

are then dried, in the customary manner, by heating for one hour at 110°, and weighed as lead sulfate.

The results of a few representative analyses follow.

TABLE I
RESULTS OF ANALYSES

Compound	% Pb	
	Calcd.	Found
Tetraphenyl lead	40.18	39.83 40.03
Tetra- <i>p</i> -bromophenyl lead	24.91	24.68 24.38
Diphenyl-di- <i>p</i> -bromophenyl lead	30.76	30.65 30.80
Triphenyl- <i>n</i> -butyl lead	41.82	41.52 41.46
Diphenyl-di- <i>isobutyl</i> lead	43.58	43.08 43.53

The authors wish to acknowledge helpful suggestions from Dr. J. A. Wilkinson.

Summary

A method is described for the quantitative estimation of total lead in non-volatile organolead compounds by decomposition with concentrated sulfuric and nitric acids.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

THE THERMAL DECOMPOSITION OF NITRITES. THE NITRITES OF TRIPHENYLETHYLAMINE AND DIPHENYLETHYLAMINE¹

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That the action of nitrous acid upon a primary aliphatic amine does *not* in general produce *exclusively* the alcohol of corresponding structure, has been pointed out by a number of investigators; an impression to the contrary regarding this fundamental class of organic reactions appears, nevertheless, to be held by many. In view of this and of the experimental results to be reported in this paper, it will not be out of place to include a few references² to researches which may in themselves be held to have demonstrated strikingly that *if conversion of an amine to an alcohol of corresponding structure be considered the "normal" course of the action, then*

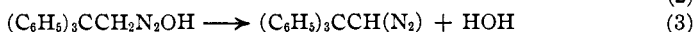
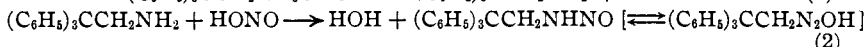
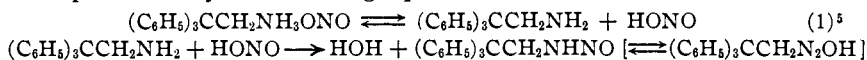
¹ This paper is based in part upon dissertations submitted to the University of Chicago by Maurice Leon Cohn and Reu Everett Hoen, in partial fulfilment of the requirements for the degree of Master of Science. An account of some of the work herein reported was presented before the Seventh Midwest Regional Meeting of the American Chemical Society at Chicago, May, 1927.

² (a) Meyer and Forster, *Ber.*, **9**, 535 (1876); (b) Demjanow, *Ber.*, **40**, 4393 (1907); (c) Wallach, *Ann.*, **353**, 318 (1907); **359**, 312 (1908); (d) Henry, *Compt. rend.*, **145**, 899 (1907); (e) Jeffreys, *Am. Chem. J.*, **22**, 36 (1899).

it must be said that observations of "abnormal" results have been at least as numerous as of the "normal." Certain of such "abnormal" results will be considered briefly in the sequel.

It has been observed in the present work that the action of heat upon an aqueous suspension of the nitrite³ of β,β,β -triphenylethylamine⁴ results in the production of triphenylethylene, $(C_6H_5)_3C:CH(C_6H_5)$, as the principal product of the reaction. The action of heat upon the nitrite in the dry state gives the same product together with a small amount of β,β,β -triphenylethylammonium nitrate.

For the interpretation of the course of these interesting changes, it has been considered most plausible to assume tentatively the series of reactions (involving the diazotization of β,β,β -triphenylethylamine) which are represented by the following equations.



The production of a diazo derivative by means of the action of nitrous acid upon an α -amino acid ester constitutes a rather well-developed method of synthesis; and there exists a conspicuous example of the isolation of a diazo derivative from the action of nitrous acid upon an amine of the type RCH_2NH_2 : amino-acetophenone, $C_6H_5COCH_2NH_2$, yields diazo-acetophenone, $C_6H_5COCH(N_2)$.⁶

Triphenyldiazo-ethane,⁷ if formed as assumed, would undoubtedly possess the property exhibited by other compounds of its type of losing nitrogen under the influence of heat. A reactive, unstable, bivalent carbon (methylene) derivative, triphenylethylidene, might result. The rearrangement of a phenyl group to the reactive bivalent carbon atom would represent the final step in the series of reactions which lead to triphenylethylene. Thus, we may have

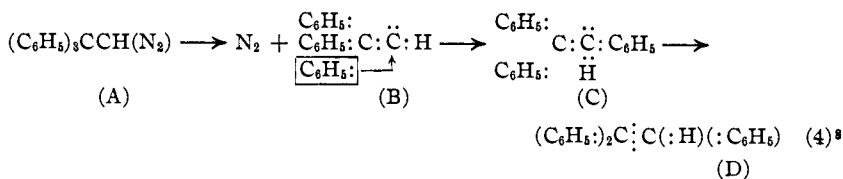
³ The salt is surprisingly stable at room temperatures (compare the experimental part). With the exception of γ,γ,γ -triphenylpropylammonium nitrite, recently prepared in this Laboratory by Hellerman and Sudzuki (unpublished work), this is probably the only nitrite of an amine of Type RCH_2NH_2 which has been isolated. The isolation of nitrites of primary amines of other types (for example, $RR'CHNH_2$) has been reported by Noyes, *Am. Chem. J.*, **15**, 539 (1893); *ibid.*, **16**, 449 (1894), and by Wallach, *Ann.*, **353**, 318 (1907).

⁴ Hellerman, *THIS JOURNAL*, **49**, 1735 (1927).

⁵ The presence of nitrate ion in the reaction mixture may be assumed, since nitrous acid and its decomposition products are by-products of the reaction. We may have $3HNO_2 \longrightarrow H^+ + NO_3^- + 2NO + H_2O$. This accounts for the appearance of β,β,β -triphenylethylammonium nitrate when the nitrite is heated in the dry state.

⁶ See Houben-Weyl, "Die Methoden der Organischen Chemie," Georg Thieme, Leipzig, 1924, Vol. 4, p. 645, for references to the literature.

⁷ A research involving the preparation of triphenyldiazo-ethane and the study of its properties is planned.



This formulation implies, of course, that the phenyl group, together with the electron pair (\cdot) which was shared between it and the adjoining carbon atom in (B), "migrates" to the bivalent carbon atom; the octet of the latter is thus completed and the *immediate* cause of instability removed. The rearrangement would leave the carbon atom bearing two phenyl groups in (C) "positive"⁹ with respect to that which gained a phenyl group; finally, we should have the shift of an electron pair which results in the formation of the electronically more symmetrical, "stable" form of the olefin (D).

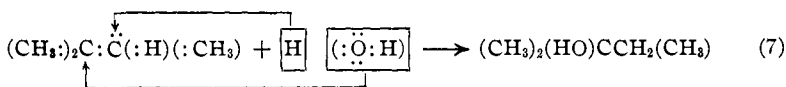
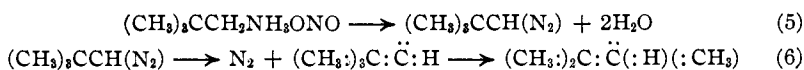
In the light of the observations recorded above and of the hypothesis which has been developed to interpret them, the essential nature of several rather mystifying reactions (involving the action of nitrous acid upon primary amines) which have been recorded in the literature, becomes less obscure. Thus, the action of nitrous acid upon trimethylethylamine, $(\text{CH}_3)_3\text{CCH}_2\text{NH}_2$, in the presence of water was found by Freund and Lenze¹⁰ to yield dimethylethyl carbinol, $(\text{CH}_3)_2(\text{C}_2\text{H}_5)\text{COH}$, and these investigators concluded that trimethylethanol, $(\text{CH}_3)_3\text{CCH}_2\text{OH}$, was formed first, and then, simply, the hydroxyl group and a methyl group exchanged positions. A much more reasonable explanation results if it is assumed that trimethylethylene in a "reactive" form is an intermediate product and this product absorbs water. $\text{H}^+(\text{OH})^-$ is added in the direction required by the polarity of the olefinic "double bond," the assumed origin of that polarity being indicated clearly by the following formulation¹¹

⁸ The role played here by the hypothetical intermediate (B) would be entirely analogous to that assumed by Professor Stieglitz for univalent nitrogen derivatives, R_3CN , in rearrangements of compounds of the types, R_3CNHX , $\text{R}_3\text{CN}(\text{N}_2)$, etc., which have been extensively investigated by Stieglitz and his collaborators. See, for example, Stieglitz and Stagner, *THIS JOURNAL*, **38**, 2046 (1916). See also Jones and Hurd, *ibid.*, **43**, 2422 (1921). Compare Hellerman and Sanders, *ibid.*, **49**, 1745 (1927).

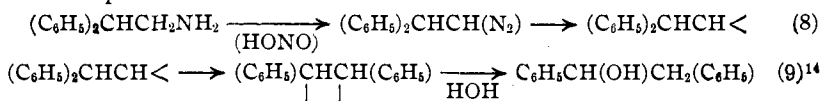
⁹ See ref. 11.

¹⁰ Freund and Lenze, *Ber.*, **24**, 2150 (1891). They were attempting to prepare β,β,β -trimethylethanol and observed the "abnormal" result cited.

¹¹ It is apparent that the appearance of an intermediate complex, $\text{RR}'\text{R}''\text{CCH}<$, where the R's represent groups or hydrogen atoms, may well account for the various types of products which have been obtained in reactions of this type (compare reference 2). The complex may add, at the bivalent carbon atom, water or unchanged primary amine, yielding, respectively, the alcohol of corresponding structure or the secondary amine (isolated as nitroso derivative). If, instead, the bivalent carbon atom is "saturated" by means of rearrangement of a group or hydrogen atom, R, an olefin, $\text{R}'\text{R}''\text{C}=\text{CHR}$, results. If, however, water has been added by the olefin in "reactive" form, an



To what extent water will be added as the final step in reactions of the type under discussion as in the case just cited, or the olefin itself produced, obviously may depend upon a number of factors such as the conditions of experiment (temperature, amount of water initially present, etc.), the solubility of the nitrite in water and the structural character of the "reactive" olefinic product of rearrangement. Triphenylethylene in its "reactive" state evidently does not add water (even when reaction is completed in aqueous suspension) but, instead, passes to its more stable form. On the other hand, it has been found here that in a related case involving the thermal decomposition of β,β -diphenylethylammonium nitrite in aqueous solution,¹² phenylbenzylcarbinol¹³ is a product in high yield. Evidently the addition of water is involved here; the changes may be summed up as follows



When a mixture of equimolar parts of β,β -diphenylethylammonium chloride and sodium nitrite was heated in the dry state, stilbene, in 76% yield, was the product. This hydrocarbon is, of course, the expected product if it is considered that essentially β,β -diphenylethylammonium nitrite has been heated in the dry state.¹⁵ In no event would phenylbenzylcarbinol be anticipated here, since this carbinol is known to become alcohol, $\text{R}'\text{R}''\text{C}(\text{OH})\text{CH}_2\text{R}$, is the product. Assumption of rearrangement of R in effect as a negative group (that is, with the shared electron pair) has seemed highly consistent with the frequent observations of the appearance of an alcohol, $\text{R}'\text{R}''\text{C}(\text{OH})\text{CH}_2\text{R}$.

¹² A solution of an equimolecular mixture of the amine hydrochloride and sodium nitrite was used; compare the experimental part.

¹³ The same carbinol [Purgotti, *Gazz. chim. ital.*, (2) 23, 226 (1893)] is obtained when the nitrite of α,β -diphenylethylamine, $(\text{C}_6\text{H}_5)_2\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)\text{NH}_2$, undergoes thermal decomposition. Purgotti actually sought to verify the structure of α,β -diphenylethylamine by means of this reaction. The risk attending the use of this type of reaction for the determination of structure of an amine is clearly seen in the experimental results herein reported.

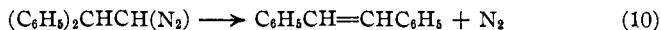
¹⁴ Other possible final products of the action were sought, but the only definite individual which could be isolated was phenylbenzylcarbinol. It is clear, however, that a phenyl group, rather than the hydrogen atom, "migrated" largely. Probably the relative "electronegativity" [Kharasch and Marker, *THIS JOURNAL*, 48, 3130 (1926)] of competing groups determines largely to what extent they shall be involved in such rearrangements.

¹⁵ Compare equation 4.

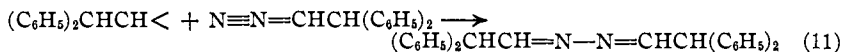
"dehydrated" to stilbene under conditions similar to those of this experiment (elevated temperature, presence of hydrogen ion).¹⁶

The Behavior of β,β -Diphenyldiazo-ethane

Of considerable interest from the point of view of the hypothesis employed in this paper for the interpretation of primary amine nitrite reactions is the behavior, observed under various conditions, of β,β -diphenyldiazo-ethane, $(C_6H_5)_2CHCH(N_2)$. It has been found that this substance,¹⁷ when heated in the presence of dilute sulfuric acid, yields stilbene¹⁸ as its decomposition product.



When heated in the presence of neutral or alkaline media, the diazo compound is found to yield diphenylacetaldazine, together with indefinite, resinous matter. The latter observation is quite in accord with the known behavior of various well-described diazo derivatives¹⁹ and the relationship between the facts here set forth may be adequately seen in the following: β,β -diphenyldiazo-ethane, when heated, may yield first nitrogen and the corresponding methylene derivative, $(C_6H_5)_2CHCH<$. The latter, in alkaline or neutral environment, in which it would be *slowly* formed in the presence of a large excess of diazo compound, may absorb unchanged β,β -diphenyldiazo-ethane with the formation of the aldazine.



In the presence of acid, where (a) decomposition of the diazo compound would presumably be accelerated and (b) synthesis of the aldazine (a substance the hydrolysis of which is accelerated by acids) be rendered improbable, the bivalent carbon intermediate should rearrange largely to the olefin



β,β -Diphenyldiazo-ethane has been assumed in the preceding section to be an intermediate product when nitrous acid acts upon β,β -diphenyl-

¹⁶ Compare (a) Limpricht and Schwanert, *Ann.*, **155**, 62 (1870); (b) Sudborough, *J. Chem. Soc.*, **67**, 605 (1895).

¹⁷ The substance, as prepared, was somewhat impure. Because of the experimental difficulties for attainment of high purity (compare the experimental part) and since the method of preparation and the properties of the compound left little doubt of its identity, it was deemed for the present purpose not necessary to expend further effort upon its purification. More extensive work upon diazo derivatives of the types, $RR'R''CCH(N_2)$ and $RR'CHCH(N_2)$, is in contemplation.

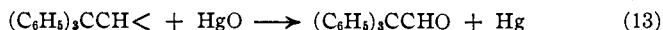
¹⁸ Phenylbenzylcarbinol would not be expected; see the preceding section.

¹⁹ See, for example, Staudinger, *Ber.*, **49**, 1884 (1916), and other articles in the *Berichte*, 1916. In his interpretations of various transformations of aliphatic diazo derivatives, Staudinger has found the assumption of intermediate methylene derivatives to be decidedly useful.

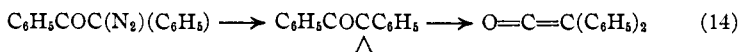
ethylamine. In the latter case the diazo compound *as formed* would presumably be converted rapidly to the bivalent carbon complex, *re-arrangement* of which, under the conditions, would evidently be a logical consequence.

Evidence for the Hypothetical Bivalent Carbon Intermediate: Synthesis of Triphenylacetaldehyde

Postulation of bivalent carbon complexes as intermediates in nitrite decompositions as has been done in this paper has seemed a logical step, especially since such complexes have already been assumed with considerable reason to be intermediates in various decompositions of aliphatic diazo compounds.²⁰ Several observations made in the course of this work appear to be decidedly in harmony with this type of hypothesis. It has been found that when β,β,β -triphenylethylammonium nitrite is heated with mercuric oxide, triphenylacetaldehyde, $(C_6H_5)_3CCHO$, appears as a product along with triphenylethylene.²¹ Triphenylacetaldehyde would be a product if a transitorily existing intermediate, triphenylethylidene, were oxidized to the aldehyde very much as isocyanides, $RNC\langle$ are oxidized under similar conditions to isocyanates.



It was considered of importance in this connection to test the applicability of this type of procedure to the case of a well-described aliphatic diazo compound to which triphenyldiazo-ethane would be strikingly related structurally, namely, the azibenzil of Curtius.²² Schroeter found²³ that the thermal decomposition of this interesting compound resulted in its rearrangement to diphenylketene.



Of exceptional theoretical interest is the observation made in this work that azibenzil, heated in the presence of moist mercuric oxide, yields 74% of benzil, $C_6H_5COCOC_6H_5$. This would, of course, be the expected product if, in the presence of mercuric oxide, "saturation" (that is, ultimate completion of the octet)²⁴ of the bivalent carbon atom in the assumed intermediate, $C_6H_5COCC_6H_5$, by an *intermolecular* oxidation-reduction rather

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than by the competing *intramolecular* oxidation-reduction (established by

²⁰ Staudinger, ref. 19.

²¹ The possibility that this observation may have resulted from the oxidation of free *amine*, present in the reaction mixture, seemed to be obviated by the experimental finding that the amine itself is not oxidized to the aldehyde or an addition product of the latter under the conditions used.

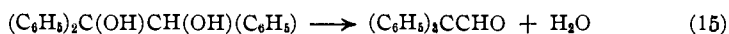
²² Curtius, *Ber.*, **22**, 2161 (1889); *J. prakt. Chem.*, [2] **44**, 182 (1891).

²³ Schroeter, *Ber.*, **42**, 2336 (1909).

²⁴ Compare equation (4) and the discussion that follows.

the rearrangement of a phenyl nucleus) which leads to diphenylketene is the preferred course.²⁵

The bearing of the results outlined in this section upon the status of the identity of triphenylacetaldehyde is of interest. Schmidlin²⁶ in 1910 reported that he had prepared this aldehyde by means of the action of triphenylmethylmagnesium chloride upon ethyl formate. His substance melted at 223.5° and possessed other surprising properties. The product obtained in this work from the action of mercuric oxide upon β,β,β -triphenylethylammonium nitrite was found to melt at 105° and to possess in general properties very unlike those of Schmidlin's compound. A literature search revealed that in 1917 Danilov²⁷ had prepared a compound having the melting point 105.5° and possessing chemical properties which left little doubt that his substance was, in fact, triphenylacetaldehyde. His preparation had been accomplished by the action of hot dilute sulfuric acid upon triphenylethylene glycol, a reaction of the pinacol-pinacolone type



Our product was proved to be in all respects identical with that of Danilov and our synthesis may be said to be conclusive of the structure of the substance, since it is the first synthesis of this aldehyde from a precursor which already possesses the triphenylmethyl group.²⁸

²⁵ Curtius and Lang [*J. prakt. Chem.*, [2] **44**, 546 (1891)] observed that azibenzil is oxidized by iodine and bromine to phenylbenzoyldi-iodomethane, $\text{C}_6\text{H}_5\text{COCI}_2\text{C}_6\text{H}_5$, and phenylbenzoyldibromomethane, respectively. Staudinger, Anthes and Pfenninger, [*Ber.*, **49**, 1936 (1916)], have studied the action of aniline and of benzoic acid upon diphenyldiazomethane. In none of the cases in which the diazo group ($=\text{N}\equiv\text{N}$) in an aliphatic diazo compound is replaced by two halogen atoms, by oxygen or by an ionogen, H^+Y^- [for example, $\text{H}^+(\text{HNC}_6\text{H}_5)^-$; $\text{H}^+(\text{OCC}_6\text{H}_5)^-$] is it necessary or desirable to postulate exclusively a path involving an intermediate bivalent carbon complex. Thus, if we assume for the structure of one of the reactive tautomers (electromers) of a diazo compound the electronic modification of the Thiele-Angeli structure proposed by Professor Noyes [THIS JOURNAL, **48**, 2405 (1926)], $\text{RR}'\text{C}::\text{N}::\text{N}$; it seems possible that the diazo compound may enter into reaction directly through the exposed pair $\cdot\cdot$ ("loss" to an oxidant; sharing with H^+) and nitrogen be lost secondarily. In the present state of our knowledge accurate evaluation of the relative importance for a given reaction of two such alternative paths is difficult; the assumption of intermediate bivalent carbon complexes has seemed most rational for the purposes of this paper.

²⁶ Schmidlin, *Ber.*, **43**, 1143 (1910).

²⁷ Danilov, *J. Russ. Phys.-Chem. Soc.*, **49**, 282 (1917); compare *C. A.*, **19**, 1488 (1925).

²⁸ The synthesis of the aldehyde by a direct oxidation of triphenylethylamine would be slightly more determinative. Such a synthesis has actually been accomplished and will be submitted in a paper by Hellerman and Cole to THIS JOURNAL.

Danilov reported that the product of reduction of the phenylhydrazone of his aldehyde was an amine, the melting point of which was 131°. β,β,β -triphenylethylamine has since been found [Hellerman, ref. 4] to melt at 132°.

Note on the Preparation of Diphenylacetonitrile

It is desired, finally, to emphasize the utility of a simple procedure employed in the course of our experimental work involving the use of thionyl chloride as dehydrating agent in the conversion of an acid amide to the corresponding nitrile. This device has already been occasionally employed.²⁹ Preparation of diphenylacetonitrile in quantity by means of the methods recorded in the literature has been found to be exceedingly troublesome. It is shown here that this nitrile may be produced rapidly in good yield by the dehydration of diphenylacetamide with thionyl chloride.³⁰

Experimental Part

Experiments Related to the Thermal Decomposition of β,β,β -Triphenylethylammonium Nitrite. Preparation of the Nitrite, $(C_6H_5)_3CCH_2NH_2ONO$.—When a small excess of a 10% solution of sodium nitrite was slowly added to a well-stirred solution of 1 g. of β,β,β -triphenylethylamine hydrochloride in 20 cc. of water, the nitrite of the amine precipitated in thin, rhomboidal plates. These were washed with ice water and dried in a vacuum desiccator over phosphorus pentoxide; decomposition point, 128°. No evidence of decomposition was found in a sample which had been stored at room temperature for several months. That the product was in fact a salt was further shown by this observation. Some of the product (which is slightly soluble in water and, of course, insoluble in ether) was shaken with a mixture of sodium hydroxide and ether; it was completely decomposed and the ether extract was found to contain free amine, while the aqueous layer retained nitrite ion.

Anal. (Dumas) Calcd. for $C_{20}H_{20}O_2N_2$: N, 8.8. Found: 8.4.

Preparation of β,β,β -Triphenylethylammonium Nitrate, $(C_6H_5)_3CCH_2NH_2ONO_2$.³¹—The nitrate, prepared in almost quantitative yield by means of the addition of an excess of 50% nitric acid to an aqueous solution of the hydrochloride, was washed with ice water and dried in a vacuum desiccator over phosphorus pentoxide; decomposition point, 239°.

Anal. (Dumas) Calcd. for $C_{20}H_{20}O_3N_2$: N, 8.4. Found: 8.2.

• **The Action of Heat upon the Nitrite in Aqueous Suspension. Formation of Triphenylethylene.**—An aqueous suspension of the nitrite (4 g.) was heated on the steam-bath for one hour; nitrogen was evolved and the mixture became "milky." The emulsion was extracted with ether. Unchanged β,β,β -triphenylethylamine was recovered from the residual aqueous solution (after the ether extraction) by means of treatment of the latter with sodium hydroxide, extraction of the alkaline mixture with ether, evaporation of the ether, and purification of the residual solid (which was compared with an authentic sample of the amine). The ether extract of the emulsion, after being washed first with hydrochloric acid and then with water, was dried over anhydrous sodium sulfate and evaporated. A viscous oil remained, which at first resisted all attempts made to promote its crystallization; after it had been permitted to stand

²⁹ (a) Hess and Dorner, *Ber.*, **50**, 392 (1917); (b) Stephen, *J. Chem. Soc.*, **127**, 1874 (1925).

³⁰ For details see the experimental part. Hellerman and Sudzuki (unpublished work) easily prepared β,β,β -triphenylpropionitrile from the parent amide by means of the same general method.

³¹ Hellerman, *THIS JOURNAL*, **49**, 1739 (1927).

for several weeks, it suddenly solidified when casually stirred. The crude product melted at 60–65°; it was found possible to effect purification by means of recrystallization from 90% ethanol. The pure product (1.5 g.) was found to melt constantly at 68° (corr.) and to be soluble in most of the common organic solvents. Analysis established the empirical formula, C_6H_4 .

Anal. Subs., 0.2028: CO_2 , 0.6970; H_2O , 0.1153. Calcd. for C_6H_4 : C, 93.75; H, 6.25. Found: C, 93.73; H, 6.32.

The melting point and the empirical formula of the substance are identical with those of triphenylethylene, $(C_6H_5)_2C=C(H)C_6H_5$. The identity of the substance was further proved by the following. When some of it was mixed with known triphenylethylene its melting point was not depressed. Further, when some of the substance was dissolved in carbon tetrachloride, treated with bromine in excess and the product isolated by means of evaporating the solvent, the melting point of the product was found to be 90°. The melting point of α,β -dibromotriphenylethane, $(C_6H_5)_2CBrC(Br)(H)C_6H_5$,³² is 92°. The melting point of the product of bromination was not depressed by admixture with some of the dibromo derivative prepared from known triphenylethylene.

The Action of Heat upon the Nitrite in the Dry State.— β,β,β -Triphenylethylammonium nitrite (0.7 g.), contained in a hard glass test-tube, was heated in an oil-bath to 135° and was maintained at that temperature for half an hour. When the temperature had reached 128° (the decomposition point) a puff of nitrogen dioxide appeared and was followed by a smooth evolution of nitrogen. The cooled "melt" was shaken with ether; all dissolved except a crystalline residue which was collected and found to weigh 0.05 g. This was found to decompose at 238° and was proved to be pure β,β,β -triphenylethylammonium nitrate by means of comparison with some of the synthetic nitrate. The ethereal filtrate (from the nitrate) was saturated with dry hydrogen chloride. A solid precipitated which was collected and found to consist of 0.2 g. of the hydrochloride of β,β,β -triphenylethylamine. From the ethereal filtrate (from the hydrochloride) there was obtained, after spontaneous evaporation of the ether, a residual oil, which was proved to consist essentially of triphenylethylene, as follows. It was treated with dilute alcohol, whereupon it solidified; the solid was crystallized from 90% alcohol and was proved to be triphenylethylene, the criteria being those employed for identification of this olefin in the preceding section.

β,β -Diphenylethylamine Hydrochloride and Sodium Nitrite

β,β -Diphenylethylamine, $(C_6H_5)_2CHCH_2NH_2$.—This amine was prepared by the method of Freund and Immerwahr,³³ which consists of the reduction by sodium of diphenylacetonitrile, $(C_6H_5)_2CH(CN)$, in alcoholic solution. The gray, pasty mass which resulted from the reduction was cautiously diluted with water, carefully neutralized with hydrochloric acid and the mixture was evaporated on a water-bath until alcohol and hydrocyanic acid were completely removed. Diphenylmethane (by-product) was removed by means of ether extraction; from the residual aqueous solution, diphenylethylamine was freed by addition of sodium hydroxide, extracted with ether and the ethereal extract treated with concentrated hydrochloric acid. The aqueous ethereal

³² Klages and Heilmann, *Ber.*, **37**, 1455 (1904).

³³ Freund and Immerwahr, *Ber.*, **23**, 2845 (1890). A modification developed by Miss Sanders (Master's Dissertation, The University of Chicago, 1925) was used. The yields were quite low due to a side reaction and it is intended to investigate later the preparation of this amine by means of a method involving the rearrangement of β,β -diphenylpropionohydroxamic acid (compare reference 4). See also the method of Rupe and Gisiger [*Helv. Chim. Acta*, **8**, 338 (1925)].

mixture was evaporated to dryness and the residual hydrochloride purified by means of dissolving it in the minimum quantity of anhydrous ethanol and reprecipitating with absolute ether. Its purity was indicated by its melting point (254.5°) and by analysis. The yields varied (7 g. of diphenylacetoneitrile gave 0.6 to 0.96 g. of amine hydrochloride).

For the preparation of diphenylacetoneitrile, the initial substance, the following method involving the dehydration of diphenylacetamide with thionyl chloride has been found far superior to any of the procedures recorded in the literature, both as to ease of preparation and yield of product.

The Preparation of Diphenylacetoneitrile Starting with Diphenylacetic Acid

Diphenylacetyl Chloride.³⁴—Pure diphenylacetic acid,³⁴ 85 g. is mixed with thionyl chloride, 135 g., in a flask fitted with a ground-in condenser ("closed" with a calcium chloride tube). The mixture is heated in an oil-bath to 45° and as the reaction proceeds (sulfur dioxide and hydrogen chloride are evolved) the temperature of the bath is gradually raised to 80°; the total period of heating is five hours. The reaction mixture is next freed from most of the excess thionyl chloride by means of distillation of the latter under reduced pressure (40–45 mm.). The residue is placed in a desiccator over sodium hydroxide under a partial vacuum. After several hours, crystallization of the diphenylacetylchloride is complete. The chloride, collected and dried, is almost pure.

Diphenylacetamide.—For the next step, the preparation of diphenylacetamide, either the dried chloride in pulverized form or the crude reaction mixture containing excess thionyl chloride, obtained as detailed above after five hours' heating of diphenylacetic acid with thionyl chloride, may be used. Either of these is added in small portions to a large excess of concentrated, aqueous ammonia, which is agitated vigorously meanwhile. The resulting precipitate is collected, triturated in a mortar with aqueous ammonia and the product is again collected and finally dried at 100°. The yield of amide (based upon diphenylacetic acid taken) is practically quantitative; the "crude" product melts at 166–168° (recorded³⁵ m. p. 165–166°; 167.5–168°). After crystallization from alcohol the product is found to melt at 167.5–168.5°.

Diphenylacetoneitrile.—Diphenylacetamide, 25 g., and thionyl chloride, 35 g., are heated together (under a return condenser protected with a calcium chloride tube) in an oil-bath (temperature of bath, 90–105°) for four hours. The resulting mixture is cautiously poured upon crushed ice in order to destroy excess thionyl chloride. The suspended solid nitrile is collected, washed with water and dried in a vacuum desiccator over sodium hydroxide. The yield of crude nitrile is almost quantitative; only a small loss should occur during the process of purification, which is conducted as follows. The product is treated with a relatively large quantity of 50% ethanol and the mixture heated to not over 55°. At this point the supernatant liquid is decanted and cooled sharply. Diphenylacetoneitrile crystallizes in white, glistening plates: m. p. 73.5–74°. The filtrate from these crystals or fresh 50% alcohol is used for several further extractions of residual crude nitrile under the conditions specified.

The Action of Heat upon β,β -Diphenylethylammonium Nitrite in Aqueous Solution.— β,β -Diphenylethylamine hydrochloride, 1.2 g., and sodium nitrite, 0.35 g., were dissolved in 35 cc. of water. Nothing precipitated. The solution was heated; when the temperature of the solution reached 65°, slow evolution of nitrogen began; at 75° the evolution became marked and droplets of an oil began to appear. Heating was continued at 75–80° for twenty minutes; at 90° for ten minutes; then the temperature was raised to the boiling point and the heating discontinued. As the mixture cooled the

³⁴ "Organic Syntheses," John Wiley and Sons, Inc., New York, Vol. III, p. 45 (1923).

³⁵ Beilstein-Prager-Jacobson, Vol. IX, page 674 (1926).

oil became converted to a crystalline mass. This was collected upon a filter (leaving filtrate A, see below), washed well with water and dried on a porous plate; weight, 0.6 g. It was very soluble in alcohol. A portion washed with dilute alcohol melted at 60–68°. The product was purified by recrystallization from dilute alcohol; m. p. 67°. The physical properties of the product indicated that it was phenylbenzylcarbinol.³⁶ For complete characterization some of the product was boiled for twenty minutes with sulfuric acid (1:4).^{16a} It was converted quantitatively to stilbene, which was identified by comparison with a sample of stilbene on hand.

Filtrate A was evaporated to dryness on the steam-bath. The residue was treated with dilute hydrochloric acid and the mixture filtered; from the filtrate by treatment with alkali, extraction with ether and treatment of the ethereal extract with hydrogen chloride, there was recovered 0.2 g. of β,β -diphenylethylamine hydrochloride. From the residual mixture of resinous and crystalline material after treatment of the first residue with acid, there was isolated a second "crop" of phenylbenzylcarbinol. No other individual could be found, although stilbene, β,β -diphenylethanol, 1,1-diphenylethylene and methyl-diphenylcarbinol were sought. The latter two might have been products if rearrangements of hydrogen atoms as well as phenyl groups had taken place.³⁷

The Action of Heat upon a Mixture of β,β -Diphenylethylamine Hydrochloride and Sodium Nitrite in Equimolecular Proportion.—An intimate mixture of diphenylethylamine hydrochloride, 0.34 g., and sodium nitrite, 0.12 g. (1 mole), contained in a hard glass test-tube was heated in a glycerine-bath; at 160° there was a slight evolution of a gas and droplets of an oil began to collect upon the walls of the tube above the mixture. At 195° the mass had become yellowish-brown in color; the heating was continued at 195° until forty minutes had elapsed after the temperature had reached 160°. The cooled reaction product was extracted with ether. A white solid consisting largely of sodium chloride remained. The ethereal extract was treated with dry hydrogen chloride and filtered from a slight quantity of amine hydrochloride. The filtrate from the hydrochloride was allowed to evaporate. The residue, which consisted of crystals embedded in viscous liquid, was washed with water and then treated with cold alcohol, whereupon white needles separated. These were recrystallized from ether and were found to melt at 124.5°. The melting point of a mixture of the product with known stilbene (recorded m. p. 125°) was also 124.5°. The yield was 0.2 g. (76%).

β,β -Dipenyldiazo-ethane

The Preparation of β,β -Diphenylethyl Urethan, $(C_6H_5)_2CHCH_2NHCOOC_2H_5$.—When 1.9 g. of β,β -diphenylethylamine hydrochloride was shaken violently with 1.5 g. of ethyl chlorocarbonate and an excess of 25% sodium carbonate, β,β -diphenylethylurethan separated as a white, crystalline solid. This was collected, washed with water and dried over sulfuric acid. The melting point, 69–70°, was not raised when the substance was crystallized from ligroin;³⁸ yield, 93%.

Anal. (Dumas) Calcd. for $C_{17}H_{19}O_2N$: N, 5.20. Found: 5.21.

The Preparation of β,β -Diphenylethyl nitroso-urethan, $(C_6H_5)_2CHCH_2N(NO)COOC_2H_5$.—After considerable experimentation, there was devised the following procedure which, carefully followed, leads to high yields of the nitroso compound.

Of thoroughly dried β,β -diphenylethylurethan, 1 g. was dissolved in 30 cc. of anhydrous ether, anhydrous sodium sulfate, about 3 g., was added, and the mixture,

³⁶ Ref. 35, Vol. VI, p. 683.

³⁷ See the theoretical section.

³⁸ Sieglitz, *Ber.*, 55, 2040 (1922), prepared the same compound by means of the rearrangement of β,β -diphenylpropionoazide in alcoholic solution.

contained in a flask, suitably protected from moisture with a calcium chloride tube, was cooled in an ice-salt bath. The gases prepared by treatment of sodium nitrite with 80% sulfuric acid and dried by calcium chloride were introduced into the ethereal mixture until the latter had assumed a dark green hue. The sodium sulfate was removed by filtration; the filtrate was placed over sulfuric acid in a desiccator connected to a suction pump and ether was allowed to evaporate at room temperature. The product was a stable, viscous, straw-colored oil; it exhibited chemical properties which are common to N-nitroso compounds. The yield was practically quantitative.

Anal. (Dumas) Calcd. for $C_{17}H_{18}N_2O_3$: N, 9.39. Found: 9.13.

β,β -Diphenyldiazo-ethane, $(C_6H_5)_2CHCH(N_2)$,³⁹— β,β -Diphenylethyl nitroso-urethan, 0.235 g., dissolved in 2 cc. of anhydrous ether (contained in a flask suitably protected from moisture) was placed in a freezing mixture at -15° . To this solution was added 0.5 cc. of absolute ethanol in which had been "dissolved" 0.025 g. of sodium. The resulting solution was permitted to remain below -10° for three hours, during which it assumed a red color which deepened progressively. The flask was quickly transferred to a vacuum desiccator which was surrounded with ice-salt mixture and which was connected with a suction pump through a line suitably protected from moisture. In this manner the solvents were evaporated at -10° to -15° . A red, semi-crystalline mass remained. An assay of this product for diazo nitrogen indicated that well over 80% of the nitroso-urethan taken had been converted to β,β -diphenyldiazo-ethane. That this diazo compound was, in fact, present was proved further by its properties (see below), particularly its conversion when heated in aqueous suspension to the dihydrazone (azine) of diphenylacetaldehyde, $[(C_6H_5)_2CHCH=N]_2$. Time was not taken to effect complete purification of the compound; this could probably be effected by means of crystallization from an appropriate solvent at low temperatures (below -10°). The diazo compound was successfully prepared several times (in up to 1 g. portions) by means of the procedure here outlined.

Decomposition of the Diazo Compound

(A) **Spontaneously.**—While the diazo compound, as prepared above, may be kept below -10° for many hours, it begins to evolve nitrogen when the temperature is permitted to rise to 0° . A sample allowed to remain above 0° for twelve hours was found to have resolved itself into a yellow resinous mass which contained no diazo nitrogen and which yielded no definite chemical individual after treatment with various solvents.

(B) **When Heated in Acid Environment:** Stilbene.— β,β -Diphenyldiazo-ethane, prepared from 0.23 g. of β,β -diphenylethyl nitroso-urethan, was gradually heated with dilute sulfuric acid (1 part acid: 4 parts water) almost to the boiling point of the acid until evolution of nitrogen had ceased. The mixture was cooled and the reddish-yellow oil which had formed was extracted with ether and recovered by means of evaporation of the solvent. The viscous residue (0.18 g.) was treated with 95% alcohol, whereupon a nearly white solid separated. The latter was washed with alcohol, collected and crystallized from ether; m. p. 122° . It was proved to be stilbene by means of comparison with an authentic sample of stilbene. It was further characterized by conversion to long, yellow needles of stilbene picryl chloride (m. p. 71°) according to the procedure of Liebermann and Palm.⁴⁰

³⁹ Our method of preparation of the compound is, of course, a modification of Von Pechmann's general procedure [*Ber.*, 27, 1888 (1894)] for the preparation of aliphatic diazo compounds. Compare Oppé, *Ber.*, 46, 1095 (1913).

⁴⁰ Liebermann and Palm, *Ber.*, 8, 378 (1875).

(C) **When Heated in Alkaline and in Neutral Environment: Diphenylacetaldehyde, $(C_6H_5)_2CHCH=NN=CHCH(C_6H_5)_2$.**—Some of the diazo compound which had been washed with cold water was mixed with water and heated on the steam-bath until evolution of nitrogen had ceased. After several hours the water was decanted from the reddish-yellow, oily product and the latter was treated with ether. A white powder, insoluble in the ether, remained. This was repeatedly treated with boiling ether until it melted constantly at 165° . The recorded melting point of diphenylacetaldehyde (prepared by treatment of diphenylacetaldehyde with hydrazine hydrate) is 165° .⁴¹

Anal. (Dumas) Calcd. for $C_{26}H_{24}N_2$: N, 7.41. Found: 7.60.

When some β,β -diphenyldiazo-ethane in the dry state was subjected to the action of heat, the aldazine was likewise found to be a product. The same product was obtained after some of the diazo compound was decomposed on the steam-bath in the presence of concentrated aqueous ammonia. No other definite compound was isolated from these various reaction mixtures.

The study of the decomposition products of β,β -diphenyldiazo-ethane and similar compounds is being continued (by L. H. and R. E. H.).

Triphenylacetaldehyde from the Action of Mercuric Oxide upon β,β,β -Triphenylethylammonium Nitrite

An intimate mixture of the nitrite (1 g.) and yellow mercuric oxide, freshly precipitated and dried over phosphorus pentoxide (5 g.), was heated for half an hour at 135° . The reaction mixture was extracted with ether. The ethereal extract, treated with dried hydrogen chloride, yielded about 0.1 g. of β,β,β -triphenylethylamine hydrochloride. The filtrate from the hydrochloride was allowed to evaporate spontaneously. The residue consisted largely of triphenylethylene in a semi-crystalline deposit on the bottom of the beaker. On the upper sides of the beaker rhomboidal plates had collected. Several of these were removed and washed with a small portion of cold 90% alcohol; m. p. 104° . The contents of the beaker were extracted with ligroin (b. p. $30-60^\circ$); the ligroin extract after evaporation of the solvent yielded well-defined plates which were recrystallized from ligroin and found to melt at $104-105^\circ$. When they were mixed with some known triphenylacetaldehyde²⁷ (m. p. 105°) the melting point was not depressed.

Triphenylacetaldehyde is not formed when triphenylethylamine is substituted for its nitrite in the above experiment.⁴²

Benzil from the Action of Mercuric Oxide upon Azibenzil⁴³

Azibenzil (phenylbenzoyldiazomethane), $C_6H_5COC(N_2)C_6H_5$, was prepared in excellent yield from benzil monohydrazone by the method of Curtius and Thun.⁴⁴ An intimate mixture of the pure diazo compound, 1 g., and moist mercuric oxide (freshly precipitated and well washed), 20 g., contained in a large test-tube, was heated in a

⁴¹ Klages and Kessler, *Ber.*, **39**, 1756 (1906).

⁴² Hellerman and Cole, unpublished work. An extended investigation of the behavior of nitrites and other salts of amines with oxides of heavy metals is in progress. A preliminary experiment has indicated that the action of mercuric oxide upon β,β -diphenylethylammonium nitrite yields diphenylacetaldehyde in addition to rearrangement products.

⁴³ We are indebted to Mr. J. R. Sudzuki who aided with the experimental work outlined under this caption.

⁴⁴ Curtius and Thun, *J. prakt. Chem.*, [2] **44**, 182 (1891).

glycerine bath to 100°. The mixture became gray due to separation of mercury. The reaction mixture was extracted with absolute alcohol. From the alcoholic extract there was obtained, after evaporation of the solvent in a stream of air (without heat), 0.7 g. of light yellow crystals of almost pure benzil. The product, recrystallized several times from alcohol, was identified by its melting point and by comparison with an authentic sample of benzil. It was further characterized by conversion to the monohydrazone, which was compared with a sample of benzil monohydrazone on hand.

Summary

1. The nitrite and nitrate of β,β,β -triphenylethylamine have been prepared and described. They are stable, solid substances at room temperature. The nitrite is one of the few nitrites of amines of Type RCH_2NH_2 which have been isolated.

2. The principal product of the action of heat upon the nitrite in aqueous suspension has been shown to be triphenylethylene. It has been shown further that the nitrite, heated in the dry state, yields also β,β,β -triphenylethylammonium nitrate.

3. An hypothesis to account for the product of thermal decomposition and to interpret the action by which it is produced has been developed. This hypothesis, which involves diazotization of the amine and subsequent formation of a transitorily existing methylene intermediate, has been found to be useful in the interpretation of various amine nitrite decompositions which have been recorded in the literature.

4. The thermal decomposition of the nitrite of β,β -diphenylethylamine has been shown to lead to phenylbenzylcarbinol or to stilbene, depending upon the conditions.

5. β,β -Diphenyldiazo-ethane has been prepared (in a somewhat impure state) and its behavior under various conditions studied. Its behavior, when heated under certain conditions, is interestingly related to the thermal behavior of β,β -diphenylethylammonium nitrite.

6. It has been shown that the action of mercuric oxide upon β,β,β -triphenylethylammonium nitrite at 135° results in the formation of triphenylacetaldehyde in addition to triphenylethylene. This is the first observation of the formation of triphenylacetaldehyde from a precursor which possesses the triphenylmethyl group.

7. It has been shown that azibenzil, heated with moist mercuric oxide, undergoes to no large extent the Schroeter rearrangement to diphenylketene, but instead gives benzil in 74% yield.

8. Improved methods for the preparation of diphenylacetamide and diphenylacetonitrile are submitted.

9. The preparation of β,β -diphenylethylnitroso-urethan, starting compound for β,β -diphenyldiazo-ethane, is described. An improved method is outlined for the preparation of the parent urethan.