

ELECTROLYTICAL REDUCTIVE ADDITION OF ACETONE TO TRIFLUOROCHLOROETHYLENE*

F. LIŠKA, V. DĚDEK and M. NĚMEC

Department of Organic Chemistry,
Institute of Chemical Technology, 166 28 Prague 6

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The electrolytical addition of acetone to trifluorochloroethylene affords 2-methyl-3,3,4-trifluoro-4-chloro-2-butanol (*I*) similarly to the radical addition of 2-propanol to trifluorochloroethylene.

The radiation-initiated addition of 2-propanol and the electrolytical reductive addition of acetone to esters of α,β -unsaturated carboxylic acids has been recently reported by Itoh and co-workers¹. Both additions afforded the same reaction product, namely, the corresponding 4,4-dimethyl- γ -butyrolactone. The 4,4-dimethyl- γ -butyrolactone was also reported to accompany the primary product from the electrolytical addition of acetone to acrylonitrile, *i.e.*, 4-methyl-4-hydroxyvaleronitrile^{2,3}. The electrolytical addition of acetone to styrene, 1,3-butadiene, stilbene⁴, and allyl alcohol⁵ affords exclusively the primary addition products, *i.e.*, the corresponding tertiary alcohols.

Fluorinated olefins react readily with numerous compounds under the conditions of radical^{6,7}, electrophilic, and nucleophilic addition reactions^{8,9}. Particularly in the nucleophilic additions of alcohols, amines, thiols, and hydrogen cyanide to fluorinated olefins and to derivatives of α,β -unsaturated esters or nitriles¹⁰, the experimental conditions are very similar. It was therefore of interest in this connection to investigate the possibility of an electrolytical addition of acetone to trifluorochloroethylene. Such a reaction would represent a novel procedure in the addition of carbonyl compounds to fluorinated olefins.

The title reaction was performed under usual reaction conditions¹, *i.e.*, trifluorochloroethylene was introduced into a solution of acetone, sulfuric acid and water and the resulting reaction mixture was subjected to electrolysis at a constant voltage of 45 V (platinum anode, mercury cathode). As the principal reaction product, there was isolated 2-methyl-3,3,4-trifluoro-4-chloro-2-butanol (*I*), *i.e.*, the same reaction product as in the addition of 2-propanol to trifluorochloroethylene under the radical conditions, namely, in additions initiated with organic initiators, ⁶⁰Co γ -radiation¹¹, and ultraviolet radiation¹². The coulombic yield of the alcohol *I* varied in the range

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carbanion *Ib* under the formation of the alcohol *I*. The ionic reaction course is assumed by Itoh and coworkers for the addition of acetone to esters of α,β -unsaturated acids¹ (type of the Michael addition) and also by Sugino and Nonaka² for the addition of acetone to acrylonitrile. On the other hand, a radical course is proposed by Brown and Lister³ for the same reaction.

EXPERIMENTAL

The IR spectra were taken on a Perkin-Elmer 225 apparatus in tetrachloromethane in the range of 800–2000 cm^{-1} and 2600–3700 cm^{-1} . The NMR spectrum was measured on a Varian XL 100 apparatus in deuteriochloroform. The mass spectrum was recorded on a Gas Chromatograph — Mass Spectrometer LKB 9000 apparatus. Gas-chromatographical analyses were performed on a Chrom 31 apparatus with a flame ionisation detector and with the use of polypropylene sebacate and Carbowax 20 M on Chromosorb W.

Electrolytical Reductive Additions

The electrolysis was performed in a glass vessel, internal diameter 30 ml, internal volume 100 ml. Mercury at the bottom was used as cathode and anode was formed by a platinum foil placed about 5 mm from the mercury surface. The electrodes were not separated by diaphragma. Prior to electrolysis, the vessel was charged with the reaction mixture and during electrolysis, trifluorochloroethylene was introduced (rate, about 3 g per h) almost to the mercury surface. In all cases, the electrolysis was performed at a constant voltage between the electrodes (45 V). The electrolysis vessel was externally cooled with iced water. When the electrolysis was accomplished, most acetone was evaporated under diminished pressure. The residue was diluted with water (50 ml) and extracted with five 10 ml portions of ether. The ethereal extracts were combined, dried over anhydrous sodium sulfate, and evaporated. Distillation of the residue afforded a liquid, b.p. 60–70°C/25 Torr. The composition of the distillate was checked by gas chromatography; the content of the alcohol *I* was about 95%. For the composition of the reaction mixtures, reaction conditions and yields of particular experiments see Table I.

REFERENCES

1. Itoh M., Taguchi T., Chung V., Tokuda M., Suzuki A.: *J. Org. Chem.* **37**, 2357 (1972).
2. Sugino K., Nonaka T.: *Electrochim. Acta* **13**, 613 (1968).
3. Brown O. R., Lister K.: *Discussions Faraday Soc.* **45**, 106 (1968).
4. Pallaud R., Nicolas M.: *Compt. Rend. Ser. C* **267**, 1834 (1968).
5. Tomilov A. P., Kljuev B. L.: *Ž. Obšč. Chim.* **39**, 470 (1969).
6. Sosnovsky G.: *Free Radical Reactions in Preparative Organic Chemistry*. MacMillan, New York 1964.
7. Walling C.: *Svobodnyje Radikaly v Rastvore* (translation from English). Izd. Inostr. Lit., Moscow 1960.
8. Chambers R. D., Mobbs R. H.: *Advan. in Fluorine Chem.* **4**, 50 (1965).
9. Paleta O.: *Chem. listy* **60**, 1363 (1966).
10. Bruson H. A.: *Org. Reactions* **5**, 79.
11. Dědek V., Liška F.: *This Journal* **32**, 4297 (1966).
12. Liška F., Dědek V., Němec M.: *This Journal* **37**, 2091 (1972).
13. Liška F., Dědek V., Holik M.: *This Journal* **35**, 1208 (1970).
14. Ebersson L., Schäfer H.: *Organic Electrochemistry*, p. 124. Springer, Berlin 1971.

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