LETTERS TO THE EDITOR

SYNTHESIS OF SOME o-CARBORANE DERIVATIVES

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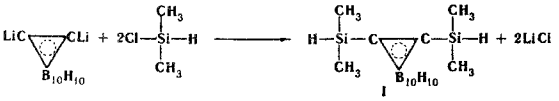
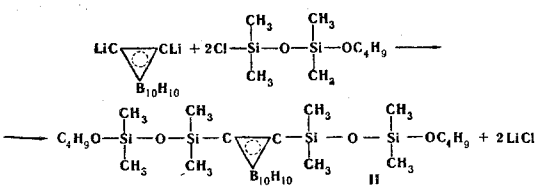
We have carried out work on the synthesis of some derivatives of o-carborane. Reaction of dilithium-o-carborane with dimethylchlorosilane has given, for the first time, 1, 2-bis(dimethylsilylhydride)o-carborane:



The product I was a viscous oily colorless liquid, bp 121°–125° C (3 mm); d_4^{20} 0.9457; n_D^{20} 1.5360. Found: C 27.8; H 9.80; B 40.75; Si 20.90%. Calculated for $C_6H_{24}B_{10}Si_2$: C 27.7; H 9.23; B 41.50; Si 21.54%.

Reaction of dilithium-o-carborane with 1-chloro-3-butoxyl-1, 1, 3, 3-tetramethyldisiloxane also gave for the first time 1, 2-bis(1-butoxy-1, 1, 3, 3-tetramethyldisiloxane)o-carborane:



Compound II was a viscous oily colorless liquid, bp 110°–115° C (10 mm). Found: H 10.0; B 20.1; Si 20.4%. Calculated for $C_{16}H_{42}B_{10}O_4Si_4$: H 9.4; B 19.5; Si 20.2%.

A low-molecular dimethylsiloxane polymer, not containing boron, was obtained along with this product.

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A NEW METHOD OF PREPARING 2-HYDRAZINOBENZO- AND NAPHTHOTHIAZOLES

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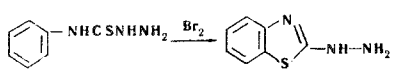
A paper recently published [1] stated that 4-phenylthiosemicarbazide cannot be cyclized to 2-hydroazinobenzothiazole by the method described in [2]. We have found that under certain conditions 2-hydrazinobenzothiazole can be obtained in 33% yield.



The method can also be used to prepare substituted 2-hydrazinobenzothiazoles, e. g. 6-ethoxy-2-hydrazinobenzothiazole. The appropriate naphthylthiosemicarbazides also give good yields of 2-hydrazinonaphtho-[1, 2]- and -[2, 1]thiazoles. In this way these hydrazines, difficultly accessible by other means, become readily accessible.

GENERAL METHOD OF PREPARING THE HYDRAZINES

A solution of 0.5 ml (0.01 mole) bromine in 15 ml $CHCl_3$ in small portions, was added with constant stirring to a suspension of 0.01 mole 4-arylthiosemicarbazide in 30 ml $CHCl_3$. The whole was left for 30 min at room temperature, then heated for 40 min on a steam-bath, when there was vigorous evolution of HBr. Then the products were cooled, the precipitate of hydrazine hydrobromide filtered off, and washed with $CHCl_3$.

In the case of 2-hydrazinobenzothiazole, the solid was gently heated in 30 ml water, and SO_2 passed. The resultant tarry reaction product was filtered off, and the filtrate neutralized with alkali. The resultant pre-

cipitate of hydrazine was filtered off, and recrystallized from EtOH. Yield 33%, mp 200°–201° C (201°–203° C [3]). 6-Ethoxy-2-hydrazinebenzothiazole was obtained in 30% yield, mp 174°–175° C (175°–176° C [3]).

4-α-Naphthylthiosemicarbazide* mp 145°–147° C (MeOH), colorless prisms, yield 33%. Found: N 19.84; S 14.73%. Calculated for $C_{11}H_{11}N_3S$: N 19.34; S 14.74%. 2-Hydrazinonaphtho[1, 2]thiazole hydrobromide was crystallized from boiling water, using active charcoal. Yield 90%. The hydrobromide was suspended in dimethylformamide, and addition of alkali liberated the hydrazine base, mp 239°–242° C, readily soluble in dimethylformamide and dioxane, less soluble in EtOH. Found: N 19.36; S 15.33%. Calculated for $C_{11}H_9N_3S$: N 19.54; S 14.89%. It reacted with benzaldehyde to give the hydrazone, mp 195°–196° C (MeOH). Found: N 14.20; S 10.61%. Calculated for $C_{18}H_{13}N_3S$: N 13.85; 10.57%.

4-β-Naphthylthiosemicarbazide*. Mp 170°–172° C (MeOH), prisms, yield 21–24%. Found: N 19.43; S 15.21%. Calculated for $C_{11}H_{11}N_3S$: N 19.34; S 14.74%.

*Prepared as described in [5].

2-Hydrazinonaphtho[2, 1]-thiazole hydrobromide prepared from it was crystallized from water, (yield 66%). The hydrazine base was separated similarly to 2-hydrazinonaphtho[1, 2]thiazole, mp 219°–220° C. 2-Hydrazinonaphtho[2, 1]thiazole reacted with CH_3CHO to give a hydrazone, mp 243°–245° C (241°–243° C [4]).

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6, 6'-SPIROBISHEXAHYDROPYRIMIDINES

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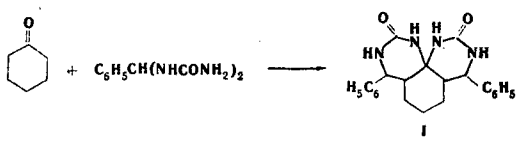
Reaction of cyclohexanone with benzalbisurea (BBU) in ethanol in the presence of HCl gave a compound of the formula $C_{22}H_{24}N_4O_2$[1]. From its IR, UV, and PMR spectra, and from information in the literature regarding the action of aliphatic ketones on urea [2–4], it can be inferred that it was 2, 2'-dioxo-4, 4'-diphenyl-5, 5'-trimethylene-6, 6'-spirobishexahydropyrimidine (I). Compound I was colorless, slightly soluble in organic solvents, mp 335° C (decomp). Found: C 70.5; 70.5; H 6.54; 6.62; N 14.7; 14.9%. Calculated for $C_{22}H_{24}N_4O_2$: C 70.2; H 6.42; N 14.9%.



I

IR spectrum (in KBr), ν cm^{-1}: NH 3200, 3400; CH_2 2860; 2920; C=O 1680 and 1660 (same intensity); absorption bands characteristic of C=C and C=N lacking. UV spectrum (in AcOH) λ_{max}, mμ (lgε): 258 (2.77); 264 (2.70); 284–302 (hump) (2.30). PMR spectrum (in CF_3COOH, internal standard TMS): CH arom δ 7.0 (singlet); NH δ 4.5 (multiplet); CH_2 and CH δ 2.0–1.0 (multiplet).

Under similar conditions condensation of 2-methylcyclohexanone and acetone with BBM gave respectively 2, 2'-dioxo-4, 4'-diphenyl-5-methyl-5, 5'-trimethylene-6, 6'-spirobishexahydropyridmidine (II), mp > 350° C, and 2, 2'-dioxo-4, 4'-diphenyl-6, 6'-spirobishexahydropyrimidine III, mp 312°–315° C (decomp). Compound III was also prepared from dibenzalacetone and urea using the method of [3].

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