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REDUCTIVE DESULFURATION OF KETONES OF THE THIOPHENE SERIES CONTAINING AN ADAMANTANE GROUP

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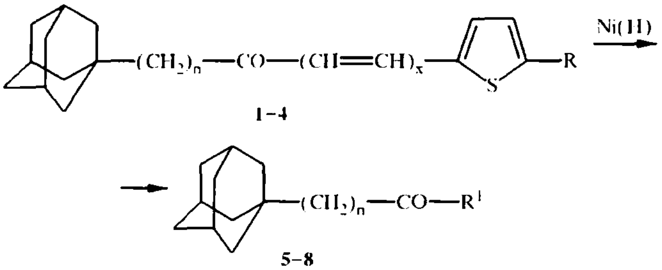
Reductive desulfuration of adamant-1-yl thien-2-yl ketone, adamant-1-ylmethyl thien-2-yl ketone, adamant-1-yl 2-(thien-2-yl)vinyl ketone, and adamant-1-yl 2,2'-bithiophen-5-yl ketone with Raney nickel in ethanol leads to the corresponding alkyl adamant-1-yl ketones with normal structures.

Keywords: reductive desulfuration, adamantane, ketones, thiophene, Raney nickel.

We previously described [1] the synthesis of some ketones of the thiophene series containing an adamantane group by acylation of thiophene and 2,2'-thiophene by adamantane-1-carboxylic, adamant-1-ylacetic, adamantane-1,3-dicarboxylic, and adamantane-1,3-diacetic acids chlorides under Friedel-Crafts conditions. According to the literature, the chemical properties of these ketones have been little studied. For example, their reduction to the corresponding secondary alcohols with sodium borohydride, and the nitration and oximation of the thiophene nucleus have been described [2, 3].

In a continuation of the study of the chemical properties of ketones of the thiophene series containing an adamantane group, the reductive desulfuration of adamant-1-yl thien-2-yl ketone (**1**), adamant-1-yl 2-(thien-2-yl)-vinyl ketone (**2**), adamant-1-yl 2,2'-bithiophen-5-yl ketone (**3**), and adamant-1-ylmethyl thien-2-yl ketone has been carried out:



1 n = 0, x = 0, R = H; **2** n = 0, x = 1, R = H; **3** n = 0, x = 0, R = thien-2-yl; **4** n = 1, x = 0, R = H;
5 n = 0, R^1 = n-C$_4$H$_9$; **6** n = 0, R^1 = n-C$_6$H$_{13}$; **7** n = 0, R^1 = n-C$_8$H$_{17}$; **8** n = 1, R^1 = n-C$_4$H$_9$

The process was carried out with Raney nickel W-7 [3] in boiling alcohol for 5-9 h to give the corresponding ketones **5-8**. The choice of these vigorous conditions is explained by the negative correlation between the steric shielding of starting thienoylalkane and the yield of their desulfuration products [4].

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TABLE 1. Physicochemical Characteristics of Alkyl Adamant-1-yl Ketones

Ketone	R_f	n_D^{23} (Lit. n_D^{23} [8])	mp of dinitrophenylhydrazone, °C (Lit. mp [8])	IR spectrum, ν, cm^{-1}	Yield, %
5	0.516*	1.4939 (1.4936)	175-178 (175-177)	2850-2950 (CH_2, Ad); 1710 (CO)	43
6*[2]	0.613*[3]	1.4920 (1.4916)	124-126 (126-128)	2850-2950 (CH_2, Ad); 1710 (CO)	31
7*[4]	0.484*	1.6995	202-203	2850-2950 (CH_2, Ad); 1710 (CO)	38
8	0.758*	1.4981	92-94 (91-92)	2850-2950 (CH_2, Ad); 1715 (CO)	41

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* Acetone-CCl_4, 1:6

*[2] ^{1}H NMR spectrum: 0.88 (3H, t, J = 7.7 Hz, CH_3); 1.25 (2H, m, $\underline{CH_2}CH_3$); 1.42 (6H, m, $3CH_2$); 1.70 (12H, t, J = 3.4 Hz, CH_2 in Ad); 1.98 (3H, sh. m., CH in Ad); 2.12 (2H, s, CH_2CO).

*[3] Eluent CCl_4.

*[4] Found, %: C 82.14; H 12.09. $C_{19}H_{32}O$. Calculated, %: C 82.55; H 11.67.

The characteristics of the ketones obtained are given in Table 1. The relatively small yields are possibly connected to insufficiently effective extraction of the products from the excess of nickel used (see also [5]). However attempts to increase the yields by multiple washings of the Raney nickel with ethanol were unsuccessful.

It may be considered that the low yields of adamant-1-yl alkyl ketones are in complete agreement with literature reports of the desulfuration of adamant-1-ylthiophenes [6, 7] and *tert*-butyl thien-2-yl ketones [4].

The structures of ketones **5**, **6**, **8** were confirmed by the agreement between their physicochemical characteristics and literature data [8, 9]. The structure of the new compound **7** was established by a combination of chemical and physical methods. From the ^{1}H NMR spectrum of ketone **6** it may be confirmed that, in agreement with the general rule [10], the CH=CH bond of the vinyl unit is hydrogenated under the chosen experimental conditions. It should be noted that we did not observe reduction of the carbonyl group. This is somewhat unexpected, however it can be explained by the steric effect of the adamantyl substituent.

Thus it has been shown that it is possible to desulfurate ketones of the thiophene series containing an adamantane substituent with Raney nickel W-7 to obtain the corresponding adamant-1-yl alkyl ketones and to establish their structure.

EXPERIMENTAL

IR spectra of nujol mulls were recorded with an IKS-22 spectrometer. ^{1}H NMR spectrum of $CDCl_3$ solutions containing HMDS as internal standard were recorded on a Bruker WP-80DS instrument at 80 MHz.

Thin-layer chromatography was carried out on Silufol UV-254 plates.

Adamant-1-yl *n*-Butyl Ketone (5). A solution of adamant-1-yl thien-2-yl ketone (2.46 g, 0.01 mol) in the minimal amount of ethanol was added to a suspension of Raney nickel W-7 (25 g) in ethanol (25 ml). The reaction mixture was boiled with stirring for 5 h. The solvent was removed, the inorganic precipitate was filtered off, and carefully washed with ether and ethanol. The washing solutions were added to the filtrate and dried over calcium chloride. After evaporation of the solvent compound **5** was obtained as a colorless, transparent liquid whose purity was confirmed by TLC. The yield and characteristics are given in Table 1.

Adamant-1-yl *n*-Hexyl Ketone (6) was prepared in an analogous manner to **5**, using ketone **2** (0.01 mol) and Raney nickel W-7 (45 g) in ethanol (45 ml). The reaction time was increased to 7 h.

Adamant-1-yl *n*-Octyl Ketone (7) was prepared in an analogous manner to **5** from ketone **3** (0.03 mol), using Raney nickel W-7 (20 g) in ethanol (20 ml). Reaction time 9 h.

Adamant-1-ylmethyl *n*-Butyl Ketone (8) was prepared in an analogous manner to **5** from ketone **4**.

2,4-Dinitrophenylhydrazones of Adamant-1-yl Alkyl Ketones. Solutions of ketones **5-8** (0.01 mol) and 2,4-dinitrophenylhydrazine (0.01 mol) in the minimal amount of acetic acid were mixed and kept at room temperature until a crystalline precipitate formed. The precipitate was filtered off, washed with water until neutral, dried, and recrystallized from ethanol. The yield was quantitative.

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