ACTION OF ORGANOLITHIUM COMPOUNDS ON 6-AZIDO-2-METHYLBENZOTHIAZOLE

L. I. Skripnik and V. Ya. Pochinok

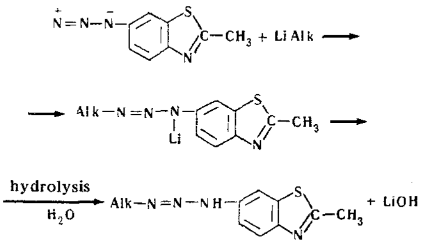
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 4, No. 6, p. 1007, 1968

UDC 547.789.6'236.2:542.957

During the interaction between 6-azido-2-methylbenzothiazole and ethyl- and n-butyllithium aliphatic-aromatic triazenes were formed. which we had previously obtained by means of organomagnesium synthesis.

In a previous report, it has been shown that, during the reaction between 6-azido-2-methylbenzothiazole and organomagnesium halide compounds, alkyl (aryl)-(2-methylbenzothiazolyl-6)triazenes [1] were formed.

Triazenes with an analogous structure have also been obtained when organolithium compounds were used. During the interaction between 6-azido-2-methylbenzothiazole and ethyl- and n-butyllithium, ethyl (2-methylbenzothiazolyl-6)triazene and n-butyl(2-methylbenzothiazolyl-6)triazene (previously described in the first report) were obtained respectively.



EXPERIMENTAL

6-Azido-2-methylbenzothiazole (I) was obtained by diazotization of 6-amino-2-methylbenzothiazole with subsequent treatment of the resulting diazonium salt with sodium azide. After crystallization from aqueous ethanol, colorless crystals were obtained with decomp. 67–68° C [1].

Ethyl and butyllithium were obtained from ethyl bromide or n-butyl chloride, respectively, in a medium of absolute ether in an atmosphere of dry nitrogen [2]. Their concentrations were determined by the acidimetric method [3].

Alkyl triazenes. The equivalent quantity of an ethereal solution of alkyllithium was added dropwise to a solution of 1.9 g (0.01 mole) of compound I in 25 ml absolute ether. The reaction mixture was cooled to −5° C and stirred vigorously. An orange precipitate was formed. The reaction mass was stirred for a further 2 hr period and the temperature was gradually increased to room temperature. The organolithium compound formed was hydrolyzed with iced water with stirring. The separated triazene was extracted with ether. The ethereal extract was carefully washed with water in order to remove alkali (determined with litmus) and dried with anhydrous sodium sulfate. After removing the ether by distillation and drying in a vacuum desiccator, the remaining light-yellow oil was crystallized.

Ethyl-(2-methylbenzothiazolyl-6)triazene. Yield, 83.4%; decomp. 75–76° C (from petroleum ether). Found %: N 25.31, 25.48. Calculated for $C_{10}H_{12}N_4S$. %: N 25.44.

n-Butyl-(2-methylbenzothiazolyl-6)triazene. Yield, 88%; decomp. 77–78° C (from petroleum ether). Found, %: N 22.34, 22.49. Calculated for $C_{12}H_{16}N_4S$. %: N 22.56.

The triazenes obtained also form silver derivatives by means of the active hydrogen atom of the triazeno group. The method of preparation and constants have been described in a previous publication [1].

REFERENCES

1. V. Ya. Pochinok and L. F. Avramenko, Ukr. khim. zh., 28, 511, 1962.
2. K. A. Kocheshkov and T. V. Talalaeva, Synthetic Methods in the Field of Organometallic Compounds [in Russian], no. 1, 1949.
3. H. Gilman, E. A. Zoellner, J. B. Dickey, and W. M. Selby, J. Am. Chem. Soc., 57, 1061, 1935.
4. L. I. Skripnik and V. Ya. Pochinok, KhGS [Chemistry of Heterocyclic Compounds], 3, 292, 1967.

14 September 1966 Kiev State University