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SYNTHESIS OF 1-(2-FURYL)-2-NITROPROPEN-3-ONES

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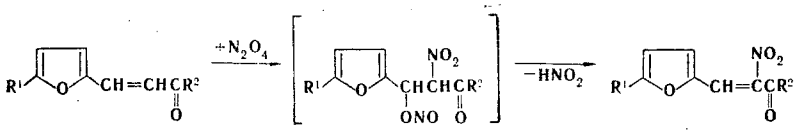
1-(2-Furyl)-2-nitropropen-3-ones were synthesized by reaction of nitrogen tetroxide with a number of α,β-unsaturated furylcarbonyl compounds. The 5-nitrofuryl derivative was obtained from 1-(2-furyl)-3-(4-methoxyphenyl)propen-3-one when the excess amount of N_2O_4 was increased. Replacement of bromine by a nitro group in the furan ring is observed in the case of the 5-bromofuryl derivative.

It is known that 1-(5-nitrofuryl)propen-3-ones have strong bactericidal and bacteriostatic properties [1]. In addition, 1-furyl-2-nitroethylene is a good repellent for application to clothing to protect against salt marsh mosquitoes and gnats and also protects leather clothing from mildew [2]. It therefore seemed of interest to synthesize 1-furyl-(substituted furyl)propen-3-ones and -propen-3-als with a nitro group in the side chain in the 2 position. Only a few of these compounds have been described [3, 4]. In order to synthesize other representatives we studied the reaction of nitrogen tetroxide with some α,β-unsaturated furylcarbonyl compounds (Ia-g).

Compounds Ia-f are converted smoothly to nitro derivatives IIa-f.



I a-f A II a-f

I-II a $R^1=CH_3$, $R^2=H$; b $R^1=R^2=CH_3$; c $R^1=H$, $R^2=C_4H_3S$ (thienyl); d $R^1=H$, $R^2=4\text{-}CH_3OC_6H_4$; e $R^1=NO_2$, $R^2=CH_3$; f $R^1=Cl$, $R^2=4\text{-}ClC_6H_4$

This reaction pathway is explained by conjugation between the electron-acceptor carbonyl group and the electron-donor furan ring. In this case the carbon atom in the 2 position has the maximum π-electron density, and reaction intermediate A is therefore formed. Splitting out of nitrous acid from A also leads to the formation of nitro compounds IIa-f.

When the amount of nitrogen tetroxide is increased above the stoichiometric value, furylpropenone Id forms, in addition to nitro ketone IId, 1-(5-nitro-2-furyl)-2-nitro-3-(4-methoxyphenyl)propen-3-one (III), which becomes the only product in the case of a considerable ex-

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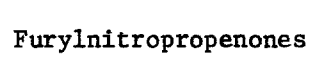
TABLE 1. Furylnitropropenones 

Compound	R¹	R²	Reaction temp., °C (reaction time, h)	mp, °C[a]	Found, %			Empirical formula	Calc., %			Yield, %
					C	H	N		C	H	N	
IIa	CH_3	H	−7(1,5)	137—138	53,0	3,8	7,8	$C_8H_7NO_4$	53,0	3,9	7,7	53
IIb	CH_3	CH_3	−15(1,5)	158—159	55,3	4,6	7,2	$C_9H_9NO_4$	55,4	4,6	7,2	24
IIc	H	C_4H_3S	−18(2)	161—162	53.0	2,9	5,7	$C_{11}H_7NO_4S$[b]	53,0	2,8	5,6	20
IId	H	4-$CH_3OC_6H_4$	−20(1,5)	176—177	61,7	4,2	5,2	$C_{14}H_{11}NO_5$	61,5	4,1	5,1	29
IIe	NO_2	CH_3	+17(1,5)	176—177	42,5	2,6	12,5	$C_8H_6N_2O_6$	42,5	2,7	12,4	56
IIf	Cl	4-ClC_6H_4	0(2)	233—234	49,8	2,4	4,4	$C_{13}H_7Cl_2NO_4$[c]	50,0	2,3	4,5	34
III	NO_2	4-$CH_3OC_6H_4$	−20(1,5)	120—121 (dec.)	52,9	3,3	8,7	$C_{14}H_{10}N_2O_7$	52,8	3,2	8,8	21

a) Crystallization solvents: alcohol for IIa-c, benzene for IId and III, and acetic acid for IIe,f. b) Found: S 13.0%. Calculated: S 12.8%. c) Found: Cl 22.6%. Calculated: Cl 22.7%.

TABLE 2. 2,4-Dinitrophenylhydrazones Va-f

Compound	mp, °C[a]	Empirical formula	N, %		Yield, %
			found	calc.	
Va	200—201	$C_{14}H_{11}N_5O_7$	19,3	19,4	90
Vb	217—218	$C_{15}H_{13}N_5O_7$	18,7	18,7	87
Vc	201	$C_{17}H_{11}N_5O_7S$[b]	16,2	16,3	81
Vd	208	$C_{20}H_{15}N_5O_8$	15,3	15,4	83
Ve	255—256	$C_{14}H_{10}N_6O_9$	20,6	20,7	80
Vf	223—224 (acetic acid)	$C_{19}H_{10}Cl_2N_5O_7$[c]	14,3	14,2	86

a) Crystallization solvents: toluene for Va, dioxane for Vb, benzene for Vc,d, dimethylformamide for Ve, and acetic acid for Vf. b) Found: S 7.5%. Calculated: S 7.5%. c) Found: Cl 14.6%. Calculated: Cl 14.4%.

cess of nitrogen tetroxide. At the same time, furfurylideneacetophenone, which does not contain a methoxy group in the benzene ring, is converted under these conditions only to 1-(2-furyl)-2-nitro-3-phenylpropen-3-one [4]; this is evidently associated with the large +C effect of the 4-methoxyphenyl grouping in the IId molecule.

The reaction of furylpropenone Ig (R^1 = Br, R^2 = 4-ClC_6H_4) with nitrogen tetroxide leads to replacement of the bromine in the furan ring by a nitro group to give IV; this is evidently explained by its high polarizability. Structure IV was proved by the agreement between its constants and those described in the literature [5] and by the absence of a melting-point depression for a mixture with an authentic sample synthesized by the method in [6].

In the IR spectra of IIa-f and III the frequencies of the stretching vibrations of the C=O groups increase (1675-1694 cm^{-1}) as compared with the corresponding frequencies of the starting compounds (1646-1670 cm^{-1}); this can be explained by the −C effect of the nitro group. The stretching vibrations of the ethylene bond are observed at 1575-1600 cm^{-1}. The out-of-plane deformation vibrations of the trisubstituted C=C bond appear at 815-840 cm^{-1}. The intense absorption bands at 1335-1387 and 1515-1580 cm^{-1} correspond to the symmetrical and asymmetrical stretching vibrations of the nitro group. The furan and thiophene rings are easily detected from the frequencies of the skeletal and out-of-plane vibrations of the rings (1400-1482, 840-890, and 700-747 cm^{-1}), and also from the stretching vibrations of the substituted heterorings at 916-935 and 1010-1035 cm^{-1}. In addition, the corresponding spectra contain characteristic absorption frequencies of the stretching vibrations of p-disubstituted benzene (1480-1520 cm^{-1}), in-plane deformation vibrations of aromatic C–H bonds (1254-1275 and 1115-1180 cm^{-1}), and vibration of a methoxy group (2845, 1255 cm^{-1}) and a C–Cl bond (740-760 cm^{-1}). The absorption band at 1390 cm^{-1} corresponds to the CH_3 group.

The synthesized nitro derivatives (IIa-f) readily form 2,4-dinitrophenylhydrazones Va-f, the IR spectra of which do not contain a band of stretching vibrations of a carbonyl group but do contain frequencies characteristic for C=N (1615 cm^{-1}) and NH (3450, 3400, and 1315 cm^{-1}) bonds.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-10 spectrometer. Thin-layer chromatography (TLC) was carried out on Silufol UV-254 plates with elution by benzene and development in UV light.

The starting Ia-g were obtained by crotonic condensation of furfural and its substituted derivatives with acetaldehyde or the appropriate ketones by known methods [7-11].

1-(5-Methyl-2-furyl)-2-nitropropen-3-al (IIa). A 1.36-g (10 mmole) sample of Ia was dissolved in 20 ml of absolute ether, and 0.92 g (10 mmole) of nitrogen tetroxide was added at −7°C. The solution was stirred at −7°C for 1.5 h, after which it was poured over 100 g of finely crushed ice. After 3 h, the ether layer was separated, and the ether was evaporated. The residue was washed successively with alcohol and ether and recrystallized from alcohol.

Compounds IIb-d,f were similarly obtained. Dinitro ketone III was synthesized by the described method when a threefold excess of nitrogen tetroxide was used.

1-(5-Nitro-2-furyl)-2-nitro-3-methylpropen-3-one (IIe). An 0.92-g (10 mmole) sample of nitrogen tetroxide was added at 17°C to a suspension of 0.91 g (5 mmole) of 5-nitrofurylpropenone Ie in 50 ml of absolute ether, and stirring was continued for 1.5 h. The solution was then poured over a mixture of 100 g of ice and 50 ml of water. The ether was evaporated to one-third of its original volume, and the resulting crystals were removed by filtration, washed with alcohol and ether, and recrystallized from acetic acid. No melting-point depression was observed for a mixture of a sample of this product with a sample of IIe obtained from 1-(2-furyl)-2-nitro-3-methylpropen-3-one by the method in [6]. Their IR spectra coincided completely.

1-(5-Nitro-2-furyl)-3-(4-chlorophenyl)propen-3-one (IV). A solution of 0.28 g (3 mmole) of nitrogen tetroxide in 3 ml of ether was added at 0°C to 0.94 g (3 mmole) of III dissolved in 50 ml of absolute ether, and the mixture was then maintained at 5°C for 1 h. It was then poured over ice, and the nitro product was isolated as in the case of IIa and recrystallized from ethyl acetate to give 0.45 g (54%) of light-yellow crystals with mp 189-190°C [5]. Found, %: C 56.1; H 2.9; Cl 12.9; N 4.9. $C_{13}H_8ClNO_4$. Calculated, %: C 56.2; H 2.9; Cl 12.8; N 5.0. The 2,4-dinitrophenylhydrazone was obtained as dark-red crystals with mp 226°C (from acetic acid). Found, %: Cl 7.9; N 15.3. $C_{19}H_{11}ClN_5O_7$. Calculated, %: Cl 7.8; N 15.3.

2,4-Dinitrophenylhydrazones Va-f. A 1-mmole sample of the ketone was dissolved by heating in 10-15 ml of ethanol, and a hot solution of 1 mmole of 2,4-dinitrophenylhydrazine in 5-10 ml of alcohol acidified with concentrated hydrochloric acid (0.5-2 ml) was added. Heating was continued for 10-40 min, after which the precipitate was removed by filtration, washed with alcohol, and recrystallized from a suitable solvent.

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5-TRIFLUOROMETHYLFURAN DERIVATIVES

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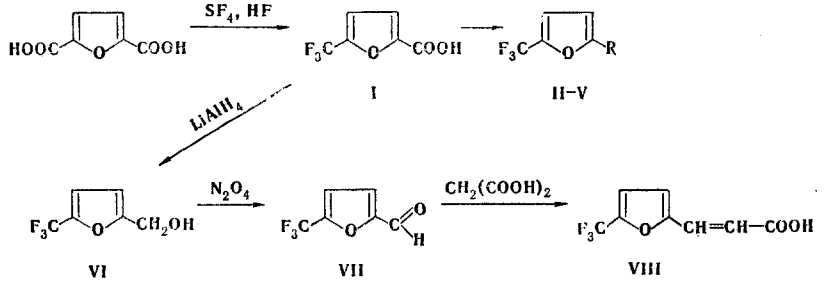
Methods for the preparation of 5-trifluoromethylfuran-2-carboxylic acid, 5-trifluoromethylfurfural, and 5-trifluoromethyl-2-aminofuran derivatives were developed.

Trifluoromethylfurans are valuable intermediates for the synthesis of physiologically active substances [1-3]. Derivatives of 5-trifluoromethylfuran, which was previously obtained by a multistep method [3], are of particular interest. 5-Trifluoromethylfuran-2-carboxylic acid, which we have previously obtained by fluorination of furan-2,5-dicarboxylic acid with sulfur tetrafluoride, could have been a convenient starting compound for the synthesis of various 5-trifluoromethylfuran derivatives. However, it was obtained in only 16% yield, and mainly 2,5-bis(trifluoromethyl)furan was obtained in the fluorination [1]. Fluorination was accomplished under severe conditions (at 185°C for 45 h). Under milder conditions the carboxyl groups were not converted to trifluoromethyl groups.

It was recently found that the fluorination of carboxylic acids with sulfur tetrafluoride in anhydrous hydrogen fluoride proceeds at a considerably lower temperature and gives the trifluoromethyl derivatives in higher yields [4]. It was found that one can realize partial fluorination of furan-2,5-dicarboxylic acid with sulfur tetrafluoride when the process is carried out in HF solution under mild conditions (at 40-50°C). 5-Trifluoromethylfuran-2-carboxylic acid (I) was obtained in 60-65% yield in this case. Thus acid I became a fully accessible compound, from which we synthesized a number of 5-trifluoromethylfuran derivatives. From acid I we obtained its methyl ester (II), acid chloride (III), amide, hydrazide (IV), and nitrile (V). Acid I and its ester II and chloride III are converted to 5-trifluoromethyl-2-hydroxymethylfuran (VI) by reduction with lithium aluminum hydride. 5-Trifluoromethylfurfural (VII) was obtained in good yield by oxidation of carbinol VI with nitrogen tetroxide.

β-(5-Trifluoromethyl-2-furyl)acrylic acid (VIII) was synthesized by condensation of aldehyde VII with malonic acid.



II R=$COOCH_3$; III R=COCl; IV R=$CONHNH_2$; V R=CN

5-Trifluoromethyl-2-nitrofuran (IX), which was previously obtained in 37% yield [2] by fluorination of 2-nitrofuran-5-carboxylic acid with sulfur tetrafluoride at 120°C, was necessary for the preparation of amino derivatives of 5-trifluoromethylfuran. When we carried

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