

SHORT
COMMUNICATIONSDedicated to Full Member of the Russian Academy of Sciences
G.A. Tolstikov on his 75th anniversary

Unusual Reaction of Chloroacetyl Chloride with 1,2-Dichloroethylene. Synthesis of 1,1,4-Trichlorobut-3-en-2-one

G. V. Bozhenkov, V. A. Savosik, E. V. Rudyakova, A. N. Mirskova, and G. G. Levkovskaya

Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences,
ul. Favorskogo 1, Irkutsk, 664033 Russia
e-mail: ggl@irioch.irk.ru

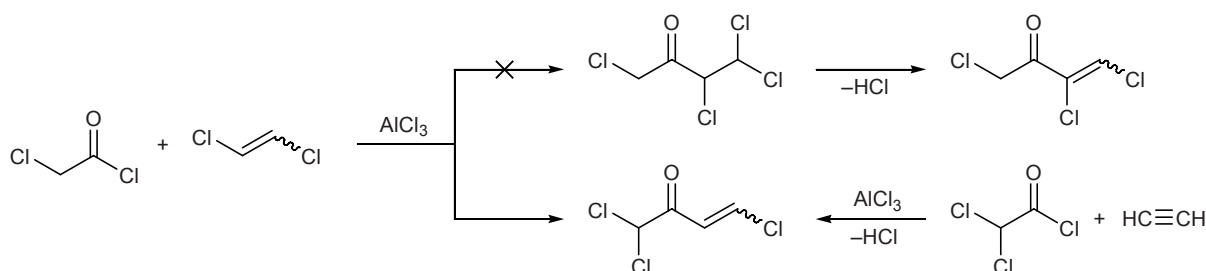
Received June 6, 2007

DOI: 10.1134/S1070428008010211

Chlorovinyl ketones are very important and promising synthons for the preparation of various highly reactive polyfunctionalized compounds, including heterocyclic ones [1]. We previously synthesized alkyl 1,2-dichlorovinyl ketones from aliphatic carboxylic acid chlorides and 1,2-dichloroethylene in the presence of aluminum chloride [2]. While continuing studies on the scope of application of the proposed procedure for the preparation of 1,2-dichloro enones, we have found that, in contrast to the only known halogen-containing 1,2-dichlorovinyl ketone, dichloromethyl 1,2-dichlorovinyl ketone [3] which was obtained from dichloroacetyl chloride and *cis*-1,2-dichloroethylene, chloroacetyl chloride reacts with a mixture of *cis* and *trans* isomers of 1,2-dichloroethylene (a large-scale commercial product) to give an unexpected product, previously unknown 2-chlorovinyl dichloromethyl ketone, whose structure was unambiguously proved by IR and ^1H and ^{13}C NMR spectroscopy, two-dimensional ^1H - ^{13}C NMR spectroscopy, mass spectrometry, and independent synthesis. By special experiment we showed that 1,2-dichloroethylene does not give rise to 2-chlorovinyl dichloromethyl ketone under analogous conditions.

Studies on the mechanism of formation of 2-chlorovinyl dichloromethyl ketone from 1,2-dichloroethylene and chloroacetyl chloride, which is likely to involve chlorotropic rearrangements, and on the reactivity of the resulting chloro enone are now in progress.

1,1,4-Trichlorobut-3-en-2-one. Chloroacetyl chloride, 70.86 g (0.62 mol), was added dropwise under stirring to a solution of 82.67 g (0.62 mol) of aluminum chloride in 100 ml of 1,2-dichloroethylene, and the mixture was stirred for 11 h at 60°C. The mixture was cooled and poured onto ice, the organic layer was separated, and the aqueous layer was extracted with methylene chloride. The extracts were combined with the organic phase, dried over CaCl_2 , filtered, and evaporated, and the residue was distilled under reduced pressure. Yield 75 g (70%), bp 57–60°C (7 mm), $n_{\text{D}}^{20} = 1.5262$. IR spectrum, ν , cm^{-1} : 3080, 3020 (=CH); 2990 (CHCl_2); 1720, 1690 (C=O); 1590, 1570 (C=C). ^1H NMR spectrum (CDCl_3), δ , ppm: 7.57 d (1H, 4-H, $J = 13.4$ Hz), 6.99 d (1H, 3-H, $J = 13.4$ Hz), 5.88 s (1H, CHCl_2). ^{13}C NMR spectrum, δ_{C} , ppm: 183.12 (C=O), 141.82 (=CH), 124.59 (=CH), 69.09 (CHCl_2). Mass spectrum, m/z (I_{rel} , %): 173 (5) [M] $^+$, 91 (60), 89



(100), 83 (10), 63 (20), 61(50), 48 (10). Found, %: C 27.63; H 1.76; Cl 61.30. $C_4H_3Cl_3O$. Calculated, %: C 27.70; H 1.74; Cl 61.33.

The IR spectrum (neat) was recorded on a Specord 75IR spectrophotometer. The 1H and ^{13}C NMR spectra were measured on a Bruker DPX-400 spectrometer at 400.13 and 100.62 MHz, respectively. The mass spectrum (electron impact, 70 eV) was obtained on a Shimadzu GCMS-QP5050A instrument (quadrupole mass analyzer, a.m.u. range 34–650).

REFERENCES

1. Kochetkov, N.K., *Usp. Khim.*, 1955, vol. 24, p. 32; Pohland, A.E. and Benson, W.R., *Chem. Rev.*, 1966, vol. 66, p. 161.
2. Bozhenkov, G.V., Levkovskaya, G.G., Larina, L.I., Ushakov, P.E., Dolgushin, G.V., and Mirskova, A.N., *Russ. J. Org. Chem.*, 2004, vol. 40, p. 1583.
3. Prins, H.J. and Haring, H.G., *Recl. Trav. Chim. Pays-Bas*, 1954, vol. 73, p. 479; *Chem. Abstr.*, 1955, vol. 49, p. 12265b.