2. A labile and a stable dibenzoyl-chloro-ethylene can be prepared by the addition of hydrogen chloride to dibenzoyl-acetylene and by the loss of hydrogen chloride from the dichlorides of dibenzoyl-ethylene.

3. A labile and a stable dichloro- and dibromo-dibenzoyl-ethylene can be prepared by the addition of chlorine and bromine to dibenzoyl-acetylene.

4. The action of alcoholates and phenolates on dibenzoyl-dibromo-ethane first forms dibenzoyl-acetylene which then immediately adds a molecule of alcohol or phenol. Similar reactions can be carried out with the dibromides and dichlorides prepared from other unsaturated 1,4-diketones.

5. The action of ammonia on dibenzoyl-acetylene or dibenzoyl-dibromo-ethane yields dibenzoyl-amino-ethylene. The action of potassium acetate in alcohol on the same substances forms dibenzoyl-hydroxy-ethylene, an unstable acidic substance.

6. The action of reducing agents on certain substituted unsaturated 1,4-diketones is discussed.

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NOTE

Does Nicotine Combine with Calcium Ions?—The existence of a calcium-nicotine combination has been claimed in a recent paper by Graham and Carr.[1] From their experimental data it may be inferred that the reputed combination is not of the nature of nicotine of crystallization but rather a union between nicotine and calcium ions which is readily formed and which is difficultly soluble in water and in the ordinary organic solvents. Such a compound would be of decided practical interest, for its properties would need consideration in analytical methods for the determination of nicotine, in commercial methods for the extraction of nicotine, in formulas for dusting powders and in the selection or preliminary treatment of waters employed for preparing nicotine sprays and dipping baths.

Thatcher[2] already has criticized the report on general principles and for its possible failure to allow for the notable volatility of nicotine under certain conditions, but has not examined all the evidence in the detail that the importance of the matter appears to demand. Graham and Carr present three lines of evidence for the existence of their hypothetical combination, which will here be discussed in their original order.

First, they failed to obtain quantitative recovery of nicotine by the Kissling method in the presence of calcium compounds, even if only the powdered calcium carbonate regularly added as an absorbent. The pres-

[1] Graham and Carr, THIS JOURNAL, **46**, 695 (1924).

[2] Thatcher, *ibid.*, **46**, 1539 (1924).

ent writer[3] long ago emphasized the danger of volatilization of nicotine in such methods as Kissling's but on the other hand showed that with proper precautions, methods in which nicotine is extracted by organic solvents from admixture with calcium carbonate, hydrate and sulfate give results in excellent agreement with those afforded by the silicotungstate method, in which of course no calcium compounds are added. Subsequent comparisons of the two methods by the Association of Official Agricultural Chemists[4] showed similar agreement. Consequently, the analytical findings of Graham and Carr need proof of an unimpeachable technique to be convincing.

The second line of evidence lay in their observations that admixture of aqueous solutions of nicotine and calcium chloride afforded a slight precipitate and that then, when sodium hydroxide was added in excess, a voluminous precipitate resulted which left behind no visible nicotine and which was insoluble in ether, whereas, in the absence of calcium chloride, the nicotine was merely salted out as a visible layer on the surface. This may all be superficially true. Even purified nicotine is likely to contain traces of impurities which are salted out and rendered visible by moderate proportions of soluble neutral salts. Calcium chloride solutions naturally yield voluminous precipitates of calcium hydroxide, insoluble in ether, when treated with sodium hydroxide. Moreover, inorganic powders are prone to adsorb, entangle and carry down oily material which otherwise would tend to float on an aqueous medium. That in fact nothing more than such a mechanical union occurs between calcium hydroxide and nicotine under the conditions outlined by Graham and Carr is indicated by the following experiments.

Experiment 1.—To 5 cc. of 0.5 *M* calcium chloride solution in a 50cc. graduated, stoppered cylinder was added 5 cc. of an aqueous 4 per cent. solution of nicotine of high purity, followed by 5 cc. of *M* sodium hydroxide solution. The mixture was frequently agitated during one hour, then left overnight. Ether was next added to the 50cc. mark and the cylinder was thoroughly shaken. After three hours, 20 cc. of the ether layer was pipetted out and delivered into a beaker containing 100 cc. of water and 1 cc. of concd. hydrochloric acid. After the mixture had been thoroughly stirred, the ether was expelled by gentle warming and finally, after cooling, nicotine was determined by precipitation with silicotungstic acid as in the A. O. A. C. official method. The residue of anhydrides weighed 0.9366 g. The residue from a check preparation, performed in a parallel manner except that water was used instead of calcium chloride solution, weighed 0.9256 g.

Experiment 2.—In this experiment *M* calcium chloride solution was

[3] Chapin, *U. S. Dept. Agr., Bur. Animal Ind. Bull.*, **133** (1911).

[4] *J. Assoc. Offic. Agr. Chem.*, **3**, 183 (1917).

used and the sodium hydroxide was the clear liquid decanted from a well-settled 1:1 solution of the C. P. substance. The mixtures were frequently agitated during 0.5 hour and then stood 1.5 hours longer before ether was added. Then they were left overnight before the ethereal solution was pipetted out for analysis. In other respects the procedure was the same as in Experiment 1. The residue of anhydrides from the preparation in which calcium chloride was added weighed 0.9871 g.; that from which calcium chloride was absent weighed 0.9723 g.

The third line of evidence was based on the claim that when a solution of pure nicotine, which naturally was alkaline, was added to a neutral solution of calcium chloride, the resulting mixture showed an acid reaction. Such a simple, yet spectacular experiment, ought to afford no difficulty, but in fact the writer has been wholly unable to observe any such effect. Into one of a pair of matched test-tubes was brought a measured portion of neutral solution of calcium chloride and into the other the same volume of water. One drop of phenolphthalein indicator solution was added to each tube and both of course remained colorless. Equal volumes of a 4 per cent. aqueous nicotine solution were then added to both tubes. A rose color developed in both, but neither immediately after mixing nor after the expiration of 24 hours did the tube containing calcium chloride show a paler color than the check tube. Both 0.5 *M* and *M* calcium chloride solutions were used and the proportion of nicotine solution to calcium chloride solution was varied progressively from 1:1 to 1:20.

The only conclusion to be drawn from the above data is that no evidence exists for the calcium-nicotine combination claimed by Graham and Carr.

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