SILYLOTROPIC REARRANGEMENTS IN SILICON-CONTAINING DERIVATIVES OF ACETOACETIC ESTER, MALONIC ESTERS, AND BENZOYLACETONE

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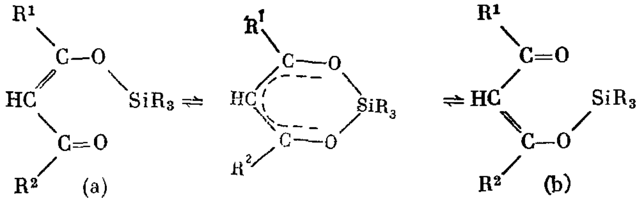
It is known that 2-trialkylsiloxy-2-penten-4-ones, $R_3SiOC(Me)=CH{-}COCH_3$, are a mixture of the Z and E isomers, in which connection intramolecular silylotropic rearrangement (SR), a 1,5-shift of the R_3Si group, is observed in the Z isomer [1-3]. cis-2-Triethylgermoxy-2-penten-4-one rearranges by the same mechanism as its Si analog, but with a lower activation energy [4]. In the present paper the PMR method was used to study the structure and silylotropy of compounds of the series $R_3SiOC(R^1)=CH{-}CO{-}R^2$, where R = Et, R^1 = Me, R^2 = OEt (I); R = Et, $R^1 = R^2$ = OMe (II); R = Me, $R^1 = R^2$ = OMe (III); R = Et, $R^1 = R^2$ = OEt (IV); and $R = R^2$ = Me, R^1 = Ph (V). It was established that (I) and (IV), similar to 2-trimethylsiloxy-2-penten-4-one (VI) [3], are a mixture of the Z and E isomers, whereas (II), (III), and (IV) are found predominantly in the Z form (Table 1).

A broadening, and then a doubling of the signals of the protons of the R^1 and R^2 groups is observed in the PMR spectra of (II)-(IV) when the temperature is lowered, which testifies to the progress of SR



The tautomeric transitions (a) ⇄ (b) in (II)-(IV) are degenerate, whereas nondegenerate tautomerism is characteristic for (I) and (V). For (I) the equilibrium is shifted

TABLE 1. PMR Parameters of Compounds $R_3SiO(R^1){-}C=CH{-}COR^2$

Compound	Isomer	Amount in mixture, %	Temp. of observation, °C	Solvent	Chemical shifts δ, ppm						
					=CH	R^1		R^2		R	
						CH_2	CH_3	CH_2	CH_3	CH_2	CH_3
(I)	E	80	25	CCl_4	5,00		2,22	4,01	1,22	0,71	0,98
	Z	20			4,94		1,85	3,99	1,22	0,71	0,98
(II)	Z	100	25	$CDCl_3$	4,25		3,62		3,62	0,72	0,98
			−60		4,30		3,65		3,67	0,72	0,98
			25	$(CD_3)_2CO$	4,24		3,57		3,57	0,72	0,98
			−60		4,28		3,50		3,68	0,72	0,98
(III)	Z	100	25	$(CD_3)_2CO$	4,30		3,58		3,58		0,33
			−60		4,30		3,61		3,46		0,33
(IV)	Z	100	25	$CDCl_3$	4,20	3,98	1,26	3,98	1,26	0,72	0,98
			0		4,20	4,12	1,32	3,87	1,22	0,72	0,98
(V)	E(a)	55	25	$CDCl_3$	6,21	7,50 (Ph)		2,40			0,36
	E(b)	25			6,11	2,17		7,50 (Ph)			0,36
	Z(a)	15			5,98	7,50 (Ph)		2,21			0,22
	Z(b)	5			5,98	2,17		7,50 (Ph)			0,22
(V)	Z(a)	15	−60	$CDCl_3$	5,98	7,50 (Ph)		2,35			0,11
	Z(b)	5			6,11	2,01		7,50 (Ph)			0,27

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TABLE 2. Activation Parameters of Silyl Migrations (a) ⇄ (b) in Z Form of Compounds $R_3SiOC(R^1) = CHCOR^2$

Compound	Population of form (a)	Observed signals	Δν, Hz	Temp. of merging, °C	K_{298}, sec^{-1}	ΔG_{298}, kcal/mole	E_a, kcal/mole	lg A
(I)	1,0							
(II)	0,5	OCH_3	14,4	12	37,1	15,3±0,2	15,1±1,0	12,6±1,0
(III)	0,5	OCH_3	11,8	10	100,0	14,8±0,2		
(IV) *	0,5	OCH_2	17,2	20	40,0	15,3±0,5		
(V)	0,75	CH_3	20,0	−5	350,0	13,9±0,2	14,0±0,7	13,5±0,9
	0,75	=CH	7,2	−20	150,0	14,4±0,3	14,2±0,9	13,9±0,7
(VI) [1, 2]	0,5	CH_3	36,6	−23	851,0	13,5±0,5	13,8±0,5	

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*The exchange rate was determined at the merging temperature of the signals.

toward the (Ia) form, where R^1 = Me, R^2 = OEt, while the signals of the (Ib) form are not observed (Table 2). For (II)-(IV) the difference in the shielding of the protons of the MeO and EtO groups, like the temperature for the coalescence of their signals, depends on the polarity of the medium and the solution concentration. This presumes the possibility of intermolecular exchange of the R_3Si groups. Previously intermolecular rearrangements with transition of the Et_3Ge group were observed in the neat 2-triethylgermoxy-2-penten-4-one and in its solutions in DMSO and pyridine [5], while the exchange of R_3Si groups was observed in binary mixtures of compounds of type $R_3SiOC(Me) = CHCOR^1$ [6]. By using the dynamic PMR method to effect a complete analysis of the line shapes [7] for (II) and (III) it was shown that the migration rate of the R_3Si group is independent of the nature of the solvent, i.e., the process is intramolecular. The dependence of the merging temperature of the signals of the protons of the alkoxy groups on the nature of the solvent is related to the effect of the medium on the chemical shifts of these protons. The kinetic parameters of the SR, found for (II), (III), and (V) by the method of complete analysis of the line shapes, and for (IV) by the merging temperature of the signals, are given in Table 2.

The R^1 and R^2 substituents in the dicarbonyl system affect both the population of the tautomeric forms and the migration rate of the R_3Si group. In [8], on the basis of the effect of the R^1 and R^2 substituents on the migration rate of the acetyl group in the compounds $MeCOOC(R^1) = CHCOR^2$, where R^1 = Me, R^2 = Me, Ph, OEt, CF_3, it was postulated that acceptor substituents decrease, while donor substituents (for example, OEt) increase the migration rate. Our observed effect of a decrease in the rate of the 1,5-shift in the compounds $Me_3SiOC(R^1) = CHCOMe$ when going from R^1 = Me (VI) to R^1 = Ph (V) (see Table 2) is in agreement with these data. However, in the case of compounds (II)-(IV), contrary to the data given in [8], a noticeable decrease in the migration rate of the R_3Si group is observed. The activation parameters of the SR in (II) and (III) are 1-1.5 kcal/mole higher than in (VI) (see Table 2). The reason evidently consists in the different signs of the induction and mesomeric effects of the substituent R^1 = OMe ($\sigma_I = 0.25$, $\sigma_C^\circ = -0.41$ [9]). Based on the induction effect, the substituents R^1 = OMe and Ph are acceptors. It may be assumed that the effect of the R^1 and R^2 substituents on the silylotropy rate in β-dicarbonyl derivatives is accomplished predominantly via the induction mechanism.

EXPERIMENTAL

The PMR spectra were recorded on a Tesla BS-487C spectrometer (80 MHz) for 10% solutions of the compounds. A complete analysis of the line shapes was done on a BÉSM-6 electronic computer using the program given in [7].

CONCLUSIONS

Using the dynamic PMR method, it was shown that the silylotropic rearrangements in the trialkylsilyl derivatives of acetoacetic ester, malonic esters, and benzoylacetone have an intramolecular character, while the substituents, framing the β-dicarbonyl fragment, affect the thermodynamic and kinetic parameters of the process.

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PERBROMIDES OF 2,4-DINITROPHENYLHYDRAZONES OF ALIPHATIC AND ALICYCLIC KETONES

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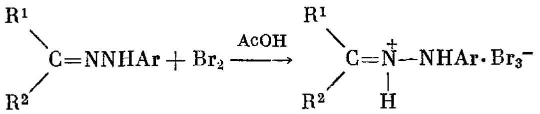
The nature of the bromination products of 2,4-dinitrophenylhydrazones (DNPH) is determined by the character of the substituents on the C atom of the hydrazone fragment. The DNPH of aldehydes, both in halogenated hydrocarbons and in AcOH, are brominated to the DNPH of acyl bromides [1, 2]. The DNPH of steroidal and aralkyl ketones in halogenated hydrocarbons are capable of bromination in the α position of the ylidene fragment [3-5].

When the DNPH of acetone (I), diethyl ketone (II), and cyclohexanone (III) were treated with excess Br_2 in AcOH, we unexpectedly isolated the crystalline products (IV)-(VI), which, based on the elemental analysis data, contained three Br atoms per hydrazone molecule. When heated or treated with hot water, alcohol, or AcOH, when chromatographed on Silufol plates, and also when stored, they slowly liberate bromine (reaction with KI in presence of acid) and are converted to the starting hydrazones (I)-(III). The stability of the compounds decreases in the order (VI) > (V) > (IV). By analogy with the well-known perbromides of quaternary ammonium and pyridinium salts [6] and the perbromides of aromatic aldehyde azines [7], such properties should be characteristic for the perbromides of the DNPH of acetone, diethyl ketone, and cyclohexanone. This assumption is confirmed by the spectral characteristics of (IV)-(VI).



(I) — (III)   (IV) — (VI)

$R^1 = R^2 = CH_3$ (I), (IV), C_2H_5 (II), (V); $R^1 + R^2 = (CH_2)_5$ (III), (VI),
$Ar = 2,4\text{-}(NO_2)_2C_6H_3$.

When compared with the spectra of the starting hydrazones (II) and (III), a broad absorption band at 2480-2550 cm^{-1} appears in the IR spectra of compounds (V) and (VI), which band is characteristic for immonium salts [8]. At the same time, a shift of 25-30 cm^{-1} toward higher frequencies is observed for the absorption band of the C=N group [νC=N in (II) 1626 cm^{-1}, in (III) 1624 cm^{-1}], which is caused by protonation of the imino N atom and was mentioned previously when forming immonium salts [8] and azine perbromides [7], and also a shift of the absorption band of the NH group toward lower frequencies by 75-100 cm^{-1} [νNH in (II) 3312 cm^{-1}, in (III) 3305 cm^{-1}]. The UV spectra of perbromides (V) and (VI) are practically analogous to the spectra of the starting hydrazones, which is also in agreement with protonation at the imino N atom [9].

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