ALKYLATION OF FURAN AND THIOPHENE WITH tert-BUTANOL IN THE PRESENCE OF THE STRONGLY ACID CATION EXCHANGER AMBERLYST 15

É. Ya. Lukevits, L. M. Ignatovich,
Yu. Sh. Gol'dberg, and M. V. Shimanskaya

UDC 547.722'732.541.128

The best of the presently known routes for the synthesis of 2-(tertbutyl)furan (I) is the Friedel–Crafts alkylation of furan-2-carboxylic acid by tert-butyl chloride and the subsequent decarboxylation of the resulting 5-(tert-butyl)furan-2-carboxylic acid in the presence of quinoline and cupric oxide at a raised temperature [1]. We have established that the alkylfuran (I) can be obtained in one stage by the reaction of furan with tert-butanol in the presence of the commercially available ("Fluka") strongly acid ion-exchange resin Amberlyst 15 (A 15) containing the SO_3H function (4.6 mg-equivalents of SO_3H groups in 1 g of resin; the water content < 3%).*

The reaction can be accomplished in two variants. According to the first, A 15 (1.15 mmole based on the SO_3H groups) is added to the solution of 1 mmole of tert-butanol in excess furan; the resulting suspension is stirred at room temperature for 24 h. Compound (I) is thereby formed in a yield of 80% based on tert-butanol.† Under analogous conditions, compound (I) is alkylated to 2,5-di(tert-butyl)furan (II) with a yield of 75%. The tert-butylation of thiophene does not proceed at room temperature, and the 3.5:1 mixture of 2- and 3-(tert-butyl)thiophene is formed in quantitative yield on heating the mixture of thiophene with tert-butanol in the presence of A 15 (80°C, 1 h).

In the second variant, the alkylation is performed in an inert solvent. For example, the yield of the alkylfuran (I) comprises 90% in the alkylation of furan (0.3 M solution in CCl_4, a 1:1.5:2 molar ratio of furan–t-BuOH–A 15, 76°C, microautoclave, 3 h). A tenfold increase in the excess of the sulfo-cation exchanger, relative to the data presented above, sharply accelerates the reaction, which stops after 30 min (∼20°C) and gives a 1:3.5 mixture of the alkylfurans (I) and (II).

The method proposed for the tert-butylation is significantly simpler than that described in the work [1] and permits selective monoalkylation, whereas the new recently proposed variant of the alkylation of aromatic and heterocyclic compounds by tert-butyl bromide, catalyzed by silica gel, only permits the isolation of the 2,5-di(tert-butyl) derivatives in the case of furan and thiophene [5].

The tert-butylation reaction does not proceed with the utilization of the weakly acid ion-exchange resin IRC-50 containing the COOH function.

Therefore, the described method of alkylation utilizing the sulfo-cation exchanger, insoluble in the reaction medium, as the acid agent can evidently serve as an effective alternative to the traditional Friedel–Crafts alkylation, which is known [6, 7] to present much difficulty in the case of five-membered heterocycles owing to the acidophobicity of these compounds.

LITERATURE CITED

1. J. Fitzpatrick, D. Milner, and P. White, Synth. Comm., 12, 498 (1982).
2. L. T. Scott and I. O. Naples, Synthesis, No. 3, 209 (1973).
3. G. M. Coppola, Synthesis, No. 12, 1021 (1984).

*For the utilization of A15 as an acid agent in organic synthesis, see e.g., [2-4].
†The yield and the ratio of the reaction products were determined from GLC data.

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga 226006.
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 853-854, June, 1986.
Original article submitted January 10, 1986.

 0009-3122/86/2206-0678$12.50

4. C. W. Jefford and G. Bernardinelli, Tetrahedron Lett., 26, 615 (1985).
5. Y. Kamitori, M. Hojo, R. Masuda, T. Izumi, and S. Tsukamoto, J. Org. Chem., 49, 4161 (1984).
6. S. H. Patinkin and B. S. Friedman, Friedel–Crafts and Related Reactions (ed. G. A. Olah), Vol. 2, Interscience, New York (1964), p. 104.
7. C. C. Price, Organic Reactions, Vol. 3, New York, (1967), p. 1.

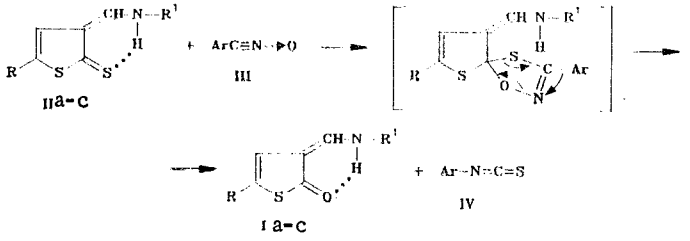
NEW METHOD OF ISOLATING N-SUBSTITUTED 3-AMINOMETHYLENETHIOL-4-EN-2-ONES

M. A. Kalik, Ya. L. Gol'dfarb, and M. M. Krayushkin

UCD 547.733.04

The methods for the synthesis of the little-studied N-substituted 3-aminomethylenethiol-4-en-2-ones (I) — thiophene analogs of aromatic o-hydroxyazomethines — are based on the application of the not readily accessible and labile hydroxy and methoxy derivatives of thiophene [1, 2].

We have found that the compounds (I) can be obtained in good yields (60-80%) by the reaction of the corresponding N-substituted mercaptoaldimines (II) with mesitylnitrile oxide (III) at 20°C for 20-30 min. The resulting oxyaldimines (Ia-c) and mesityl isothiocyanate (IV) are separated by chromatography on silica gel utilizing hexane [for compound (IV)] and $CHCl_3$ [for the substances (I)] as the eluents.



I, II a,b R=Et, c R=OMe; a,c R^1=*cyclo*-C_6H_{11}, b R^1=β-$C_{10}H_7$; Ar=2,4,6-$Me_3C_6H_2$

The structure and composition of the compounds obtained were confirmed by the data of the elemental analysis, IR, UV, PMR, and mass spectra. The oxyaldimines (Ia, b) were identical to the samples previously described by us [2] according to the mps and the spectra. Compound (Ic), $C_{12}H_{17}NO_2S$, had a yield of 70% and mp 119-121°C (from alcohol). The PMR spectrum in $CDCl_3$ was as follows: 3.75 (3H, singlet, OCH_3), 5.38 (1H, singlet, 4-H), 7.00 (1H, doublet, CH=N, $J_{CH,NH}$ = 13.5 Hz), and 9.00 ppm (1H, broad singlet, NH). The mass spectrum (m/z, J, %) was as follows: 239 (100) (M^+), 224 (70), 157 (80), 142 (85), and 114 (20).

The conversion observed can be considered as the selective 1,3-dipolar cycloaddition of the nitrile oxide (III) at the thiocarbonyl group of the mercaptoaldimine (II), and the subsequent opening of the resulting oxathiazole ring with the accompanying migration of the aryl residue to the nitrogen and the elimination of the isothiocyanate (IV) [3].

LITERATURE CITED

1. P. Demerseman, J. P. Lechartier, A. Cheutin, M. J. Desvoe, and P. Royer, Compt. Rend., 254, 1652 (1962).
2. Ya. L. Gol'dfarb and M. A. Kalik, Khim. Geterotsikl. Soedin, No. 2, 178 (1971).
3. Ch. Grundmann and P. Grunanger, The Nitrile Oxides, Springer-Verlag, Berlin (1971), p. 122.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow.
117913. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 854-855, June, 1986. Original article submitted February 3, 1986.

