155. *The Action of Phosphoryl Chloride on the Toluene-*p*-sulphonyl Derivative of β-Anilinopropionic Acid.*

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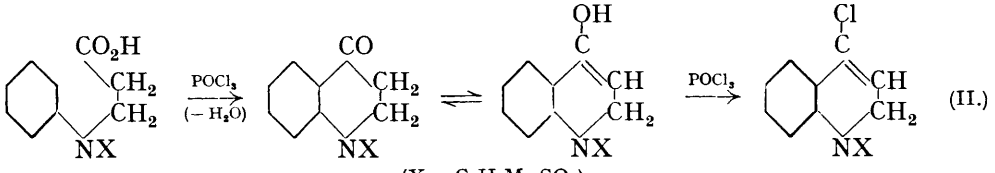
This reaction was studied by Clemo and Perkin (J., 1924, **125**, 1608; 1925, **127**, 2297) in their synthesis of 4-keto-1 : 2 : 3 : 4-tetrahydroquinoline and, according to them, the product is 3-chloro-4-keto-1-toluene-*p*-sulphonyl-1 : 2 : 3 : 4-tetrahydroquinoline (I). The formation of this compound, as pointed out by the authors, apparently involves direct chlorination by phosphoryl chloride, and, furthermore, the compound is converted into 4-keto-1 : 2 : 3 : 4-tetrahydroquinoline by boiling concentrated hydrochloric acid and into 4-methoxyquinoline by refluxing with methyl-alcoholic potash.

These facts appeared so remarkable to the author that the structure of the compound was reinvestigated. Examination of the analytical data given by Clemo and Perkin shows that their calculated values are erroneous and that the values they actually found agree closely with the alternative structure proposed for this compound, namely, 4-chloro-1-toluene-*p*-sulphonyl-1 : 2-dihydroquinoline (II), the formation of which is readily explicable, as are now also the two conversions mentioned above :



(II.)

(X = $C_6H_4Me{\cdot}SO_2$).

The analytical data for (I) and (II) are as follows, Clemo and Perkin's erroneously calculated values for (I) being added in italics :

	C.	H.	O.	N.	Cl.	S.
Calc. for (I)	57·23%	4·17%	14·31%	4·17%	10·58%	9·54%
Calc. for (II)	60·09	4·38	10·02	4·38	11·11	10·02
Found (Clemo and Perkin)	59·7	4·36	(10·04)	4·8	10·9	10·2
Found (author)	60·21	4·51	—	—	—	—
	60·0	*4·5*	—	*4·5*	*10·6*	*9·5*

The corresponding chloro-compounds, described by Clemo and Perkin in the second publication (*loc. cit.*), prepared from *m*- and *p*-toluidine, *p*-anisidine and *p*-phenetidine should similarly be formulated as the 1-toluene-*p*-sulphonyl derivatives of 5-methyl-, 7-methyl-, 6-methyl-, 6-methoxy-, and 6-ethoxy-4-chloro-1 : 2-dihydroquinoline respectively. The authors gave a complete analysis for the compound from *p*-anisidine (*loc. cit.*, p. 2306), found that the data did not correspond to those required for 3-chloro-4-keto-6-methoxy-1-toluene-*p*-sulphonyltetrahydroquinoline, and suggested that the compound might be 3-chloro-6-methoxy-1-toluene-*p*-sulphonyldihydroquinoline.

The experimental results obtained by Clemo and Perkin in the preparation of (II) and 4-keto-1 : 2 : 3 : 4-tetrahydroquinoline have been confirmed, but it has also been found that in the preparation of the former a small quantity of 4-chloroquinoline is produced. A similar case of oxidation occurs when 4-keto-1 : 2 : 3 : 4-tetrahydroquinoline is refluxed with phosphoryl chloride, 4-chloroquinoline being obtained, and identified by conversion into 4-anilinoquinoline.

4-Methoxyquinoline was prepared from 4-chloroquinoline by the methods of Meyer (*Monatsh.*, 1906, **27**, 257) and of Clemo and Perkin. In both cases the product had m. p. 41°, the result obtained by Clemo and Perkin thus being confirmed.

Experimental.

Following the method of Clemo and Perkin for the prepn. of (II), the aq. filtrate, after removal of (II), was rendered alkaline and steam-distilled; a small quantity of 4-chloroquinoline, m. p. 34°, was obtained, which was further identified by conversion into 4-anilinoquinoline,

m. p. 201° (Ephraim, *Ber.*, **1893**, **26**, 2229, gives 198°). 4-Chloroquinoline picrate and 4-anilinoquinoline picrate form small yellow needles, m. p. 217° (decomp.) and 195° respectively, from EtOH.

4-Chloroquinoline, prepared quantitatively by refluxing 4-hydroxyquinoline (Camps, *Ber.*, **1901**, **34**, 2708) with $POCl_3$ for 30 min., removing the excess of $POCl_3$ on the water-bath under diminished press., adding H_2O, making the solution alkaline, and steam-distilling it, was converted into 4-anilinoquinoline by refluxing with $PhNH_2$ ($1\frac{1}{4}$ mols.) for 2 hr. in AcOH. The base and its picrate were identical, respectively, with the compounds described above.

Treatment of 4-chloroquinoline with Na (1 atom), dissolved in MeOH, in a sealed tube at 140° for 3 hr. gave a quant. yield of 4-methoxyquinoline, b. p. 171°/22 mm., m. p. 41°, identical with the product obtained by the method of Clemo and Perkin (*loc. cit.*). 4-Methoxyquinoline picrate formed small, yellow, silky needles, m. p. 203°, from EtOH, and the mercurichloride had m. p. 199° (decomp.), in agreement with Clemo and Perkin.

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