

[CONTRIBUTION FROM THE LABORATORY OF THE UNIVERSITY OF BUFFALO]

FURTHER STUDIES IN KETO-ENOL DETERMINATION

BY GLADYS A. MICHALEK AND HOWARD W. POST

RECEIVED DECEMBER 9, 1931

PUBLISHED MAY 7, 1932

Previous work of ours¹ included evidence that ethyl α -phenylacetate exists in the enol form to the extent of about 28.6% at room temperatures. Later work by K. von Auwers² presented values of approximately 39.2% for the same property.

We did not find in our first contribution sufficient agreement between bromine titration values representing the enol content of ethyl α -phenylacetate and like figures derived from refractive indices by von Auwers, Brühl or anyone else, in spite of the existence of corrections which might be applied to the latter. It should be noted also that this ester required several days to reach equilibrium after distillation even when the same type of Pyrex glass was used for all operations and for all containers throughout the work.

We have accordingly repeated our work in the hope of being able to reconcile our values with those of von Auwers.

Preparation of the Ester.—Ethyl α -phenylacetate was prepared by the same method outlined in our first paper on this subject. The hydrolysis of acetobenzyl cyanide was, however, modified in that the solution was kept at room temperature instead of at zero degrees during the addition of hydrochloric acid and later was poured into water at room temperature instead of ice water. As in earlier work fractionation was carried out under vacuum using a flask with fractionating column attached. The ester was first collected over a range of fifteen degrees and refractionated to boil at 145–147° under 11 mm. pressure. Two batches of crude ester were purified separately in order to have a check on the index of refraction. Both showed an index of refraction of 1.5130 at 20° when given time to reach equilibrium. Freshly distilled material always showed a high index.

Bromine Titration.—Titration of the enol content was carried out as before. The sample, which was weighed by difference, was introduced into 30 cc. of alcohol at -7° and sufficient freshly prepared alcoholic bromine solution added quickly to give a slight color, which was immediately discharged with alcoholic β -naphthol solution. To this was added 10 cc. of 5% potassium iodide solution and the whole heated on the steam-bath for twenty minutes in the dark, then titrated with *N*/10 sodium thiosulfate solution. The latter had a factor of 1.1227 at 20°. The buret was calibrated and found to be correct at 20° within the accuracy of the titration.

Some trouble was experienced in obtaining β -naphthol sufficiently pure that it could effectively remove the excess of bromine. Distillation of β -naphthol followed by two recrystallizations from water gave a product requiring not more than 0.3 cc. of thiosulfate solution to discharge the color

¹ Post and Michalek, *THIS JOURNAL*, **52**, 4358 (1930).

² Von Auwers, *ibid.*, **53**, 1496 (1931).

of the blank. Calculations were made with and without this correction, however; in the actual titration the amount of thiosulfate accounted for in this way is probably much smaller since the excess of bromine is much less. We know of no way of calculating the actual excess of thiosulfate used in the titration due to the impurity of the β -naphthol. In the previous work a correction of 0.5 cc. was made in the results.

Temp., °C.	Na ₂ S ₂ O ₃ , cc.	Sample, g.	DATA	
			Titrated	% Enol Corrected
21.5	19.8	0.7353	31.15	30.68
22.0	16.0	.6213	29.76	29.18
22.0	17.9	.6911	29.93	29.44
22.0	13.9	.5256	30.59	29.93
Average			30.36	29.81

Conclusions.—Our results agree within the limits of experimental error with those of our former paper. In view of the discrepancy still existing between these values and those of von Auwers, we are forced to conclude that the only further light which can be thrown on the question should come from an isolation of enol and keto in the pure state, followed by a determination of the refractive index and the bromine titration value of each.

Summary

The enol content of ethyl α -phenylacetoacetate has been redetermined both by bromine titration and by the determination of the refractive index. The values so obtained check within the limits of experimental error with those previously published by the authors.

BUFFALO, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF BIOLOGICAL CHEMISTRY, COLLEGE OF PHYSICIANS AND SURGEONS, COLUMBIA UNIVERSITY]

BENZENESULFONYLGUANIDINES¹

BY H. T. CLARKE AND H. B. GILLESPIE

RECEIVED DECEMBER 10, 1931

PUBLISHED MAY 7, 1932

In the course of an investigation, now in progress, of the benzenesulfonyl derivatives of proteins and peptides, it became necessary to ascertain the effect of *benzenesulfonyl chloride upon guanidine and its derivatives under various conditions*. Ackermann² treated guanidine carbonate with benzenesulfonyl chloride in the presence of excess sodium hydroxide, thereby obtaining the sparingly soluble benzenesulfonylguanidine. He also reported failure to produce a sparingly soluble derivative of arginine under analogous conditions. The corresponding β -naphthalenesulfonyl

¹ Work supported by a research grant from The Chemical Foundation.

² Ackermann, *Z. physiol. Chem.*, **47**, 366 (1906).