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A SAFE AND EFFICIENT PROCEDURE TO PREPARE ALKYL AND ALKOXYALKYL CHLORIDES AND DICHLORIDES BY CATALYTIC DECOMPOSITION OF THE CORRESPONDING ALKYL AND ALKOXYALKYL CHLOROFORMATES AND BISCHLOROFORMATES WITH HEXABUTYLGUANIDINIUM CHLORIDE

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**A SAFE AND EFFICIENT PROCEDURE TO
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HEXABUTYLGUANIDINIUM CHLORIDE**

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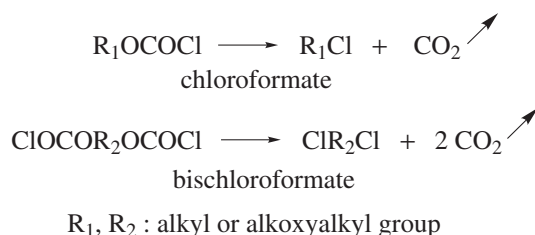
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ABSTRACT

Small amounts of hexabutylguanidinium chloride (0.01 mol%) decomposes pure chloroformates or bischloroformates with different lengths of carbon chains by a semicontinuous process to diminish run-away risk, leading to chloride compounds with high yield and purity.

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*Scheme 1.*

Alkyl chlorides and dichlorides are largely used to prepare herbicides and drugs (1–5). They are generally prepared by decomposition of the corresponding chloroformates or bischloroformates in the presence or not of a catalyst (Sch. 1).

Without a catalyst, these exothermic reactions of decomposition (6) lead to the formation of many by-products (olefin (7) or rearranged alkyl chlorides (8)). This does not occur in the presence of catalysts (e.g., amides (9) and the tertiary amines or their hydrochlorides (10–12)). In this case, the reaction is carried out with large quantities of catalyst (up to 43 mol%).

Other catalysts, such as phosphonium or quaternary ammonium salts (13,14), which are thermally unstable, lose their activity during the reaction and cannot be recycled.

Recently, Foulon et al. (15) used a hexasubstituted guanidinium salt (hydrochlorate of hexabutylguanidinium chloride: HBGC · HCl), which is thermally stable, to decompose small quantities (1 mmol) of monochloroformates with short carbon chains (≤ 8) at 100°C and with 0.5% of catalyst in the presence of monochlorobenzene as solvent. In this case, the kinetics of the reaction is fast.

Preliminary experiments were carried out by using Foulon's conditions to the decomposition of a more significant quantity (10 mmol) of *n*-octyl chloroformate. It was found that violent and very exothermic reactions were produced, even in the case of chloroformate with longer carbon chains ($\text{R}_1 = \text{CH}_3(\text{CH}_2)_9$) or bischloroformate ($\text{R}_2 = (\text{CH}_2)_8$). The reduction to 0.01% of the quantity of catalyst was not successful to control the decomposition of the *n*-octyl chloroformate.

Such results led us to modify these experimental conditions so that they could be applicable to the decomposition of large quantities of mono and bischloroformates. Reactions were carried out in absence of organic solvent to facilitate synthesis scale transfer. Variable length of carbon chain (between 4 and 18) was also considered.



Table 1. Thermogravimetric Analysis of the Chloroformates and Bischloroformates Studied

Products	Decomposition Temp. (°C)
$\text{ClOCO}(\text{CH}_2)_4\text{OCOCI}$	142
$\text{ClOCO}(\text{CH}_2)_6\text{OCOCI}$	142
$\text{ClOCO}(\text{CH}_2)_8\text{OCOCI}$	150
$\text{ClOCO}(\text{CH}_2)_{10}\text{OCOCI}$	165
$\text{ClOCO}(\text{CH}_2)_{12}\text{OCOCI}$	170
$\text{O}(\text{CH}_2\text{CH}_2\text{OCOCI})_2$	143
$(\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCOCI})_2$	160
$\text{O}(\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCOCI})_2$	163
$\text{CH}_3(\text{CH}_2)_{15}\text{OCOCI}$	160
$\text{CH}_3(\text{CH}_2)_{17}\text{OCOCI}$	163

RESULTS AND DISCUSSION

The studied chloroformates or bischloroformates were first synthesized without catalyst and solvent by reaction of corresponding alcohol with phosgene (16).

In order to avoid the formation of by-products by thermal decomposition of chloroformates and bischloroformates (7,8), we first determined their decomposition temperatures by thermogravimetric analysis (Table 1).

Table 1 shows that, for compounds belonging to the same family, the longer the alkyl or alkoxyalkyl chain is, the more thermally stable the chloroformate or bischloroformate becomes. For all the studied compounds, the decomposition temperatures are equal to or higher than 142°C. Thus, maximum temperature of the reaction should not exceed 140°C if catalytic decomposition is desired (instead of thermal degradation).

In order to avoid the violence of the reaction observed with Foulon's conditions, chloroformates and bischloroformates were introduced gradually into the reactor containing a catalyst: $\text{HBGC} \cdot \text{HCl}$ (0.01 mol%/total amount of chloroformates and bischloroformates), which was previously dissolved in chloroformate (1000 g/g catalyst). In the case of the decomposition of butyl 1,4-bischloroformate and bis(ethyl 2-chloroformate)ether, the catalyst was dissolved in the corresponding chlorinated compound (1000 g/g catalyst) because the decomposition of these bischloroformates is fast and violent. The chloroformate feed rate was varied so that the reaction temperature was kept between 110 and 115°C. However, total reaction time was fixed to 4 h. Results obtained at the end of various reactions are shown in Table 2.



Table 2. Catalytic Decomposition of Chloroformate or Bischloroformate in the Presence of HBGC·HCl (0.01 mol%)

Chloroformate's R ₁ and R ₂ Groups	Feed Time	Yield ^a (%)	Purity ^a (%)	Products Other Than Chlorides ^b
R₁				
-(CH ₂) ₄ ^{-c}	2:50	91	97	Carbonate and polycarbonate
-(CH ₂) ₆ ⁻	2:30	93	98	Chloroformate
-(CH ₂) ₈ ⁻	2:00	94	96	Chloroformate
-(CH ₂) ₁₀ ⁻	1:00	97	>99	Small amount of carbonate and polycarbonate
-(CH ₂) ₁₂ ⁻	0:20	88	92	Carbonate and polycarbonate
O(CH ₂) ₂ ^{-c}	2:00	91	>99	No impurity
(CH ₂ OCH ₂ CH ₂) ₂ ⁻	2:30	97	>99	Small amount of carbonate and polycarbonate
O(CH ₂ CH ₂ OCH ₂ CH ₂) ₂ ⁻	1:50	81	87	Carbonate and polycarbonate
R₂				
CH ₃ (CH ₂) ₁₅ ⁻	0:50	92	97	Chloroformate
CH ₃ (CH ₂) ₁₇ ⁻	0:20	90	94	No impurity

^a Analysis of crude reaction medium by CPG by internal calibration.

^b Analysis by IR; chloroformate ($\nu_{\text{CO}} \approx 1780 \text{ cm}^{-1}$); carbonate ($\nu_{\text{CO}} \approx 1750 \text{ cm}^{-1}$).

^c The HBGC·HCl is dissolved in the chlorinated compound and not in chloroformate.

The shorter the carbon chain of R₁ or R₂ is, the longer the substrate feed takes. The decomposition kinetics is very fast for the compounds bearing short carbon chains (15) (≤ 8) and obliges to decrease the feed rate to limit the heat generation. The mechanism being a S_N2 one (15), the nucleophilic attack of the chloride ion of catalyst on the α carbon of the -O(CO)Cl function would be easier and faster for these small molecules. The viscosity of the reaction medium increases with the length of R₁ and R₂ which is unfavorable to the diffusion of the catalyst molecules leading to a decrease of yield. This fact was especially marked for R₁ = (CH₂)₁₂, O(CH₂CHOCH₂CH₂)₂ and R₂ = CH₃(CH₂)₁₇.

Other compounds yielded chlorinated derivatives in more than 90% with purity higher than 96%. In all the cases, yield values were minimized because of a stripping of the chlorinated compound by CO₂ during the reaction. The by-products present in small quantities (carbonates or polycarbonates) arose from the secondary reactions between catalyst and the chloroformate or bischloroformate (15) (Sch. 2).



Alcohols and diols were Aldrich products. Phosgene and HBGC · HCL were furnished by SNPE. Alkylchloride, alkylchloride, and alkoxyalkylchloride used as standards for GC analysis were purchased from Aldrich and Fluka.

General Procedure for the Synthesis of Chloroformate and Bischloroformate. Phosgene (1 eq./OH function) was introduced in a reactor cooled at -10°C . Then, alcohol or diol (1 eq.) and phosgene (2 eq./OH) were added simultaneously into the reactor, maintaining the mixture temperature lower than 10°C . When the alcohol or diol was solid at room temperature, we had to use a heated dropping funnel. The reaction medium was stirred for 3 h at room temperature. Finally the excess of phosgene was removed by a stream of nitrogen through the solution for one night.

General Procedure for the Decomposition of Chloroformate and Bischloroformate. The HBGC · HCl (1×10^{-4} eq./total amount of chloroformates and bischloroformates) was solubilized in chloroformate (or bischloroformate) or corresponding alkyl chloride (or dichloride) (1000 g/g catalyst). The complement of chloroformate (or bischloroformate) was added dropwise to the mixture in such a way as to maintain the temperature lower than 115°C and have a regular carbon dioxide gas evolution. The reaction mixture was stirred at 120°C for a 4-h total reaction time.

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REFERENCES

1. Yago, K.; Kawada, K.; Uchibori, T.; Zen, S.; Tomonaga, F. *Yakugaku Zasshi* **1992**, *112* (10), 723.
2. Kanazawa, A.; Ikeda, T.; Endo, T. J. *Polym. Sci. Part A: Polym. Chem.* **1993**, *31* (12), 3003.
3. Edwards, K.J.; Hardcastle, I.R.; Jarman, M.; Neidle, S.; Laughton, C.A. GB Patent 2,266,530, Nov 03, 1992.
4. Weis, A.L.; Chen, S.-F.; Reddy, P.S.; Mittakandi, M.; Dexter, D.L.; Woynarowski, J.M. WO Patent 96 03,384, Oct 1, 1996.
5. Park, J.; Falcetta, J.J. WO Patent 96 06,603, July 03, 1996.
6. Rigamonti, F. *Chem. Engin. Sci.* **1992**, *47*, 2653.
7. Lewis, E.S.; Herndon, W.C. *J. Am. Chem. Soc.* **1961**, *83*, 1955.
8. Clinch, P.W.; Hudson, H.R. *J. Chem. Soc., Chem. Com.* **1968**, 925.





HEXABUTYLGUANIDINIUM CHLORIDE

373

9. Richter, R.; Tucker, B. J. *Org. Chem.* **1983**, *48* (5), 2625.
10. Flinckinger, E.; Trieschmann, H.-G. DE Patent 821 207, Nov 15, 1951.
11. Weickmann, A. DE Patent 857 350, Nov 11, 1952.
12. Neumayr, F.; Decker, M. EP Patent 025 829, April 1, 1981.
13. Widder, R.; Decker, M. EP Patent 375 920, July 4, 1990.
14. Briody, R.G.; Manner, J.A. US Patent 4,814,524, March 21, 1989.
15. Foulon, F.; Fixari, B.; Picq, D.; Le Perchec, P. *Tetrahedron Lett.* **1997**, *38* (19), 3387.
16. Matzner, M.; Kurkjy, R.P.; Cotter, R.J. *Chem. Rev.* **1964**, *64*, 645.

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