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3-DINITROBENZOYLHYDRAZONES OF ORGANOSILICON CARBONYL COMPOUNDS

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One of the authors [1] previously found a new reagent for the carbonyl group–3,5-dinitrobenzoylhydrazide (I). In contrast to 2,4-dinitrophenylhydrazine, semicarbazide, and hydroxylamine, it readily forms well crystallizing 3,5-dinitrobenzoylhydrazones with aldehydes and ketones of various structures.

It was of considerable interest to investigate the behavior of (I) toward aldehydes and ketones containing the silicon atom. We investigated the reaction of (I) with organosilicon carbonyl compounds for the example of the reactions with α,β-silicoacetylenic aldehydes and ketones, as well as γ- and ε-silicon containing saturated ketones and ketones of more complex structure. The investigation showed that (I) forms readily crystallizing 3,5-dinitrobenzoylhydrazones (II) with characteristic melting points with organosilicon aldehydes and ketones (table).

$$R_3SiC{\equiv}C-\underset{\substack{|\\R'}}{C}=O+NH_2-NHCOC_6H_3(NO_2)_2$$

$$\rightarrow R_3SiC{\equiv}C-\overset{\substack{R'\\|}}{C}=N-NHCOC_6H_3(NO_2)_2$$

$$R_3Si(CH_2)_nCOR''+NH_2-NHCOC_6H_3(NO_2)_2$$

$$\rightarrow R_3Si(CH_2)_n\underset{\substack{|\\R''}}{C}=N-NHCOC_6H_3(NO_2)_2,$$

where R and R"-CH_3; C_2H_5; C_3H_7; R'-H; CH_3; C_2H_5; $CH{=}CH_2$; $C{\equiv}C{-}CH{=}CH_2$; C_6H_5; n–2 and 4.

In addition, the tendency of organosilicon aldehydes and ketones to form (II) and their yields depend to a considerable degree on their structure (see the table). Thus, the α,β-silicoacetylenic aldehydes 1 and 2 in the table form (II) more readily than the α,β-silicoacetylenic ketones 8, 9, and 10. However, they are less reactive with (I) than are silicoacetylenic ketones containing electronegative radicals near the carbonyl group (11-13). Saturated organosilicon ketones (3-5) form (II) somewhat better than their silicoacetylenic analogs (8-10). As the distance of the carbonyl atom from the silicon atom increases, the tendency to form (II) decreases (6,7). Thus, the reactivity of organosilicon carbonyl compounds can be followed by the reaction of 3,5-dinitrobenzoylhydrazide. 3,5-Dinitrobenzoylhydrazones of organosilicon aldehydes and ketones represent white crystalline substances with characteristic melting points, crystallizing readily from alcohol and melting without decomposition.

EXPERIMENTAL

The 3,5-dinitrobenzoylhydrazones (II) were produced in the following way: about 0.001 mole (I) was dissolved with heating in 10 ml of ethanol, and 0.0015 mole of the organosilicon carbonyl compound was added. The mixture was heated for half an hour at 50-60° and allowed to crystallize. If no precipitate formed, then it was precipitated by adding distilled water. The hydrazones obtained were recrystallized from ethanol.

CONCLUSIONS

The reaction of 3,5-dinitrobenzoylhydrazide with organosilicon aldehydes and ketones was investigated. It was shown that this reagent forms readily crystallizing 3,5-dinitrobenzoylhydrazones and is suitable for the identification of organosilicon carbonyl compounds.

Item no.	Carbonyl compounds	3,5-Dinitrobenzoylhydrazone	M.p., °C	Found, %				Calculated, %				Yield after recrystallization, %
				C	H	Si	N	C	H	Si	N	
1	$(CH_3)_3SiC \equiv C-CHO$	$C_{13}H_{14}N_4O_5Si$	195	46,35	4,18	8,58	17,03	46,70	4,19	8,38	16,76	58
2	$(CH_3)_2C_2H_5SiC \equiv C-CHO$	$C_{14}H_{16}N_4O_5Si$	172	48,33	4,61	8,27	16,28	48,27	4,62	8,05	16,07	56
3	$(CH_3)_3Si(CH_2)_2COCH_3$	$C_{14}H_{20}N_4O_5Si$	130	48,10	5,80	7,93	—	47,70	5,72	7,97	—	57
4	$(CH_3)_3Si(CH_2)_2COC_2H_5$	$C_{15}H_{22}N_4O_5Si$	142	49,10	6,11	7,56	—	49,18	6,05	7,66	—	55
5	$(C_2H_5)_3Si(CH_2)_2CO(CH_2)_2CH_3$	$C_{18}H_{28}N_4O_5Si$	118	—	—	—	—	—	—	—	—	50
6	$CH_3(C_2H_5)_2Si(CH_2)_4COCH_3$	$C_{18}H_{28}N_4O_5Si$	90	53,02	7,08	—	13,73	52,93	6,91	—	13,71	22
7	$(C_2H_5)_3Si(CH_2)_4COCH_3$	$C_{19}H_{30}N_4O_5Si$	96	54,45	7,07	—	13,32	54,01	7,16	—	13,25	23
8	$(CH_3)_2C_2H_5SiC \equiv C-CO-CH_3$	$C_{15}H_{18}N_4O_5Si$	84	50,18	5,03	7,97	15,49	49,71	5,00	7,71	15,45	40
9	$(CH_3)_2C_2H_5SiC \equiv C-CO-C_2H_5$	$C_{16}H_{20}N_4O_5Si$	86	50,94	5,37	6,99	—	51,04	5,36	7,43	—	43
10	$(CH_3)_3SiC \equiv C-CO-CH_3$	$C_{14}H_{16}N_4O_5Si$	99	48,40	4,82	8,02	16,11	48,27	4,62	8,05	16,07	41
11	$(CH_3)_3SiC \equiv C-CO-C_6H_5$	$C_{19}H_{18}N_4O_5Si$	190	56,07	4,46	6,77	13,70	55,60	4,38	6,82	13,65	73
12	$(CH_3)_3SiC \equiv C-CO-CH=CH_2$	$C_{15}H_{16}N_4O_5Si$	101	5,00		7,96		49,99		7,79		98
13	$(CH_3)_3SiC \equiv C-CO-C \equiv C-CH=CH_2$	$C_{17}H_{16}N_4O_5Si$	85	—	—	—	—	—	—	—	—	71

LITERATURE CITED

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