XCIV.—*Estimation of Hydroxyl Groups in Carbon Compounds.*

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TSCHUGAEFF (*Ber.*, 1902, 35, 3912) has described a process for detecting hydroxyl radicles in carbon compounds by the aid of Grignard's magnesium methyl iodide, the basis of the method being the determination of the amount of methane evolved when dry ethereal solutions of the hydroxyl derivative and Grignard's compounds are mixed. The reaction proceeds according to the equation $R\cdot OH + CH_3\cdot MgI = R\cdot O\cdot MgI + CH_4$, and the methane is collected in a Knop's nitrometer. It is stated that the volume of gas usually approximates to that

required by theory, although the method is not recommended for quantitative purposes.

In our examination of the red compounds formed by the union of *s*-trinitrobenzene with arylamines (Trans., 1901, 79, 522; 1903, 83, 1334), we wished to use some simple method for detecting and estimating hydroxyl radicals. In experimenting with Tschugaeff's method, we have found that quantitative results cannot be obtained owing to three following sources of error: (1) When a Knop's nitrometer with india-rubber connections is used, the water slowly permeates this material and reacts with the Grignard reagent, evolving methane. (2) When the reaction is conducted in a vessel filled with ordinary air, slow absorption of the oxygen by the magnesium methyl iodide occurs (compare Bouveault, *Bull. Soc. chim.*, 1903, 29, 1051). (3) When ether is employed as solvent, slight alterations in temperature produce considerable variations in the volume, owing to the change in the vapour pressure of the liquid.

We have overcome these difficulties by working in an atmosphere of dry nitrogen in place of ordinary air, using amyl ether as solvent and collecting the gas over dry mercury in a Lunge nitrometer or Hempel burette.

We first attempted to use toluene as a solvent, but found that in this medium, magnesium does not react with methyl iodide. A combination could not be detected even on boiling, but the addition of a little dry ether (5 c.c.) caused a slight reaction which became brisker as more of the liquid was introduced.

Blaise (*Compt. rend.*, 1901, 132, 839) states that the magnesium alkyl haloids are only formed in the presence of ether, and that this substance plays an important chemical part in the reaction. Our experiments indicate that other ethers may be employed in place of ethyl ether and that the reaction depends to a considerable extent on the presence of the C·O·C group in the molecule of the solvent.*

Preparation of the Magnesium Methyl Iodide Solution.

The amyl ether employed was dried over calcium chloride, boiled for several hours with metallic sodium, treated with a small amount (5 c.c.) of the amyl ether solution of magnesium methyl iodide, and again boiled with sodium, then left for several hours over phosphoric oxide, and finally distilled.

Dry magnesium turnings (6·09 grams) were added to 100 c.c. of the dry ether, and 35·5 grams of methyl iodide dissolved in 20 c.c. of the ether were then introduced. The reaction which began when the

* Tschelinzeff (*Ber.*, 1904, 37, 2084) has since shown that dimethylaniline may be substituted for ether.

mixture was gently warmed on the sand-bath was allowed to proceed at the ordinary temperature, and finally completed by heating the mixture for about half an hour. As a rule some 13—14 per cent. of the magnesium was not dissolved and the clear solution was decanted from this residue and made up to 200 c.c. with pure amyl ether. The solution should be kept out of contact with the atmosphere as far as possible because it absorbs moisture, oxygen, and carbon dioxide.

Estimation of Hydroxyl Radicles.

A stout flask of about 200 c.c. capacity is fitted with a doubly bored india-rubber stopper, which carries a stopcock reaching nearly to the bottom of the flask, and a short tube which is fitted by means of a length of thick-walled india-rubber tubing to a Lunge nitrometer or Hempel burette filled with dry mercury. Dry amyl ether (10—20 c.c.) and 0.10—0.25 gram of the substance are placed in the flask and an excess—about 15 c.c.—of the amyl ether solution of magnesium methyl iodide is placed in a small tube, which is lowered into the flask in a vertical position. The air in the flask is displaced by dry nitrogen, the flask is then attached to a Hempel burette filled with dry mercury and the apparatus left for 2 to 4 hours to attain a constant temperature. The height of the mercury, the temperature, and pressure are noted, and after mixing the two solutions and shaking vigorously, the level of the mercury is adjusted and the volume read off with the usual precautions.

A blank experiment was made in order to show that no gas is evolved when the magnesium methyl iodide solution is mixed with dry amyl ether. The flask was then heated in a glycerol bath first for 10 minutes at 120°, and then for 10 minutes at 140°. A small amount of white solid separated but there was no change in the volume of the gas.

The following hydroxyl derivatives have been used:— α - and β -naphthols, resorcinol, acetoxime, chloral hydrate, ethyl salicylate, pyrogallol, quinol, deoxybenzoin, benzoin, ethyl acetoacetate, and *o*-nitrophenol: the results obtained are tabulated on p. 936.

In addition to these compounds, we have experimented with two ketonic substances, namely, benzophenone and benzil, which do not contain hydroxyl groups and which cannot react in a tautomeric enolic form. In the former case, the results obtained were entirely negative; with benzil, on the other hand, a small amount (some 6 c.c. from 0.26 gram of the ketone) of gas was evolved, the origin of which we are not able to explain.

Notes on the Experiments.

Nos. 1, 2, and 3. The naphthols and their magnesium derivatives dissolved readily in cold amyl ether.

Nos. 4, 5, 6, and 7. Resorcinol, acetoxime, chloral hydrate, and ethyl salicylate dissolved readily in cold amyl ether. When the solutions were mixed with the magnesium methyl iodide a small amount of white precipitate was obtained in the case of resorcinol and acetoxime.

No. of expt.	Substance.	Weight.	Vol. of gas in c.c.	Temp.	Pressure in mm.	Vol. at N.T.P.	Theory.
1	α -Naphthol.....	0.2322	36.2	9°	756.5	34.9	36.0
2	„.....	0.2665	42.4	9	754	40.7	41.3
3	β -Naphthol.....	0.2239	36.0	10	751	34.3	34.7
4	Resorcinol.....	0.1852	78.6	9.3	751.6	75.2	75.2
5	Acetoxime.....	0.1301	41.1	9	759	39.7	39.8
6	Chloral hydrate.....	0.1440	40.9	9.2	763	39.7	38.8
7	Ethyl salicylate.....	0.2792	37.8	11	776	37.1	37.5
8	Pyrogallol.....	0.1264	69.8	9	757	67.3	67.2
9	Quinol.....	0.1190	51.5	12	768	49.9	48.3
10	Deoxybenzoin.....	0.2757	4.45	9.4	737	4.2	31.4
11	„.....	0.3000	3.45	9	761	3.3	34.2
12	„.....	0.2804	4.78	13.6	756.2	4.5	32.0
13	Benzoin.....	0.2814	31.9	14	762.4	30.5	29.6
14	Ethyl acetoacetate...	0.2290	37.3	11.8	767.2	36.1	39.3
15	„.....	0.2150	35.7	11.3	762	34.4	36.9
16	<i>o</i> -Nitrophenol.....	0.1980	38.1	11.3	762	36.7	31.8

* The vapour pressure of the amyl ether has been neglected in all the experiments.

No. 8. Pyrogallol itself dissolved readily in the ether, but the addition of the magnesium methyl iodide solution produced a copious white precipitate.

No. 9. Quinol was sparingly soluble in cold amyl ether, but dissolved readily on warming. In this experiment, when the reading had been taken before mixing, the flask and its contents were heated to 120° in a glycerol bath until the hydroxy-compound was dissolved; the two solutions were mixed, thoroughly shaken, kept at 120° for 20 minutes, and then allowed to cool and the volume ascertained. The heating was repeated, but no further increase occurred.

Nos. 10, 11, 12, 14, and 15. These experiments are interesting, as

they deal with ketonic compounds which are capable of reacting in their enolic tautomeric forms. The results obtained indicate the enolising action of Grignard's reagent, the effect being more marked in the case of ethyl acetoacetate, which, according to W. H. Perkin (*Trans.*, 1892, 61, 808), consists almost entirely of the ketonic form, and yet reacts in this case as if it were almost entirely in the enolic form. It follows from these results that this method is useless for the investigation of tautomeric substances of the keto-enolic type.

A fourth experiment conducted with deoxybenzoin gave a somewhat lower result, namely 1.2 c.c. of gas from 0.2882 gram.

No. 13. The benzoin was only sparingly soluble in amyl ether in the cold, and therefore, when the first reading had been taken, the flask was heated to about 120° in order to dissolve the benzoin, and after cooling somewhat, the two solutions were mixed, heated for 20 minutes at 120°, allowed to cool, and the volume of gas read off.

No. 16. When the two solutions were mixed, a reddish-brown precipitate was obtained, and a gas was evolved; the latter, after 4 hours at the ordinary temperature, amounting to 38.1 c.c.; this quantity is greater than that required for one hydroxyl group. When left for another 8 hours at the ordinary temperature, an additional 5 c.c. of gas were evolved, and after heating at 115–120° for 20 minutes, there was a further increase of 13 c.c., making a total of 56.1 c.c. The high results obtained with *o*-nitrophenol appears to be due to the presence of the nitro-group, as other nitro-derivatives not containing hydroxyl groups, for example, *m*-dinitrobenzene, evolve a gas when mixed with the magnesium methyl iodide solution, and the volume of gas is considerably increased when the mixture is heated.

It is possible that this evolution of gas is due to the nitro-compound reacting as the tautomeric nitrosophenol or quinone oxime,

but no definite conclusions can be drawn until further experiments have been made.

In each experiment 2–3 hours were allowed to elapse after the flask had been attached to the measuring tube before any readings were taken, due allowance being made for changes of temperature and pressure.

As Tschugaeff informs us that he is conducting further experiments on hydroxy-derivatives, we are not proceeding in this direction, but at present are engaged in applying the method to the determination of amino- and imino-groups.

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