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NEW SYNTHESIS OF BUTANE AND CYCLOHEXANE COMPOUNDS CONTAINING TWO FURAN FRAGMENTS

E.I. MAMMADOV, G.A. ZAIDOVA

Azerbaijan Technical University
AZ1073, Baku, H. Cavid pr. 25
e-mail: zaida.zaid88@gmail.com
e-mail: mammadov.elman@rambler.ru

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ABSTRACT

The reaction of adipic acid with thionyl chloride ($SOCl_2$) yields the dichloride anhydride of the corresponding acid. It has been established that, regardless of whether 1,4-cyclohexanedicarboxylic acid is in the cis- or trans-form, its reaction with PCl_3 produces only the dichloride anhydride of trans-1,4-cyclohexanedicarboxylic acid. In the electrophilic addition of adipic and trans-1,4-cyclohexandicarboxylic acid dichlorides to 3-chloro- and 2-methyl-3-chloropropenes in the presence of $AlCl_3$, 1,2,11,12-tetrachloro-2,11-H(CH_3)dodecane-4,9-diones and trans-1,4-di-[3-H(CH_3)-3,4-dichlorobutanoyl-1]cyclohexanes were obtained, which upon vacuum distillation form 1,4-difuryl derivatives of butane and cyclohexane. Structures of difurans are confirmed by IR and NMR ^1H spectroscopy and chemical transformations. Furan compounds with maleic anhydride form Diels-Alder adducts.

INTRODUCTION

Furan and its derivatives are frequently encountered in the composition of natural compounds, they exhibit physiological activity and are widely used in the development of effective pharmaceuticals as well as chemical agents employed in plant protection [1–5].

The broad range of application fields of furan compounds has provided a strong impetus for research directed toward their synthesis by new methods.

Saturated and unsaturated chloroketones are promising starting materials for the synthesis of heterocyclic compounds containing one or two heteroatoms [6–14]. The electrophilic addition reactions of acid chlorides to unsaturated hydrocarbons, their chloro-substituted derivatives, and allylic-type chlorides represent one of the favorable approaches for the synthesis of saturated and unsaturated chloroketones [6, 9–11, 13–16].

It is known that the electrophilic addition reactions of acid chlorides to 3-chloropropene (allyl chloride) and 2-methyl-3-chloropropene (methallyl chloride) in the presence of $AlCl_3$ proceed according to Markovnikov's rule, and that the nature of the products formed depends on the structure of the corresponding carboxylic acids. Thus, when the acid chlorides of acetic, propionic, and butyric acids are used, a mixture of saturated and unsaturated chloroketones is mainly obtained, whereas higher aliphatic carboxylic acid chlorides ($\geq C_4$) as well as cycloalkane

carboxylic acid chlorides yield 2- and 2,4-substituted furan derivatives [6, 10, 12, 17–19].

In the presented article, valuable heterocyclic compounds containing two furan fragments were obtained by the method described.

EXPERIMENTAL SECTION

IR spectra were recorded on a Thermo Scientific Nicolet IS10 FT-IR spectrophotometer, and ^{1}H NMR spectra were measured on a "Bruker AM-360" instrument using internal standards TMS or HMDC.

The purity of the synthesized furans (4a–d) was determined by thin-layer chromatography (TLC) on "Sulufol UV-254" plates.

Commercial reagents, including 3-chloropropene (2a), 2-methyl-3-chloropropene (2b), adipic acid, and *cis*- and *trans*-1,4-cyclohexanedicarboxylic acids, were used as starting materials.

1. Synthesis of difuran compounds 4a–d.

1.1. 1,4-di-(2-furyl)butane (4a). A mixture of 14.7 g (0.11 mol) $AlCl_3$ and 80 ml of dry dichloroethane was cooled to −20 °C, and then, under stirring, 8.35 g (0.05 mol) of dichloranhydride 1a and 9.2 g (0.12 mol) of 3-chloropropene (2a) were added sequentially. The reaction mixture was stirred until it reached room temperature, quenched with 5% HCl solution, and the organic layer was separated, while the aqueous layer was extracted with ether (2 × 100 ml). The combined organic layer and ether extracts were successively washed with water, 10% $NaHCO_3$ solution, and again with water, and dried over anhydrous $CaCl_2$. The solvents were removed, and the residue was distilled under vacuum in a nitrogen atmosphere. This afforded 4g (42% yield) of 1,4-di-(2-furyl)butane (4a) with the following characteristics: $t_{boil.}$ 108-109 °C/3mm; n_D^{20} 1.4955. IR spectrum (cm^{-1}): 3125, 3155(ν_{CH}); 1517, 1598 ($\nu_{C=C,C=C}$); 880 (δ_{CH}). ^{1}H NMR spectrum(δ, ppm): 1.65 (4H, m, furyl-CH_2-); 2.58 (4H, m, -CH_2-CH_2-); 5.9 (H^3-cyclo, 2H, m); 6.13 (H^4-cyclo, 2H, m); 7.2 (H^5-cyclo, 2H, m). TLC: R_f 0.53, eluent – hexane: benzene 3:1.

1.2. 1,4-di-[2-(4-metylfuryl)]butane (4b). Using the above method 1.1, adipic acid dichloranhydride (1a) and 2-methyl-3-chloropropene (2b) afforded 1,4-di-[2-(4-methylfuryl)]butane (4b): yield 51%; $t_{boil.}$ 117 – 119 °C/3mm; n_D^{20} 1.4930. IR spectrum (cm^{-1}): 3130 (ν_{CH}); 1534, 1610 ($\nu_{C=C,C=C}$); 889 (δ_{CH}). ^{1}H NMR spectrum (δ, ppm): 1.4-1.9 (4H, m, furyl-CH_2-); 1.85 (6H, d, J=8 Hs, 2C^4-CH_3); 2.4-2.9 (4H, m, -CH_2-CH_2-); 5.72 (H^3-cyclo, 2H, m); 6.94 (H^5-cyclo, 2H, m). TLC: R_f 0.61, eluent – hexane: benzene - 3:1.

Using the above method (1.1), difurans 4c and 4d were synthesized from the reaction of *trans*-1,4-cyclohexanedicarboxylic acid dichloranhydride (1b) with 3-chloropropene (2a) or 2-methyl-3-chloropropene (2b).

1.3. Trans-1,4-di-(2-furyl)cyclohexane (4c). Yield 53%; $t_{melting}$ 84-85 °C (CH_3OH). IR spectrum (cm^{-1}): 3130, 3135(ν_{CH}); 1510, 1606 ($\nu_{C=C,C=C}$); 889 (δ_{CH}). ^{1}H NMR spectrum (δ,ppm): 1.1-2.4 (10H-cyclo, m); 5.82 (H^3-cyclo, 2H, m); 6.1 (H^4-cyclo, 2H, m); 7.14 (H^5-cyclo, 2H, m). TLC: R_f 0.56, eluent - $CHCl_3$: hexane - 1:1.

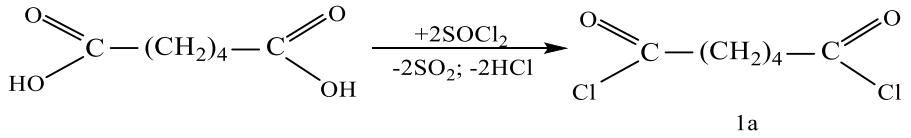
1.4. Trans-1,4-di-[2-(4-metyfuril)]cyclololohexane (4d). Yield 57%; $t_{melting}$ 100-101°C (CH_3OH). IR spectrum (cm^{-1}): 2950(ν_{CH}); 1532, 1606 ($\nu_{C=C,C=C}$); 895 (δ_{CH}). ^{1}H NMR spectrum (δ, ppm): 1.2-2.1 (10H-cyclo, m); 1.8 (6H, d, J=8 Hs, 2C^4-CH_3); 5.6 (H^3-cyclo, s, 2H); 6.8 (H^5-cyclo, 2H, m). TLC: R_f 0.49, eluent - $CHCl_3$:hexane - 1:1.

RESULTS AND DISCUSSION

The dichlorides of adipic and trans-1,4-cyclohexanedicarboxylic acids (1a,b) were taken to synthesize heterocyclic compounds containing two furan rings.

The dichloride of adipic acid (1a) was obtained from the reaction of the acid with thionyl chloride (scheme 1).

Scheme 1.

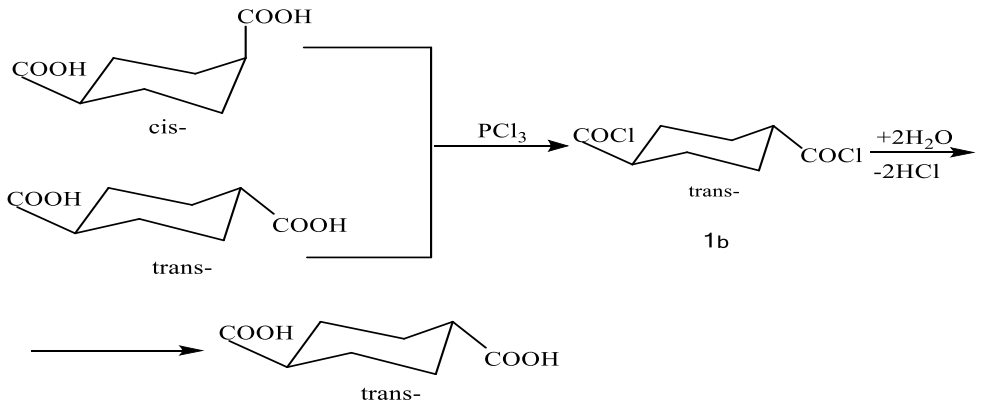


1a

The dichloride (1a) was used without purification, as it readily decomposes upon distillation.

It was determined that, regardless of whether 1,4-cyclohexanedicarboxylic acid is taken in the cis- or trans-form, the reaction with PCl_3 yields only the dichloride of *trans*-1,4-cyclohexane dicarboxylic acid. Hydrolysis of the dichloride (1b) with water affords exclusively *trans*-1,4-cyclohexanedicarboxylic acid (scheme 2).

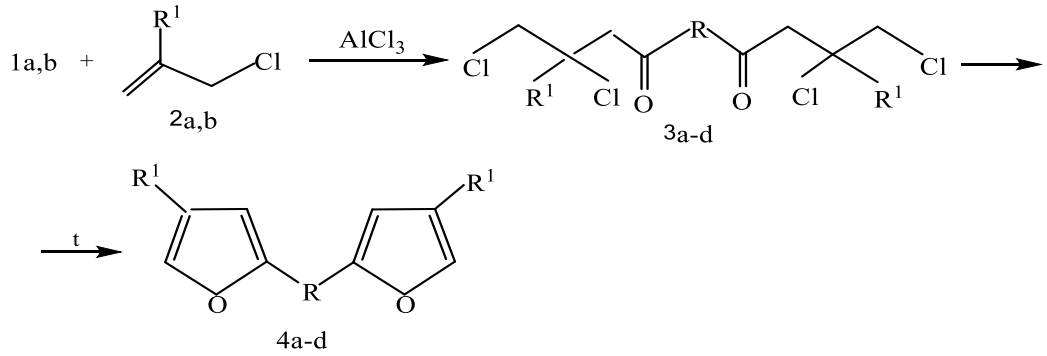
Scheme 2.



1b

Reaction of the dichlorides 1a,b with 3-chloropropene (2a) and 2-methyl-3-chloropropene (2b) in the presence of $AlCl_3$ afforded 1,2,11,12-tetrachloro-2,11-H(CH_3)-dodecane-4,9-dione (3a,b) and *trans*-1,4-di-[3-H(CH_3)-3,4-dichlorobutanoyl-1]cyclohexane (3c,d) (scheme 3).

Scheme 3.



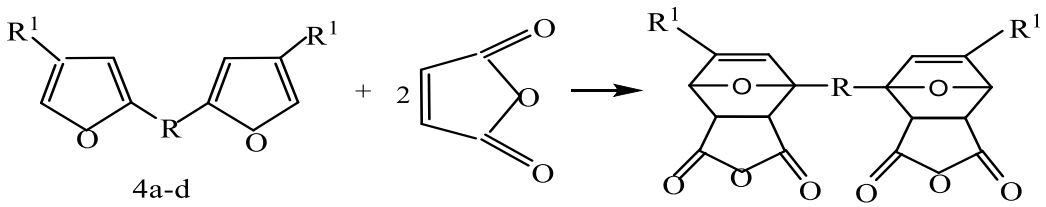
R= −$(CH_2)_4$− (1a; 3a,b; 4a,b); *trans*-1,4-cyclo-C_6H_{10} (1b; 3c,d; 4c,d); R^1 = H (2a; 3a,c; 4a,c); CH_3 (2b; 3b,d; 4b,d).

During vacuum distillation of the tetrachloroketones (3a–d), heterocyclization occurs, leading to the formation of 1,4-difuryl derivatives of butane (4a,b) and cyclohexane (4c,d) (scheme 3).

The structures of the difurans (4a–d) were confirmed based on IR and ^{1}H NMR spectral data as well as chemical transformations.

In the furan compounds 4a–d, the furan rings participate in a Diels–Alder reaction with maleic anhydride, forming the corresponding Diels–Alder adducts (scheme 4) [20].

Scheme 4.



Here, R and R^1 - are the ones shown in the 3rd scheme.

The IR spectra of the difuran compounds (4a–d) exhibit absorption bands characteristic of the furan ring (cm^{-1}): 2950-3150 (ν_{CH}); 1598-1610 ($\nu_{C=C}$); 1510-1534 ($\nu_{C=C}$); 880-895 ($\boldsymbol{\delta}_{CH}$) (experimental section).

In the ^{1}H NMR spectra of compounds 4a–d, the protons of the 1,4-substituted butane (cyclohexane) fragments appear at δ 1.4–2.9 (1.1–2.4) ppm, while the protons of the furan ring are observed as characteristic multiplets at δ 5.6–7.2 ppm (experimental section).

Thus, a two-step, efficient method has been developed for the synthesis of butane and cyclohexane difuryl derivatives based on the reaction of the dichlorides of adipic and *trans*-1,4-cyclohexanedicarboxylic acids with 3-chloropropene and 2-methyl-3-chloropropene.

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