J. Chem. Research (S), 2000, 4–5
J. Chem. Research (M), 2000, 0112–0129

Oligomerization of acrylic acid derivatives by a reaction with the alkylcopper(I)-phosphine complex

Michiharu Mitani*, Chitsakon Pakjamsai, Teruko Tsuchida and Hidekazu Kudoh

Department of Chemistry and Material Engineering, Faculty of Engineering, Shinshu University, Wakasato, Nagano 380-8553, Japan

Reaction of alkylcopper(I)phosphine complexes with electron-deficient olefins affected preferentially the products based on oligomerization, *e.g.* the product obtained by sequential conjugated addition, trimerization and cyclization from methyl methacrylate and the dimerization product from butyl acrylate.

Conjugated carboxylic acid derivatives such as acrylates are polymerized through the action of the metal compounds. On the other hand, organocuprates afford the Michael-type adducts by the reaction with some conjugated esters.[5] We herein report that organocopper – phosphine complexes bring about the formation of the products based on the head-to-tail dimeri- or trimerization of acrylic acid derivatives.

When methyl methacrylate (**1a**) was introduced at 0 °C for 30 min into a reaction system formed by the addition of a THF solution containing $CuBr(PPh_3)_2$ to BuMgBr in Et_2O, 2,4-dimethoxycarbonyl-6-pentyl-2,4,6-trimethylcyclohexanone (**2a**), which appears to be derived from cyclization following trimerization of **1a** triggered by the addition of the butyl group, was afforded as the major product (66% yield) along with a dimerization product **3a** (10% yield) and a trace amount of a 1,4-conjugated adduct. Although **2a** has been reported to be formed by the reaction of **1a** with dibutylmagnesium or the butyl Grignard reagent, it has been afforded as a minor product in the complex mixture.[8] The type **2** product ($R_2 = CH_2OCH_3$) has also been formed, although as a by-product of the reaction of **1a** in the presence of sodium methoxide and methanol.[9] In the proposed reaction, the formation method of the $CuBr(PPh_3)_2$ complex that occurs due to the mixing of CuBr and PPH_3 in THF proved critical for this oligomerization reaction. This is revealed by the results indicating that oligomers **2a** and **3a** were not afforded by subjection of **1a** to the reaction system generated from mixing of the Grignard reagent with a white gel formed by prolonged stirring (about 10 min) after addition of CuBr to a THF solution containing PPh_3 or with a light brown solution formed by addition of PPh_3 to a suspension containing CuBr, whereas the formation of **2a** and **3a** in the above-mentioned reaction was realized by the reaction of **1a** in the system formed from mixing Grignard reagent with a transparent solution generated through stirring for about 3 min after addition of CuBr to a THF solution containing PPh_3. Choice of solvent also had a strong influence on the performance of the proposed reaction, *i.e.*. use of THF rather than Et_2O for preparation of the Grignard reagent resulted in low conversion (19%) of **1a** along with no formation of **2a** and **3a**, whereas a transparent solution of the CuBr-phosphine complex was not formed in an ether solvent. Next, the effects of the amount of the PPh_3 ligand were investigated. The reaction without the phosphine ligand resulted in no formation of **2a** and **3a**, despite a large consumption of **1a**, and the mole ratio of CuBr to PPh_3 of 2 was found to be best. The influence of halides in the copper(I) salts and the Grignard reagent was examined, and the bromides (*i.e.* CuBr and BuMgBr) were revealed to be advantageous.

Some Grignard reagents, other than the n-butyl reagent, were also examined. Ethylmagnesium bromide was found to result in a slightly lower yield of trimerization product **2b** as well as enhanced formation of dimerization product **3b**, and the branched (*i.e.* sec- and tert-butyl) Grignard reagents also revealed similar tendencies, whereas the allyl Grignard reagent brought about no consumption of **1a**. Furthermore, use of lithium reagent (*i.e.* BuLi) rather than the Grignard reagent resulted in the formation of only a small amount of **2a** (3% yield), although **1a** was almost completely consumed. These results are listed in Table 4. GC analysis of products **2** and **3** revealed that these products consist of almost completely pure diastereomers, with the exception of **2b** which is a 1.5:1 diastereomeric mixture.

Table 4 Reaction of **1a** with the RM-$CuBr(PPh_3)_2$ system[a]

RM	**1a** conversion (%)	Product (yield/%)	
n-BuMgBr	88	**2a** (66)	**3a** (10)
EtMgBr	93	**2b** (61)	**3b** (18)
sec-BuMgBr	82	**2c** (47)	**3c** (14)
tert-BuMgCl	100	**2d** (21)	**3d** (19)
AllylMgBr	0		
n-BuLi[b]	86	**2a** (3)	

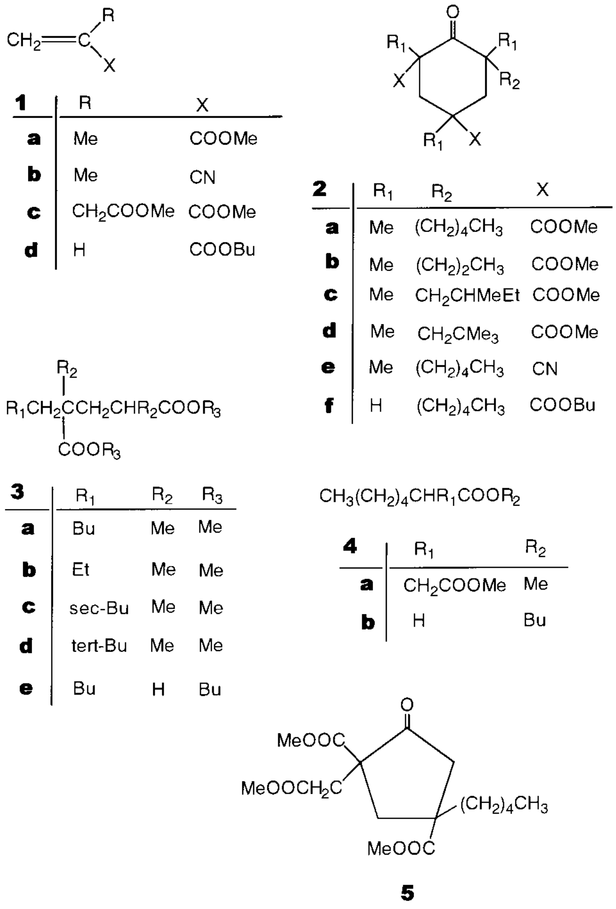
[a]Reaction temperature = 0 °C. [b]Hexane solution.

Next, the effects of varying the phosphine ligand were examined. The phosphine bearing an electron-donating substituent, *i.e.* tris(p-methoxyphenyl)phosphine, and the sterically demanding substituent, *i.e.* tri(o-tolyl)phosphine, reduced the formation of **2a** and **3a** somewhat compared with the use of triphenylphosphine. Triphenylphosphite also diminished the yield of **2a**, despite enhancement of the formation of **3a**. Alkylphosphines (*i.e.* tri-n-butylphosphine and tricyclohexylphosphine) brought about an increase in the yield of **2a**, 72 and 71%, respectively. Use of diphosphinoalkaline ligands resulted in the propane derivative showing preferential formation of **2a** (76%) compared with methyl, ethyl and butyl derivatives (48, 41 and 18%, respectively).

Various electron-deficient olefins other than **1a** were subjected to the reaction in the BuMgBr – CuBr–PPh_3 system. Methacrylonitrile (**1b**) gave the cyclohexanone derivative **2e**, which consists of a single diastereomer and appears to be formed according to the same reaction sequence as that in **2a** from **1a**. On the other hand, dimethyl ithaconate (**1c**) and butyl acrylate (**1d**) afforded the 1:1 conjugate adducts (**4a** and **4b**) along with the products (**5** and **3e**) derived from dimerization after the conjugate addition, the products of the latter type being preferentially formed compared to those of the former type. Gas chromatographic analysis revealed that **5** is composed of the diastereomeric mixture in a ratio of 15:11. The reaction of **1c** using trialkylphosphines (*i.e.* Bu_3P and cyc-hex_3P) as a ligand rather than PPh_3 was performed in order to bring about the enhanced formation of the dimerization-derived products **5**. These results are listed in Table 6. Next, the effects of ligands, reaction temperature and Lewis acid additive upon the reaction of **1d** were investigated. As with ligand, Bu_3P and cyc-$hexyl_3P$ increased the yields of the

---

* To receive any correspondence.



1	R	X
a	Me	COOMe
b	Me	CN
c	CH_2COOMe	COOMe
d	H	COOBu

2	R_1	R_2	X
a	Me	$(CH_2)_4CH_3$	COOMe
b	Me	$(CH_2)_2CH_3$	COOMe
c	Me	$CH_2CHMeEt$	COOMe
d	Me	CH_2CMe_3	COOMe
e	Me	$(CH_2)_4CH_3$	CN
f	H	$(CH_2)_4CH_3$	COOBu

3	R_1	R_2	R_3
a	Bu	Me	Me
b	Et	Me	Me
c	sec-Bu	Me	Me
d	tert-Bu	Me	Me
e	Bu	H	Bu

$CH_3(CH_2)_4CHR_1COOR_2$

4	R_1	R_2
a	CH_2COOMe	Me
b	H	Bu

5

Fig. 1

dimerization product **3e** (62 and 65%, respectively), and, in the bis(diophenylphosphino)alkane series, the propane derivative characteristically diminished the formation of **3e** and **4b** in contrast to the enhanced formation of **2a** from **1a**. Lowering of the temperature to –40 °C afforded a slight increase in the yields of **3e** and **4b** (59 and 22%, respectively), and raising the temperature to the reflux temperature remarkably decreased the yields of **3e** and **4b** (14 and 3%, respectively). Addition of Lewis acids (Me_3SiCl, BF_3, $TiCl_3$, $AlCl_3$ and $AlMe_3$) resulted in somewhat diminished yields of **3e** along with enhanced formation of **4b**, except when using $TiCl_4$, although BF_3 and $TiCl_4$ affected only slight formation of the trigomerization product **2f**, as judged from GC – MS analysis.

An alkylcopper(I)-phosphine complex may be reasonably assumed to be an actual working intermediate in our reaction system which consists of an alkyl Grignard reagent and a copper(I)halide phosphine complex.[10] The reason why this putative intermediate preferentially forms oligomers by the reaction with acrylate derivatives may be a result of steric congestion or back-donating stabilization of the copper(I) intermediate due to the phosphine ligand to impede progression of polymerization.

Techniques: ^1H and ^{13}C NMR, IR, MS

References: 13

Tables: 7

Table 1: Reaction of methyl methacrylate (**1a**) with the BuMgBr-CuBr(PPh_3) n system

Table 2: Influence of CuX and BuMgX upon reaction of **1a**

Table 3: Influence of reaction temperature upon reaction of **1a**

Table 5: Influence of phosphine ligand upon reaction of **1a** with the BuMgBr-CuBr system

Table 7: Influence of phosphine ligand, reaction temperature and Lewis acid additive upon reaction of butyl acrylate (**1d**) with the BuMgBr-CuBr system

Received 28 June 1999; accepted 14 October 1999
Paper 9/05176G

References cited in this synopsis

5 J. Munch-Petersen, *Acta Chem. Scand.* 1958, **12**, 2007; E.-L. Lindstedt, M. Nilsson, T. Olsson, *J. Orgmet. Chem.* 1987, **334**, 255: B.H. Lipshutz, J.A. Kozlowski, D.A. Parker, K.E. McCarthy, *J. Orgmet. Chem.* 1985, **285**, 437; Y. Yamamoto, S. Yamamoto, H. Yatagai, Y. Ishihara and K. Maruyama, *J. Org. Chem.* 1982, **47**, 119.
8 F.H. Owens, W.L. Myers and F.E. Zimmerman, *J. Org. Chem.* 1961, **26**, 2288.
9 Th. Volker, A. Neumann and U. Baumann, *Makromol. Chem.* 1963, **63**, 182.
13 H.O. House, W.L. Respess and G.W. Whitedides, *J. Org. Chem.* 1966, **31**, 3128.