

## ABOUT SOME REACTIONS OF 4'-NITRO-2'-HYDROXY-CHALCON

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4'-nitro-2'-hydroxy chalcon was transformed into 7-nitro flavonol and chalcondibromide, prepared from chalcon by addition of bromine and was converted into 7-nitro-flavone by alkaline and hydrochloric acid ring closure.

The transformation of chalcondibromides prepared from chalcon containing an ortho-hydroxyl group by adding bromine to flavone is widely known, as well as the alkaline  $H_2O_2$  oxidation of chalcones yielding the corresponding flavonol.

These reactions have been realised in the nitro-hydroxy-chalcon group with 5'-nitro-2'-hydroxy chalcon [1]. The present work reports the above mentioned reactions with 4'-nitro-2'-hydroxy chalcon.

As to the reactions it is worthy to mention that 4'-nitro-2'-hydroxy chalcon dibromide can be prepared not only by cooling, but also at reflux-temperature with almost the same yield as in the former case. It should also be mentioned that hydrogen cyanide cannot be added to nitrohydroxy-chalcon or other chalcones applied by us for other investigations [2]. The failure of this reaction in the case of chalcones containing a nitro group has already been established by other authors, too [3].

Furthermore, it should be emphasized that 7-nitro-flavone can be prepared from 4'-nitro-2'-hydroxy chalcon dibromide not only by means of an alkaline, but also by hydrochloric acid ring closure. Flavone has not yet been prepared in this way from nitrohydroxy-chalcon dibromides, only from other chalcondibromides [4].

7-nitro-flavone obtained by us by alkaline and hydrochloric acid ring closure has been prepared otherwise, too [5].

### Experimental

*Experiments with hydrogen-cyanide addition.* 0,27 g (1 mmole) 5'-nitro-2'-hydroxy-chalcon (m. p. 179 °C) was dissolved in 10 ml dimethyl-formamide and 0,07 ml glacial acetic acid was added. The solution was heated to 50 °C and dropwise an aqueous solution of 0,13 g (2 mmole) of KCN was added under constant stirring. Thereafter, the solution stirred for about 2 hours at the same temperature. It was kept for two days at room temperature, then diluted with distilled water, the precipitate was filtered, washed and after drying it was recrystallized from 1:1 mixture of ethanol-ethylacetate. M. p. 179 °C, M. p. of mixture: 179 °C, thus we recovered unchanged ketone.

The experiment was carried out with the above quantities by means of acidic cooling and boiling as like with chloroform acetone and methanol solutions on applying acidification by sulphuric acid. The initial substance was recovered in all these cases.

*4'-nitro-2'-hydroxy-chalcondibromide.* 0,27 g (1 mmole) chalcon was dissolved in 30 ml chloroform and 0,1 ml (0,31 g) (2 mmole) bromine was added. The solution was kept in a refrigerator for four hours at +5 °C, thereafter it was dried in vacuo and recrystallized from glacial acetic acid. Yellow needles were obtained. Yield: 0,34 g, 79%, M. p. 188 °C. Analysis: Calculated Br 37,2; Found 36,9%.

*7-nitro-flavone.* 0,1 g 4'-nitro-2'-hydroxy-chalcon dibromide was suspended in 5 ml methanol and 1 ml NaOH of a 10% aqueous solution was added to this suspension. A substance formed which was recrystallized after washing with methanol from acetone. M. p. 233 °C. Analysis: Calculated C 67,4%, H 3,4%; Found C 67,4% H 3,4%.

0,1 g dibromide was boiled for 48 hours in a mixture of 40 ml ethanol and 16 ml cc HCl. After cooling the separated substance was recrystallized from acetone, and a substance mp 233 °C, was obtained. There was no mp depression with flavone prepared by alkaline ring closure.

*7-nitro-flavonol.* 0,3 g 4'-nitro-2'-hydroxy-chalcon was dissolved in a mixture of 20 ml ethanol and 20 ml NaOH of 5%, then 5 ml of 17% H<sub>2</sub>O<sub>2</sub> was added to the solution. After standing for a night at room temperature it was poured into 25 ml ice water and acidified with 1:1 HCl. The separated precipitate was recrystallized from glacial acetic acid and substance which did not melt till 250 °C was recovered. Analysis: C 67,9%; H 3,2%. Thus the substance is not flavonol, but its structure has not been clarified as yet.

From the filtrate of glacial acetic acid ester crystallization a crystalline substance was obtained by evaporation. Mp. 251 °C. According to analysis it is flavonol. Calculated C 63,6; H 3,2; Found C 63,9, H 3,4.

## О НЕКОТОРЫХ РЕАКЦИЯХ 4'-НИТРО-2'-ГИДРОКСИ ХАЛКОНА

Дь. Шипос и Й. Йекл

4'-нитро-2'-гидрокси халкон был превращен щелочным окислением H<sub>2</sub>O<sub>2</sub> в 7-нитрофлавонол, а халкон-дибромид, изготовлен из халкона присоединением брома был превращен в 7-нитрофлавонол замыканием кольца щелочью и хлористоводородной кислотой.

### References

- [1] Christian, C. M., G. C. Amin: Chem. Ber., 90, 1287 (1957).
- [2] Sipos, Gy., I. Dobó, B. Czukur: Acta Phys. et Chem. Szeged, 8, 160 (1962).
- [3] Kanthi, R. B., K. S. Nargund: U. Karnatak. Univ. 2, 8 (1957).
- [4] Pendse, H. K., S. D. Limaye: Rasayam 2, 90 (1955).
- [5] Bapat, D. S., K. Venkataramen: Proc. Indian. Acad. Sci., 42, 336 (1935).

### Erratum

to the paper J. HEVESI "On the Relative Yield and the Degree of Polarization of Viscous Fluorescent Solutions Quenched by KJ" published in Acta Phys. et Chem. Szeged, **8**, 16–24 (1962).

Figure 4 of the paper should be replaced by the following

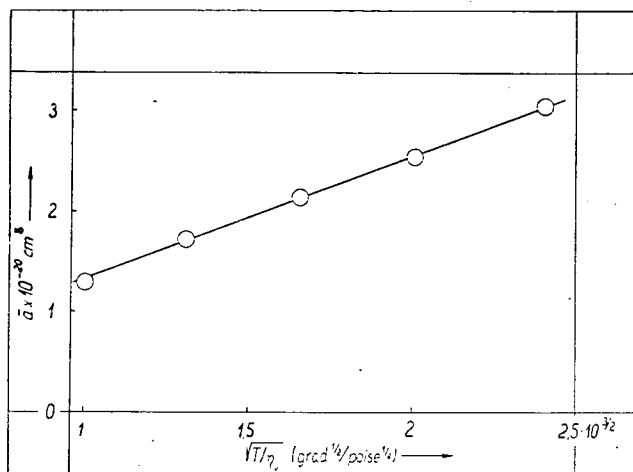


Fig. 4.

The experimental data used in the paper are quoted here (see J. Hevesi: Dissertation, Szeged, 1961. Table 9.):

$t$ (°C)	$\bar{a}$ ( $\times 10^{-20}$ $\text{cm}^{-3}$ )	$\sqrt{T/\eta} \cdot 10^{3/2}$ (grad <sup>1/2</sup> /poise <sup>1/2</sup> )
20	1,290	1,002
30	1,721	1,309
40	2,131	1,658
50	2,528	2,008
60	3,041	2,407

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