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Chemistry. — “Action of Potassium hypochlorite on Cinnamide”¹.

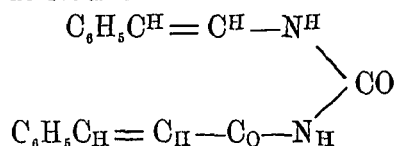
By Dr. R. A. WEERMAN (Communicated by Prof. HOOGWERFF).

(Communicated in the meeting of September 29, 1906).

From the experiments of BAUCKE¹⁾ on propiolamide and those of FREUNDLER²⁾, VAN LINGE³⁾ and JEFFREYS⁴⁾ on cinnamide it appears that in the case of these unsaturated acids, the HOFMANN reaction to prepare an amine from an amide by means of a halogen and an alkali does not succeed.

As to the non success we may form two hypotheses: first of all that the double bond⁵⁾ prevents the intramolecular rearrangement of atoms which must be assumed in the HOFMANN reaction, and secondly that the amine supposed to be formed, in this case $C_6H_5CH=CHNH_2$, suffers decomposition under the said circumstances.⁶⁾

The first, however, is *not* the case as from cinnamide may be prepared the urea derivative:



where consequently one-half of the amide has undergone the transformation.

This being a case of an unsaturated amide, it is necessary to make use of the modification proposed by HOOGWERFF and VAN DORP and not to work with free halogen. Further the hypochlorite solution must not contain any free alkali; on account of the insolubility of cinnamide and the consequent inertness, an alcoholic solution is employed.

Although at first sight it appears strange that in alcoholic solution the urea derivative is formed and not the urethane, this may be explained by the experiments of STIEGLITZ and EARLE⁷⁾, which show that isocyanates react very readily with halogen-amides⁸⁾.

¹⁾ Rec. 15, 123.

²⁾ BULL [3] 17, 420.

³⁾ Dissertation VAN LINGE, Bazel 1896.

⁴⁾ Am. Chem. Journ. 22, 43.

⁵⁾ On account of the great analogy existing between the LOSSEN transformation of hydroxamic acids and the HOFMANN reaction, this first supposition was not very probable, as THIELE had prepared from the acylated cinnamohydroxamic acid the urethane $C_6H_5CH=CH-NH-CO-C_6H_5$. A second indication, though less conclusive, in the more distant analogy between the BECKMANN rearrangement and the HOFMANN reaction was the formation of isochinolin from the oxime of cinnamaldehyde. (Ber. 27, 1954).

⁶⁾ THIELE, Ann. 309 197

⁷⁾ Am. Chem. Journ. 30, 412. C 1904, I, 239.

⁸⁾ This is the reason why, in the preparation of urethanes according to JEFFREYS, the sodium ethoxide should be added all at once.

In order to prepare the urea derivative, the cinnamide is dissolved in eight times its weight of 96 pCt. alcohol, and when cooled to the temperature of the room the hypochlorite solution, prepared according to GRAEBE ¹⁾, is slowly dropped in, the free alkali being neutralised with 2N hydrochloric acid immediately before use. For every 2 mols. of amide, 1 mol. of potassium hypochlorite should be added. The liquid gets warm, and very soon a crystalline mass composed of very slender needles is deposited. After a few hours the mass is collected at the pump; this does not go very readily on account of the fine state of division. The yellowish mass is treated with hot alcohol and then washed with water. A fairly pure urea derivative is thus obtained (m. p. about 218). By recrystallisation once or twice from glacial acetic acid it is obtained pure in needles (m. p. 225—226).

0,1733	0,1654	0,1654	0,0894	0,1863	13,9	0,4682	0,4467	765
			gm.	gm.	CC.N	gm.	gm.	m.M.
			yielded	„ „ „	at		„ „	
					19½°			
			Found	73,68		5,78		
					pCt. C		pCt. H	9,70 pCt. N
				73,66		5,85		

Theory $C_{18}H_{16}N_2O_2$: 73,95 pCt. C 5,51 pCt. H 9,59 pCt. N

The compound is insoluble at a low temperature in water, ligroin, alcohol, methyl alcohol, ether, carbon disulphide and benzene; at the boiling temperature slightly soluble in alcohol and benzene and freely so in glacial acetic acid, chloroform and acetone. It is insoluble in alkalis or acids.

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Astronomy. "*Mutual occultations and eclipses of the satellites of Jupiter in 1908.*" By Prof. J. A. C. OUDEMANS.

(Communicated in the meeting of September 29, 1906).

N.B. In the present communication the four satellites of Jupiter, known since 1608, have been denoted by I, II, III and IV in accordance with their mean distances from the planet. The further letters *n* and *f* indicate whether the satellite is *near* or *far*, i.e. whether it is in that half of the orbit which is nearest to or furthest from the Earth. The joventric longitudes as well as the geocentric amplitudes are counted in "signs" and "degrees", the latter beginning from the superior

¹⁾ Ber. 35, 2753.