NOTES.

9-Benzhydrylanthrone and iso*Dianthranyl.* By EDWARD DE BARRY BARNETT and NORMAN FREDERICK GOODWAY.

9-Benzhydrylanthrone.—Anthrone (8 g.), potassium hydroxide (100 c.c. of 25% solution), and crude benzhydryl chloride (20 c.c.) were boiled (about 20 minutes) until the colour of the solution became pale: it was found to be inadvisable to carry the heating beyond this point. The product was cooled, washed with water, triturated with ether, and recrystallised from glacial acetic acid and from benzene–light petroleum; it was then colourless and melted at 188—189° (Found: C, 89·9; H, 5·7. $C_{27}H_{20}O$ requires C, 90·0; H, 5·5%). This *benzhydrylanthrone*, when heated on the water-bath with pyridine and acetic anhydride, yielded 9-benzhydrylanthranyl acetate which, after recrystallisation from glacial acetic acid, melted at 234—235°, and not at 228—229° as stated by

Padova (*Compt. rend.*, 1909, **149**, 219; *Ann. Chim.*, 1910, **19**, 393), who obtained it by boiling diphenylmethyleneanthrone with zinc dust, sodium acetate, and acetic anhydride.

iso*Dianthranyl.*—Benzhydrylanthrone (10 g.) and zinc dust (20 g.) were boiled with 100 c.c. of glacial acetic acid and 20 c.c. of concentrated hydrochloric acid, added during 45 minutes. After boiling for a further period of one hour, the hot solution was filtered and the crystals which separated on cooling were recrystallised twice from glacial acetic acid containing a little hydrochloric acid and twice from toluene. The pale yellow, crystalline product melted at 312° after some decomposition at about 308° (Found: C, 94·8; H, 5·2. Calc. for $C_{28}H_{18}$: C, 94·9; H, 5·1%). The acetic acid liquor from the above preparation contained diphenylmethane.

This *iso*dianthranyl is quite different from the colourless dianthranyl (m. p. above 360°) obtained by Barnett and Matthews (J., 1923, **123**, 380) by the reduction of anthrone, but is probably identical with the dianthranyl (m. p. 300°) described by Schulze (*Ber.*, 1885, **18**, 3034), Liebermann and Gimbel (*Ber.*, 1887, **20**, 1854) and Eckert and Hofmann (*Monatsh.*, 1915, **36**, 497). It is remarkable that neither Barnett and Matthews (*loc. cit.*) nor Schlenk (*Annalen*, 1928, **463**, 165) has been able to obtain the product described by the above workers, although Schlenk (*loc. cit.*) obtained a dianthranyl, m. p. 304°, by the action of sodiodiphenylmethane on 9-bromoanthracene. Schlenk's product is probably identical with that described above, his analytical figures suggesting that his specimen was not quite pure. He attributes the isomerism to the presence of two different types of anthracene complex due to the non-coplanar nature of the anthracene ring system (compare Bergmann and Mark, *Ber.*, 1929, **62**, 750).—SIR JOHN CASS TECHNICAL INSTITUTE, LONDON, E.C.3. [*Received, March 2nd,* 1929.]

Preparation of o-*Nitroacetophenone.* By WILLIAM OGILVY KERMACK and JAMES FERGUS SMITH.

THE preparation of *o*-nitroacetophenone from ethyl *o*-nitrobenzoylacetoacetate (Needham and Perkin, J., 1904, **85**, 151) through *o*-nitrobenzoylacetic acid is tedious, and the yield is unsatisfactory.

o-Nitroacetophenone was obtained by Gevekoht (*Annalen*, 1883, **221**, 323) by refluxing ethyl *o*-nitrobenzoylacetoacetate with five times its volume of dilute sulphuric acid (1 part of concentrated acid and 2 parts of water), a small quantity of *o*-nitrobenzoylacetone being formed as a by-product.

In attempts to obtain *o*-nitroacetophenone by Gevekoht's method, 50%, 36%, and 28% (by weight) acid being used, the yields of *o*-nitroacetophenone and *o*-nitrobenzoylacetone were 27% and 52%, 22% and 68%, and 16% and 70%, respectively, of the theoretical. It would seem from the above that, when ethyl *o*-nitrobenzoylacetoacetate is heated with dilute sulphuric acid, hydrolysis of the ester group and elimination of carbon dioxide take place primarily; the acetyl group in the resulting *o*-nitrobenzoylacetone not being readily susceptible to hydrolysis, *o*-nitroacetophenone is not obtained to any great extent.

It was obviously essential to remove the acetyl group before hydrolysis of the ester group took place. This was achieved by refluxing for 7 hours an alcoholic solution of the ester containing 10% by weight of sulphuric acid, the acetyl group being removed as ethyl acetate. An amount of water equal to the volume of alcohol used was then added, and the whole distilled until the liquid had been reduced to its original volume; the ethyl acetate and the bulk of alcohol were thus removed. The residue was refluxed for about an hour and cooled, and the *o*-nitroacetophenone extracted in ether. The extract yielded practically nothing to dilute alkali solution, showing that very little, if any, *o*-nitrobenzoylacetone had been formed. The yield of *o*-nitroacetophenone (redistilled) exceeded 75% of the theoretical. Results almost as good were obtained when the fission of the acetyl group was carried out by a 50% aqueous-alcoholic solution containing 10% of sulphuric acid.

It is difficult to explain the fact that Gevekoht, using aqueous sulphuric acid, obtained *o*-nitroacetophenone as his main product. It is possible that some alcohol may have been present. The method here described, in which hydrolysis is carried out by alcoholic sulphuric acid, may prove of use in other cases where it is desired to eliminate an acetyl group without removal of a carboxyl group.

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The Stability of Diazonium Salts of the Triazole Series. By JOSEPH REILLY and DENIS MADDEN.

THE rate of decomposition of diazonium salts of the pyrazole and pyrazolone series obeys approximately the unimolecular law (J., 1925, **127**, 2936). The decomposition of triazolediazonium salts is more rapid and at least two reactions are proceeding simultaneously. Substitution of alkyl groups tends towards stabilisation, which is also influenced by the nature of the alkyl group; *e.g.*, the *iso*butyl derivative decomposes more slowly than the corresponding methyltriazolediazonium salt under similar conditions. The nature of the anion and the amount of acid present also influence the stability. The comparative stability may be judged from the following table, which gives the c.c. of gas evolved from 0·002 g.-mol. of the various triazoles at 55° in presence of 6 mols. of acid.

	15 Mins.		30 Mins.	
	Nitrate.	Chloride.	Nitrate.	Chloride.
5-Amino-1 : 2 : 4-triazole	22·0	27·7	26·8	33·1
5-Amino-3-methyl-1 : 2 : 4-triazole	19·5	22·1	23·2	28·4
5-Amino-3-ethyl-1 : 2 : 4-triazole	19·0	22·0	23·0	30·8
5-Amino-3-*iso*propyl-1 : 2 : 4-triazole	18·1	19·4	23·6	26·8
5-Amino-3-*iso*butyl-1 : 2 : 4-triazole	13·1	16·6	19·2	26·1

5-*Amino*-3-*ethyl*-1 : 2 : 4-*triazole Nitrate.*—Aminoguanidine nitrate (25 g.) was gently heated under reflux with 20 g. of propionic acid and a few c.c. of water for 24 hours. An aqueous solution of the product was made faintly alkaline with potassium carbonate and evaporated to dryness. An ethyl acetate extract of the residue, on treatment with concentrated nitric acid, yielded 5-*amino*-3-*ethyl*-1 : 2 : 4-*triazole nitrate* (17 g.), m. p. 167° after recrystallisation from warm ethyl acetate–ethyl alcohol (Found: N, 40·15. $C_4H_8N_4,HNO_3$ requires N, 40·0%). The nitrate dissolved readily in hot water and hot ethyl alcohol.

5-*Amino*-3-*ethyl*-1 : 2 : 4-*triazole* crystallised from ethyl acetate had m. p. 152° (Found : N, 49·7. $C_4H_8N_4$ requires N, 50·0%).

3-*Ethyl*-1 : 2 : 4-*triazole*-5-*azo*-β-*naphthylamine* crystallised from ethyl alcohol in bright red needles, m. p. 259° after darkening at 242° (Found : N, 31·7. $C_{14}H_{14}N_6$ requires N, 31·6%). 3-*Ethyl*-1 : 2 : 4-*triazole*-5-*azo*-β-*naphthol* crystallised from ethyl alcohol in orange-red needles, m. p. 180—181° (Found : N, 26·4. $C_{14}H_{13}ON_5$ requires N, 26·2%). 3-*Ethyl*-1 : 2 : 4 - *triazole* - 5 - *azoacetylacetone*, obtained as a yellow precipitate when sodium acetate was added to a solution of the diazonium salt and acetylacetone, melted at 236° after recrystallisation from ethyl alcohol (Found: N, 31·2. $C_9H_{13}O_2N_5$ requires N, 31·4%). 5-*Diazo*-3-*ethyl*-1 : 2 : 4-*triazole chloroaurate* readily decomposed when heated (Found : Au, 45·4. $2C_4H_5N_5Cl_3Au,H_2O$ requires Au, 45·5%).

5-*Amino*-3-iso*butyl*-1 : 2 : 4-*triazole nitrate*, prepared by heating 20 g. of *iso*valeric acid (b. p. 173—174°) and 20 g. of aminoguanidine nitrate for several hours, and isolated (16 g.) in the same way as the ethyl homologue, crystallised from hot ethyl acetate–ethyl alcohol in silvery needles, m. p. 171° (Found : N, 34·6. $C_6H_{12}N_4,HNO_3$ requires N, 34·5%).—UNIVERSITY COLLEGE, CORK. [*Received, December* 14*th*, 1928.]