

level from the others, or to accident. The first of these possibilities is eliminated by side views, which show that at full metaphase the chromosomes lie in a flat plate; while the early anaphases show the daughter chromosomes separating in two flat parallel plates. The second possibility is, I think, wholly excluded in the case of *Anasa* by (1) the great number of cells from different individuals that show 21 chromosomes (often a smaller number, in my experience never in a single instance 22); (2) the equally constant appearance of 22 chromosomes in the female; and above all (3) the fact that in *Anasa* and some of the other genera *the smaller number in the male is shown by the size relations to be consistently owing to the absence of a particular chromosome*—in *Protenor* always one member of the largest pair that appears in the female, in *Anasa* always a member of one of the largest two pairs. It is manifestly impossible that this should be due to accident. As to the passage of the lagging odd chromosome without division to one pole in the second division, I do not think the most critical observer who examines the demonstrative evidence given by very large numbers of cells in my preparations can have the slightest doubt.

I, therefore, think that as far as the first three points are concerned, my results on *Anasa* will sooner or later receive full confirmation at the hands of other observers. Paulmier himself, after reexamining his own preparations, was thoroughly convinced of his error regarding the spermatogonial number—an error that was a natural one at the time his work was done. The most careful search has failed to discover the original of the group from which he figured 22 chromosomes, or any other agreeing with it in number. Montgomery's confirmation of my result as opposed to his own earlier one is known. The consistent and cumulative corroboration given by so many other genera of Hemiptera (including one of the Homoptera recently studied by Miss Stevens), some of them far more favorable for study than *Anasa*, speaks for itself.

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NOTES ON ORGANIC CHEMISTRY

DIAZONIUM PERCHLORATES

THE chemical activity of perchloric acid and the fact that, under certain conditions, it is explosive, are matters of common knowledge, it is also generally known that many of the diazonium (diazo) salts, such as benzenediazonium nitrate, $C_6H_5N:NNO_3$, are likewise explosive and their instability is often very great. It might be anticipated, therefore, that diazonium perchlorates, if they could exist at all, would prove to possess an unusual degree of energy and that their study, although it might be attended with danger, would yield results of considerable general interest. A number of such compounds have recently been described, simultaneously, by D. Vorländer,¹ and by K. A. Hofmann and H. Arnold.² The object of the former was to endeavor to discover some basic substance which, with perchloric acid, would form a sparingly soluble salt that could be employed instead of potassium perchlorate for the quantitative determination of the acid. This result has not been attained, but it is found that an immediate, voluminous precipitate is formed when phenylacridine sulphate is added to a 1 per cent. perchloric acid solution, and that a turbidity is produced when a 0.1 per cent. solution of the acid is used. Hofmann and Arnold desired to obtain some sparingly soluble diazonium salts. The preparation of *benzenediazonium perchlorate*, $C_6H_5N:NClO_4$, is very simple. Aniline (2 grams) is mixed, at a temperature of 0°, with water (200 c.c.), concentrated hydrochloric acid (6 c.c.), commercial perchloric acid (10 c.c.) and sodium nitrate (1.5 grams). The perchlorate immediately crystallizes out in colorless needles, which are strongly doubly refractive. Even in the moist state this compound explodes with great violence if rubbed or struck with articles of stone or iron. When dry the explosive power of the substance is, of course, very much greater. If a few centigrams are dropped on blocks of hard wood, deep holes are torn in them, but the explosion is so local in its effect that vessels of thin glass, placed a

¹ Ber. 39, 2713 (1906).

² Ibid., 39, 3146 (1906).

few inches away from the seat of disturbance, are uninjured.

The sensitiveness of the orthotoluene derivative is even greater than that of the above benzene compound, because in the moist state it explodes if it be touched with a porcelain stirring rod.

Chemically, these compounds are relatively stable and can be retained in a cool place for a day without change.

A considerable number of other diazonium perchlorates are described in the two papers quoted; in general, they exhibit the interesting contrast of being slightly *less* explosive than the two salts described above, but *considerably more* unstable chemically.

PREPARATION AND PROPERTIES OF BENZOYL NITRATE

THE formation of an acid chloride, such as acetyl chloride, CH_3COCl , from an acid and phosphorus pentachloride, is one of the most generally applicable reactions known. The corresponding bromides are available in moderate numbers, but only a very few of the iodides or fluorides have been prepared and, with these exceptions, no compounds are known containing an inorganic acid radicle in place of chlorine. For this reason, as well as on account of its properties which are described below, the isolation of *benzoyl nitrate*, $\text{C}_6\text{H}_5\text{COONO}_2$, is a matter of considerable interest. A preliminary announcement on the subject some months ago by F. Francis¹ has been followed up with a fuller account by him self² and T. H. Butler.³ The compound is prepared by mixing together, at about -15° , benzoyl chloride and well-dried, finely divided silver nitrate. The product is an oil which is extremely sensitive to moisture. It may be filtered through dry filter paper, but if the latter contains the ordinary amount of moisture the nitrate reacts with explosive violence. In sealed tubes, at the ordinary temperature, the nitrate changes gradually into benzoic anhydride and, apparently, nitrogen pentoxide.

¹ *Jour. Chem. Soc.*, **89**, 1 (1906).

² *Ber.*, **39**, 3795 (1906).

³ *Ibid.*, **39**, 3804 (1906).

At 100° the change is similar, except that nitrogen peroxide and oxygen are formed, and at higher temperatures the reaction is so rapid as to produce an explosion. In nitrobenzene solution the nitrate is transformed slowly, to the extent of 60 per cent. in six months, into metanitrobenzoic acid. Other non-ionizing solvents bring about the same change, but less rapidly.

In its reactions benzoyl nitrate behaves as a nitrating agent, as an oxidizing agent, or as a means of introducing a benzoyl radicle. Alcohol yields ethyl nitrate; aromatic hydrocarbons, phenols, and their ethers give, with ease, chiefly mono-nitroderivatives. As examples of oxidation may be mentioned the transformation of thiophenol and hydrazobenzene into diphenyldisulphide and azobenzene, respectively. Primary aromatic and secondary aliphatic amines yield benzoyl derivatives, $\text{C}_6\text{H}_5\text{CONHR}$, but secondary aromatic amines form nitrosamines. With the exception of paratolylmethylnitramine, $\text{CH}_3\text{C}_6\text{H}_4\text{N}(\text{NO}_2)\text{CH}_3$, these are unstable and pass into nitro secondary amines, such as $\text{CH}_3\text{C}_6\text{H}_5(\text{NO}_2)\text{NHCH}_3$.

One of the chief points of interest in connection with the nitrating action of benzoyl nitrate is that it permits of this reaction being realized in the complete absence of water, a condition which, hitherto, has been unattainable. The nearest previous approximation to it was by the use of diacetyl orthonitric acid, $(\text{CH}_3\text{COO})_2\text{N}(\text{OH})_2$. One result of such change in the conditions of reaction is that orthonitroaniline, which can only be obtained to the extent of about 10 per cent. in admixture with its isomers by the ordinary methods of nitration, is formed quantitatively by the action of benzoyl nitrate on acetanilide.

Metanitrobenzoyl nitrate, $\text{O}_2\text{NC}_6\text{H}_4\text{COONO}_2$, and *butyryl nitrate*, $\text{CH}_3\text{CH}_2\text{CH}_2\text{COONO}_2$, are also formed by the action of the respective chlorides on silver nitrate, hence it would appear that such compounds are always produced, as intermediate steps, in the reaction of an acid chloride on a metallic nitrate.

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