Russian Chemical Bulletin, International Edition, Vol. 53, No. 11, pp. 2647—2649, November, 2004

Brief Communications

A novel method for the synthesis of dichloroalkenes

V. G. Nenajdenko,[a]* A. V. Shastin,[b] V. M. Muzalevskii,[a] and E. S. Balenkova[a]

[a]Department of Chemistry, M. V. Lomonosov Moscow State University,
Leninskie Gory, 119992 Moscow, Russian Federation.
Fax: +7 (095) 932 8846. E-mail: nen@acylium.chem.msu.ru
[b]Institute of Problems of Chemical Physics, Russian Academy of Sciences,
142432 Chernogolovka, Moscow Region, Russian Federation.
E-mail: shastin@icp.ac.ru

A novel convenient method for the synthesis of dichloroalkenes was developed. The method involves catalytic olefination of hydrazones of aliphatic carbonyl compounds with bromo(trichloro)methane.

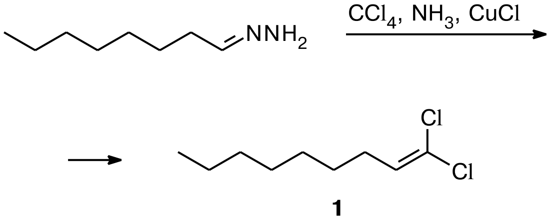
Key words: olefination, carbonyl compounds, hydrazones, bromotrichloromethane, catalysis, copper salts, dichloroolefins.

Construction of new carbon-carbon bonds is a key problem in modern organic chemistry, while transformation of carbonyl compounds into olefins is one of the most general approach to construction of new C=C bonds.[1] Earlier,[2] catalytic olefination was discovered as a novel reaction. It was found that treatment of *N*-unsubstituted benzaldehyde hydrazones with CCl_4 in the presence of bases and catalytic amounts of cuprous chloride affords β,β-dichlorostyrenes.

gem-Dichloroolefins are valuable products of organic synthesis and are used to obtain chloroacetylenes,[3] acetylenes,[4] and alkali metal acetylenides.[5] In addition, the *gem*-dichloroolefin fragment is part of the structure of pyrethroids (*e.g.*, cypermethrin and cyfluthrin) widely used as pesticides.[6]

Our preceding attempted syntheses of dichloroolefins by catalytic dichloromethylenation of aliphatic carbonyl compounds gave the target dichloroalkenes in low yields. For instance, in the reaction of octanal hydrazone with CCl_4, the yield of 1,1-dichlorononene (**1**) was 15% (Scheme 1).[7]

Scheme 1

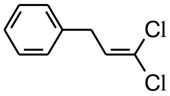
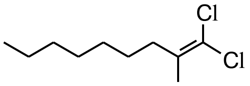
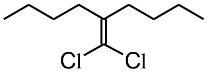
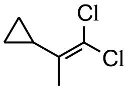
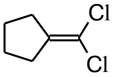
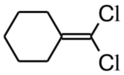
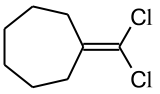
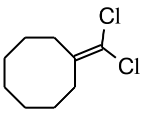
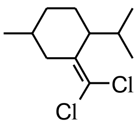
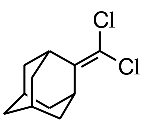


Later,[8] it was demonstrated that bromotrichloromethane is a more reactive alkenylating reagent

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 2538—2540, November, 2004.

than tetrachloromethane, even in the presence of a catalyst (0.5 mol. % CuCl). In the present work, with the aim of extending the range of the target products, we carried out reactions with a wide set of aliphatic aldehydes and ketones and obtained dichloroalkenes in satisfactory to good yields (the yield of compound **1** increased to 60%). The products obtained contain both alkyl substituents and small rings and have framework and cyclic structures (Scheme 2, Table 1). To attain the highest possible yields, a solution of an *in situ* prepared hydrazone was added to a solution of bromotrichloromethane, aqueous ammonia, and cuprous chloride in DMSO (according to the "normal" procedure, polyhaloalkane is added to a solution of hydrazone, a base, and a catalyst). The reversed order of mixing the reagents ensures significantly higher concentrations of polyhaloalkane and the catalyst with respect to hydrazone than in the case of normal order of addition; as shown earlier,[2] this should increase the yield of the target olefin.

Table 1. Dichloroolefins from aliphatic carbonyl compounds

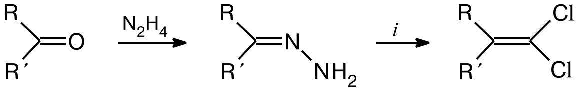
Dichloroalkene	Yield (%)*
 **(2)**	68
 **(3)**	63
 **(4)**	43
 **(5)**	55 (34)
 **(6)**	42
 **(7)**	70 (38)
 **(8)**	60 (36)
 **(9)**	44 (15)
 **(10)**	27
 **(11)**	25

* The yields given in parentheses were attained in the normal order of addition of $CBrCl_3$ to hydrazone.

For some carbonyl compounds, we used both ways of mixing the reagents (see Table 1). It turned out that the reversed order of addition increases the yields of the target alkenes by 10 to 30% and the yield of the cyclooctanone derivative increased nearly three times.

According to the data obtained, the yield of the alkene strongly depends on the spatial environment of the carbonyl group. For instance, when passing from phenylacetaldehyde and relatively non-hindered heptyl methyl ketone to noticeably more hindered dibutyl ketone, the yields of dichloroalkenes **2**—**4** decrease from 60—70 to 43%. In the series of cyclic ketones, the yields of alkenes containing from five- to eight-membered rings show a parallel change with the energy of the ring strain: **5** < **6** > **7** > **8** (see Scheme 2).

Scheme 2



2—11

i. $CBrCl_3$, 0.5 mol.% CuCl

Thus, we developed a novel simple and convenient method for the synthesis of dichloroalkenes from hydrazones of aliphatic carbonyl compounds. The main advantages of the method proposed are easy-to-perform reactions, inexpensive starting reagents, minimum amounts of a catalyst. The yields of the target alkenes are comparable with the yields attained *via* other methods.[1]

Experimental

^1H and ^{13}C NMR spectra were recorded on a Varian VXR-400 spectrometer (400 MHz and 100 MHz, respectively) in $CDCl_3$ with Me_4Si as the internal standard. IR spectra were recorded on a UR-20 spectrophotometer (thin film). TLC analysis was carried out on Silufol UV-254 plates; spots were visualized with an acidified solution of $KMnO_4$, the iodine vapor, and UV light. Column chromatography was carried out on Merck silica gel (63-200 mesh).

Synthesis of dichloroalkenes (general procedure). An argon-prefilled flask was charged with hydrazine hydrate (0.5 mL, 10 mmol) and DMSO (5 mL). A solution of a carbonyl compound (10 mmol) in 5 mL of DMSO was added dropwise with vigorous stirring. After the reaction was completed (monitoring by TLC), the solution of the hydrazone obtained was added to a vigorously stirred mixture of $CBrCl_3$ (5 mL), 25% aqueous ammonia (3 mL), and CuCl (0.005 g, 0.5 mol. %) for 0.5 h. The reaction mixture was stirred until the gas ceased to evolve (5—30 min for different substrates) and then poured into water (300 mL). The product was extracted with dichloromethane (3×100 mL) and the combined extract was dried over sodium sulfate. The solvents were removed *in vacuo* and the residue was purified by column chromatography with hexane as the eluent.

The ^{1}H NMR spectra of compounds **1**, **2**, and **4**—**11** are identical with those previously reported for **1**,[9] **2**,[10] **4**,[11] **5**, **8**, **9**,[12] **6**,[13] **7**, **11**,[14] and **10**.[15]

1,1-Dichloro-2-methylnon-1-ene (3). The yield was 63%, colorless oil, R_f 0.84 (hexane). Found (%): C, 56.90; H, 8.21. $C_{10}H_{18}Cl_2$. Calculated (%): C, 57.42; H, 8.67. IR, ν/cm^{-1}: 1620 (C=C). ^{1}H NMR, δ: 2.23 (t, 2 H, C(3)H_2, J = 7.3 Hz); 1.85 (s, 3 H, CH_3—C=C); 1.43 (pent, 2 H, C(4)H_2, J = 7.3 Hz); 1.32—1.24 (m, 8 H, C(5)H_2, C(6)H_2, C(7)H_2, C(8)H_2); 0.88 (t, 3 H, Me, J = 7.3 Hz). ^{13}C NMR, δ: 135.37 (C(1)); 113.99 (C(2)); 35.41, 31.77, 29.21, 29.10, 26.98, 22.64, 19.80, 14.07.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 03-03-32052a).

References

1. V. N. Korotchenko, V. G. Nenajdenko, A. V. Shastin, and E. S. Balenkova, *Usp. Khim.*, 2004, **73**, 1039 [*Russ. Chem. Rev.*, 2004, **73** (Engl. Transl.)].
2. A. V. Shastin, V. N. Korotchenko, V. G. Nenajdenko, and E. S. Balenkova, *Tetrahedron*, 2000, **56**, 6557.
3. P. Vinczer, S. Sztruhar, L. Novak, and C. Szantay, *Tetrahedron Lett.*, 1992, **33**, 683.
4. Z. Wang, S. Campagna, G. Xu, M.E. Pierce, J. M. Fortunak, and P. N. Confalone, *Tetrahedron Lett.*, 2000, **41**, 4007.
5. E. Hajime, N. Tsutomu, I. Masahiko, and N. Masazumi, *Tetrahedron Lett.*, 1981, **22,** 4441.
6. V. K. Promonenkov, T. G. Perlova, L. N. Andreeva, L. M. Levit, I. K. Kolchin, E. S. Nemets, A. M. Katunskii, E. Yu. Balashova, I. I. Eliseeva, V. V. Akshentsev, M. Ya. Pushina, V. A. Kasparov, E. D. Butova, V. V. Krotov, A. A. Fokin, and P. A. Krasutskii, *Piretroidy. Khimiko-tekhnologicheskie aspekty* [*Pyrethroids. Aspects of Chemical Technology*], Khimiya, Moscow, 1992, 336 pp. (in Russian).
7. V. N. Korotchenko, Ph.D. (Chem.) Thesis, M. V. Lomonosov Moscow State University, Moscow, 2003, 198 pp.
8. V. G. Nenajdenko, V. N. Korotchenko, A. V. Shastin, D. A. Tyurin, and E. S. Balenkova, *Zh. Org. Khim.*, 2004, **40**, No. 12 [*Russ. J. Org. Chem.*, 2004, **40** (Engl. Transl.)].
9. P. Vinczer, S. Sztruhar, L. Novak, and C. Szantay, *Org. Prep. Proc. Int.*, 1992, **24**, 540.
10. P. Jubault, C. Feasson, and N. Collignon, *Bull. Soc. Chim. Fr.*, 1994, **131**, 1001.
11. F. Karrenbrock, H. J. Schafer, and I. Langer, *Tetrahedron Lett.*, 1979, 2915.
12. A. D. Ketley, A. J. Berlin, E. Gorman, and L. P. Fesher, *J. Org. Chem.*, 1966, **31**, 305.
13. W. T. Brady and A. D. Patel, *Synthesis*, 1972, 565.
14. P. J. Kropp, S. A. McNeely, and R. D. Davis, *J. Am. Chem. Soc.*, 1983, **105**, 6907.
15. T. Parella, F. Sanchez-Ferrando, and A. Virgili, *Magn. Reson. Chem.*, 1997, **35**, 30.

Received June 29, 2004;
in revised form August 30, 2004