The reaction mixture was heated to 80 °C; at this temperature, the exothermic reaction began, and the temperature rapidly raised to 110-120 °C. This temperature was maintained by gradual addition of the solution of AlMe<sub>3</sub> over a period of 10-15 min. Then the reaction mixture was additionally heated for 10-15 min at 120-130 °C, cooled to 80 °C, and AsMe<sub>3</sub> was gradually distilled off by slow evacuation of the system. The distillation was terminated at 50 °C and 16 Torr under conditions of reflux of di-n-butyl ether when the reflux condenser was flooded. The setup was filled with the inert gas. AsMe<sub>3</sub> frozen in the liquid-nitrogen trap (1.5-2 g) was recondensed into the trap with AsMe<sub>3</sub> maintained at -80 °C. Then the whole amount of AsMe<sub>3</sub> was distilled using a vacuum system in a Stock-type apparatus and finally distilled under argon with a rod-and-disk type dephlegmator (120 mm), b.p. 52 °C. 23.6 g of AsMe3 was obtained, yield 98.5 %.

The waste reaction mixture, viz., the suspension and the solution of methylalumoxanes in di-*n*-butyl ether, was quenched with 10 % HCl; di-*n*-butyl ether was separated from the aqueous solution, through which a flow of hydrogen sulfide was passed. No precipitation of  $As_2S_3$  was observed, which indicated that arsenic was completely extracted from  $As_2O_3$ .

The high rate of the formation of  $AsMe_3$  by the procedure suggested makes it possible to prepare up to 100 g of  $AsMe_3$  over a period of 5–6 h.

The reaction in diglyme was carried out in a similar way at a temperature of up to  $140 \, ^{\circ}$ C.

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# ESR spectroscopic study on the addition of PhCONHCHCO<sub>2</sub>Me radicals to alkenes and spin traps

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Using ESR spectroscopy, the rate constants for the addition of PhCONHCHCO<sub>2</sub>Me radicals to alkenes CH<sub>2</sub>=CXY (X = Me, Y = Ph; X = H, Y = Ph; X = Me, Y = CO<sub>2</sub>Me; X = H, Y = CO<sub>2</sub>Me; X = H, Y = CN) and nitrosodurene were determined at 22 °C. It is shown that a linear dependence exists between the donor-acceptor properties of the substituents at the vinyl group and the rate constants for the addition.

Key words: spin trap method, rate constants for addition, alkenes.

Addition of acyclic carbon-centered radicals to compounds with multiple bonds is successfully used to form carbon-carbon and carbon-element bonds regio- and stereoselectively.<sup>1-7</sup> The rate of the radical addition to mono- and disubstituted alkenes essentially depends on the polar properties of substituents,<sup>8</sup> which manifests

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itself markedly in the case of electrophilic radicals  $CCl_3$ ,<sup>9</sup> R $CCl_2$ <sup>10</sup> and RR'CH (RR' =  $CO_2R^{2,11}$ , CN<sup>7</sup>), when one or more electron-acceptor groups are connected with the  $\alpha$ -carbon atom of the radical.

Involvement of radicals of the XNHCRCOY type in addition processes will allow one to obtain multifunctional adducts and telomers, which are so necessary in organic synthesis.<sup>2,5</sup> As a rule, the stage of addition is decisive in the formation of adducts in chain processes of interaction with unsaturated compounds, irrespective of the method of initiation.<sup>2,3</sup> In this connection, rate constants of the addition of the PhCONHCHCO<sub>2</sub>Me (R) radical to CH<sub>2</sub>=CXY (X = Me, Y = Ph (1); X = H, Y = Ph (2); X = Me, Y = CO<sub>2</sub>Me (3); X = H, Y = CO<sub>2</sub>Me (4); X = H, Y = CN (5)) and to a spin trap, nitrosodurene (ND), were determined in this work using the ESR method.

# **Results and Discussion**

Radicals R<sup>·</sup> were generated by detaching the bromine atom from PhCONHCHBrCO<sub>2</sub>Me with Re(CO)<sub>5</sub><sup>·</sup> radicals, which are formed in the light-induced decomposition of Re<sub>2</sub>(CO)<sub>10</sub> ( $\lambda \approx 366$  nm).<sup>12</sup> ESR spectra of spin-adducts (SA) of radicals R<sup>·</sup> with 2-methyl-2-nitrosopropane (MNP) are characterized by the following values:  $a_N = 14.75$ ,  $a_{\beta-N} = 2.75$ , and  $a_{\beta-H} =$ 1.10 Oe, which are close to the corresponding values of the HFC constants of spin-adducts of radicals of the XNHCHCOY type with MNP,<sup>13</sup> and those of SA of radicals R<sup>·</sup> with nitrosodurene give  $a_N = 14.0$ ,  $a_{\beta-N} =$ 2.25, and  $a_{\beta-H} = 4.50$  Oe. Steady concentrations of the spin-adducts of PhCONHCHCO<sub>2</sub>Me radicals with nitrosodurene against the initial concentration of the trap<sup>14</sup> are given below.

Using this dependence and taking the rate constant  $(k_0)$  for the interaction of the nitroxyl radicals RN(O)Ar (hereinafter, Ar = 2,3,5,6-Me<sub>4</sub>C<sub>6</sub>H) with radicals R<sup>+</sup> to be equal to  $2 \cdot 10^8$  L mol<sup>-1</sup> s<sup>-1</sup>,<sup>14</sup> we determined the rate constant for the addition of radicals R<sup>+</sup> to ND, which is equal to  $1.5 \cdot 10^7$  L mol<sup>-1</sup> s<sup>-1</sup> at 22 °C. Its value is close to the values of addition constants of secondary acyclic radicals to ND.<sup>15</sup>

Besides the signals of the spin-adducts of radicals R with ND, the ESR spectra of the products of photochemical interaction of PhCONHCHBrCO<sub>2</sub>Me with compounds 1-5 in the presence of  $\text{Re}_2(\text{CO})_{10}$  and ND also had the bands of the spin-adducts of RCH<sub>2</sub>CXY radicals (Table 1, Figs. 1 and 2) with the trap. Generation of the radicals detected can be described by Scheme 1.

The concentrations of radicals A and B become steady upon interaction of radicals R<sup> $\cdot$ </sup> and RCH<sub>2</sub>CXY with A and B.

**Table 1.** The HFC constants of the spin-adducts of  $RCH_2CXY$  radicals with nitrosodurene, which were obtained upon the addition of radicals R<sup>+</sup> to  $CH_2=CXY^*$ 

x	Y	a <sub>N</sub> /Oe	a <sub>β-H</sub> /Oe	
Me	Ph	13.6	_	
Н	Ph	13.8	3.9	
Me	CO <sub>2</sub> Me	13.2	_	
Н	CO <sub>2</sub> Me	13.5	8.2	
Н	ĊŇ	13.2	6.9	

• The signals of  $RCH_2CXY$  are also observed in the ESR spectra along with the signals of the spin-adducts of RN(O)Ar radicals with nitrosodurene (see Figs. 1 and 2).



Fig. 1. a. The ESR spectrum of the spin-adducts of radicals PhCONHCHCO<sub>2</sub>Me (R) and RCH<sub>2</sub>CHPh with ND.  $[ND]_0 = 2.42 \cdot 10^{-3}$ ,  $[2]_0 = 1.745$  mol L<sup>-1</sup>. b. The simulated spectrum.



Fig. 2. a. The ESR spectrum of the spin-adducts of radicals PhCONHCHCO<sub>2</sub>Me and RCH<sub>2</sub>CMeCO<sub>2</sub>M with ND.  $[ND]_0 = 2.12 \cdot 10^{-3}$ ,  $[3]_0 = 2.805$  mol L<sup>-1</sup>. b. The simulated spectrum.

x	Y	[CH <sub>2</sub> =CXY]	[ONAr] <sub>0</sub> · 10 <sup>3</sup>	[A] · 10 <sup>6</sup>	[ <b>B</b> ] · 10 <sup>6</sup>	$k_2 \cdot 10^{-3}$
			/mol L <sup>-1</sup>			
Me	Ph	1.55	2.42	178.7	17.4	12.0
Н	Ph	1.75	2.42	174.0	6.2	9.8
Me	CO <sub>2</sub> Me	2.80	2.12	63.7	14.2	3.5
Н	CO <sub>2</sub> Me	5.53	0.3	145.6	38.4	1.5
Н	ĊŇ	4.17	3.07	59.8	1.23	0.3

**Table 2.** The steady concentrations of RN( $\dot{O}$ )Ar (A) and RCH<sub>2</sub>CXYN( $\dot{O}$ )Ar (B) radicals and the rate constants for the addition ( $k_2$ ) to CH<sub>2</sub>=CXY at 22 °C

$$\left. \begin{array}{c} \mathbf{R}^{*} + \mathbf{A}^{*}(\mathbf{B}^{*}) \\ \mathbf{R}CH_{2}CXY + \mathbf{A}^{*}(\mathbf{B}^{*}) \end{array} \right\} \xrightarrow{k_{4}} \text{ Nonradical products}$$

From the above-said, the rate constant for the addition  $(k_2)$  of radicals R<sup> $\cdot$ </sup> to monomers (M) can be presented by the following expression (1).<sup>15</sup>

$$k_{2} = \frac{k_{1}k_{3}[ND]_{0} + k_{1}k_{2}([A]_{st} + [B]_{st})}{k_{3}[M]_{0}}[B]_{st}/[A]_{st}$$
(1)

One can accept the value of  $4.0 \cdot 10^6 \text{ Lmol}^{-1} \text{ s}^{-1}$  for the rate constants for the addition of RCH<sub>2</sub>CHPh and RCH<sub>2</sub>CMePh radicals to ND and the value of  $2.0 \cdot 10^7 \text{ Lmol}^{-1} \text{ s}^{-1}$  for all the other adduct-radicals;  $k_4 = 2.0 \cdot 10^8 \text{ Lmol}^{-1} \text{ s}^{-1}$  at 22 °C.<sup>15,16</sup> Taking into account these assumptions from the experimental data obtained (Table 2), the rate constants of addition of radicals R to monomers 1–5 were calculated according to the expression (1).

In the case of addition of RBr to monomers M, which is described by Scheme 2, the relative yields of RMBr adducts will be determined by the rates of addition of radicals R<sup> $\cdot$ </sup> to M. A linear dependence (r =0.98) between the donor-acceptor properties (e) of the substituents at the vinyl group and the values of rate constants for the addition (see Table 2) allows us to estimate, using e values for alkenes,<sup>17</sup> the rate constants for the addition of radicals R<sup> $\cdot$ </sup> to them as well as the

#### Scheme 1

PhCONHCHBrCO<sub>2</sub>Me (RBr) + Re(CO)<sub>5</sub> · ---  
R · + Re(CO)<sub>5</sub>Br  
R · + ONAr 
$$\xrightarrow{k_1}$$
 RN( $\dot{O}$ )Ar  
A  
R · + CH<sub>2</sub>=CXY  $\xrightarrow{k_2}$  RCH<sub>2</sub>CXY  
RCH<sub>2</sub>CXY + ONAr  $\xrightarrow{k_3}$  RCH<sub>2</sub>CXYN( $\dot{O}$ )Ar  
B

relative yields of adducts (provided that the rate of the chain transfer is much higher than the growth rate). For example, it follows from the results obtained that the ratio between the yields of radical-adducts  $RCH_2CXY$  and adducts  $RCH_2CXYBr$  in the addition of radicals R<sup>+</sup> to hex-1-ene (6) and to compounds 4 and 5 will be equal to 1, 0.2, and 0.04 ( $k_2 = 7.0 \cdot 10^3 L mol^{-1} s^{-1}$  in the case of the reaction of radicals R<sup>+</sup> with compound 6 because the *e* value for 6 is  $-0.28^{-17}$ ). A similar ratio for the yields of adducts (NC)<sub>2</sub>CHCH<sub>2</sub>CXYI was obtained<sup>6</sup> in the addition of (NC)<sub>2</sub>CHI to compounds 6, 4, and 5: 1 : 0.1 : 0.03 (the rates of detachment of iodine from (NC)<sub>2</sub>CHI with radicals (NC)<sub>2</sub>CHCH<sub>2</sub>CXY are considerably higher than the rates of addition of the latter to CH<sub>2</sub>=CXY).

## Scheme 2

$$Re(CO)_5$$
 + PhCONHCHBrCO<sub>2</sub>Me (RBr)  $\longrightarrow$   $Re(CO)_5Br + R^{-1}$ 

$$R' + M \xrightarrow{k_2} RM'$$

 $RM' + RBr \xrightarrow{k_5} RMBr + R'$ 

2R<sup>•</sup> - K<sub>6</sub> Nonradical products

## Experimental

ESR spectra were recorded on an SE/X-2547 spectrometer. The reaction mixtures were degassed in glass cylindrical vials according to a "freezing—evacuation—thawing" procedure (several cycles) and irradiated with light ( $\lambda = 366$  nm) in the resonator of the spectrometer. Benzene was used as the solvent. Nitrosodurene was preliminarily dissolved in dichloromethane before addition to reaction mixtures. The ratio between steady concentrations of nitroxyl radicals was calculated from simulated spectra (see Figs. 1 and 2). The concentrations of spin-adducts were determined with the use of 2,2,6,6-Me<sub>4</sub>-4,4-(PhCO)<sub>2</sub>C<sub>5</sub>H<sub>4</sub>NO<sup>-</sup> radicals as a standard (the radical concentration was  $3.0 \cdot 10^{-3}$  mol L<sup>-1</sup>). PhCONHCHBrCO<sub>2</sub>Me was prepared by the procedure described earlier.<sup>18</sup>

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# A new synthesis of (Z, E)-tetradec-11-enyl acetate, the sex attractant of the omnivorous leafroller (*Archips podana*)

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A four-step synthesis of the title pheromone was elaborated starting from accessible (Z)-cyclooctene and but-l-ene.

Key words: cometathesis, pheromones, omnivorous leafroller.

It is known that the main components of the sex pheromone of the omnivorous leafroller are (Z)- and (E)-tetradec-11-enyl acetates with the ratio of Z/E-isomers from 50/50<sup>-1</sup> to 63/37, and that the latter composition is the most efficient.<sup>2</sup>

Two approaches to the synthesis of monoenic components of insect pheromones are most popular in the laboratory and technological practice. The first approach is based on the use of acetylenic compounds followed by the stereoselective hydrogenation.<sup>3</sup> The second approach is based on the Wittig reaction.<sup>3</sup> Considerable attention has been given recently to the use of the catalytic cometathesis for the synthesis of components of insect pheromones, because this makes it possible to decrease substantially the number of synthetic stages and to use accessible petroleum raw material.<sup>4-6</sup> We have previously reported<sup>6</sup> on the successful application of this approach for the synthesis of monoenic components of pheromones with double bonds in positions 6–11. For example, a mixture of (Z, E)-isomers of tetradec-11-enyl acetate was obtained by the cometathesis of (Z)-cyclodecene and but-1-ene followed by the selective hydroboration—oxidation of (Z, E)-tetradeca-1,11-diene to (Z, E)-tetradec-11-en-1-ol, whose acetylation gave

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