NOTES.

The Decomposition of Carbon Monoxide in the Silent Electric Discharge. By ERWIN OTT.

MESSRS. LUNT and MUMFORD have had the kindness to send me the proof of their recent paper (this vol., p. 1711) on the above subject, in which they state that the brown solid polymeride of carbon suboxide deposited during the decomposition produces traces of oxalic acid when dissolved in water, whereas the polymerides of C_3O_2, prepared from malonic acid and phosphoric oxide (see Diels and Wolf, *Ber.*, 1906, **39**, 689; Diels and Meyerheim, *Ber.*, 1907, **40**, 359) do not produce oxalic acid on such treatment.

I have previously shown (*Ber.*, 1922, **55**, 2129; 1925, **58**, 774) that the C_3O_2 prepared by Diels's method is soon polymerised by traces of phosphorus compounds, and that the unimolecular C_3O_2

is also polymerised in a very short time by the electric discharge, even when largely diluted with carbon monoxide. It is clear that the polymerisation of C_3O_2 by different means and in different circumstances (in the liquid state and in the gaseous state, when very diluted with an indifferent gas) can produce different products.

Lunt and Mumford would therefore appear not to have disproved the fact that the brown solid has been formed by polymerisation of C_3O_2 produced according to the equation $4CO = C_3O_2 + CO_2$ which has been established by several quantitative determinations of the ratio $CO_2/[C_3O_2 + (C_3O_2)_x]$.—THE UNIVERSITY, MUNSTER (WESTFALIA), GERMANY. [*Received, July 29th*, 1929.]

Application of Semicarbazones to the Determination of Ketones.

By STIG VEIBEL.

HOBSON (this vol., p. 1384) has described a micro-method for determining semicarbazones and its application to the analysis of ketones, based on the method of Maselli (*Gazzetta*, 1905, **35**, i, 267) for determining semicarbazide, *viz.*, hydrolysis of the semicarbazide to hydrazine and ammonia. He states that hydrolysis with boiling 15% hydrochloric acid is complete after 7—8 hours and uses mercuric chloride as an oxidising agent.

Two years ago (*Bull. Soc. chim.*, 1927, **41**, 1410) I described a very similar method for the identification of aldehydes and ketones, which could be employed as a micro-method. The hydrolysis is carried out with 15—20% sulphuric acid (in the case of very slightly soluble semicarbazones, with 45% sulphuric acid) and is complete in ½ hour, and iodic acid is used as the oxidising agent.

The essential difference between the two methods seems to be, however, that according to Hobson it is necessary to destroy the hydrazine as it is formed during the hydrolysis, and this may be done by using a mixture of hydrochloric acid and mercuric chloride; whereas, in my method, the iodic acid is added after hydrolysis is complete. Hobson states that the liberated ketone may cause a partial reduction of hydrazine to ammonia. I have never found any evidence of such reduction: this may be due to the fact that the amount of hydrazine reduced during the hydrolysis in Hobson's method (7 hours' heating) is some 2—3% only, and consequently in my method (½ hour hydrolysis) the amount reduced would be within the limits of experimental error.

Hobson states that his method may be employed for the quantitative determination of ketones in mixtures, and suggests that the semicarbazone may be separated from the excess of semicarbazide by washing with water. Not all semicarbazones, however, are so slightly soluble in water that this method of purification may be employed without considerable loss of semicarbazone.—THE UNIVERSITY, COPENHAGEN. [*Received, July 18th,* 1929.]

The Direct Dibromination of m-*Bromophenol.* By HERBERT HENRY HODGSON and JOSEPH NIXON.

THE addition of bromine (2 mols.) to a solution of *m*-bromophenol in glacial acetic acid gives 3 : 4 : 6-tribromophenol (compare Kohn and Strassmann, *Monatsh.*, 1925, **45**, 597, who did not decide whether 3 : 4 : 6- or 2 : 3 : 4-tribromophenol was produced). Its constitution is established as follows: 3 : 4 : 6-*Tribromo*-2-*nitrophenol* is obtained when a mixture of 16 g. of bromine and 30 c.c. of glacial acetic acid is added to a solution of 11 g. of 3-bromo-2-nitrophenol (Hodgson and Moore, J., 1926, 157) in 50 c.c. of glacial acetic acid and the whole is shaken, warmed until free bromine has disappeared, diluted with water until slightly turbid, warmed until the turbidity has disappeared, and allowed to cool. Recrystallised from light petroleum, the product (long, pale yellow needles) has m. p. 109° (Found: Br, 63·9. $C_6H_2O_3NBr_3$ requires Br, 63·8%). By treatment with dilute sodium hydroxide solution and methyl sulphate it yields 3 : 4 : 6-tribromo-2-nitroanisole, which crystallises from alcohol in pale yellow needles, m. p. 105° (Found: Br, 61·6. Calc. for $C_7H_4O_3NBr_3$: Br, 61·5%). This ether also melts at 105° when mixed with the tribromonitroanisole (m. p. 105°) prepared by nitrating the tribromoanisole obtained from the above tribromophenol as described by Kohn and Strassmann (*loc. cit.*).

3-Bromo-2-nitrophenol thus behaves towards bromine in the anticipated manner.—TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, September 12th,* 1929.]

Some Phenanthrene Derivatives. By ROBERT KENNETH CALLOW and JOHN MASSON GULLAND.

THE directions given by Austin (J., 1908, **93**, 1760) for the nitration of 9-bromophenanthrene are incomplete, and the best yield of 9-bromo-10-nitrophenanthrene was obtained as follows. Nitric acid (*d* 1·45; 5 c.c.) was slowly dropped into a hot solution of 9-bromophenanthrene (20 g.) in acetic acid (20 c.c.) and acetic anhydride (8 c.c.), and the mixture heated on the water-bath for 20 minutes. The solid product (20 g.) which separated on cooling was crystallised from toluene (yield, 13·7 g.) and then from acetone (yield, 8 g.; m. p. 175—190°). This material was suitable for most purposes, but further crystallisation from acetone afforded a product, m. p. 195—203°. Austin records 195° for material crystallised from toluene, and 209° for a specimen obtained by a laborious method of purification.

Dinitrophenanthrene.—Phenanthrene was nitrated as described by Schmidt and Heinle (*Ber.*, 1911, **44**, 1488), but nitric acid of *d* 1·5 instead of 1·45 was used. The solid fractions obtained by the extraction with alcohol there described and crystallisation from acetic acid had melting points above that of 9-nitrophenanthrene, and repeated crystallisation from acetic acid yielded a sparingly soluble *dinitrophenanthrene* in pale buff needles, m. p. 255—260° (Found: C, 62·7; H, 3·1; N, 10·4. $C_{14}H_8O_4N_2$ requires C, 62·7; H, 3·0; N, 10·4%).

9-*Phenanthrylaminoacetonitrile.*—A solution of 9-aminophenanthrene (2 g.) and potassium cyanide (1·5 g.) in formaldehyde solution (3 c.c. of 40%), alcohol (30 c.c.), and water (10 c.c.) was boiled under reflux for 2½ hours, and water was then added until the solution became slightly cloudy. The solid which separated on cooling, together with a further crop obtained by evaporating the mother-liquor (total, 1·8 g.), was crystallised from xylene and then from methyl alcohol; 9-*phenanthrylaminoacetonitrile* separated in light brown needles, m. p. 231—235°, which tenaciously retained a molecule of solvent (Found in material dried at 100°: C, 76·7; H, 6·1; N, 10·7. $C_{16}H_{12}N_2,CH_3{\cdot}OH$ requires C, 77·3; H, 6·1; N, 10·6%). When this substance was heated under reflux for 3 hours with boiling 10% sodium hydroxide solution, ammonia was evolved, and acidification of the solution yielded a white precipitate of 9-phenanthrylglycine, m. p. 199—201°, which dissolved readily in methyl and ethyl alcohols, forming fluorescent solutions. The yellow solution of this acid in boiling acetic acid rapidly deposited a brown flocculent precipitate, possibly 2 : 5-diketo-1 : 4-di-(9′-phenanthryl)piperazine, which separated from xylene as a brown microcrystalline powder, m. p. 203—206° (decomp.), and was soluble in warm, though insoluble in cold, sodium hydroxide solution.

When a mixture of formaldehyde solution (0·6 c.c. of 40%) and acetic acid (3 c.c.) was added to a solution of 9-aminophenanthrene (1·4 g.) in acetic acid (14 c.c.), a yellow powder separated immediately. It was insoluble in the usual solvents, but crystallisation from nitrobenzene or anisole yielded a very small amount of yellow prisms, m. p. above 320°, which may have been diphenanthracridine (Found: C, 90·2; H, 5·3. Calc. for $C_{29}H_{17}N$: C, 91·8; H, 4·5%) or a complex acridine derivative.

Our thanks are due to the Chemical Society for a grant which partly defrayed the cost of this investigation.—THE DYSON PERRINS LABORATORY, OXFORD. [*Received, July* 30*th*, 1929.]