Synthesis of New Fragrances from Furfural

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From the point of view of their sensory properties, furan derivatives are important flavor components of a number of food products, especially those which have been "processed thermally," i.e., by baking, frying, boiling or roasting. More than 80 compounds of the furan-derived group were found in such food products,[1] of which the major ones are characterized in Table I.

A number of furan-derived compounds obtained chemically by synthesis and not found in nature have been described in literature. Some of them have fragrances that are interesting,[2] although not always characterized in detail.

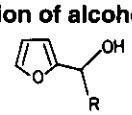
The present paper discusses the synthesis and fragrance characterization of several new furan derivatives and a few known compounds which have not yet been described in detail. These are alkylfurylcarbinols and 2,2-dialkylfurylpropanal derivatives obtained both from furfural and furfuryl alcohol.

Alkylfurylcarbinols and Their Acetates

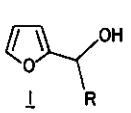
Alkylfurylcarbinols [**1**] are known and have been described in literature.[2] They are obtained, usually with high yields, as products of the Grignard reaction of furfural with alkylmagnesium halides where anhydrous diethyl ether is the most commonly used solvent. The flavors of alkylfurylcarbinols though, have not been described yet. The same refers to their acetates [**2**].

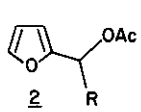
A number of alkylfurylcarbinols [**1**] were obtained in the present research work using a modified Grignard reaction described recently for the synthesis of alkylfurylcarbinols.[3] The inconvenient diethyl ether was replaced with a THF-

Table II. Fragrance characterization of alcohols with the formula



R	Method	Yield (%)	Boiling point [°C]	[Torr]	Mol. weight	Fragrance
C_2H_5	A	85	69	8	126	chemical
C_3H_7	A	77	92	12	140	chemical
C_4H_9	A	80	111	11	154	chemical
C_5H_{11}	B	82	111	7	168	strong, with a mushroomnote
iso-C_5H_{11}	B	75	101	7	168	strong, non-perfumery
C_6H_{13}	B	75	115	8	182	strong flower with note of *Lilium Candida*
C_7H_{15}	B	76	126	7	196	mild, flower, with a note of rose





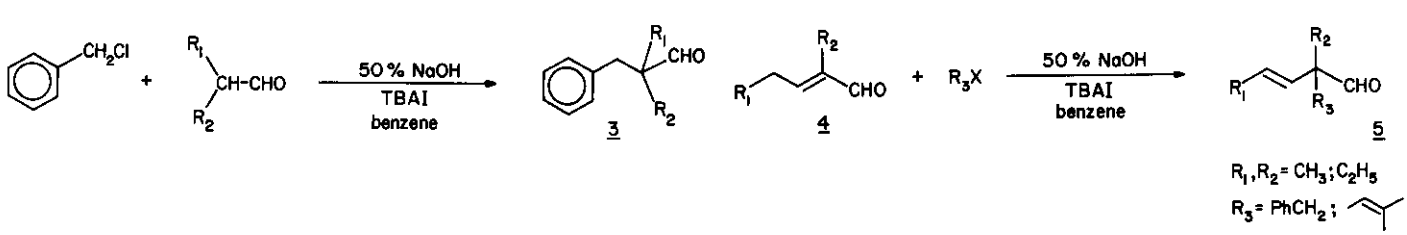


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Table I. Major natural fragrances of furan derivatives

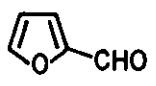
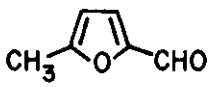
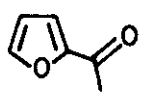
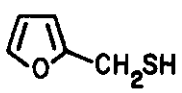
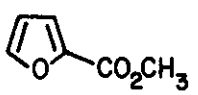
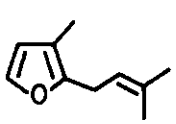
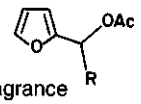
Formula and name	Occurrence	Fragrance
 Furfural	coffee, cocoa, roasted and boiled meat, bread	sharp and penetrating, close to that of fresh baked bread, when diluted
 5-Methyl-furfural	coffee, cocoa, roasted and boiled meat, bread	caramel-spicy, with a note of bitter almonds
 Acetylfuran	coffee, cocoa, roasted and boiled meat, bread	sweet and balmy, slightly burnt
 Furfuryl-mercaptan	roasted coffee	close to that of fresh roasted coffee, when diluted
 Furan-carboxylic acid methyl ester	coffee, cocoa, peanuts	pleasant, fruity with a note of mushrooms
 Rose furan	Bulgarian rose oil	rosy with a fruit note

Table III. Fragrance characterization of acetates with the formula 

R	Yield (%)	Boiling point [°C]	[Torr]	Mol. weight	Fragrance
C_2H_5	85	66	11	168	fruity
C_3H_7	82	72	10	182	fruity with a flower note
C_4H_9	83	82	10	196	fruity with a flower note
C_5H_{11}	80	108	8	210	flower, green with a note of *Ledum palustre*
iso-C_5H_{11}	81	105	10	210	delicate, fruity with a note of pear
C_6H_{13}	79	127	9	224	pleasant, fruit-flowery
C_7H_{15}	80	135	10	238	weak, flowery

benzene mixture and furfural was introduced to a magnesium suspension dropwise with alkyl bromide in the form of a suspension (Method A). A conventional two-step procedure (Method B) was used with less reactive chlorides. Alcohols [**1**] were obtained with yield in the range 75-85%. The products and their fragrances are characterized in Table II. The alcohols were esterified with acetic acid in the presence of anhydrous sodium acetate to produce their respective acetates [**2**] with yield in the range 80-85% (Table III).[4]

2,2-Dialkylfurylpropanal Derivatives

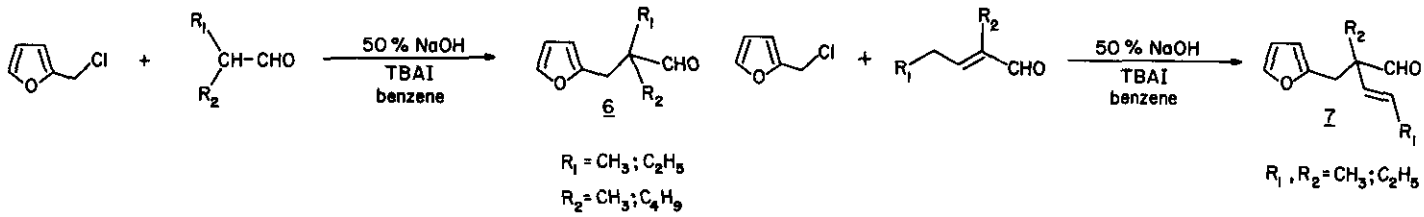
The possibility of using the phase-transfer catalysis to synthesize fragrances was first reported by Dietl and Brannock, in a paper on the synthesis of 2,2-dialkylphenylpropanal [**3**] and its derivatives from benzyl chloride and isobutyraldehyde and 2-ethylhexanal.[5]

The aldehyde-derived products such as acetals, alcohols and their esters gave interesting fragrances. Synthesis of fragrances by C-alkylation, with phase-transfer catalysis, of α, β-unsaturated aldehydes [**4**] with reactive halides such as benzyl or prenyl chloride was developed afterwards.[6,7]

Both aldehydes [**4**] and aliphatic aldehydes such as propanal or n-butanal react when used in a suitable excess. At reaction conditions (50% NaOH), the aldehydes undergo crotonic condensation to form aldehydes [**4**] which further react in situ with halides to aldehydes [**5**]. The reaction involves only reactive benzyl- and allyl halides.

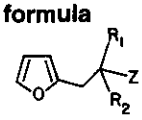
The present study was based on the reaction of aldehyde C-alkylation with furfuryl chloride, shown in Scheme 1, to synthetize 2,2-dialkylfurylpropanals and further appropriate alcohols and their acetates.

The derived products are characterized in Tables IV and V.[8] As shown in these tables, both aldehyde [**6**] (R_1, R_2=CH_3) and aldehyde [**3**] produce a penetrating aldehyde-fatty fragrance which makes them useless in perfumery. By blocking the aldehyde group (cyclic acetal), a much milder, flowery fragrance was obtained. Its alcohol derivative, however, gave a more interesting and relatively rare flavor of



Scheme 1

Table IV. Fragrance characterization of compounds with the formula



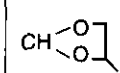
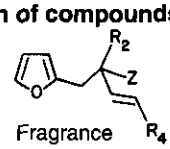
Z	R_1	R_2	Yield (%)	Boiling point [°C]	[Torr]	Mol. weight	Fragrance
CHO	CH_3	CH_3	66	55	5	152	penetrating, aldehyde-fatty
	CH_3	CH_3	88	78	3.5	210	flower with an indol-jasmin note
CHO	C_2H_5	C_4H_9	60	105	5	208	strong, wood-flower
CH_2OH	CH_3	CH_3	85	63	4	154	fresh, yeasty with a note of fusel oil
CH_2OH	C_2H_5	C_4H_9	88	98	4	210	fresh, flower
CH_2OAc	CH_3	CH_3	80	74	4	196	fruity, with a note of banana
CH_2OAc	C_2H_5	C_4H_9	82	91	1	252	rare, fresh, flower-green

Table V. Fragrance characterization of compounds with the formula



Z	R_1=R_2	Yield (%)	Boiling point [°C]	[Torr]	Mol. weight	Fragrance
CHO	CH_3	45	90	13	178	strong, flower-mushroom with a note of humus
CHO	C_2H_5	55	109	9	206	pleasant, mushroom-flower with a fruity note
CH_2OH	CH_3	88	99	12	180	penetrating, flower with a note of sweet pea
CH_2OH	C_2H_5	85	118	9	208	pleasant, fresh, flower with a fruity note
CH_2OAc	CH_3	80	86	7	206	pleasant, mushroom-flower
CH_2OAc	C_2H_5	83	108	5.5	250	pleasant, flower-mushroom

fresh yeast with a note of fusel oil. Elongation of its side aliphatic chains produced a more flowery fragrance (aldehyde [**6**]). Also its alcohol and acetate derivatives gave pleasant flower fragrances.

Introduction of an unsaturated bond into its side chain produced a distinct note of mushrooms. Their alcohol derivatives produced pleasant, rare, flower fragrances and can be of interest to perfume producers along with their acetates which give flower-mushroom flavors.

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References

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5. HK Dietl and KC Brannock, Tetrahedron Lett 1273 (1973)
6. US Patent 4010207 (1976)
7. US Patent 4380675 (1981)
8. J Nowicki and J Gora, Pol J Chem, in press