Intramolecular cyclization of chloral allyl hemiacetal under the action of the $Fe(CO)_5$—DMF system

*T. T. Vasil'eva,[a] A. V. Ivanov,[b] K. I. Kobrakov,[b] K. Laihia,[c] E. Kolehmainen,[c] V. K. Korolev,[b] N. A. Kuz'mina,[a] and A. B. Terent'ev[a]**

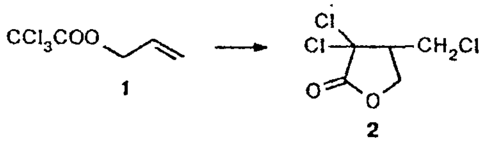
[a]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail terent@ineos.ac.ru
[b]*A. N. Kosygin Moscow State Textile Academy, 1 ul. Malaya Kaluzhskaya, 117918 Moscow, Russian Federation*
[c]*Chemistry Department, University of Jyvaskyla, 40351 Jyvaskyla, Finland.*
Fax: (358) 1460 2501

Chloral allyl hemiacetal undergoes cyclization in the presence of the $Fe(CO)_5$—DMF system to form 3,3,5-trichloro-2-hydroxytetrahydropyran rather than a butyrolactone derivative.

Key words: chloral allyl hemiacetal, cyclization, $Fe(CO)_5$—DMF, 3,3,5-trichloro-2-hydroxytetrahydropyran.

Generally, intramolecular cyclization of radicals containing the radical center and the double bond at positions 1 and 5 affords substituted five-membered cyclic compounds.[1] Using allyl trichloroacetate (**1**) as an example, it was demonstrated that its cyclization initiated with the $Fe(CO)_5$—DMF metal complex system[2] or copper salts[3] gave the corresponding butyrolactone (**2**) (Scheme 1).

Scheme 1

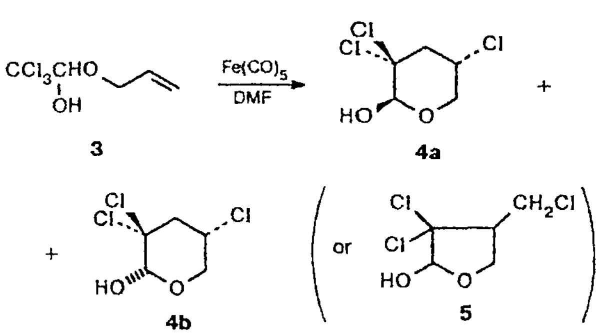


The structure of the resulting compound was established by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry.[3]

In studies of cyclization of a structurally similar compound, *viz.*, chloral allyl hemiacetal (**3**), under analogous conditions, we obtained an unexpected product (Scheme 2).

According to the ^{1}H and ^{13}C NMR spectral data, the reaction product was a 1 : 1 mixture of two compounds whose compositions corresponded to compounds **4** or **5**. The results of ^{1}H and ^{13}C NMR spectral studies demonstrated (see below) that one of these compounds is hydroxytetrahydropyran (**4a**). The second product could be either its diastereomer (compound **4b**) or hydroxytetrahydrofuran (**5**). A choice between these structures presented difficulties because the chemical shifts for some signals in the ^{13}C NMR spectrum of this compound differ substantially from those for the structurally similar analogs of compounds **2** and **4** reported in the literature.[3–5] With the aim of unambiguously establishing the structures of these molecules, the ^{13}C NMR spectrum of a mixture of isomers of compound **4** was recorded with the use of the 2D ^{13}C,^{13}C INADEQUATE technique[6] (Table 1 and Fig. 1), which allows one to isolate sets of signals of individual isomers from the overall spectrum and to determine the number and the nature of the neighbors at each C atom. The basis for this method is the detection of interactions between covalently bonded C atoms. From Fig. 1 it is clearly seen that the NMR spectrum contains two sets of signals belonging to different compounds.

Scheme 2



In addition, ^{1}H,^{1}H homocoupling (for the CH_2 groups) and ^{1}H,^{13}C heterocoupling (for the CH groups) were revealed. This made it possible to elucidate the nature of the group to which a particular C atom belongs, the

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 750—752, April, 1999.

Table 1. ^{13}C and ^{1}H NMR spectral data for the isomers of 3,3,5-trichloro-2-hydroxytetrahydropyran* (**4a** and **4b**)

δ_C	$^{1}J_{C,H}$/Hz	δ_H	$^{1}J_{H,H}$/Hz
		Isomer **4a**	
95.38 (CH, C-2)	177.2	4.78 (H-2)	
86.88 (C, C-3)	—	—	—
46.93 (CH_2, C-4)	141.7	2.64 (H-4a)	$J_{H-4a,H-4e}$ = 13.6, $J_{H-4a,H-5a}$ = 10.9
	135.7	2.59 (H-4e)	$J_{H-4e,H-5a}$ = 5.3, $J_{H-4e,H-6e}$ = 1.5
50.14 (CH, C-5)	154.5	3.93 (H-5a)	$J_{H-5a,H-6a}$ = 11.0
63.31 (CH_2, C-6)	156.9	3.75 (H-6a)	$J_{H-6a,H-6e}$ = 11.1
	147.2	3.43 (H-6e)	$J_{H-6e,H-5a}$ = 5.4
		Isomer **4b**	
98.48 (CH, C-2)	167.2	4.14 (H-2)	
88.55 (C, C-3)	—	—	—
52.02 (CH_2, C-4)	142.4	1.91 (H-4a)	$J_{H-4a,H-4e}$ = 14.0
	132.6	2.68 (H-4e)	
49.40 (CH, C-5)	156.3	3.66 (H-5a)	$J_{H-5a,H-6e}$ = 4.8, $J_{H-5a,H-6a}$ = 11.2, $J_{H-5a,H-4e}$ = 4.5, $J_{H-5a,H-4a}$ = 11.4
71.27 (CH_2, C-6)	155.6	3.59 (H-6e)	$J_{H-6a,H-6e}$ = 11.3, $J_{H-6e,H-4e}$ = 2.7
	144.5	2.83 (H-6a)	

* The assignment is arbitrary.

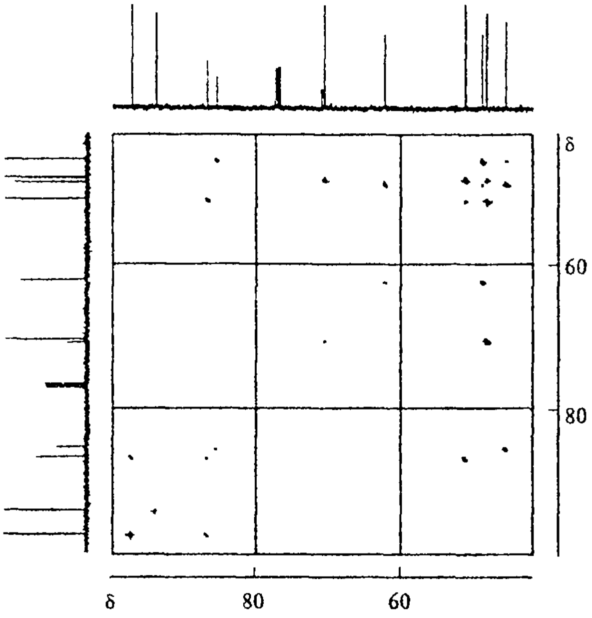


Fig. 1. $^{13}C,^{13}C$ INADEQUATE spectra for a mixture of isomers **4a,b** (shift of the scale to within 1 ppm is possible).

number of its neighbors, and the sequence of bonding of C atoms in the compounds under study for each ^{13}C signal. Thus compound **4a** is characterized by the presence of two C atoms (δ 95.38 and 63.31), which are bound to two and one O atoms, respectively, and have one adjacent C atom each, and of three C atoms having two adjacent C atoms each. The presence or absence of $^{1}H,^{13}C$ heterocoupling indicates the group of atoms (CH_2, CH, or C) to which a particular C atom belongs. In the case of the spectrum of compound **4b**, analogous conclusions can be drawn. A molecule with structure **5** should contain one C atom bound to three adjacent C atoms and the CH_2Cl group bonded to only one C atom, which is not actually observed. The number of signals as well as their multiplicity in the ^{1}H NMR spectra correspond to the molecular structures proposed for compounds **4a** and **4b**.

Thus, it was demonstrated that the isomeric compound is the second diastereomer of hydroxytetrahydropyran **4a** (*i.e.*, **4b**). An analogous product was prepared by the reaction of chloral with allyl alcohol in the presence of CuCl.[7]

The reasons for the difference in the results of cyclization of compounds **1** and **3** lies apparently in the fact that the nature of the functional groups of the initial compounds affects substantially the mechanism of cyclization.

Experimental

Preparative GLC was carried out on an LKhM-80 chromatograph (steel column (1300×9 mm) with 20% SKTFT-50X on Chromaton-N-AW; helium as the carrier gas (120 mL min^{-1}); katharometer as the detector). The ^{1}H and ^{13}C NMR spectra were recorded on Bruker WP-200 (200 MHz), JEOL JNM GSX 270 FT, and Bruker Avance DRX500 (125.77 MHz) spectrometers in $CDCl_3$ or C_6H_6. The chemical shifts are given in the δ scale relative to Me_4Si. The assignment of the signals was made with the use of the $^{1}H,^{13}C$ HMQC correlation[8,9] for the data obtained using the INADEQUATE technique.[6]

Chloral allyl hemiacetal (3).[10] When chloral and an equimolar amount of allyl alcohol were mixed, the reaction mixture spontaneously warmed up to 85 °C and turned yellow. The mixture was kept for 2 h and distilled off. The yield was 85%. B.p. 109—109.5 °C (*cf.* Ref. 10: b.p. 116 °C), n_D^{20} 1.4871, d_4^{20} 1.3759. ^{1}H NMR, δ: 5.90 (m, 1 H, CH=); 5.35 (m, 2 H, CH_2=); 4.85 (s, 1 H, CH); 4.38 (m, 2 H, CH_2O); 3.47 (s, 1 H, OH).

Cyclization of chloral allyl hemiacetal (3) in the presence of the $Fe(CO)_5$—DMF system. A mixture of hemiacetal **3** (0.2 g, 1 mmol) and $Fe(CO)_5$ (0.04 g, 0.2 mmol) in DMF (0.44 g, 0.6 mmol) and benzene (9.5 mL) was heated for 3 h in a sealed tube at 145 °C. The reaction mixture was passed through a SiO_2 layer to remove resinification products. Then the reaction product was isolated by preparative GLC. **3,3,5-Trichloro-2-hydroxytetrahydropyran (4)** was obtained in 30% yield, n_D^{20} 1.5179, d_4^{20} 1.5201. Found: MR 40.95. Calculated: MR 40.86. Found (%): C, 29.71; H, 3.42; Cl, 51.26. $C_5H_7Cl_3O_2$. Calculated (%): C, 29.23; H, 3.43; Cl, 51.77. The ^{1}H and ^{13}C NMR spectra, which were recorded using the INADEQUATE technique, of the isomers of compound **4** are given in Table 1 and Fig. 1.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 96-03-33430) and the International Association for the Promotion of Cooperation with Scientists from the Newly Independent States of the Former Soviet Union (INTAS, Grant 96-1990).

References

1. J. Baldwin, *J. Chem. Soc., Chem. Commun.*, 1976, 734.
2. A. B. Terent'ev, T. T. Vasil'eva, N. A. Kuz'mina, E. I. Mysov, and Yu. N. Belokon', *Izv. Akad. Nauk, Ser. Khim.*, 1997, 796 [*Russ. Chem. Bull.*, 1997, **46**, 764 (Engl. Transl.)].
3. H. Nagashima, K. Seki, N. Ozaki, H. Wakamatsu, K. Itoh, Y. Tomo, and J. Tsuji, *J. Org. Chem.*, 1990, **55**, 985.
4. A. J. de Haag, *Org. Magn. Reson.*, 1974, No. 6, 233.
5. L. de Buyck, *Bull. Chem. Soc. Belg.*, 1990, **99**, 121; 1992, **101**, 392.
6. D. L. Turner, *J. Magn. Reson.*, 1982, **49**, 175.
7. K. I. Kobrakov, F. V. Ivanov, V. K. Korolev, and A. B. Terent'ev, *Khim. Geterotsikl. Soedin.*, 1998, 130 [*Chem. Heterocycl. Compd.*, 1998 (Engl. Transl.)].
8. A. Bax, R. H. Griffey, and B. L. Hawkins, *J. Magn. Reson.*, 1983, **55**, 301.
9. A. Bax and S. Subramanian, *J. Magn. Reson.*, 1986, **67**, 565.
10. B. Oglialoro, *Ber.*, 1874, **7**, 1462.

Received October 13, 1998;
in revised form October 29, 1998