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Organic reactions without organic solvents and oils and fats as renewable raw materials for the chemical industry

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Abstract

The use of organic solvents should be minimized as far as possible to reduce atmospheric volatile organic compounds (VOCs). Examples of solvent-free organic syntheses are described. The increasing usage of renewable feedstocks taking advantage of the synthetic potential of nature is another way to avoid organic solvents. Most important is the development of chemical products, i.e., coatings that can be processed without organic solvents. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Sustainable development has become a key ideal as the 20th century comes to a close (WCED, 1987). On the journey that is supposed to translate this ideal, with its far-reaching environmental, economic and social objectives, into the real world of the 21st century, chemists will be confronted with some very demanding tasks. They must develop products that can be manufactured in environmentally acceptable ways with minimum consumption of energy and raw materials, also maintaining as favorable an ecological balance as possible. During their lifetime these products must be of use to humans without harming them and must not pollute the environment. Thus, chemistry will make important contributions to the ecological, economic and social dimensions of sustainable development, by making optimal use of resources, and consumers will be provided at affordable prices with environmentally benign products according to their needs.

In this process the organic solvents are especially important, as they are generally used in large quantities, and as they are volatile organic compounds (VOCs). These are ecologically harmful being a cause for photochemical smog, and their use should therefore be minimized as far as possible or even avoided. Thus, the emissions of VOCs from different industrial sectors in Germany (1995: 1.090 kt) have to be reduced to 300–450 kt until the year 2010 (May, 1998). A thorough treatment of toxicology, occupational health, environmental and legal aspects, and of the uses of organic solvents had been given by Stoye (1993). Chemists are challenged to solve this problem as an important contribution to a sustainable development.

In chemical industry organic solvents are of course recovered and recycled wherever possible. However, in practice this is only rarely accomplished with complete efficiency by end of the pipe technologies, which means that some organic solvents from chemical production will inevitably escape and severely pollute the environment. In 1995 the emissions from chemical industry in Germany amounted to 26 kt (May, 1998). More important with respect to emissions of VOCs (1995: >1.000 kt) is the processing of chemical products especially coatings (348 kt), adhesives (60 kt), printing inks (72 kt) and others (400 kt) including plastic processing and

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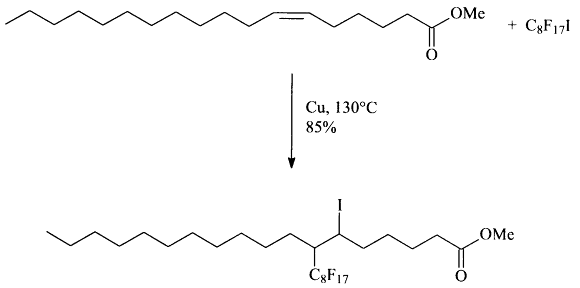

Fig. 1. Copper initiated addition of perfluorooctyl iodide to methyl petroselinate (Metzger et al., 1996).

foaming, industrial cleansing, building protection agents, cosmetics, pharmaceutical industry, metalworking, food extraction and aerosols (May, 1998) giving evidence that chemical products have to be invented that can be processed without or at least with reduced amounts of organic solvents. Thus, on the way to a sustainable future chemists have to develop methods to reduce VOC emissions by production-integrated environmental protection and most important by product-integrated environmental protection (Christ, 1999). Alternatives under investigation as solvents for organic reactions are water (Li and Chan, 1997) and supercritical gases, in particular CO_2 (Jessop and Leitner, 1999).

2. Solvent-free organic syntheses

The best solvent from an ecological point of view is without doubt no solvent. There are of course a great many reactions that can already be carried out in the absence of solvent. Examples that spring to mind are the numerous industrially important gas-phase reactions and many polymerizations. Diels–Alder and other pericyclic reactions are also often carried out without solvent. Reports on solvent-free reactions have, however, become increasingly frequent and specialized over the past few years. Areas of growth-include reactions between solids (Toda, 1995; Tanaka and Toda, 2000), between gases and solids (Kaupp and Schmeyers, 1995), and on supported inorganic reagents (Clark, 1994), which in many cases are accelerated or even made possible through microwave irradiation (Varma and Saini, 1997). There are also reactions in which at least one reactant is liquid under the conditions employed, which means that the solvent that would normally be used can simply be left out (Metzger, 1998a,b). We thought that radical reactions should be best suited to perform such reactions because of minor influence of solvent.

Simple heating of perfluoroalkyl iodides with an alkene in the presence of copper powder to 130°C gives the addition product in good yields (Metzger et al., 1996). In the example of Fig. 1 the alkene used is methyl petroselinate which is contained to 50–70% in the seed oil of coriander and is an interesting renewable feedstock. This simple reaction can be applied also to further haloalkanes containing electron withdrawing substituents such as 2-iodoalkanoates and 2-iodonitriles. The example given in Fig. 2 reveals the reaction mechanism. Electron transfer from copper gives an α-ester radical that is added to the alkene. The adduct radical is cyclized to the cyclopentylmethyl radical and iodine transfer yields the product. 2-iodoalkanoates can be formed from the corresponding bromo compounds in situ by addition of a stoichiometric amount of sodium iodide to the reaction mixture followed by addition and lactonization (Fig. 3) being an interesting example of a three-step reaction without isolation of intermediate products. That is another important principle of environmentally benign organic syntheses. Compared to analogous, well-known reactions using different transition metal complexes and salts as initiators in solvents such as benzene, acetonitrile, dichloromethane, 1,2-dichloroethane (Metzger and Mahler, 1995a,b) the solvent-free system is obviously environmentally more benign with

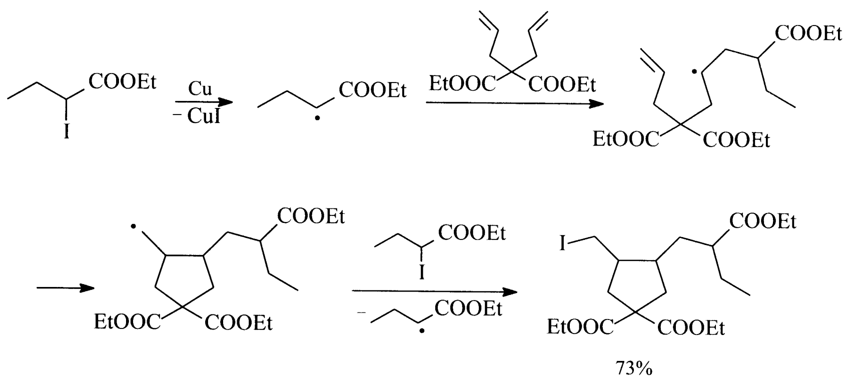

Fig. 2. Mechanism of the copper initiated addition of ethyl 2-iodobutanoate to diethyl diallylmalonate (Metzger et al., 1997).

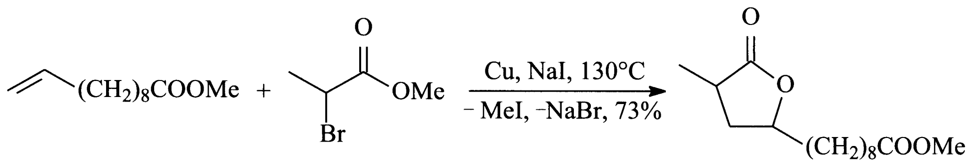

Fig. 3. Copper initiated addition of methyl 2-bromopropionate to methyl 10-undecenoate in the presence of sodium iodide (Metzger and Mahler, 1995a,b; Metzger et al., 1997).

respect to the criteria of minimum consumption of energy and raw materials and reduced amounts of waste.

3. Renewable feedstocks: syntheses of new oleochemicals by additions to unsaturated fatty compounds

Biosyntheses normally occur in the absence of organic solvents. Thus, the use of renewable feedstocks in chemical industry taking advantage of the synthetic potential of nature is also (in addition to all the other advantages, i.e., reduction of carbon dioxide emission, biodegradibility) important from the point of view of the reduction of VOCs. We have been interested in syntheses using fats and oils as renewable feedstocks. Unsaturated fatty compounds such as oleic acid, petroselinic acid, erucic acid, ricinoleic acid, linoleic and linolenic acid, finally 10-undecenoic acid (Fig. 4) and also the respective esters, alcohols and native oils are alkenes, and contain an electron-rich C,C-double bond that can be functionalized in many different ways by reactions with electrophilic reagents. During the last few years we have

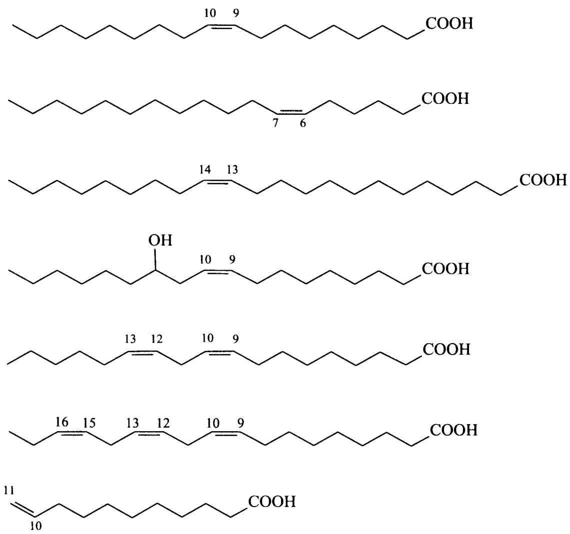

Fig. 4. Unsaturated fatty compounds from renewable feedstocks: oleic acid; petroselinic acid; erucic acid; ricinoleic acid; linoleic acid; linolenic acid; 10-undecenoic acid.

been reporting on numerous C,C-bond forming additions for example to oleic acid giving a great variety of interesting branched and long-chain fatty compounds with potentially new and interesting properties. Some typical examples are given in Fig. 5 (Biermann et al., 2000). Recent developments in the synthesis of new fatty acid derivatives of industrial importance were edited by Knothe and Derksen (1999). Interestingly, life cycle analysis of the production of the important detergent lauryl sulphate based on renewable versus petrochemical feedstocks revealed important ecological advantages of the former (Hirsinger and Schick, 1995).

4. Sustainable coatings

As pointed out in Section 1 the processing of coatings is an important source of VOCs. Until the early 1980s paints usually contained 50–70% of solvents. Considerable efforts have since been made to reduce the solvent content of paints significantly and abandon use of solvents with the highest hazard potential. High-solid paints and especially waterborne systems have replaced many traditional coating materials in industry, handicrafts and households (Biethan, 1991). However, these new paints are not totally free of solvent. Thus, in high-solid paints, some percent of auxiliary solvents are used to reduce the viscosity, as well as to optimize degassing and the flow properties. Waterborne solvents contain as well auxiliary solvents as solubilizers in amounts of 2–15%, depending on the binder (Stoye, 1993).

Powder coating is the coating method that is totally solvent free (Meyer, 1991). Recently, epoxidized vegetable oils and their derivatives have found industrial application as cross-linkers in environmentally friendly solvent-free powder coatings and can serve as building blocks for the preparation of binders based on renewable feedstock exhibiting good drying properties (Buisman et al., 1999).

Radiation-curable systems are also solvent free. Thus, there is no solvent recovery problem and no pollution. However, most radiation-curable systems are based on acrylates (Philips, 1991). Recently, epoxidized vegetable oils have found application in cationic curable coatings upon exposure to UV radiation (Crivello and Narayan, 1992). Life cycle analysis of coatings based on

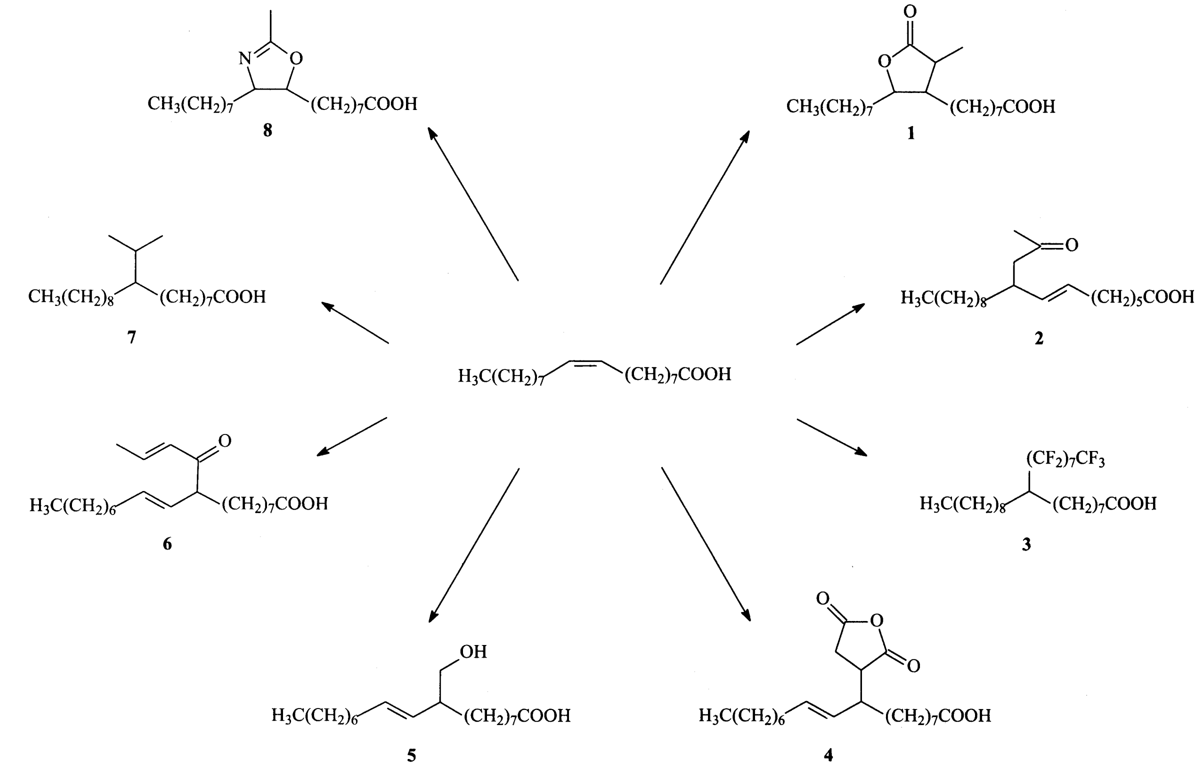

Fig. 5. Some interesting new fatty compounds formed by additions to methyl oleate: radical additions (1–3); thermal ene addition (4); cationic addition of formaldehyde (5), Friedel-Crafts acylation (6) (Biermann et al., 2000), Friedel-Crafts alkylation (7) (Biermann and Metzger, 1999); and formation of oxazolines (8) via epoxy stearic acid (Metzger et al., 1999).

acrylates compared to epoxidized vegetable oils revealed an important ecological advantage of the latter (Diehlmann and Kreisel, 2000).

5. Conclusion

On the way to a sustainable development the use of organic solvents should be minimized as far as possible to reduce VOCs in atmosphere. Examples for solvent-free syntheses have been described and become increasingly frequent. The use of renewable feedstocks in chemical industry should be intensified as another form of the reduction of VOCs. Chemical products must be developed that can be processed avoiding the use of organic solvents.

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