

New Synthetic Odoriferous Compounds

By Libor Červený, Antonín Marhoul and Vlastimil Růžicka, Institute of Chemical Technology, Prague, Czechoslovakia

New compounds possessing interesting odoriferous properties can be prepared by employing comparatively simple procedures and may be applied in perfume compositions. 4-Phenyl-1,3-dioxan is the common starting compound used in the synthesis of all eighteen new synthetic odoriferous compounds.

Readily available 4-phenyl-1,3-dioxan (1) is obtained by Prins's reaction, i.e., by condensing styrene and formaldehyde in the presence of acid catalysts.^{1,2} It has no distinctly odoriferous properties as such; it ranks among balsamic types and is not used alone in the perfumery. On the other hand, it can be employed as a starting compound in the synthesis of a large variety of compounds, some of which were newly synthesized; while in others obtained by a known procedure, some interesting odours were detected which earlier had escaped attention due to an inadequate purification or isolation of these compounds from reaction mixtures, or simply due to lack of interest in this field.

New synthetic odoriferous compounds based on 4-phenyl-1,3-dioxan are reviewed in figure 1.

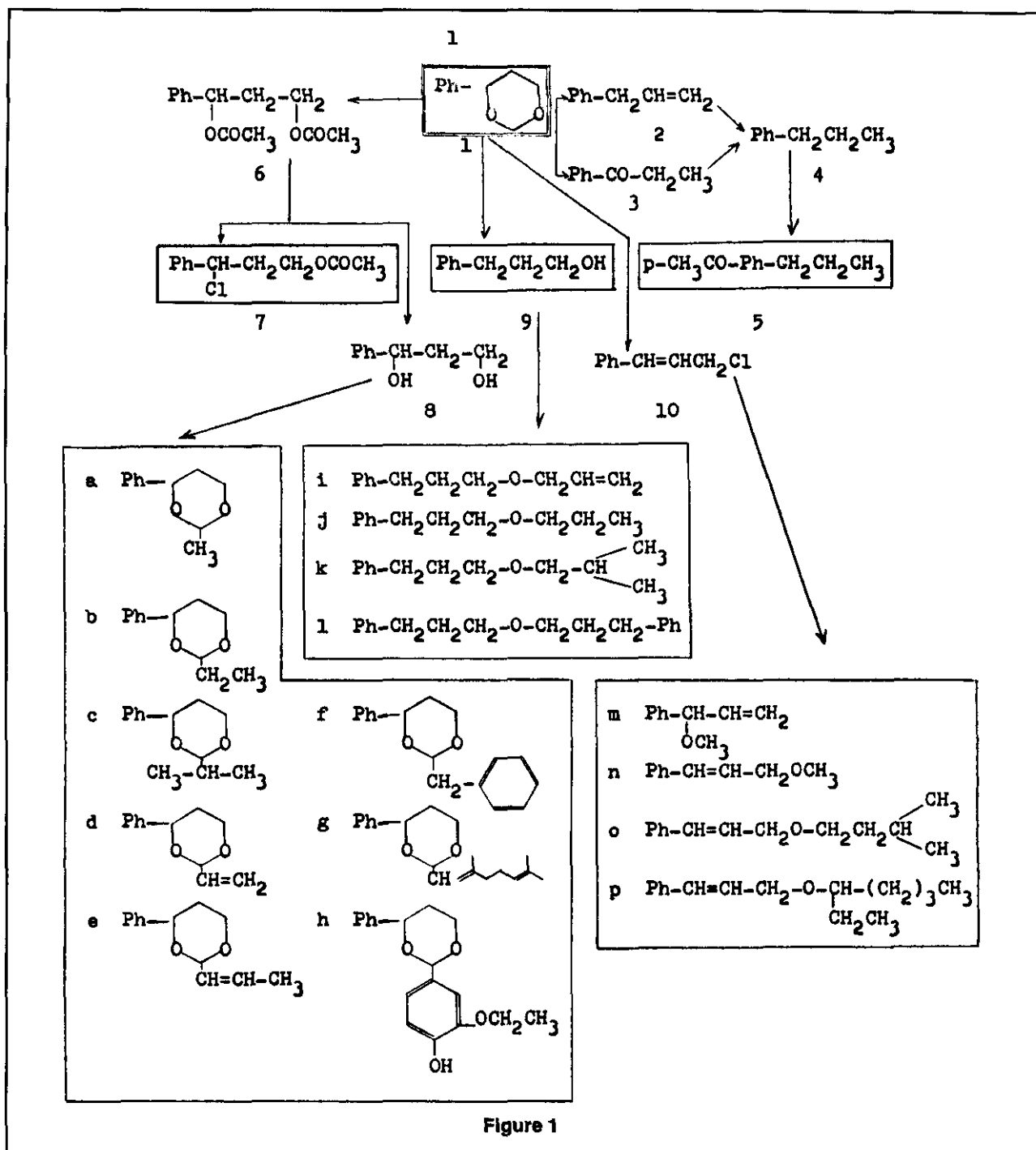
By splitting 4-phenyl-1,3-dioxan on some catalysts, for example those based on copper, it is

possible to obtain allylbenzene (2);^{3,4} splitting the compound on palladium catalysts in an inert atmosphere yields propiophenone (3).^{5,6} Both these compounds are otherwise not easily available and are obviously best prepared by the route involving the splitting of 4-phenyl-1,3-dioxan. Hydrogenation of both compounds mentioned above leads to n-propylbenzene (4), the synthesis of which by employing other procedures is also very difficult because the usual Friedel-Crafts alkylations yield cumene.

n-Propylbenzene is also formed in the hydrogenolysis of 4-phenyl-1,3-dioxan to 3-phenyl-1-propanol (9), using catalysts based on CuO-Cu₂O₃-MnO as a minority side product.⁵ Its isolation by rectification is very easy.

Acetylation of n-propylbenzene allows us to obtain p-n-propylacetophenone (5), a new synthetic odoriferous compound with a pronounced scent, corresponding to that of derivatives of jasmine.⁷ The odour resembles very much that of methyljasmonate and methylhydrojasmonate, and the compound can therefore be suitably used in jasmine perfumes and "phantasies," and also in flower and wood compositions.

Acidolysis of 4-phenyl-1,3-dioxan leads to 1-phenyl-1,3-propanedioldiacetate (6).^{1,8} In it-



self, this compound has no pronounced odour, but possesses fixation properties and may be employed, for example, instead of benzylsalicylate. In addition to the known splitting to cinnamylacetate, an important odoriferous compound, it also gives 3-chloro-3-phenylpropanolacetate (7), if treated with hydrogen chloride.⁹⁻¹¹ The latter product resembles 2-phenylethylacetate, is durable and also stable in soaps where no undesirable coloration develops.

Base-catalyzed hydrolysis or transesterification with methanol applied to 1-phenyl-1,3-propano-

dioldiacetate yields 1-phenyl-1,3-propanediol (8), a nonodoriferous compound with good fixation properties and possessing repellent effects.¹² The secondary-bound hydroxyl group can be split-off by hydrogenolysis, thus yielding a known synthetic aromatic compound, 3-phenyl-1-propanol (9), which, of course, is more suitably prepared by direct route from 4-phenyl-1,3-dioxan.^{5,13} By reacting 1-phenyl-1,3-propanediol with some aldehydes, cyclic acetals (2-substituted 4-phenyl-1,3-dioxans) possessing an interesting odour were obtained.¹⁴⁻¹⁶

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The odor characteristics may be described thus:

- condensation with acetaldehyde gives 2-methyl-4-phenyl-1,3-dioxan (a) with a weak fruit note
- with propionaldehyde we have 2-ethyl-4-phenyl-1,3-dioxan (b) with fruit-flower odour
- with isobutyraldehyde we get 2-isopropyl-4-phenyl-1,3-dioxan (c) whose odour is fruity to mushroom
- with acrolein: 2-ethylidene-4-phenyl-1,3-dioxan (d), mushroom odour
- with crotonaldehyde: 2-propylidene-4-phenyl-1,3-dioxan (e), also mushroom odour
- with phenylacetaldehyde: 2-benzyl-4-phenyl-1,3-dioxan (f), flower scent
- with citral: 2-(3,7-dimethyl-2,6-heptadienyl)-4-phenyl-1,3-dioxan (g), lemon-scented
- with ethylvaniline we obtain 2-(3-ethoxy-4-hydroxyphenyl)-4-phenyl-1,3-dioxan (h), the ethylvaniline-helliotropine-cocoa type

The advantage of all acetals consists in their stability in an alkaline medium and, hence, in the possibility to use them in soaps and detergents.

New Ether Compounds

Another group of new odoriferous compounds are ethers derived from 3-phenyl-1-propanol. They can be obtained by reacting alkoxides with the respective alkyl halides in the presence of phase transfer catalysts.¹⁷

3-Phenylpropylallylether (i) resembles lavedin and is suitable in compositions of the chypre, fougère, lavender and like types.

3-Phenylpropylpropylether (j) has a green-waxy odour, 3-phenylpropylisobutyric ether (k) is mushroom with hyacinth nuance, and di(3-phenylpropyl)-ether (l) has a flower (hyacinth) odour and may be appropriately used in combinations with styrax.

The dioxan ring of 4-phenyl-1,3-dioxan may also be destroyed with hydrochloric acid in the presence of ammonium chloride with formation of cinnamylchloride.^{10,18} A group of odoriferous ethers can be derived from the latter (m-p). These are obtained by a reaction between cinnamylchloride and alcohols in an alkaline medium. With a weak base (Na_2CO_3 , K_2CO_3), the allyl rearrangement takes place simultaneously, so that the resulting product is also an ether of the phenylallyl type, along with allylcinnamylether.^{10,19} Of these compounds, an ether prepared from methanol and cinnamylchloride in the presence of potassium carbonate was of particular interest—namely, 3-methoxy-3-phenyl-

propene (m), a compound possessing spicy odour, which may serve as a substitute of petit-grain, bergamot, or mycelion. Its poorer durability is of course a drawback. Cinnamyl-methylether (n) formed at the same time has a cinnamon-waxy odour. It may also be prepared independently from methanol and cinnamyl-chloride in the presence of a strong base (NaOH, KOH), when no allyl rearrangement occurs.^{10,19} Cinnamylisoamylether (o), cyclamen to wax scented, and cinnamyl-2-ethylhexylether (p), scented like drying straw, can be prepared in a similar manner.

Acknowledgment

The authors thank Dr. F. Vonášek, k.p. Astrid Prague, for careful reading of the manuscript and valuable comments.

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Address correspondence to Libor Červený, Prague Institute of Chemical Technology, Dept. of Organic Technology, Suchbátarova 5, 16628 Praha 6, Czechoslovakia.

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