C—C Bond Formation between Electron-Rich and Electron-Poor Alkenes in a One-Pot Synthesis

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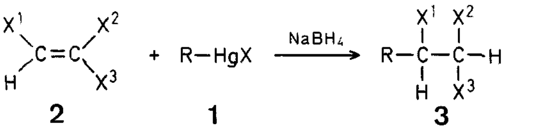
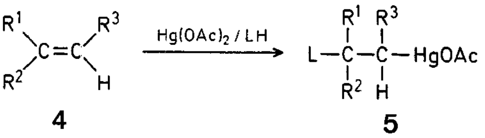
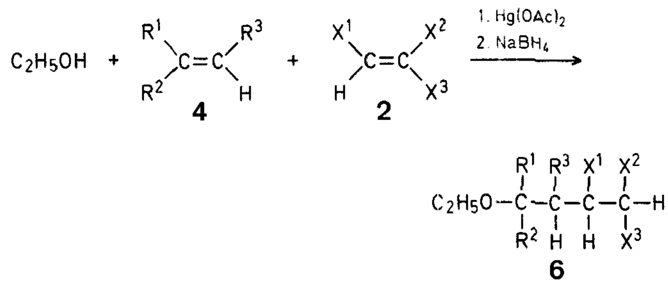
The reduction of alkylmercuric salts (**1**) in the presence of electron-poor alkenes (**2**) yields products **3** via a radical-chain reaction[1].



An efficient synthesis of alkylmercuric salts (**5**) is the addition of mercury(II) acetate to electron-rich alkenes (**4**) in a nucleophilic solvent LH[2].



The combination of solvomercuration and reductive demercuration provides a method for C—C bond formation between electron-rich and electron-poor alkenes[3]. We have now observed that these two reaction steps can be carried out in a one-pot synthesis without isolation of the organomercuric compound **5** and without changing the solvent if ethanol is used.



The effect of the substituents X^1, X^2, and X^3 on the yield of **6** is shown by the reactions of alkenes **2** with cyclopentene [**4**, R^1-R^3=$(CH_2)_3$, R^2=H] (Table 1) and the effect of the substituents R^1, R^2, and R^3 is shown by the reactions of alkenes **4** with acrylonitrile (**2**, X^1=X^2=H, X^3=CN) (Table 2). The overall yields of these two-step reactions are 50–75% if X^1, X^2, X^3 at alkenes **4** are powerful electron-withdrawing substituents. The smaller yields with styrene and dichloroethene reflect the low reactivity of these alkenes in addition reactions with alkyl radicals[4].

Alkanes or Substituted Alkanes (6); General Procedure:

A suspension of mercury(II) acetate (4.1 g, 13 mmol) in ethanol (10 ml) is mixed with alkene **4** (20 mmol) at 20 °C. After the mercury(II) acetate has dissolved, mercury(II) oxide (1.5 g, 7.0 mmol) is added in four portions. The colorless solution is diluted with dichloromethane (100 ml) and the alkene **2** (60 mmol). The mixture is then cooled to 0 °C, sodium borohydride (1.5 g, 40 mmol) is added quickly and stirring is continued for 1 h. The excess of sodium borohydride is de-

Table 1. Substituted Cyclopentanes [**6**, R^1-R^3=$(CH_2)_3$, R^2=H] from Alkenes **2** and Cyclopentene

6	X^1	X^2	X^3	Yield [%][a]	b.p.[b] [°C/0.1 torr]	Molecular formula[c]	I.R. (film) ν [cm^{-1}]	^{1}H-N.M.R. ($CDCl_3$/TMS$_{int}$) δ [ppm]
a	H	H	—CN	65	85°	$C_{10}H_{17}NO$ (167.3)	2260 (CN)	1.15, 1.18 (t, 3H, J=7.0 Hz); 1.4–2.0 (m, 9H); 2.40 (t, 2H, J=7.0 Hz); 3.2–3.8 (m, 3H)
b	H	H	—$COOCH_3$	60	75°	$C_{11}H_{20}O_3$ (200.3)	1740 (CO)	1.16, 1.18 (t, 3H, J=7.0 Hz); 1.4–2.0 (m, 9H); 2.37 (t, 2H, J=7.0 Hz); 3.3–3.6 (m, 3H); 3.66 (s, 3H)
c	H	H	—CO—CH_3	51	60°	$C_{11}H_{20}O_2$ (184.3)	1715 (CO)	1.16, 1.18 (t, 3H, J=7.0 Hz); 1.4–2.0 (m, 9H); 2.14 (s, 3H); 2.49 (t, 2H, J=7.0 Hz); 3.2–3.7 (m, 3H)
d	H	H	C_6H_5	15	105°	$C_{15}H_{22}O$ (218.3)		1.16, 1.18 (t, 3H, J=7.0 Hz); 1.2–2.1 (m, 9H); 2.62 (t, 2H, J=7.0 Hz); 3.2–3.8 (m, 3H); 7.2 (mc, 5H)
e	H	Cl	—CN	66	100°	$C_{10}H_{16}ClNO$ (201.7)	2270 (CN)	1.16, 1.18 (t, 3H, J=7.0 Hz); 1.4–2.5 (m, 9H); 3.1–3.9 (m, 3H); 4.4–4.8 (m, 1H)
f	H	Cl	Cl	21	110°	$C_9H_{16}Cl_2O$ (211.1)		1.16, 1.18 (t, 3H, J=7.0 Hz); 1.4–2.5 (m, 9H); 3.2–3.8 (m, 3H); 5.80, 5.83 (t, 1H, J=6.5 Hz)
g	—CN	H	—CN	66	115°	$C_{11}H_{16}N_2O$ (192.3)	2260 (CN)	1.16, 1.18, 1.19 (t, 3H, J=7.0 Hz); 1.3–2.3 (m, 7H); 2.4–4.1 (m, 6H)
h	—$COOCH_3$	CH_3	—$COOCH_3$	37	95°	$C_{14}H_{24}O_5$ (272.3)	1735 (CO)	1.16, 1.19 (t, 3H, J=7.0 Hz); 1.24, 1.27 (d, 3H, J=7.0 Hz); 1.4–2.4 (m, 7H); 2.6–3.1 (m, 2H); 3.2–3.8 (m, 3H); 3.67 (mc, 6H)

[a] Yield based on alkene **4** (cyclopentene).
[b] Temperature of the bath.
[c] The microanalyses were is satisfactory agreement with the calculated values: C, ±0.35; H, ±0.13; N, ±0.10.

0039-7881/82/0932-0735 $ 03.00

Table 2. 5-Ethoxyalkanenitriles (**6**, $X^1=X^2=H$, $X^3=CN$) from Alkenes **4**, Ethanol, and Acrylonitrile

6	R[1]	R[2]	R[3]	Yield [%][a]	b.p.[b] [°C/0.1 torr]	Molecular formula[c]	I.R. (film) ν [cm⁻¹]	^{1}H-N.M.R. ($CDCl_3$/TMS_{int}) δ [ppm]
i	*n*-C_4H_9	H	H	65	60°	$C_{11}H_{21}NO$ (183.3)	2260 (CN)	0.90 (mc, 3H); 1.18 (t, 3H, J=7.0 Hz); 1.1–1.9 (m, 10H); 2.38 (mc, 2H); 3.1–3.7 (m, 3H)
j	C_6H_5	H	H	48	115°	$C_{13}H_{17}NO$ (203.3)	2260 (CN)	1.16 (t, 3H, J=7.0 Hz); 1.5–2.0 (m, 4H); 2.25 (mc, 2H); 3.34 (mc, 2H); 4.15 (mc, 1H); 7.25 (mc, 5H)
k	C_2H_5	CH_3	H	53	50°	$C_{10}H_{19}NO$ (169.3)	2260 (CN)	0.84, 0.85 (t, 3H, J=7.0 Hz); 1.10 (s, 3H); 1.16 (t, 3H, J=7.0 Hz); 1.4–1.9 (m, 6H); 2.37 (mc, 2H); 3.32 (q, 2H, J=7.0 Hz)
l	*t*-C_4H_9	CH_3	H	10	85°	$C_{12}H_{23}NO$ (197.3)	2250 (CN)	0.92 (s, 9H); 1.12 (t, 3H, J=7.0 Hz); 1.14 (s, 3H); 1.3–2.0 (m, 4H); 2.2–2.4 (m, 2H); 3.46 (q, 2H, J=7.0 Hz)
m	CH_3	H	CH_3	75	45°	$C_9H_{17}NO$ (155.2)	2260 (CN)	0.90 (d, 3H, J=6.5 Hz); 1.07, 1.09 (d, 3H, J=6.0 Hz); 1.16, 1.17 (t, 3H, J=7.0 Hz); 1.4–2.1 (m, 3H); 2.40 (mc, 2H); 3.1–3.8 (m, 3H)
n	H	—$(CH_2)_4$—		68	100°	$C_{11}H_{19}NO$ (181.20)	2250 (CN)	1.16, 1.18 (t, 3H, J=7.0 Hz); 0.8–2.5 (m, 13H); 2.7–3.0 (m, 1H); 3.2–3.8 (m, 2H)
o	CH_3	CH_3	CH_3	60	100°	$C_{10}H_{19}NO$ (169.3)	2260 (CN)	0.90 (d, 3H, J=7.0 Hz); 1.07 (s, 3H); 1.14 (s, 3H); 1.14 (t, 3H, J=7.0 Hz); 1.2–2.2 (m, 3H); 2.2–2.6 (m, 2H); 3.38 (q, 2H, J=7.0 Hz)

[a] Yield based on alkene **4**.
[b] Temperature of the bath.
[c] The microanalyses were is satisfactory agreement with the calculated values: C, ±0.35; H, ±0.20; N, ±0.32.

stroyed with water (30 ml) and the liquid layers are decanted and separated. The water layer is extracted with dichloromethane (3 x 30 ml) and the combined organic phases are filtered through a funnel covered with magnesium sulfate. Distillation yields products **6**.

This work was supported by the Fonds der Chemischen Industrie. U. L. thanks the Studienstiftung des Deutschen Volkes for a graduation scholarship.

Received: February 8, 1982

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0039-7881/82/0932-0736 $ 03.00