COMMUNICATIONS TO THE EDITOR

CIS- AND TRANS-FORMS OF 2,5-DIMETHYL-3-HEXENE-2,5-DIOL

Sir:

In THIS JOURNAL, **62,** 2615 (1940), is an article entitled "Rearrangement of Unsaturated 1,4-Glycols. II. *cis*- and *trans*-Forms of 2,5-Dimethyl-3-hexene-2,5-diol," by J. R. Johnson and O. H. Johnson.

These authors investigated the crystals of Bourguel, m. p. 101°, but could obtain none of the γ-oxide by dehydrating them, and drew the conclusion that they represented the *trans*-form of the ethylenic glycol, 2,5-dimethyl-3-hexene-2,5-diol.

These authors have apparently overlooked an investigation of these crystals by I. Zalkind and S. Bukhovets (*J. Gen. Chem.*, U. S. S. R., **7,** 2417 (1937); *Chem. Abstr.*, **32,** 2086[1] (1938)) where we found them not to be an ethylenic derivative at all but another crystalline form of the acetylenic glycol, 2,5-dimethyl-3-hexine-2,5-diol. Naturally, therefore, this substance does not give any γ-oxide on dehydration. We could also show that the α-form of dimethyl-hexenediol is obtainable free from any trace of the acetylenic glycol and is not a mixture but another form of the ethylenic glycol with a m. p. of 75°.

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U. S. S. R. I. ZALKIND

RECEIVED MAY 20, 1941

CIS- AND TRANS-FORMS OF 2,5-DIMETHYL-3-HEXENE-2,5-DIOL. CORRECTION

Sir:

At the time when our experiments with these glycols were carried out,[1] we were not aware of the recent work of Zalkind and Bukhovets.[2] Our synthesis of the *cis*-form from methyl maleate definitely confirmed Bourguel's assignment of the *cis*-configuration to the β-form of the glycol, m. p. 69–70°. Our efforts to synthesize an authentic *trans*-glycol from methyl fumarate were unsuccessful but we had no reason to doubt Bourguel's assignment of the *trans*-configuration to the glycol melting at 101°. He had obtained this form in 30% yields by treating the acetylenic glycol with a large excess of metallic sodium in methyl alcohol,[3] and believed it to be a new form of the ethylenic glycol.

Professor Zalkind erred in stating that we drew any conclusions concerning the configurations of the glycols from the dehydration experiments, since we have little faith in this method by itself as a basis for the assignment of configurations. All of the evidence known to us at that time was compatible with Bourguel's interpretation and we merely assumed that his conclusions were correct.

Recent experiments in this Laboratory with Bourguel's glycol, m. p. 101°, have given complete confirmation of Zalkind's contention that it is merely a second crystalline modification of the acetylenic glycol. In the presence of platinum catalyst the compound m. p. 101° took up *four* atoms of hydrogen and gave the saturated glycol, 2,5-dimethylhexane-2,5-diol, m. p. 88.5°; with a palladium catalyst the compound took up only two atoms of hydrogen and gave the *cis*-form of the ethylenic glycol, m. p. 68–69°. In both cases the hydrogenated glycols were obtained in 88–90% yields and their identity was established by mixed melting points with authentic samples.

These results leave no doubt that Bourguel's *trans*-form is spurious and that our experiments were made with a form of the acetylenic glycol instead of the ethylenic glycol. Our experimental data should now be corrected as follows. Page 2619: The dichloride obtained by the action of hydrochloric acid should be designated as 2,5-dichloro-2,5-dimethyl-3-hexine, and the product of dehydration as 2,5-dimethylhexadiene-1,5-ine-3. Our conclusions relating to the relative reactivity of the alleged *cis*- and *trans*-forms should be stricken from the literature.

It is hoped that further experimental work will overcome the difficulty of obtaining an authentic *trans*-form of the ethylenic glycol. Zalkind's α-form of the ethylenic glycol, m. p. 75°, cannot be assigned the *trans*-configuration in the absence of rigorous experimental proofs, as it may prove to be merely another crystalline modification of the *cis*-form.

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(1) Johnson and Johnson, THIS JOURNAL, **62,** 2615 (1940).

(2) Zalkind and Bukovets, *J. Gen. Chem.* (U. S. S. R.), **7,** 2417 (1937); *C. A.*, **32,** 2086 (1938).

(3) Bourguel and Rambaud, *Bull. soc. chim.*, [4] **47,** 185 (1930).