stocks accumulated in the course of our work on the synthesis of porphyrins. Precise details of the synthesis of any examples are available from K.M.S.

Acknowledgment. This research was supported by grants from the U.S. Office of Naval Research (N00014-85-C-0317), Aquanautics Corporation (Emeryville, CA), and the Instituto Nacional de Investigaçao Cientifica (Portugal, J.A.S.C. and M.G.P.M.S.N.). We thank Professors J. Simao and I. Montenegro (Braga, Portugal) and Drs. M. M. Al. Arab and K. R. Barqawi (Yarmouk, Jordan) for advice and assistance. H.D.T. is a Fulbright Scholar in Davis, from Yarmouk University, Jordan.

Synthesis of ω-Unsaturated Acids

Stanley B. Mirviss

Stauffer Chemical Company, Eastern Research Center, Dobbs Ferry, New York 10522

Received February 10, 1987 (Revised Manuscript Received November 28, 1988)

A short, high-yield method for the synthesis of ω-unsaturated acids has been developed that precludes any double-bond migration or hydrogenation. Key is the coupling reaction between Grignards of ω-unsaturated alkyl halides and the bromomagnesium salt of ω-bromo fatty acids. The reaction has been successfully extended to ω-bromo nitriles. The use of ω-chloro acids or α-bromo acids gives lower yields of heterocoupling products and substantial homocoupling. A catalyst study shows Li_2CuCl_4 to yield the most heterocoupling of several catalysts tried for the chloro acids, and Ni(II) or Cu(I) are best for the α-bromo acids.

ω-Unsaturated acids are of interest for use as ultra thin-layer photoresists[1] and for the synthesis of ω-radioiodinated fatty acids for use as myocardial imaging agents.[2] The syntheses in the literature involve many steps.[1a,3] The products are not adequately pure for photoresists because of the small amounts of double-bond migration and hydrogenation that occur in the final synthesis step. This is the Wolff–Kishner reduction (or the Huang–Minlon modification) of the intermediate ω-unsaturated keto acids. These side reactions have been noted before.[4a] Even the milder reduction conditions used by Hunig[4b] or the sodium borohydride reduction of the tosyl hydrazone of the keto group are reported[4c] to give small amounts of these side reactions.

The long-chain ω-unsaturated fatty acid molecules align on a solid surface as a Langmuir–Blodgett film or monolayer oriented so that the polar carboxylic acid groups are at the solid surface. The double-bond end groups are exposed unhindered for polymerization by high-energy radiation. Traces of byproducts with internal double bonds, no double bonds, or shorter or longer chain lengths will terminate polymer chain propagation by the X-ray or electron-beam polymerization of the terminal double bonds. Thus, high purity is necessary for high resolution in the photoresist by electron-beam microlithography.[1c]

A shorter route than those reported and especially one that precludes double-bond migration and/or hydrogenation was successfully used for the synthesis of ω-tricosenoic acid (22-tricosenoic acid) V, a particularly suitable ω-unsaturated fatty acid.[1] The ω-bromododecanoic acid I was prepared by the reaction of cyclododecanone with peroxytrifluoroacetic acid to form the lactone,[5] lactone hydrolysis with dilute sodium hydroxide to produce 12-hydroxydodecanoic acid,[6] and then conversion of the hydroxy acid to 12-bromododecanoic acid with 48% hydrobromic acid in the presence of sulfuric acid.[7] The product after recrystallization showed no evidence of 11-bromododecanoic acid (NMR, GC) and had properties identical with the literature.

$$\underset{\text{I}}{\mathrm{Br(CH_2)_{11}CO_2H}} + \mathrm{C_2H_5MgBr} \xrightarrow{\text{THF}} \underset{\text{II}}{\mathrm{Br(CH_2)_{11}CO_2MgBr}} + \mathrm{C_2H_6} \tag{1}$$

$$\mathrm{CH_2{=}CH(CH_2)_9OH} + \mathrm{SOCl_2} \xrightarrow{\mathrm{C_5H_5N}} \underset{\text{III}}{\mathrm{CH_2{=}CH(CH_2)_9Cl}} \tag{2}$$

$$\text{III} + \mathrm{Mg} \xrightarrow{\text{THF}} \underset{\text{IV}}{\mathrm{CH_2{=}CH(CH_2)_9MgCl}} \tag{3}$$

$$\text{II} + \text{IV} \xrightarrow[\text{THF}]{\mathrm{Li_2CuCl_4}} \underset{\text{V}}{\mathrm{CH_2{=}CH(CH_2)_{20}CO_2H}} \tag{4}$$

Compound III was prepared in 91% yield from 10-undecenyl alcohol and thionyl chloride with properties identical with those reported for III made by another route.[8] The method of Baer and Carney[9] was used for the coupling reaction. The reaction of the Grignard IV (made from III) with II (the bromomagnesium salt of I) in the presence of dilithium tetrachlorocuprate in tetrahydrofuran gave V, after hydrolysis of the reaction product. The

---

(1) (a) Barraud, A.; Rosilio, C.; Ruaudel-Teixier, A. *J. Colloid Interface Sci.* **1977**, *62*, 509. (b) Barraud, A.; Rosilio, C.; Ruaudel-Teixier, A. *Thin Solid Films* **1980**, *68*, 91. (c) Barraud, A.; Rosilio, C., Ruaudel-Teixier, A. *Solid State Tech.* **1979**, Aug, 120. (d) Fariss, G.; Lando, J.; Rickert, S. *Thin Solid Films* **1983**, *99*, 305. Peterson, I. R.; Russell, G. J.; Roberts, G. G. *Ibid.* **1983**, *109*, 371.

(2) Kabalka, G. W.; Gooch, E. E.; Otto, Ch. *J. Radioanal. Chem.* **1981**, *65*, 115.

(3) (a) Stenhagen, E. *Arkiv Kemi, Min. O. Geol.* **1949**, *1*[13], 99. (b) Bowman, R. E.; Fordham, W. D. *J. Chem. Soc.* **1952**, 3945.

(4) (a) Sisido, K.; Kawanisi, M. *J. Org. Chem.* **1962**, *27*, 3722. (b) Hunig, S.; Eckardt, W. *Ber.* **1962**, *95*, 2498. (c) Gunstone, F. D.; Ismail, I. A. *Chem. Phys. Lipids* **1967**, *1*, 209.

(5) Huisgen, R.; Ott, H. *Tetrahedron* **1959**, *6*, 253.

(6) Smissman, E.; Muren, J.; Dahle, N. A. *J. Org. Chem.* **1964**, *29*, 3517.

(7) Jocelyn, P. C.; Polgar, N. *J. Chem. Soc.* **1953**, 132; *Organic Synthesis*; Wiley: New York, 1941; Collect. Vol. I, p 29.

(8) Bergbreiter, D. E.; Whitesides, G. M. *J. Org. Chem.* **1975**, *40*, 779.

(9) Baer, T. A.; Carney, R. L. *Tetrahedron Lett.* **1976**, 4697.

0022-3263/89/1954-1948$01.50/0 © 1989 American Chemical Society

yield of unpurified V varied from 91 to 100%. Recrystallization gave high purity V suitable for the above purpose. The overall yields from undecenyl alcohol were 83–91% and from cyclododecanone were 55–61%. These results are to be compared with prior overall yields of 8%[3a] and 35%[1a] (no yield values are given in ref 3b). Baer[9] mentions the formation of small amounts of diacid from homogeneous coupling of the ω-bromo acid. In this case 1,24-tetracosadioic acid would be formed; none was noted by GC/MS. It was found that traces of copper could be removed by washing with an aqueous solution of EDTA and citric acid. The product was also free of magnesium, sodium, and lithium ions; the absence of metal ions is important for the production of photoresists.

It was found that the coupling reaction with IV is applicable to the shorter chain ω-bromo fatty acids, $Br(CH_2)_nCO_2H$, where n is 7 and 5 with 74 and 90% yields, respectively. A small amount of ketonic byproduct from reaction of the carboxylate salt with the Grignard was noted. This had not been noted by Baer[9] or with the longer chain, $n = 11$, acid. To explore this further, the very short chain Grignard, C_2H_5MgBr, was used in 100% excess with the bromo acid, $n = 10$ (3 mol of C_2H_5MgBr/mol of bromo acid). An 84% yield of tridecanoic acid was obtained with only a 2% yield of 10-bromodecyl ethyl ketone, a 3% yield of dodecyl ethyl ketone, and a 2% yield of decyl ethyl ketone. Thus, coupling is much preferred to reaction of the Grignard with the carboxylate group, even with a large excess of Grignard. The last-mentioned ketone indicates there was also some reductive reaction taking place that resulted in replacement of the bromo group by hydrogen.

A bromo dibasic acid, α-bromosuccinic acid, gave a 60% yield of the coupling product with IV, 10-undecenylsuccinic acid, plus the reduction products, succinic acid (5% yield) and 1-undecene (6% yield), and the homocoupling product, 1,21-docosadiene, VI (37% yield). A small amount (2–3% yield) of furmaric acid was also formed by dehydrobromination. The homocoupling product from the bromosuccinic acid, 1,2,3,4-butanetetracarboxylic acid, is too water soluble to have been recovered from the reaction product in aqueous media. The homocoupling product from Grignard IV was not noted by Baer[9] but was noted in related coupling reactions with reduced silver as catalyst[10,14] and with copper salts.[14]

Another extension of the reaction was to use a bromo nitrile, 4-bromovaleronitrile with IV. Grignards are known to react in high yield with the nitrile group of nitriles in the presence of a copper(I) catalyst.[11] On the other hand, aryl zinc halides react by coupling with bromoacetonitrile and a nickel(II) catalyst in 37–92% yield.[12] With the Li_2CuCl_4 catalyst heterocoupling was the predominant reaction and 14-pentadecenylnitrile was formed in 60% yield. The homocoupling product, VI, was formed in low (7%) yield and the reduction product of IV, 1-undecene, in 14% yield. No dinitrile coupling product or product of CN group involvement was noted.

Use of an aryl Grignard, (4-vinylphenyl)magnesium bromide, gave a low (13%) yield with 11-bromoundecanoic acid of the hetrocoupling product, which was 11-(p-vinylphenyl)undecanoic acid. This is similar to the low (21%) yield with the same Grignard and a bromopropionate ester with a Ni(II) catalyst.[13] In the former case, most of the styrene compound was polymerized and most of the bromo acid was recovered unchanged. The only homocoupling product was from the bromo acid. The literature does not show a cause for the low yield with the Ni(II) catalyst. The mechanism for the formation of the homocoupling product with the bromo acid might occur via an alkyl exchange between the Grignard and the bromo carboxylate salt[15] followed by homocoupling.

When (4-vinylbenzyl)magnesium chloride was used with 11-bromoundecanoic acid, no polymerization occurred. The Grignard coupled to form 1,2-bis(4-vinylphenyl)ethane in 71% yield. This is in agreement with the reported tendency of benzyl Grignards to couple.[14,16] A 10% yield of the heterocoupling product, 12-(p-vinylphenyl)dodecanoic acid, was obtained.

The use of a secondary carbon bromo acid, α-bromooctanoic acid, VII, with IV and the Li_2CuCl_4 catalyst gave a low (18%) yield of heterocoupling product, 7-carboxy-17-octadecene. Most of IV and VII were homodimerized to VI (52% yield) and 7,8-dicarboxytetradecane, VIII (75% yield), respectively. The greater amount of homocoupling with the secondary bromo acid than with the primary is in agreement with prior results with secondary and primary alkyl bromides.[10] This has been attributed to a more facile displacement reaction of an alkylcopper(I) with a primary than with a secondary alkyl bromide.[10,17] The use of Cu_2Cl_2 and $Ni(Acac)_2$ as catalysts in the reaction of VI with IV gave twice as much heterocoupling, 42 and 35%, respectively, as Li_2CuCl_4. The amount of heterocoupling is still markedly less than with the primary bromo acids. If the Cu(II) catalyst functions by first reduction to Cu(I) or an alkylcopper(I), then one would expect essentially equivalent results with both copper catalysts. Of course, that was not the case. Also, the degree of homocoupling was greater with the Cu(II) catalyst than with the Cu(I) catalyst, especially for the formation of VI (52 vs 12%). Compound VII treated with just Li_2CuCl_4 and no Grignard gave a small amount of VIII (more than stoichiometry).

It was interesting to see if chloro acids could be used in the coupling with Grignards, especially in view of very poor prior reported results with alkyl chlorides.[14] The reaction of 5-chlorovaleric acid, IX, with IV only gave a 29% yield of heterocoupled product, 15-hexadecenoic acid, with the appearance of significant amounts of homocoupled products. This contrasts sharply with the results with the similar bromo acid, 6-bromocaproic acid. The bromo acid gave a 90% yield of heterocoupled product and no homocoupled products. The chloro acid, IX, was reacted with n-octylmagnesium chloride, X, in place of IV with a variety of transition metal catalysts. Even lower yields (5–14%) of heterocoupled product were obtained. There were very little homocoupled products formed, and considerable chloro acid was recovered unchanged with considerable octane from X. These catalysts include $Ni(Acac)_2$, $Co(Acac)_2$, Cu_2Cl_2, and $PdCl_2((C_6H_5)_3P)_2$. In all these cases, products of reaction of the Grignard with the carboxyl group were noted in low yields. These were 1-chloro-5-tridecanone and the olefin dehydration product of the tertiary alcohol formed from the ketone and the Grignard. The olefin has the structure 1-chloro-5-(n-octyl)-4-tridec-

---

(10) Tamura, M.; Kochi, J. *Synthesis* **1971**, 303.

(11) Weiberth, F. J.; Hall, S. S. *J. Org. Chem.* **1987**, *52*, 3901–3904.

(12) Freijd, T.; Klingstedt, T. *Synthesis* **1987**, 40–41.

(13) Amono, T.; Yoshikawa, K.; Ogawa, T.; Sano, T., Ohuchi, Y.; Tanami, T.; Ota, T.; Hatayama, K.; Higuchi, S.; Amanuma, F.; Sota, K. *Chem. Pharm. Bull.* **1986**, *34*, 4653–4662.

(14) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978; Chapter 14.

(15) Reference 14, pp 379–380.

(16) Kharasch, M. S.; Reinmuth, O. *Grignard Reactions of Nonmetallic Substances*; Prentice-Hall: New York, 1954; pp 134–135, 1054–1056.

(17) Reference 14, p 383.

Table I. Reaction of Grignards with 4-Chlorovaleric Acid MgBr Salt and Various Catalysts

catalyst	tridecanoic or 15-hexadecenoic acids	hexadecane or VI	sebacic acid	valeric acid	4-chlorovaleric acid	octane or undecene	1-chloro-5-tridecanone	1-chloro-5-(*n*-octyl)-4-tridecene
Li_2CuCl_4	29	13	6	4.5	12	47	0	0
$Ni(Acac)_2$	7	2	trace	0.4	31	80	5	trace
Cu_2Cl_2	13.5	2.6	4	1	30	64	1.7	25
$PdCl_2((C_6H_5)_3P)_2$	18	2	2	2	52	76	0.4	3.0
$Co(Acac)_2$	6	0.5	4	7	43	71	trace	3.0

ene. From these studies it appears that the Li_2CuCl_4 is the best catalyst for heterocoupling of Grignards with primary halo acids, but Cu(I) and Ni(II) were better for secondary bromo acids.

It was not possible to prepare a Grignard from 2-chloroethyl vinyl ether under a variety of conditions although there was reaction with magnesium with the formation of insoluble magnesium salts. This is similar to the results with bis(β-chloroethyl) ether.[18] The reaction of IV with 4-carboxylbenzyl chloride gave considerable polymer, which contained benzylphenyl groups apparently from benzyl self-ring alkylation. No benzyl halide homocoupling product was found.

Experimental Section

10-Undecenyl Chloride, III. To a solution of 100 g (0.588 mol) of 10-undecenyl alcohol and 2 g of pyridine was added 75 g (0.63 mol) of $SOCl_2$ dropwise over a period of 45 min at 25 °C. The solution was heated at 65 °C for 5 h. CH_2Cl_2 (100 mL) was added, and the solution was washed twice with H_2O, dried with $MgSO_4$, filtered, and CH_2Cl_2 evaporated. The residue (103 g) by GC analysis showed a purity of 99.3% III with 0.7% alcohol; IR showed no OH band and absorbance at 1641 cm^{-1}.[8] Distillation (6-in. jacketed Vigreaux column) gave 94 g of III (bp 104–105 °C at 6 mm) (GC showed no alcohol; 100% III).

12-Bromododecanoic Acid, I. Cyclododecanone was treated with trifluoroacetic acid according to ref 5 to form the lactone, dodecanolid (yield 75%; bp 111–115 °C at 8 mm). The lactone was hydrolyzed according to the procedure of ref 6 to form 12-hydroxydodecanoic acid (yield 92%; mp 82–4 °C). The hydroxy acid was converted to 12-bromododecanoic acid, I, with 48% HBr in the presence of H_2SO_4 according to ref 7 (yield 88%; mp 52–55 °C).

22-Tricosenoic Acid, V. Preparation of IV. A well-dried and N_2-flushed flask was charged with 2.2 g of Mg ribbon (92 mmol), 80 mL of dry THF, 16.6 g (88 mmol) of III, and a small crystal of I_2. The mixture was stirred at reflux 2 h; no Mg was left.

Preparation of II. A solution of 25 g (90 mmol) of I in 100 mL of dry THF was reacted under N_2 with 32.3 mL of 2.85 M EtMgBr in Et_2O added over a period of 30 min at 0 °C until no further gas evolved.

Reaction of II and IV. To the THF solution of II was added 9 mL of a 0.2 M solution of Li_2CuCl_4 in THF[10] (1.8 mmol) at −10 °C. The solution was cooled to −20 °C and stirred vigorously while the solution of IV was added over a period of 45 min. After 1.5 h of stirring at −20 °C and then 2 h at 25 °C, 125 mL of 10% H_2SO_4 was added to the dark blue reaction mixture. The white solid present went into solution. The reaction mixture was extracted with 100 mL of toluene twice. The combined toluene extracts were washed with 5% H_2SO_4, dried over $MgSO_4$, and then flash distilled to give 29–32 g (91–100% yield; mp 68–71 °C; MS showed no detectable $HO_2C(CH_2)_{24}CO_2H$ or any other mass C_{23}; NMR showed no detectable CH_3; IR showed only $CH{=}CH_2$ unsaturation[1a]). Recrystallization from hexane solution washed with an aqueous solution of EDTA and citric acid gave white platelets, mp 73–74 °C (97 mol % purity by DSC). High-vacuum drying (1.0 mm) gave mp 74.5 °C (99 mol purity, DSC) (lit.[1a,2] mp 73.5–74 °C, 74.3–74.5 °C, 75 °C) (X-ray fluorescence showed no detectable Na, Li, Mg, K, Cu, Br, or I). A second recrystallization did not alter the 74.5 °C mp.

Reaction of IV with Other $Br(CH_2)_nCO_2H$. *n* = 7. The reactions were carried out similar to those for *n* = 11 above. The product 18-nonadecenoic acid, mp 58–60.5 °C (lit.[2] mp 59–60 °C), was isolated in 74% yield (20.1 g) after recrystallization from hexane. There was also obtained from the 20.6 g (92 mmol) of 8-bromooctanoic acid and 16.6 g (88 mmol) of I 3.75 g (28% yield) of *n*-octanoic acid and traces of 1-undecene and VI. Product identifications were made by MS and analysis by GC on the silylated material.

***n* = 5.** The reactions were carried out as for *n* = 11. The product 16-heptadecenoic acid, mp 47–49 °C (lit.[19] mp 48–50 °C) was isolated in 90% yield (12 g) after hexane recrystallization. Trace amounts of 1-undecene and *n*-octanoic acid were also formed.

Reaction of 100% Excess C_2H_5MgBr with 11-Bromoundecanoic Acid. A solution of 33.0 g (124 mmol) of 11-bromoundecanoic acid in 200 mL of dry THF was reacted under N_2 with 124 mL of a 3 M solution of C_2H_5MgBr in Et_2O (372 mmol) at −10 to −20 °C, and then 9 mL of 0.2 M Li_2CuCl_4 in THF was added. After 2 h of stirring at −20 °C, the reaction was stirred 1 h at 25 °C and then worked up as above. The silylated product by GC analysis was found to contain 28.7 g (84% yield) of *n*-tridecanoic acid, 3.7 g (8% recovery) of 11-bromoundecanoic acid, 2.05 g (6% yield) of 1,22-docosanedioic acid,[21] 0.7 g (2% yield) of 10-bromodecyl ethyl ketone, 0.8 g (3% yield) of dodecyl ethyl ketone, and 0.5 g (2% yield) of decyl ethyl ketone.

Reaction of IV with α-Bromosuccinic Acid. The reactions were carried out as above with 18.1 g (92 mmol) of α-bromosuccinic acid, 62 mL of 3 M C_2H_5MgBr in Et_2O (186 mmol), and 92 mmol of IV with 9 mL of a 0.2 M THF solution of Li_2CuCl_4. The product after workup was found by GC and MS after silylation to contain 9.9 g (40% yield) of α-(10-undecenyl)succinic acid, 5.2 g (37% yield) of 1,21-docosadiene, 2.6 g (16% recovery) of 10-undecenyl chloride, 0.9 g (6% yield) of 1-undecene, 1.1 g (10% yield) of fumaric acid, 0.5 g (5% yield) of succinic acid, and 3 g (22% yield) of α-ethylsuccinic acid. By NaOH solution extraction of a THF solution of the product followed by HCl acidification and MIBK extraction, it was possible to separate the acidic components from the neutrals. The acidic material could be separated by fractional crystallization with a toluene/acetone/hexane mixture to isolate first the fumaric acid, mp 280–287 °C, and then a mixture of succinic and ethylsuccinic acids, mp 171–183 °C, and finally 10-undecenylsuccinic acid, mp 53–58 °C after methanol/water recrystallization.

Reaction of IV with 5-Bromovaleronitrile. The reaction was carried out as above with 85 mmol of IV and 16.3 g (100 mmol) of 5-bromovaleronitrile in 100 mL of dry THF. The product after the usual workup was found by GC and MS to contain 11.4 g (60% yield) of 14-pentadecenyl nitrile, 2.0 g (12% recovery, 80% of excess) of 5-bromovaleronitrile, 1.1 g (7% recovery) of 10-undecenyl chloride, 1.8 g (14% yield) of 1-undecene, and 0.9 g (7% yield) of VI.

Reaction of (4-Vinylphenyl)magnesium Bromide with 11-Bromoundecanoic Acid. The (4-vinylphenyl)magnesium bromide was prepared from 2.24 g (92 mmol) of magnesium turnings, activated with a few crystals of I_2, in 75 mL of dry THF and 16.9 g (92 mmol) of 4-bromostyrene. The reaction tends to be vigorously exothermic, and dry ice cooling is needed to maintain

---

[18] Reference 16, p 36.

[19] Hunig, S.; Echardt, W. *Ber.* **1962**, *95*, 2493.

[20] Barry, V. C.; Twomey *Proc. Roy. Irish Akad.* **1947**, *51B*, 145–151; *Chem. Abstr.* **1947**, *41*, 4454.

[21] Drake, N. L.; Carhart, H. W.; Mozingo, R. *J. Am. Chem. Soc.* **1941**, *63*, 617–620.

the temperature at 15–20 °C. If the reaction temperature is allowed to rise above 50 °C or is kept at 25 °C for more than 2 h, polymerization occurs. The Grignard solution was added to a solution of 24.5 g (92 mmol) of 11-bromoundecanoic acid in 150 mL of dry THF prereacted with first 31 mL of a 3 M solution of ethylmagnesium bromide in Et_2O and then 9 mL of 0.2 M Li_2CuCl_4 in THF. The temperature was maintained at −25 to −30 °C. The reaction product was worked up in the usual manner. It was not possible to crystallize any material from the total product with various solvents, but it was possible to remove the acidic products by dilute caustic extraction of a THF–MIBK solution (some emulsion problems occurred). The remaining neutral material was primarily polymer. GC and MS analyses on the silylated acidic components showed 3.5 g (13% yield) of 11-(*p*-vinylphenyl)undecanoic acid, 2.3 g (10% yield) of 1,20-docosanedioc acid,[21] 0.5 g (4% yield) of undecanoic acid, 0.5 g (3% yield) of 10-undecenoic acid, and 17 g (70% recovery) of 11-bromoundecanoic acid.

Reaction of (4-Vinylbenzyl)magnesium Bromide and 11-Bromoundecanoic Acid. The Grignard was prepared from 13.8 g (90.5 mmol) of 4-vinylbenzyl chloride in 75 mL of dry THF and 2.24 g (92 mmol) of magnesium turnings. The reaction was very exothermic, and dry ice cooling was needed to hold the temperature at 25 °C. However, only 71% of the Mg was converted after 3.5 h. The Grignard solution was reacted with 24.5 g (92 mmol) of 11-bromoundecanoic acid prereacted with 92 mmol of a 3 M solution of EtMgBr in Et_2O and then with 9 mL of an 0.2 M THF solution of Li_2CuCl_4 all at −20 to −25 °C. After 1.5 h additional at −20 °C, the reaction mixture was worked up. The silylated product analyzed by GC and MS was shown to contain 7.4 g (71% yield) of 1,2-bis(4-vinylphenyl)ethane, 2.6 g (10% yield) of 12-(4-vinylphenyl)dodecanoic acid, 1.4 g (8% yield) of 1,22-docosanedioic acid,[21] and 11.1 g (45% recovery) of 11-bromoundecanoic acid.

Reaction of IV and 4-Carboxybenzyl Chloride. An 85-mmol THF solution of IV was reacted with 19.9 g (92 mmol) of 4-carboxybenzyl chloride pretreated with 92 mmol of EtMgBr solution and then with 9 mL of 0.2 M Li_2CuCl_4 solution at −20 to −25 °C. The bulk of the product was polymeric. The polymer contained benylphenyl groups and carboxylic acid groups based on IR on a KBr pellet.

Reaction of IV with 2-Bromooctanoic Acid. Li_2CuCl_4 Catalyst. The reaction was carried out as above with 85 mmol of IV and 19.0 g (85 mmol) of 2-bromooctanoic acid in 150 mL of dry THF treated first with 87 mmol of EtMgBr and then with 9 mL of 0.2 M Li_2CuCl_4 in THF. The reaction product after the usual workup and silylation was found to contain by GC and MS 9 g (74.5% yield) of VIII, which partially crystallized out, mp 91.5–94.5 °C (recrystallized heptane) (diacid and not anhydride by ^{13}C NMR) (lit.[20] mp 95–6 °C), 6.8 g (52% yield) of VI, 4.4 g (18% yield) of 7-carboxy-17-octadecene,[22] 0.1 g (0.5% recovery) of 2-bromooctanoic acid, 0.1 g (1% recovery) of III and 1.2 g (9% yield) of 1-undecene.

$Ni(Acac)_2$ Catalyst. The reaction was carried out as above with Li_2CuCl_4 except for the use of 0.46 g (1.8 mmol) of anhydrous $Ni(Acac)_2$. The product after the workup and silylation was found to contain by GC 8.8 g (35% yield) of 7-carboxy-17-octadecene,[22] 1.3 g (10% yield) of VI, 8.6 g (70% yield) of VIII, 1.3 g (10% yield) of 1-undecene, 0.3 g (2% recovery) of III, and a trace of octanoic acid.

Cu_2Cl_2 Catalyst. The reaction was carried out as above with Li_2CuCl_4 except for use of 0.18 g (1.8 mmol) of anhydrous Cu_2Cl_2. The product after workup was found to contain 10.5 g (42% yield) of 7-carboxy-17-octadecene,[22] 1.5 g (12% yield) of V, 7.0 g (52% yield) of VIII, 1.2 g (9% yield) of 1-undecene, 0.7 g (5% yield) of octanoic acid, and 0.1 g of II.

Li_2CuCl_4 Catalyst without IV. The reaction was run identical with the above except that no IV was used. The product was by GC analysis mostly 2-bromooctanoic acid (86% recovery), but it included 1.7 g (14% yield) of VIII and an unidentified component.

Reaction of 4-Chlorovaleric Acid and IV or *n*-OctylMgBr with Various Catalysts. A solution of 13.7 g (100 mmol) of 4-chlorovaleric acid was treated with 100 mmol of EtMgBr as a 3 M Et_2O solution at −20 °C. After 20 min 1.95 mmol of catalyst was added followed by 100 mmol of Grignard IV as a THF solution or *n*-octylmagnesium bromide as a 2.3 M solution in Et_2O, at −20 °C with good stirring. After 1.5 h at −20 °C, the product was warmed to the ambient and worked up. The results based on GC and MS analysis of the silylated product are tabulated in Table I. The Li_2CuCl_4 was used with IV and the other catalysts with the octyl Grignard.

Registry No. I, 73367-80-3; II, 119011-61-9; III, 872-17-3; IV, 108712-21-6; V, 65119-95-1; VI, 53057-53-7; VII, 2623-82-7; VIII, 5815-35-0; Li_2CuCl_4, 15489-27-7; $Ni(Acac)_2$, 3264-82-2; Cu_2Cl_2, 75763-85-8; $PdCl_2((C_6H_5)_3P)_2$, 13965-03-2; $Co(Acac)_2$, 14024-48-7; $Br(CH_2)_7CO_2H$, 17696-11-6; $Br(CH_2)_5CO_2H$, 4224-70-8; C_2H_5MgBr, 925-90-6; 10-undecenyl alcohol, 112-43-6; cyclododecanone, 830-13-7; dodecanolid, 143-07-7; 12-hydroxydodecanoic acid, 505-95-3; 18-nonadecenoic acid, 76998-87-3; 4-chlorovaleric acid, 32607-54-8; octanoic acid, 124-07-2; 16-heptadecenoic acid, 65119-97-3; 11-bromoundecanoic acid, 2834-05-1; *n*-tridecanoic acid, 638-53-9; 1,22-docosanedioic acid, 505-56-6; 10-bromodecyl ethyl ketone, 119011-62-0; dodecyl ethyl ketone, 18787-66-1; decyl ethyl ketone, 1534-26-5; α-bromosuccinic acid, 923-06-8; α-(10-undecenyl)-succinic acid, 119011-63-1; 10-undecenyl chloride, 2473-03-2; 1-undecene, 821-95-4; fumaric acid, 110-17-8; succinic acid, 110-15-6; α-ethylsuccinic acid, 636-48-6; 5-bromovaleronitrile, 5414-21-1; 4-bromostyrene, 2039-82-9; (4-vinylphenyl)magnesium bromide, 18120-63-3; 11-(*p*-vinylphenyl)undecanoic acid, 94865-70-0; undecanoic acid, 112-37-8; 10-undecenoic acid, 112-38-9; (4-vinylbenzyl)magnesium bromide, 45966-75-4; 4-vinylbenzyl chloride, 1592-20-7; 1,2-bis(4-vinylphenyl)ethane, 48174-52-3; 12-(4-vinylphenyl)dodecanoic acid, 119011-64-2; 4-carboxybenzyl chloride, 1642-81-5; octylmagnesium bromide, 17049-49-9; 7-carboxy-17-octadecene, 119011-65-3; 15-hexadecenoic acid, 4675-57-4; hexadecane, 544-76-3; sebacic acid, 111-20-6; valeric acid, 109-52-4; octane, 111-65-9; undecene, 28761-27-5; 1-chlorotrideca-5-none, 119011-66-4; 1-chloro-5-(*n*-octyl)-4-tridecene, 119011-67-5.

---

[22] Browning, E.; Woodrow, A. W.; Adams, R. *Ibid.* **1930**, *52*, 1281–1283.