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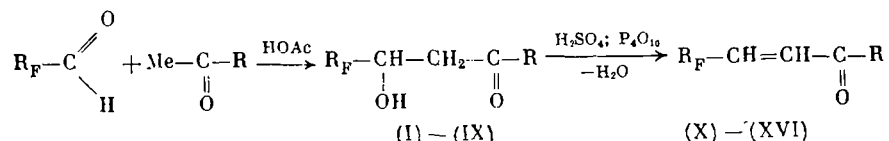
POLYFLUORINATED  $\alpha,\beta$ -UNSATURATED KETONES

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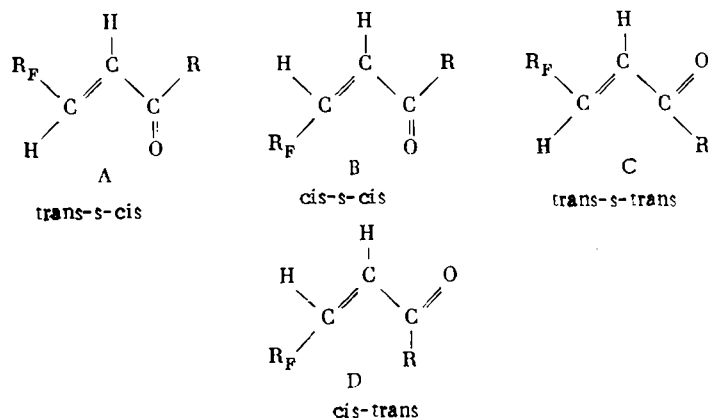
The  $\alpha,\beta$ -unsaturated ketones ( $\alpha,\beta$ -UK), particularly those groups containing fluoroalkyl groups, are of interest as highly reactive compounds having two nonequivalent electrophilic centers and also as promising monomers and intermediate products in the synthesis of biologically active compounds. In the literature there is information principally on the synthesis and properties of trifluoromethyl-containing  $\alpha,\beta$ -UK [1-8], although in many cases the introduction of long fluoroalkyl substituents alters the reactivity and properties of the compounds substantially [9].

In the present investigation, by boiling polyfluorinated aldehydes with methylketones in glacial acetic acid, we have obtained for the first time the polyfluorinated  $\beta$ -hydroxyketones (I)-(IX), the dehydration of which has been used to synthesize the corresponding polyfluorinated  $\alpha,\beta$ -UK (X)-(XVI) (Table 2), and their structure and reactions with the nucleophiles  $\text{NH}_3$ ,  $\text{PhNH}_2$ ,  $\text{MeOH}$  have been studied



The structure of (I)-(XVI) has been confirmed by elemental analysis, and also by IR and PMR spectra. In the IR spectra of (I)-(IX) OH and C=O bands are observed in the regions of 3600 and 1670-1690  $\text{cm}^{-1}$ . The presence of an asymmetrical C atom in the  $\beta$ -hydroxyketones (I)-(IX) determines the characteristic AB system in the PMR spectra of the  $\text{CH}_2$  protons at 3.9-3.8 ppm [10].

In the IR spectra of (X)-(XVI) the OH absorption appears and the C=C band appears in the region 1630-1650  $\text{cm}^{-1}$ . In the PMR spectra of the  $\alpha,\beta$ -UK (X)-(XVI) two doublets of trip-



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TABLE 1. Polyfluorinated  $\beta$ -Hydroxyketones

Com- pound	R <sub>F</sub>	R	Yield, %	mp, °C	Found Calculated, %			Molecular formula	IR spectrum, $\nu$ cm <sup>-1</sup>		PMR spectrum $\delta$ , ppm		
					C	H	F		C=O	OH	CH	CH <sub>2</sub>	OH
(I)	H(CF <sub>2</sub> ) <sub>2</sub>	Ph	40	96-97	$\frac{52.90}{52.81}$	$\frac{4.50}{4.03}$	$\frac{30.20}{30.37}$	C <sub>11</sub> H <sub>10</sub> F <sub>4</sub> O <sub>2</sub>	1675	3600	4.8 m	3.5 m	5.3 d
(II)	H(CF <sub>2</sub> ) <sub>4</sub>	<i>t</i> -Bu	53	36-37	$\frac{40.02}{40.01}$	$\frac{3.74}{4.27}$	$\frac{46.08}{46.03}$	C <sub>11</sub> H <sub>14</sub> F <sub>8</sub> O <sub>2</sub>	1700	3600	4.7 m	2.9 m	3.7 m
(III)	H(CF <sub>2</sub> ) <sub>4</sub>	Ph	61	89-90	$\frac{44.63}{44.59}$	$\frac{3.01}{2.88}$	$\frac{44.10}{43.43}$	C <sub>13</sub> H <sub>10</sub> F <sub>8</sub> O <sub>2</sub>	1670	3600	4.9 m	3.2 m	4.9 m
(IV)	C <sub>4</sub> F <sub>9</sub>	Me	80.5	34-35	$\frac{31.46}{31.39}$	$\frac{2.79}{2.34}$	$\frac{55.80}{55.85}$	C <sub>8</sub> H <sub>7</sub> F <sub>9</sub> O <sub>2</sub>	1720	3500	4.8 m	3.0 m	3.9
(V)	C <sub>4</sub> F <sub>9</sub>	Et	40.29	43-44	$\frac{33.48}{33.76}$	$\frac{3.19}{2.83}$	$\frac{53.1}{53.41}$	C <sub>9</sub> H <sub>10</sub> F <sub>9</sub> O <sub>2</sub>	1725	3600	4.7 m	3.8 m	3.6
(VI)	C <sub>4</sub> F <sub>9</sub>	<i>t</i> -Bu	59.60	52-53	$\frac{37.74}{37.95}$	$\frac{3.66}{3.76}$	$\frac{49.3}{49.10}$	C <sub>11</sub> H <sub>13</sub> F <sub>9</sub> O <sub>2</sub>	1700	3600	4.9 m	3.0 m	3.8 c
(VII)	C <sub>4</sub> F <sub>9</sub>	Ph	72.5	86-87	$\frac{42.22}{42.41}$	$\frac{2.85}{2.46}$	$\frac{46.50}{46.44}$	C <sub>13</sub> H <sub>9</sub> F <sub>9</sub> O <sub>2</sub>	1690	3600	5.0 m	3.5 m	5.5 d
(VIII)	C <sub>4</sub> F <sub>9</sub>	<i>p</i> -BrPh	75.5	100-101	$\frac{35.2}{34.92}$	$\frac{2.05}{1.8}$	$\frac{38.05}{38.24}$	C <sub>13</sub> H <sub>9</sub> F <sub>9</sub> BrO <sub>2</sub>	1690	3600	4.8 m	3.4 m	-
(IX)	H(CF <sub>2</sub> ) <sub>n</sub>	Ph	87.3	75-76	$\frac{40.05}{40.02}$	$\frac{2.25}{2.24}$	$\frac{50.90}{50.64}$	C <sub>15</sub> H <sub>10</sub> F <sub>12</sub> O <sub>2</sub>	1630	3600	5.0 m	3.5 m	5.4 d

TABLE 2. Polyfluorinated  $\alpha, \beta$ -Unsaturated Ketones

Compound	R <sub>F</sub>	R	Yield, %	bp, (p, mm Hg)	Found Calculated, %			Molecular formula	PMR spectrum, $\delta$ , ppm*	
					C	H	F		H <sub><math>\alpha</math></sub>	H <sub><math>\beta</math></sub>
(X)	C <sub>4</sub> F <sub>9</sub>	Me	97,6	50 (10)	33,67 33,35	2,10 1,75	59,30 59,35	C <sub>8</sub> H <sub>5</sub> F <sub>9</sub> O	6,7 M	6,7 M
(XI)	C <sub>4</sub> F <sub>9</sub>	<i>t</i> -Bu	98,3	59-61 (15)	40,01 40,01	3,43 3,30	54,70 51,78	C <sub>11</sub> H <sub>11</sub> F <sub>9</sub> O	7,24 M	5,8 M
(XII)	C <sub>4</sub> F <sub>9</sub>	Ph	78,5	98-99 (5)	44,90 45,55	2,51 2,01	48,98 48,78	C <sub>13</sub> H <sub>7</sub> F <sub>9</sub> O	7,6 M	6,9 M
(XIII)	C <sub>4</sub> F <sub>9</sub>	<i>p</i> -BrPh	80,5	28-29 †	36,20 36,38	4,99 4,41	39,70 39,83	C <sub>13</sub> H <sub>6</sub> F <sub>9</sub> BrO	7,6 M	6,9 M
(XIV)	H(CF <sub>2</sub> ) <sub>4</sub>	<i>t</i> -Bu	93,4	82-84 (5)	42,32 42,28	3,87 4,00	48,3 48,68	C <sub>11</sub> H <sub>12</sub> F <sub>8</sub> O	6,75 M	5,85 M
(XV)	H(CF <sub>2</sub> ) <sub>4</sub>	Ph	95,3	104 (5)	46,89 47,01	2,93 2,43	45,4 45,75	C <sub>13</sub> H <sub>8</sub> F <sub>8</sub> O	7,8 M	7,4 M
(XVI)	H(CF <sub>2</sub> ) <sub>6</sub>	Ph	89,4	148 (10)	41,49 41,68	2,08 1,87	52,6 52,73	C <sub>15</sub> H <sub>8</sub> F <sub>12</sub> O	7,7 M	6,9 M

\*  $^1J_{H_{\alpha}H_{\beta}} = 15$ ,  $^3J_{H_{\beta}F} = 10,6 - 12,5$ ,  $^4J_{H_{\alpha}F} = 2 - 2,4$  Hz.  
 † mp.

TABLE 3. IR and Raman Spectra of Polyfluorinated  $\alpha,\beta$ -Unsaturated Ketones

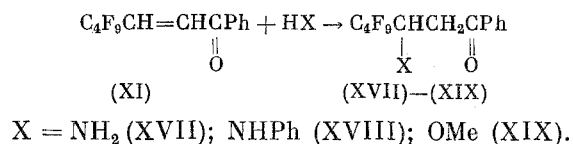
Compound	IR spectrum ( $\nu$ , $\text{cm}^{-1}$ )			Raman spectrum ( $\nu$ , $\text{cm}^{-1}$ )	
	$\nu_{as}$ C=O	$\nu_s$ C-C	CH=	$\nu_{as}$ C=O	$\nu_s$ C=C
(X)	1700 s, 1710 s	1660 s	985	1715 w 1699 s	1661 s
(XI)	1690 s	1630s	965	1708 w	1649s
(XII)	1690s	1650s	970	1688 w	1644 s
(XIII)	1700 s	1650s	970		
(XV)	1680s	1640s	960		
(XVI)	1685 s	1645 s	970		

lets are observed at 6.9 and 7.9 ppm, caused by the spin-spin coupling of the olefin protons with the  $\text{CF}_2$  group of the substituent. For  $\alpha,\beta$ -UK, apart from the cis-trans isomerism relative to the C=C bond, a rotational isomerism is possible, caused by rotation around the C-C single bond.

The presence in the IR spectra of absorption bands from nonplanar torsion-deformation vibrations of C-H for a double bond ( $\nu = 975\text{-}980 \text{ cm}^{-1}$ , Table 3) [11] and the high value of the spin-spin coupling constant of the olefin protons ( $J_{\text{HH}} = 15 \text{ Hz}$ , see Table 2) indicate unambiguously the transconfiguration of the olefin protons (forms A, B) [10]. Here attention should be paid to the high intensity of the band from the C=C bond in the IR spectra of the  $\alpha,\beta$ -UK. It can be suggested that here, as in the case of mesityl oxide [12], the order of the vibrational frequencies of a diene system having a cis-configuration is inverted. To confirm this hypothesis we recorded the Raman spectra of compounds (X)-(XII), in which the intensity of the high-frequency band (the antiphase vibration,  $\nu_{as} = 1685\text{-}1706 \text{ cm}^{-1}$ ) drops sharply and the intensity of the low-frequency band of the syn-phase vibration ( $\nu_s = 1640\text{-}1660 \text{ cm}^{-1}$ ) (see Table 3) increases.

Taking into account the criterion of the s-cis conformation of the  $\alpha,\beta$ -UK [12, 13], it can be concluded that (X)-(XII) exist in the s-cis conformation (form A). However, an s-trans configuration also for (X) is not excluded, since the doublet of the carbonyl band in the Raman spectrum is converted to a singlet and the intensity of the band at  $1650 \text{ cm}^{-1}$  increases. This fact can be explained by the volume substituents in (XI) and (XII) (t-Bu, Ph) hindering the rotation round the C-C bond, in contrast to Me substituents.

A comparison of the intensities of the C=O and C=C bands in the IR spectra of (XIII)-(XVI) also enables us to propose an s-cis conformation for them. It has been shown for the example of (XI) that, like their nonfluorinated analogs, polyfluorinated  $\alpha,\beta$ -UK add on ammonia, primary amines, and methanol through the  $\beta$ -carbon atoms to form the corresponding  $\beta$ -fluoroalkyl-substituted ketones (XVII)-(XIX)



It should be noted that polyfluorinated  $\beta$ -aminovinyl ketones, which can be considered as the  $\beta$ -substituted analogs of  $\alpha,\beta$ -UK also add on nucleophilic reagents through the  $\beta$ -carbon atom [15]. In the IR spectra of (XVII)-(XIX) the C=C band ( $1640\text{-}1660 \text{ cm}^{-1}$ ) disappears, the appearance of the broadened band of NH being observed simultaneously in the region  $3350\text{-}3390 \text{ cm}^{-1}$  for (XVII)-(XVIII). In the PMR spectra the signals from the olefin protons of  $\alpha,\beta$ -UK also disappear and the signals of protons bound with secondary and tertiary C atoms appear, the nature of the spin-spin coupling of the CH proton with  $\text{CH}_2$  and  $\text{CF}_2$  indicating  $\beta$ -addition.

#### EXPERIMENTAL

The PMR spectra of compounds (XVI) and (XIX) were recorded on a Tesla BS-567A spectrometer (100 MHz) in  $\text{CDCl}_3$ , the spectra of compounds (XVII) and (XVIII) on a Perkin-Elmer R-12B spectrometer (60 MHz) in  $\text{CD}_3\text{COCD}_3$  and  $\text{CDCl}_3$  relative to TMS. The IR spectra were recorded on a UR-20 spectrometer and the Raman spectra on a Ramanor HG-2S spectrometer using excitation by an argon laser. The polyfluorinated aldehydes were prepared as in [16].

Synthesis of Polyfluorinated  $\beta$ -Hydroxyketones (I)-(IX). A solution of 0.1 mole polyfluorinated aldehyde and 0.11 mole of methylketone (0.55 mole for acetone) in 75 ml of glacial acetic acid was refluxed for 40-50 h. The cooled mixture was diluted with a fivefold amount of water, and the resulting precipitate filtered off. The aqueous solution was extracted with ether (3  $\times$  75 ml), the extract washed with water, and the ether distilled off. The remainder was combined with the residue, washed with petroleum ether cooled to 0°C, and recrystallized from CCl<sub>4</sub>. The data from elemental analysis, the yields, and constants are presented in Table 1.

Synthesis of Polyfluorinated  $\alpha,\beta$ -Unsaturated Ketones (X)-(XVI). To 0.1 mole of the  $\beta$ -hydroxyketone was added 100 ml of conc. H<sub>2</sub>SO<sub>4</sub> and the mixture allowed to stay overnight. The reaction mass was poured into a beaker containing ice and extracted with ether. The extract was washed with water, then dried over MgSO<sub>4</sub>. The ether was distilled off, the residue distilled under vacuum, and the compounds (XI)-(XVI) obtained. When preparing (X) the corresponding  $\beta$ -hydroxyketone was distilled over P<sub>4</sub>O<sub>10</sub> under vacuum. The data from elemental analysis, the yields and constants are presented in Tables 2 and 3.

1-Phenyl-4,4,5,5,6,6,7,7,7-nonafluoro-3-amino-1-heptanone (XVII). 0.02 mole of (XII) was dissolved in 100 ml of absolute ether and placed in a 500-ml steel autoclave. Into the autoclave was introduced an excess of dry NH<sub>3</sub> and it was heated on a water bath for 1 h. After cooling the autoclave was discharged, the ether distilled off, and the residue recrystallized from n-hexane or CCl<sub>4</sub>. Yield 66.8%, mp 45-46°C. IR spectrum ( $\nu$ , cm<sup>-1</sup>) 1685 (C=O), 3350, 3440 (NH<sub>2</sub>). PMR spectrum ( $\delta$ , ppm): 3.1-3.3 m (2H, A B), 3.8-4.6 m (1H), 7.2-8.2 m (5H), 1.4 s (2H). Found, %: C 42.97, H 3.18, F 46.5. C<sub>13</sub>H<sub>10</sub>F<sub>9</sub>NO. Calculated, %: C 42.52, H 2.74, F 46.56.

1-Phenyl-4,4,5,5,6,6,7,7,7-nonafluoro-3-(N-phenylamino)-1-heptanone (XVIII). 0.02 mole of (XII) and 0.05 mole of aniline were dissolved in 50 ml absolute benzene and refluxed for 3 h. The benzene was distilled off and the residue recrystallized from n-hexane. Yield of (XVIII): 50.1%, mp 135°C. IR spectrum ( $\nu$ , cm<sup>-1</sup>) 1680 (C=O), 3390 (N-H). PMR spectrum ( $\delta$ , ppm): 3.6 d (2H), 5.2 m (H), 6.6-8.2 m (10H). Found, %: C 51.42, H 3.44, F 38.1, N 2.95. C<sub>19</sub>H<sub>14</sub>F<sub>9</sub>NO. Calculated, %: C 51.49, H 3.18, F 38.57, N 3.16.

1-Phenyl-4,4,5,5,6,6,7,7,7-nonafluoro-3-methoxy-1-heptanone (XIX). 0.02 mole of (XII) was dissolved in 50 ml of absolute methanol, 0.1 g NaOH added, and the mixture refluxed, the course of the reaction being monitored by TLC. The alcohol was evaporated off and the residue sublimed under vacuum. Yield 75%, mp 44.5°C. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1685 (C=O). PMR spectrum ( $\delta$ , ppm); 3.4 m (5H), 4.7 m (1H), 7.3-8.0 m (5H). Found, %: C 42.82, H 2.65, F 44.90. C<sub>14</sub>H<sub>11</sub>F<sub>9</sub>O<sub>2</sub>. Calculated, %: C 43.89, H 2.90, F 44.73.

## CONCLUSIONS

1.  $\beta$ -Hydroxyketones and  $\alpha,\beta$ -unsaturated ketones with  $\beta$ -fluoroalkyl substituents have been prepared. It has been shown that the latter exist predominantly in the trans-s-cis form irrespective of the length of the fluoroalkyl substituent.

2. As with the hydrocarbon analogs and the isomeric polyfluorinated  $\beta$ -aminovinylketones, polyfluorinated  $\alpha,\beta$ -unsaturated ketones react with nucleophilic reagents to form  $\beta$ -substituted ketones.

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