reached -30 °C it was kept 15 min at this temperature. At 25 °C, silica gel (50 g) was added, the solvents were evaporated and the dry residue was poured on top of a column filled with fresh silica gel (100 g). The products were isolated by elution with hexane and subsequent distillation. - **1,14-Pentadecadiene (3)** ^[26] : 81%; mp -16 to -15 °C; bp 120 - 121 °C/4 mmHg; n_D^{20} 1.4463. - ¹H-NMR : 5.83 (2 H, ddt, *J* 16.9, 10.0, 6.5), 5.01 (2 H, dq, *J* 17.0, 2.0), 4.94 (2 H, ddt, *J* 10.1, 2.0, 1.0), 2.06 (4 H, qt, *J* 7.6, 1.2), 1.4 (m, pent-like), 1.3 (14 H, m, s-like). - Analysis : calc. for C₁₅H₂₈ (208.39) C 86.46, H 13.54; found 86.11, 13.76%. - **1,15-Hexadecadiene (4)** ^[26] : 78%; mp -2.5 to -1.5 °C; bp 94 - 96 °C/1 mmHg; n_D^{20} 1.4545. - ¹H-NMR : 5.84 (2 H, ddt, *J* 17.2, 10.5, 6.6), 5.01 (2 H, dq, *J* 17.3, 1.6), 4.96 (2 H, ddt, *J* 10.2, 2.0, 1.0), 2.07 (4 H, qt, *J* 6.9, 1.4), 1.4 (4 H, m), 1.3 (16 m, s-like). - Analysis : calc. for C₁₆H₃₀ (222.42) C 86.40, H 13.60; found C 86.40, H 13.60%. - **1,16-Heptadecadiene (5)** ^[27] : 85%; mp -2 to 0 °C; bp 100 - 101 °C/0.5 mmHg; n_D^{20} 1.4485. - ¹H-NMR : 5.84 (2 H, ddt, *J* 17.5, 10.5, 6.8), 5.01 (2 H, dq, *J* 17.5, 1.7), 4.94 (2 H, ddt, *J* 10.5, 2.0, 1.2), 2.06 (4 H, qt, *J* 6.9, 1.2), 1.4 (4 H, m, pent-like), 1.28 (18 H, s). - **1,17-Octadecadiene (6)** ^[26] : 75%; mp 3 - 4 °C; bp 106 - 108 °C/0.5 mmHg; n_D^{20} 1.4555. - ¹H-NMR : 5.85 (2 H, ddt, *J* 17.0, 10.5, 6.6), 5.01 (2 H, dq, *J* 17.5, 2.0), 4.95 (2 H, ddt, *J* 10.4, 2.0, 1.0), 2.06 (4 H, qt, *J* 6.5, 1.2), 1.4 (2 H, m), 1.3 (20 H, m, s-like). - **1,18-Nonadecadiene (7)** : 88%; mp 12.5 - 13.5 °C; bp 112 - 114 °C/0.2 mmHg; n_D^{20} 1.4555. - ¹H-NMR : 5.84 (2 H, ddt, *J* 17.5, 10.5, 6.7), 5.01 (1 H, dq, *J* 17.5, 1.7), 4.96 (2 H, dm, *J* 10.5), 2.07 (4 H, qt, *J* 6.4, 1.5), 1.4 (4 H, m), 1.3 (22 H, m). - Analysis : calc. for C₁₉H₃₆ (264.50) C 86.28, H 13.72; found C 86.18, H 13.89%.

b) *1,\omega*-Dichloroalkanes : At -75 °C, solutions of the oligomethylenebis(magnesium bromide) (50 mmol, approx. 1.5 M in tetrahydrofuran), 6-chlorohexyl *p*-toluenesulfonate (100 mmol, 1 M in tetrahydrofuran) and dilithium trichlorocuprate ^[6,7] (0.8 mmol, 1 M in tetrahydrofuran) were mixed. The temperature was allowed to raise slowly, in the course of 5 h, to 25 °C and the products were isolated as described in the preceding paragraph. - **1,17-Dichloroheptadecane (13)** : 81%; mp 26.0 - 27.5 °C; bp 165 - 167 °C/0.5 mmHg. - ¹H-NMR : 3.56 (4 H, t, *J* 6.7), 1.80 (4 H, pent, *J* 7.2), 1.45 (4 H, symm. m), 1.3 (22 H, m, s-like). - Analysis : calc. for C₁₇H₃₄Cl₂ (309.37) C 66.00, H 11.07; found C 66.07, H 11.05%. - **1,18-Dichlorooctadecane (14)** ^[28] : 76%; mp 50.5 - 51.5 °C. - ¹H-NMR : 3.56 (4 H, t, *J* 6.9), 1.79 (4 H, pent, *J* 7.3), 1.45 (4 H, symm. m), 1.3 (24 H, m, s-like). - **1,20-Dichloroeicosane (15)** ^[29] : 88%; mp 54.0 - 55.5 °C. - ¹H-NMR : 3.55 (4 H, t, *J* 6.9), 1.79 (4 H, pent, *J* 7.3), 1.3 (26 H, m, s-like).

c) *O,O'*-Oligomethylene bisacetals : Solutions of the ω -(methoxymethoxy)alkylmagnesium chloride (115 mmol, approx. 1 M in tetrahydrofuran), the oligomethylene di-*p*-toluenesulfonate (50 mmol, approx. 0.5 M in tetrahydrofuran) and dilithium trichlorocuprate ^[6, 7] (1.0 mmol, 1 M in tetrahydrofuran) were combined at -75 °C. The reaction was conducted and the mixture worked up as described in the preceding paragraphs (Sections 3.a and 3.b). - **1,14-Bis(methoxymethoxy)tetradecane (8)** : 81%; mp 22.0 - 22.5 °C; bp 115 - 118 °C/0.5 mmHg. - ¹H-NMR : 4.63 (4 H, s), 3.53 (4 H, t, *J* 6.5), 3.38 (6 H, s), 1.60 (4 H, pent, *J* ~ 6.5), 1.3 (20 H, m, s-like). - Analysis : calc. for C₁₈H₃₈O₄ (318.50) C 67.88, H 12.03; found C 67.76, H 11.88%. - **1,17-Bis(methoxymethoxy)heptadecane (9)** : 84%; mp 29.5 - 31 °C; bp 163 - 165 °C/0.5 mmHg. - ¹H-NMR : 4.62 (4 H, s), 3.51 (4 H, t, *J* 6.7), 3.37 (6 H, s), 1.59 (4 H, pent, *J* 7.2), 1.3 (26 H, m, s-like). - Analysis : calc. for C₂₁H₄₄O₄ (360.58) C 69.95, H 12.30; found C 70.18, H 12.39%. - **1,18-Bis(methoxymethoxy)octadecane (10)** : 92 and 94% (using deca- and hexamethylene di-*p*-toluenesulfonate); mp 36.5 - 38.0 °C. - ¹H-NMR : 4.63 (4 H, s), 3.52 (4 H, t, *J* 6.7), 3.37 (6 H, s), 1.60 (4 H, pent, *J* 7.0), 1.3 (28 H, m). - Analysis : calc. for C₂₂H₄₆O₄ (374.61) C 70.54, H 12.38; found C 70.51, H 12.19%. - **1,22-Bis(methoxymethoxy)docosane (11)** : 84%; mp 48.5 - 50.5 °C. - ¹H-NMR : 4.63 (4 H, s), 3.52 (4 H, t, *J* 6.9), 3.37 (6 H, s), 1.60 (4 H, pent, *J* 7.2), 1.3 (28 H, m, narrow). - Analysis : calc. for C₂₆H₅₄O₄ (430.71) C 72.50, H 12.64; found C 72.70, H 12.54%. - **1,18-Bis(1-methoxy-1-methylethoxy)octadecane (12)** : 71%; mp 40 - 41 °C. - ¹H-NMR : 3.37 (4 H, t, *J* 6.6), 3.19 (6 H, s), 1.55 (4 H, pent, *J* 6.5), 1.35 (12 H, s), 1.3 (28 H, m, s-like). - **1,18-Octadecanediol** ^[29] (by acid hydrolysis of 12) : mp 98 - 99 °C. - **1,18-Octadecamethylene diacetate** ^[27] (from 12 and acetic anhydride) : mp 59.0 - 60.5 °C. - Analysis : calc. for C₂₂H₄₂O₄ (370.57) C 71.31, H 11.42; found C 71.60, H 11.10%.

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