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AN EFFICIENT DOUBLE CHLORINATION OF OLEFINS BY tert-BUTYL HYPOCHLORITE

Wataru SATO, Nobuo IKEDA, and Hisashi YAMAMOTO*

Department of Applied Chemistry, Nagoya University

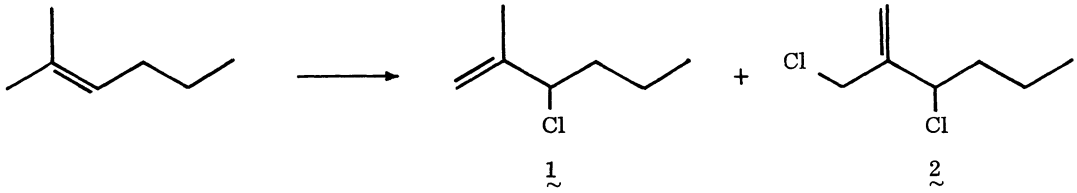
Chikusa, Nagoya 464

Allylic dichlorides can be prepared regioselectively and in good yields from simple olefins by tert-butyl hypochlorite in the presence of silica gel.

The conversion of olefins into allylic halides is very often an important and necessary organic transformation. Several newer methods have been appeared recently, among which are the followings: (1) arylselenenyl chloride or aryldiselenide with NCS;[1] (2) hypochlorite ion;[2] (3) electrochemical approach.[3] We wish to report a simple and efficient one-step procedure for the conversion of olefins into allylic dichlorides under mild conditions via treatment of the olefins with tert-butyl hypochlorite in the presence of silica gel.

2-Methyl-2-hexene was converted either to 3-chloro-2-methyl-1-hexene or to 3-chloro-2-chloromethyl-1-hexene depending on the choice of reaction conditions. Some of our results are summarized in Table I. Unfortunately, the exact role of silica gel for the present reaction is not yet clear and, in some cases, the chlorination can proceed equally well in the absence of silica gel (entry 6). However, in the absence of silica gel, the chlorination proceeds more slowly or (in hexane) not at all under the conditions specified. Furthermore, without silica gel, the product yield varied considerably from one experiment to another.[4]

Table I. Chlorination of 2-Methyl-2-hexene

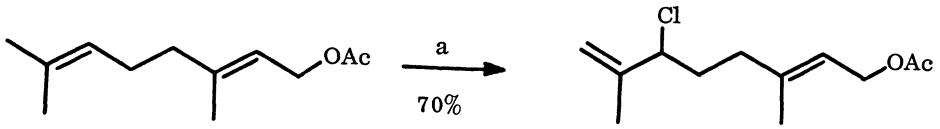


1 2

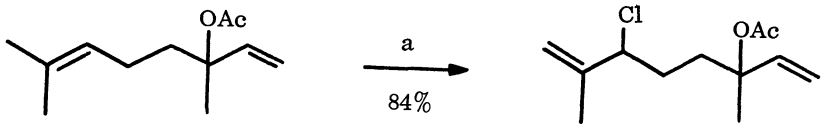
Entry	t-BuOCl	Solvent	Silica gel[a]	Product (%)[b] 1	2	Entry	t-BuOCl	Solvent	Silica gel[a]	Product (%)[b] 1	2
1	1.05	Hexane	-	3	-	6	1.05	$CHCl_3$	-	57	-
2	1.05	Hexane	+	69	-	7	2.1	$CHCl_3$	+	19	38
3	2.1	Hexane	+	73	5	8	2.1	Ether	-	53	13
4	1.05	CH_2Cl_2	-	9	-	9	2.1	Ether	+	5	69
5	1.05	CH_2Cl_2	+	59	-						

[a]Merk (7731) Silica Gel 60G for thin layer chromatography was used. Other silica gels with equal efficiencies are: Merk (9385) Silica Gel 60 and Woelm (04662) for column chromatography. [b]Yields were estimated by ^1H NMR measurments of the distilled products.

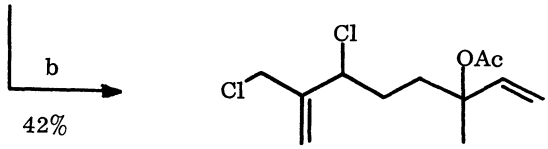
The reaction of tert-butyl hypochlorite with a number of olefins led to efficient chlorination as indicated, for example, by eq. 1-4, which also summarize experimental conditions.



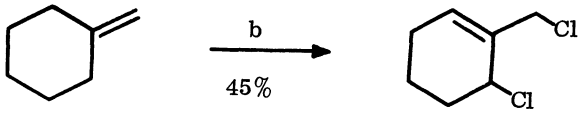
(1)[c]



(2)



(3)



(4)

Yields are for purified products isolated by column chromatography on silica gel (pre-cooled at 0 °C). Reagents and conditions: a: tert-butyl hypochlorite (1.05 equiv)-silica gel-hexane at 0 °C for 30 min and at room temperature for 1 h; b: tert-butyl hypochlorite (2.4 equiv)-silica gel-ether at 0 °C for 1 h; c: None of the β-chloroacetate (a regioisomer) was produced from this reaction.

The following experimental procedure is representative of the conversion: A solution of 2-methyl-2-hexene (2.76 ml, 20 mmol) in dry ether (80 ml) was cooled to 0 °C. Silica gel (5 g, Merk (7731) Silica Gel 60G) was added. tert-Butyl hypochlorite (5.70 ml, 48 mmol) was added dropwise via hypodermic syringe over a period of 5 min. The mixture was stirred at 0 °C for 30 min and at room temperature for 1 h. Slightly yellow color was discharged during this period. The colorless suspension was poured into aqueous sodium sulfite and the product was extracted with pentane. The combined organic layers was washed with water and dried over sodium sulfate and concentrated in vacuo. The remaining liquid was distilled (bp 100 °C, 10 mmHg) to give the dichloride 2 as a colorless oil (2.47 g, 74%). ^{1}H NMR spectrum of this product indicated the presence of (<5%) of the monochloride 1.

References

1) T. Hori and K. B. Sharpless, J. Org. Chem., 44, 4204 and 4208 (1979).
2) S. G. Hegde, M. K. Vogel, J. Saddler, and T. Hrinyo, Tetrahedron Lett., 21, 441 (1980); tert-Butyl hypochlorite with penicillin derivatives, see R. D. G. Cooper, ibid., 21, 781 (1980).
3) S. Torii, K. Uneyama, T. Nakai, and T. Yasuda, Tetrahedron Lett., 22, 2291 (1981).
4) The protonated form of tert-butyl hypochlorite was known to be a more powerful electrophilic reagent, see, L. W. Hartel and L. A. Paquette, J. Am. Chem. Soc., 101, 7620 (1979).

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