CLEAVAGE OF DI- AND TRIOXACYCLOHEXANES BY TRIMETHYLIODOSILANE

M. G. Voronkov, V. G. Komarov, A. I. Albanov, I. M. Korotaeva, and É. I. Dubinskaya

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In this paper, as a continuation of studying the reaction of trimethyliodosilane (I) with oxacyclanes [1-5], we studied its reaction with 1,4-dioxane (II), 1,3,5-trioxane (IIIa), and 2,4,6-trimethyl-1,3,5-trioxane (IIIb).

Contrary to the data in [6], we were able to cleave (II) using (I).

$$Me_3SiI\ (I) + (II) \rightarrow [ICH_2CH_2OCH_2CH_2OSiMe_3] \xrightarrow{Me_3SiI} ICH_2CH_2I\ (IV) + Me_3SiOCH_2CH_2OSiMe_3\ (V)$$

$$2\,(I) + (V) \rightarrow (IV) + 2Me_3SiOSiMe_3$$

Varying the (I):(II) mole ratio from 1:1 to 4:1 has no effect on the yield of 1,2-diiodoethane (IV), when based on starting (I). However, the yield of 1,2-bis(trimethylsiloxy)ethane (V) decreases with increase in the amount of (I), since its further cleavage by excess (I) occurs, which is confirmed by specially reacting (V) with (I). Thus, at a (I)/(II) ratio = 4:1 the reactants are almost quantitatively converted to (IV) and HMDS (98%). In contrast, the use of excess (II) permits directing the reaction toward the formation of (V), whose yield is 53% when an equimolar ratio of the reactants is used.

From (I) and the trioxanes (III) under analogous conditions are easily formed the bis(iodomethyl)(VIa) and bis(α-iodoethyl) (VIb) ethers:

$$(I) + (IIIa, b) \rightarrow RHICOCIHR\ (VIa, b) + Me_3SiOSiMe_3$$

R = H (a); CH_3 (b).

The maximum yield of (VIa, b) is reached using a (I):(III) mole ratio = 3. The yields of HMDS and (VI) decrease when the amount of (I) is increased. Compound (VIa) is not cleaved by (I) even at 150°C for 10 h (Table 1).

EXPERIMENTAL

The PMR spectra were obtained on a Tesla BS-487C spectrometer (80 MHz) using 20% CCl_4 solutions, while the GLC determinations were run on an LKhM-72 chromatograph (using a 1-m-long column packed with 10% PMS-100 deposited on Chromaton N-AW-HMDS and helium as the carrier gas) under isothermal and programmed conditions.

The reactions were run in a dry argon atmosphere. Trimethyliodosilane (I) was obtained as described in [7].

Reaction of 1,4-Dioxane (II). To 7.2 g (0.082 mole) of (II) was added 32.9 g (0.164 mole) of (I) in drops. Then the mixture was heated for 3 h at 40°. Distillation gave 3.9 g (30%) of HMDS, bp 96°, 22 g (95%) of ICH_2-CH_2I (IV), mp 79°. Found: C 8.31; H 1.23; I 90.93%. $C_2H_4I_2$. Calculated: C 8.52; H 1.43; I 90.05%. PMR spectrum (δ, ppm): 3.5 s (CH_2I); 5.9 g (34%) of 1,2-bis(trimethylsiloxy)ethane (V), bp 60° (4 mm); d_4^{20} 0.8422, n_D^{20}

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TABLE 1. Reaction of Trimethyliodosilane (I) with Trioxanes (III)

Trioxane	(I)/(IIIa, b) mole ratio	Yield, %	
		(VI)	HMDS
(IIIa)	1	96	91
	2	96	95
	3	99,5	98,5
	4	67	60
	6	46	50
(IIIb)	2	93	94
	3	97	96
	4	70	70

1.4031. Found: C 46.02; H 10.82; Si 27.01%. $C_8H_{22}Si_2O_2$. Calculated: C 46.61; H 10.75; Si 27.25%. PMR spectrum (δ, ppm): 0.08 s [$(CH_3)_3SiO$]; 3.55 s (OCH_2).

Reaction of 1,3,5-Trioxane (IIIa) and 2,4,6-Trimethyl-1,3,5-trioxane (IIIb). To 5.2 g (0.058 mole) of (IIIa) was added dropwise in 30 min 35 g (0.174 mole) of (I). The mixture was heated for 10 h at 40°. Distillation gave 13.8 g (98%) of HMDS and 25.8 g (99.5%) of bis(iodomethyl) ether (VIa), bp 62° (5 mm); d_4^{20} 2.8259; n_D^{20} 1.6720. Found: C 8.17; H 1.07; I 87.53%. $C_2H_4OI_2$. Calculated: C 8.06; H 0.75; I 88.04%. PMR spectrum (δ, ppm): 5.62 s (ICH_2O).

α,α'-Diiododiethyl ether was obtained in a similar manner from (IIIb), bp 71° (5 mm), d_4^{20} 2.2213; n_D^{20} 1.5750. Found: C 14.73; H 2.46; I 78.03%. $C_4H_8OI_2$. Calculated: C 14.74; H 2.47; I 77.88%. PMR spectrum (δ, ppm): 6.09 m (OCH_2I); 2.17 d (CH_3C).

Reaction of 1,2-Bis(trimethylsiloxy)ethane (V). To 16.9 g (0.08 mole) of (V) was added 32.9 g (0.164 mole) of (I) in drops and the mixture was heated for 6 h. We isolated 12.6 g (95%) of HMDS and 22.7 g (98%) of 1,2-diiodoethane (IV).

CONCLUSIONS

The reaction of Me_3SiI with 1,4-dioxane gives 1,2-diiodoethane, 1,2-bis(trimethylsiloxy)ethane, and hexamethyldisiloxane, while reaction with 1,3,5-trioxane and 2,4,6-trimethyl-1,3-5-trioxane respectively gives the α,α'-diiodomethyl and ethyl ethers and HMDS.

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