FUNCTIONALIZATION OF SATURATED HYDROCARBONS IN THE PRESENCE OF APROTIC ORGANIC SUPERACIDS.

2.* SINGLE-STAGE SYNTHESIS OF THIOESTERS $R^1CO{-}SR$ FROM n-ALKANES OR CYCLOALKANES (RH), ELEMENTAL SULFUR, AND COMPLEXES $R^1COBr \cdot 2AlBr_3$

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It has been found for the first time that n-alkanes and cycloalkanes (RH) can interact with elemental sulfur at ~20°C. These reactions go forward in the presence of aprotic organic superacids with the composition $R^1COBr \cdot 2AlBr_3$, leading to the formation of thioesters $R^1CO{-}SR$ in satisfactory yields.

Selective functionalization of saturated hydrocarbons is one of the promising directions in organic synthesis. Continuing our studies on functionalization of paraffins in the presence of aprotic organic superacids $R^1CO^+Al_2X_7^-$ [1, 2], we have found that certain n-alkanes and cycloalkanes (RH), at temperatures of 0-20°C in CH_2Br_2 solution, react with elemental sulfur and complexes $R^1CO^+Al_2Br_7^-$ generated in solutions of the systems $R^1COBr \cdot 2AlX_3$, forming thioesters $RS{-}COR^1$ (I):

$$R{-}H + S_8 + R^1CO^+Al_2Br_7^- \rightarrow R{-}S{-}COR^1, \qquad (I)$$

RH = C_3-C_5 n-alkanes, cyclopentane, or cyclohexane; R^1 = Me, Pr, or Ph.

The yields of the thioesters (I) with a reaction time of 1-4 h are 25-60% (other than from n-pentane) as calculated on sulfur; a 0.5 mole ratio of sulfur to complex is optimal (Table 1).

In all cases, the thioesters (I) are the main sulfur-containing products (and for the n-alkanes the only such products) from conversion of the saturated hydrocarbons. In the reactions of cyclopentane and cyclohexane, small quantities of the corresponding dicycloalkyl sulfides are formed as byproducts (yield 3-9%). It is also important to note that (I) always consists of a single isomer (R = i-C_3H_7, sec-C_4H_9, cyclo-C_5H_9, or cyclo-C_6H_{11}, respectively).

As can be seen from Table 1, the reactions of propane and cycloalkanes give rather good yields in the synthesis of the thioesters (I). Thioacylation of n-butane is selective only during the course of a limited interval of time (2.5 h at 0°C and 1 h at 20°C). When the reaction time is extended, the products include not only sec-BuSCOMe but also compounds with the empirical formulas C_3H_7SCOMe and $C_5H_{11}SCOMe$, which are obtained by the interaction of sulfur with the products of n-butane conversions. Let us also note that the reaction we have found, the thioacylation of alkanes and cycloalkanes, is always accompanied by the formation of products that do not contain sulfur, such as saturated and unsaturated ketones $RCOR^1$ and $R_{(-2H)}COR^1$, and in the case of cyclohexane, dimethyldecalins as additional products [3].

Thioacylation of n-alkanes that are more susceptible to fragmentation cannot be accomplished efficiently. Thus, the yield of product in the thioacylation of n-pentane (Table 1) is no greater than 12%, even under conditions such that splitting of the n-pentane is suppressed by considerable dilution of the reaction mixture [4].

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*For previous communication, see [1].

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TABLE 1. Synthesis of Thioesters R^1CO-SR (I) from Alkanes and Cycloalkanes (RH), Elemental Sulfur, and Complexes $R^1CO^+Al_2Br_7^-$ in CH_2Br_2 ($RH:S_8:R^1CO^+Al_2Br_7^-$ = 7:0.5:1)

Alkane (RH)	R^1	T, °C	Time, h	$RS-COR^1$ (I)	Yield of (I), % on S_8
C_3H_8	Me	20	2	$MeCO-S-CHMe_2$	47
$n-C_4H_{10}$	Me	0	2,5	$MeCO-S-CH(Me)Et$	29
$n-C_4H_{10}$	Me	20	1	»	25
$n-C_4H_{10}$	Me	20	2	»	27*
$n-C_5H_{12}$	Me	0	2	$MeCO-S-C_5H_{11}$	12
cyclo-C_5H_{10}	Me	0	2	MeCO-S-cyclo-C_5H_9	45†
cyclo-C_6H_{12}	Me	0	4	MeCO-S-cyclo-C_6H_{11}	60†
cyclo-C_6H_{12}	Pr	0	4	PrCO-S-cyclo-C_6H_{11}	52†
cyclo-C_6H_{12}	Ph	0	4	PhCO-S-cyclo-C_6H_{11}	34†

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*Also formed are $MeCO-S-C_3H_7$ and $MeCO-S-C_5H_{11}$, yield 29%.

†Also formed are dicycloalkyl sulfides, yield 3-9%.

TABLE 2. Spectral Characteristics of Thioesters (I)

Compound (I)	Mass spectrum, m/z	^1H NMR spectrum, δ, ppm from TMS
$MeCO-SCHMe_2$	43, 76, 74, 118, 75, 77, 61, 59, 60, 103	2.0 (MeCO), 1.1 d (2Me, 6H); 3.7 septet (CH, 1H)
$MeCO-SCH(Me)Et$	43, 77, 56, 132, 57, 88, 76, 75, 61, 103	1.9 (MeCO); 1.0 t(Me, 3H); 1.3 d (Me, 3H); 1.6 d.quin. (CH_2, 2H); 3.7 sextet (CH, 1H)
MeCO-S-cyclo-C_5H_9	43, 68, 77, 69, 67, 144, 101, 76, 60	
MeCO-S-cyclo-C_6H_{11}	43, 82, 67, 77, 83, 81, 55, 114, 158, 115	2.0 (MeCO); 1.3 m (3CH_2, 6H); 1.8 m (2CH_2, 4H); 3.8 m (CH, 1H)
PrCO-S-cyclo-C_6H_{11}	71, 105, 43, 55, 83, 82, 67, 186, 81	
PhCO-S-cyclo-C_6H_{11}	105, 77, 139, 106, 67, 55, 83. 220. 82	

It is significant that hydrocarbons with a tertiary carbon atom (isobutane, methylcyclohexane, adamantane) are usually more susceptible to reactions with electrophilic and radical reagents; either they may not form thioesters (I) at all under the conditions investigated (methylcyclohexane, adamantane) or they may form the thioesters with very low yields, 5% in the case of isobutane.

Let us note that in the presence of $AlBr_3$ or an equimolar complex $MeCOBr \cdot AlBr_3$, which does not bring about conversions of paraffins under mild conditions [2], no organic sulfur compounds are formed.

It is known that organic sulfur compounds can be formed from saturated hydrocarbons and sulfur in the presence of Lewis acids at elevated temperatures; however, such reactions are nonselective and inefficient. Thus, n-butane reacts with sulfur in the presence of $AlCl_3$ at 125-135°C to form a mixture of diisopropyl sulfide, dibutyl sulfide, isobutyl mercaptan, diisobutyl sulfide, 4,5-dimethyl-1,2-thiol-3-thione, and a large quantity of hydrogen sulfide [5, 6]. It should be noted that reactions of paraffins with elemental sulfur at ~20°C were previously unknown. Future investigations will be directed at the mechanism of the conversions that have been observed.

EXPERIMENTAL

The saturated hydrocarbons and methylene bromide were purified and dried by standard procedures; their boiling points matched those reported in the literature. The aluminum bromide was purified by vacuum sublimation and stored under argon. Commercial acetyl bromide, pure grade (ch) was redistilled twice in an argon atmosphere over a small quantity of PBr_5.

The course of the reaction was followed by GLC in a Biochrom-1 chromatograph with a capillary glass column 0.25 m × 0.22 mm (stationary liquid phase OV-101). The structure of the reaction products was established by chromatography/mass spectrometry in a Cratos MS 25RF instrument, and also by means of ^1H NMR and IR spectra, recorded in Bruker WP 200 SY and UR-10 spectrometers, respectively. The spectral characteristics of the compounds obtained as products are listed in Table 2. All of the thioesters (I) and the dicycloalkyl sulfides have intense peaks of the molecular ions for which the directions of decomposition are consistent with the proposed structures. The structure of the radicals in (I) was proven unambiguously by the multiplicity and position of signals in the ^1H NMR spectra. The presence of the carbonyl group in (I) was confirmed by IR spectroscopic data, $\nu CO = 1696$ cm^{-1}.

The thioesters (I) used in the ^1H NMR and IR spectroscopic studies were separated from the reaction mixtures by column chromatography on silica gel. In this operation, the nonpolar components of the reaction mixtures were eluted with hexane, after which the eluent was replaced by benzene to obtain the desired compounds, collecting the fraction with $R_f = 0.4-0.5$ and monitoring the purity of the product by GLC.

Standard Experimental Procedure. To 1.6 g (6 mmoles) of $AlBr_3$, 0.37 g (3 mmoles) of AcBr and 4 ml of CH_2Br_2 were added slowly. The resulting solution was cooled to 0°C, after which 0.048 g (1.5 mmoles) of powdered sulfur and 1.8 g (21 mmoles) of cyclohexane were added. The homogeneous solution was stirred 4 h at 0°C. The reaction mixture was poured onto ice, extracted with ether, and dried with $MgSO_4$. Obtained 0.14 g (0.9 mmole) of cyclo-$C_6H_{11}SCOMe$, yield 60% calculated on sulfur, and also 0.01 g (0.5 mmole) of dicyclohexyl sulfide, yield 3.5%.

The reactions with the other saturated hydrocarbons were carried out in the same manner, except for the propane. The propane was condensed, with cooling, in a test tube containing a solution of the complex $R^1COBr \cdot 2AlBr_3$ and a weighed sample of sulfur; the test tube was closed tightly, placed in an autoclave, and held for the required time at ~20°C under external pressure of propane so as to avoid breaking the tube.

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