[CONTRIBUTION FROM THE DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY, AND THE FIXED NITROGEN INVESTIGATIONS UNIT, BUREAU OF CHEMISTRY AND SOILS]

Aliphatic Diazo Compounds. The Preparation and Rearrangement of Diazo-β,β,β-triphenylethane[1]

BY LESLIE HELLERMAN AND R. L. GARNER

It was shown in the first paper[2] of this series that the thermal decomposition of the crystalline nitrite of β,β,β-triphenylethylamine results principally in the formation of triphenylethylene, a rearrangement product. This and the analogous behavior of β,β-diphenylethylammonium nitrite constitute unusually striking illustrations of so-called "abnormal" decompositions of primary amine nitrites of the types RCH_2NH_3ONO and $RR'CHNH_3ONO$, resulting in internal rearrangements.[3]

The intermediate stages involved in such deaminations are of theoretical interest and, perhaps indirectly, of concern for certain analytical methods of biochemistry.[4]

On the basis of much work recorded in this field, the assumption was made that diazo-β,β,β-triphenylethane, or its "hydrate," $(C_6H_5)_3CCH_2\text{-}N{=}NOH$, might be involved intermediately in the decomposition of β,β,β-triphenylethylammonium nitrite, the initial stage of the reaction being essentially a diazotization of the parent amine. The desirability of testing further whether a significant parallelism exists in the mode of decomposition of amines with nitrous acid and of aliphatic diazo compounds, made attractive the preparation of diazo-β,β,β-triphenylethane, more especially since the investigation of this compound promised to disclose matters of fresh interest for the chemistry of the aliphatic diazo group and possibly for the theory of molecular rearrangements.[5]

For the synthesis of the diazo compound, β,β,β-triphenylethylamine was converted to the ethyl urethan, which, in turn, was transformed into its crystalline N-nitroso derivative by suitable treatment with nitrous gases. From this, by appropriate treatment with sodium ethylate[6] there was obtained the desired diazo compound, $(C_6H_5)_3CCH({=}N_2)$.

The latter, purified by crystallization at low temperatures and stored in a dark desiccator, remains undecomposed for several weeks. It suffers rearrangement under a variety of conditions, with the formation of nitrogen and triphenylethylene.

$$(C_6H_5)_3CCH({=}N_2) \longrightarrow N_2 + (C_6H_5)_2C{=}CH(C_6H_5) \quad (1)$$

There is revealed a striking correspondence in the decomposition and rearrangement of diazo-β,β,β-triphenylethane and the nitrite of the related amine.

The arrangement is readily effected by the addition, to solutions of the diazo compound, of finely divided metals or a trace of iodine[7] or by the action of acids upon the solid substance. Other conditions include thermal decomposition of the substance, dry or heated with water. The latter decomposition leads also to a second product, triphenylacetaldazine, in approximately 5% yield.

$$2(C_6H_5)_3CCH({=}N_2) \longrightarrow N_2 + (C_6H_5)_3CCH{=}N{-}N{=}CHC(C_6H_5)_3 \quad (2)$$

Azines are frequently formed intermolecularly from aliphatic diazo compounds.

A good illustration of the rearrangement tendency of this diazo compound is furnished by its behavior with "nitrous gases." The action is complex, for the resulting polymerized mass yields but little of the only definite product that can be readily recovered, namely, triphenylnitroethylene, $(C_6H_5)_2C{=}C(NO_2)(C_6H_5)$. No non-rearranged addition product could be isolated. On the other hand, a most interesting observation was the formation of the identical rearrangement product, triphenylnitroethylene, from the parent

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[1] (a) Abstract of Part I of a thesis submitted by R. L. Garner in partial fulfilment of the requirements for the degree of Doctor of Philosophy, The Johns Hopkins University. (b) Presented before the Organic Division of the American Chemical Society, Buffalo, September, 1931. (c) The properties of α-diazo-γ,γ,γ-triphenylpropane will be discussed in a later paper by Hellerman and Garner.

[2] Hellerman, Cohn and Hoen, THIS JOURNAL, **50**, 1716–1729 (1928).

[3] For references to such behavior in the decompositions of even simple aliphatic amines (*e. g.*, *n*-propylamine) with nitrous acid, see Beilstein, vol. 4 (1922 and 1929).

[4] Van Slyke, *J. Biol. Chem.*, **9**, 183 (1911); *ibid.*, **12**, 275 (1912); Schmidt, *ibid.*, **82**, 587 (1929).

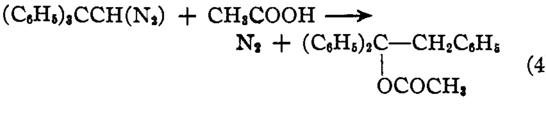
[5] Compare the preliminary observations upon diazo-β,β-diphenylethane.[2]

[6] *Cf.* von Pechmann, *Ber.*, **27**, 1888 (1894); Oppe, *ibid.*, **46**, 1097 (1913).

[7] Titration with iodine is not an entirely reliable method for the analysis of aliphatic diazo compounds. *Cf.* Wegscheider and Gehringer, *Monatsh.*, **24**, 364 (1903); *ibid.*, **29**, 525 (1908); Staudinger and Kupfer, *Ber.*, **45**, 505 (1912).

amine, $(C_6H_5)_3CCH_2NH_2$, treated with nitrous gases under comparable conditions.

From the point of view of rearrangement mechanism, the decomposition of diazo-β,β,β-triphenylethane with acids is of unusual interest. Although the decomposition of the solid diazo compound by glacial acetic acid resulted only in its rearrangement to triphenylethylene, the action of the same acid *in ether or petroleum ether* solution yielded a second and unanticipated rearrangement product, benzyldiphenylmethyl acetate.



$$(C_6H_5)_3CCH(N_2) + CH_3COOH \longrightarrow N_2 + (C_6H_5)_2\underset{\displaystyle OCOCH_3}{\underset{|}{C}}{-}CH_2C_6H_5 \qquad (4)$$

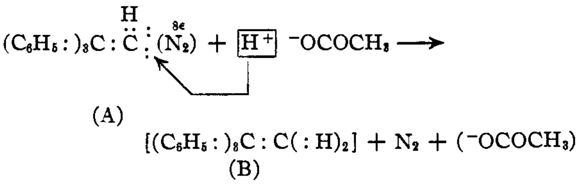
Similarly, the action of benzoic acid produced benzyldiphenylmethyl benzoate. The appearance of these esters was the more striking because they had not been described previously; the parent alcohol, benzyldiphenylcarbinol is very readily dehydrated to triphenylethylene.

Discussion

Hellerman, Cohn and Hoen offered a schematic electronic interpretation of the *thermal* rearrangement of diazo-β,β,β-triphenylethane. There was assumed, as a first step, the fission of the diazo compound into a molecule of nitrogen and an intermediate fragment $(C_6H_5:)_3C:\ddot{C}:H$, followed by the intramolecular rearrangement of this fragment. However, in those decompositions of aliphatic diazo compounds which are induced by hydrogen ions, halogens, and numerous other reagents including certain mercuric and organomercuric salts,[8] the transformations, whether essentially intramolecular or intermolecular, may be considered to be *initiated* by addition reactions, effecting virtually the elimination of nitrogen from the diazo molecules.

In this investigation it has been found that the reaction of diazo-β,β,β-triphenylethane and acetic or benzoic acid (in solution) leads, *not* to the ester of corresponding structure, but exclusively to (a) triphenylethylene, and (b) an ester related structurally to this olefin. The following scheme illustrates these rearrangements and at the same time accounts significantly for the non-formation of α-phenyl-β,β-diphenylethyl acetate, $(C_6H_5)_2CHCH(C_6H_5)OCOCH_3$, and benzoate as rearrangement products, isomeric with the esters actually obtained.

(a) *Reaction initiated by the addition of H^+ and the "loss" of N_2.*[9]



$$(C_6H_5:)_3C:\overset{H}{\ddot{C}}\vdots(\overset{8e}{N_2}) + \boxed{H^+}\ {}^-OCOCH_3 \longrightarrow$$

(A)

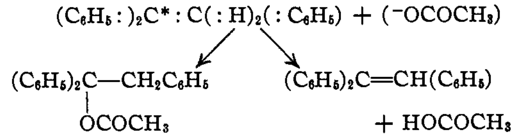
$$[(C_6H_5:)_3C:C(:H)_2] + N_2 + ({}^-OCOCH_3)$$

(B)

(b) *Apparent shift of an electron pair with a phenyl group.*

$$(C_6H_5:)_3C:C(:H)_2 \longrightarrow (C_6H_5:)_2C^*:C(:H)_2(:C_6H_5)$$

(c) *Uni-directional absorption of an acetate ion to complete the octet of the carbon atom designated (*) in the first rearrangement product, or, alternatively, loss of a proton and the formation of an olefin.*



Experimental Part

The Preparation of Ethyl N-β,β,β-Triphenylethyl Carbamate.—To an aqueous suspension of β,β,β-triphenylethylamine,[10] 20 g., was added sodium carbonate, 8 g., and ethyl chlorocarbonate, 8 g., and the mixture was shaken until there was no more evidence of reaction. After thorough trituration of the granular product, the latter was again shaken vigorously for half an hour during which there were added further small portions of ethyl chlorocarbonate and sufficient sodium carbonate solution to keep the mixture slightly alkaline. The mixture was shaken with an excess of sodium carbonate and the solid product collected, *triturated in the presence of warm dilute hydrochloric acid to remove any unchanged amine*, again collected, thoroughly washed with warm water and dried in a vacuum desiccator. The product was crystallized from purified ligroin (b. p. 60–90°) and recrystallized from the same solvent; yield, 16 g.; m. p. 94°. The analysis has already been reported. Unchanged amine, 4 g., was recovered from the hydrochloric acid washings.

Ethyl N-Nitroso-N-β,β,β-triphenylethyl Carbamate, $(C_6H_5)_3CCH_2N(NO)COOC_2H_5$.—For the preparation of this compound, pure carbamate, freed from traces of amine and crystallized as described in the preceding section, must be used. To the finely powdered carbamate, 9 g., contained in a three-necked flask, suitably protected from moisture and fitted with an oil-sealed stirrer and appropriate inlet and outlet tubes, was added 200 cc. of pure, dry ether and 10 g. of anhydrous sodium sulfate (freshly heated and cooled over phosphoric anhydride). The flask was cooled in an ice-bath. Into the vigorously stirred solu-

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(8) Hellerman and Newman, THIS JOURNAL, **54**, 2859 (1932); note especially the discussion on pp. 2862–2863.

(9) In the decomposition of diazo compounds or "diazohydrates," intermediate in amino nitrite decompositions, a similar step might be involved. *Cf.* Ref. 2 and Whitmore and Langlois, *ibid.*, **54**, 3442 (1932). The formula (A) is used for convenience and is intended to be non-committal as regards the fine structure of the diazo grouping.

(10) Hellerman, *ibid.*, **49**, 1735 (1927).

tion were conducted gases produced by the action of 80% sulfuric acid upon sodium nitrite and dried by passage through two calcium chloride towers. When the solution had become deep green, it was filtered quickly from the sodium sulfate and concentrated by means of a stream of dry air passed over the surface of the liquid (contained in a beaker which had been placed in a suitably fitted desiccator in order to afford protection from atmospheric moisture). Clusters of pale yellow crystals soon appeared. After about half of the solvent had been removed, the beaker was placed in an ice–salt bath for a few minutes; the product was collected, washed with a little chilled ether and at once placed in a vacuum desiccator which contained beakers of phosphoric anhydride, solid sodium hydroxide and chipped paraffin. The product (8 g.) was pure. For analysis, it was recrystallized from ether with the aid of cooling with solid carbon dioxide. The resulting pale yellow elongated plates decomposed at 114° (corr.) in a bath preheated to 110°.

Anal. (Dumas) Calcd. for $C_{23}H_{22}N_2O_3$: N, 7.5. Found: N, 7.7.

The Preparation of Diazo-β,β,β-triphenylethane.—To ethyl N-nitroso-N-triphenylethyl carbamate, 13 g. (0.034 mole), contained in a dry flask fitted with a calcium chloride tube and cooled in an ice–salt bath, was added sodium-dried ether, 100 cc. There was then added a solution of sodium ethylate previously prepared from 1.4 g. of sodium (C. P.) and 15 cc. of absolute ethanol and the resulting mixture was permitted to stand for three hours during which it was agitated occasionally. From the mixture, protected from moisture in a suitable apparatus and still maintained at about −15°, the ether was removed in a current of dry air. The operation was completed by permitting the residue to stand for several hours at 0° over paraffin and phosphorus pentoxide in a partially evacuated desiccator. The semi-crystalline mass was freed from inorganic contaminants by trituration in ice water. The crude diazo compound was collected on a filter, washed with ice water and at once placed in a desiccator over phosphorus pentoxide. The substance was thus obtained almost pure in practically quantitative yield; decomposition pt., 75°. For analysis it was recrystallized from a mixture, by volume two-thirds dry ether and one-third low-boiling ligroin (purified by permanganate), by dissolving the substance in a minimum quantity of the solvent at room temperature and cooling the resulting solution in a carbon dioxide–ether bath. The diazo compound was obtained as orange-yellow, slightly rhomboidal plates, decomposing at 78–80° (corr.) in a bath preheated to 75°.

It was proved by analysis that the "diazo" nitrogen of the molecule was, in fact, its total nitrogen. Assays of the "diazo" nitrogen were conducted, with the aid of a suitably constructed apparatus, as follows. The weighed sample was contained in a test-tube fitted with a two-holed rubber stopper through which were properly inserted (a) a delivery tube connected, in turn, to an azotometer, and (b) one arm of a three-way stopcock by means of which there was first introduced a current, suitably controlled, of pure, thoroughly dried carbon dioxide followed by a measured volume of glacial acetic acid. The apparatus was "swept out" with carbon dioxide, during which the diazo compound was kept at 0° and remained undecomposed. Admission of about 1 cc. of acetic acid accomplished the decomposition of the substance with the evolution of nitrogen. The latter was swept into the azotometer and measured.

Anal. Calcd. for $C_{20}H_{16}N_2$: N, 9.9. Found: (diazo nitrogen) 10.3; (Dumas) 10.2.

Decomposition of Diazo-β,β,β-triphenylethane

A sample of the diazo compound was permitted to stand over phosphoric anhydride and sodium hydroxide in a desiccator at 5° for two months, during which the substance decomposed partially. This material was then exposed to the air at room temperature for a week. A white solid resulted; m. p. 68–69°; m. p. of a mixture with authentic triphenylethylene,[11] 69° (recorded m. p. 67–68°).

Decomposition with Copper or Iodine as Catalyst.—To an ether solution of the diazo compound (at 25°) was added a little copper (Naturkupfer C); a steady evolution of nitrogen took place. When the yellow color of the solution had vanished, the solvent was evaporated; there remained an oily residue, which crystallized when "seeded" with triphenylethylene, with which it was proved to be identical.

From a solution of some of the diazo compound in chloroform or in ether, nitrogen was evolved briskly upon the addition of a minute crystal of iodine. The decomposition product was found to be triphenylethylene.

Thermal Decomposition.—Diazo-β,β,β-triphenylethane, 2 g., was heated with 25 cc. of water; a gradual evolution of a gas took place at 70–80°; to ensure complete decomposition, the mixture was heated at 100° for half an hour. The suspended gummy product was separated and taken up in ether. After filtration of the latter, there remained a small amount of white crystals (0.13 g.), which did not melt when heated to 300°. From the ether filtrate was isolated 1.7 g. of pure triphenylethylene. An analysis of the high-melting product indicated that it was triphenylacetaldazine.

Anal. (Dumas) Calcd. for $C_{40}H_{32}N_2$: N, 5.2. Found: N, 5.6.

Preparation of β,β,β-Triphenylacetaldazine.—When 1.2 g. of triphenylacetaldehyde[12] in ethanol solution was heated on the water-bath with 0.07 g. of 90% hydrazine hydrate, a white crystalline precipitate resulted. This was collected and extracted with portions of boiling ether; yield, 0.8 g. The compound did not melt when heated to 300°. An analysis indicated it to be β,β,β-triphenylacetaldazine.

Anal. (Dumas) Calcd. for $C_{40}H_{32}N_2$: N, 5.2. Found: N, 5.1.

The action upon triphenylacetaldehyde of an excess of hydrazine led to the formation of a white product, probably the hydrazone, melting at 140°. This was slightly soluble in ether and was readily oxidized by mercuric oxide.

Decomposition in the Presence of Acids.—The diazo compound, 1 g., vigorously decomposed when treated with 20 cc. of 25% sulfuric acid. The mixture was heated

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[11] Hell and Wiegandt, *Ber.*, **37**, 1429 (1904); Klages and Heilmann, *ibid.*, **37**, 1455 (1904).

[12] Daniloff and Danilova, *ibid.*, **59**, 387 (1926).

slightly to ensure complete decomposition and the product was extracted with ether. The extract was washed, dried, and the ether removed. The residual oil solidified when stirred with a little ethanol. The resulting white crystalline solid was collected, washed with a little cold 95% ethanol, dried, and identified as triphenylethylene by comparison with an authentic sample on hand. The olefin was obtained in practically quantitative yield.

After some of the diazo compound was treated with glacial acetic acid, the product obtained after removal of the acid was likewise proved to be triphenylethylene.

Decomposition of Diazo-β,β,β-triphenylethane in Solution by Acids

Acetic Acid: Formation of Benzyldiphenylmethyl Acetate $(C_6H_5CH_2)(C_6H_5)_2C(OCOCH_3)$.—When glacial acetic acid, 15 cc., was permitted to drop slowly into a solution of 5 g. of the diazo compound in 100 cc. of ether, a brisk evolution of nitrogen followed the addition of each drop and the solution gradually became colorless. White crystals began to separate almost at once. After crystallization was complete, the product was collected and washed with a little ether; yield, 2.5 g. The filtrate yielded triphenylethylene *and no other product.* The same reaction products were obtained when the decomposition was carried out in ligroin solution. The product slightly soluble in ether was found to be but slightly soluble in most common organic solvents. Recrystallized from acetone, it was obtained as thick, rhomboidal plates which melted at 175.5° (corr.). The substance was proved to be benzyldiphenylmethyl acetate, hitherto unknown, by its analysis and by its saponification to benzyldiphenylcarbinol.

Anal. Calcd. for $C_{22}H_{20}O_2$: C, 83.5; H, 6.4. Found: C, 83.55; H, 6.5.

When a chloroform solution of the ester was treated with bromine, the product, obtained by evaporation of the solvent, was found to melt at 92°, the melting point of triphenyl-α,β-dibromoethane.

A sample of the ester and an excess of a 10% solution of potassium hydroxide in methanol were heated together at the boiling point of the solvent for two hours. The solvent was distilled in a vacuum and the residue was treated with water and extracted with ether. The extract was dried and the ether removed. The residue was an oil which crystallized. The product was collected and washed with a little cold ethanol. It melted at 85°; m. p. of a mixture with known benzyldiphenylcarbinol, 86° (recorded m. p. 89°). The hydrolysis product was readily dehydrated to triphenylethylene by the action of boiling acids.

It was hardly to be anticipated that synthetic triphenylethylene in ether or ligroin solutions would combine with such acids as acetic, benzoic and malonic; that these additions do not take place was demonstrated by suitable tests. Moreover, preliminary attempts to prepare benzyldiphenylmethyl acetate from the carbinol by conventional methods led to the isolation of triphenylethylene, the product of its dehydration.

Benzoic Acid: Formation of Benzyldiphenylmethyl Benzoate, $(C_6H_5CH_2)(C_6H_5)_2C(OCOC_6H_5)$.—To diazo-β,β,β-triphenylethane, 1.5 g., dissolved in 25 cc. of dry ether, was added, little by little, benzoic acid, 0.65 g. Glistening crystals precipitated rapidly. They were collected and recrystallized from acetone; yield, 0.64 g.; m. p. 179.5° (corr.). A second fraction of the ester was obtained by partial evaporation of the filtrate. The final residue was found to be triphenylethylene. The identity of the ester was established by its analysis and by its saponification with 20% methanolic potassium hydroxide, the product of which was found to be benzyldiphenylcarbinol, identical with an authentic sample and with the saponification product of benzyldiphenylmethyl acetate.

Anal. Calcd. for $C_{27}H_{22}O_2$: C, 85.7; H, 5.9. Found: C, 85.4; H, 6.0.

Triphenylnitroethylene

From β,β,β-Triphenylethylamine by the Action of Nitrogen Trioxide.—The amine, 2.5 g., sodium sulfate (freshly dehydrated), 5 g., and dry ether, 125 cc., were placed in a three-necked flask, fitted with an oil-sealed, mechanical stirrer, and inlet and outlet tubes. The reagents were suitably protected from moisture, cooled to −15°, and vigorously stirred. Into the solution were conducted the gases obtained from the action of 80% sulfuric acid upon sodium nitrite and treated by passage through a tower containing sodium nitrite and two towers of calcium chloride. After an hour the operation was interrupted and the solution was concentrated (at −5°) by means of passing a rapid stream of dried air through the reaction vessel. When the mixture had the consistency of a paste, 50 cc. of dry ether was added, and the evaporation continued. This was twice repeated. The residue was taken up in ether; the solution was filtered from the sodium sulfate admixed with some β,β,β-triphenylethylammonium nitrite[2] that had been formed, and the solvent evaporated. The residual yellow gum was stored for twelve hours over solid sodium hydroxide, phosphorus pentoxide and chipped paraffin in a vacuum desiccator. It was then treated with a little 95% ethanol and warmed *slightly;* yellow crystals separated. These were collected and dried. The product weighed 0.57 g. After recrystallization from acetone, it melted at 174°. Its nitrogen content (Dumas) and physical characteristics indicated its identity with triphenylnitroethylene, $(C_6H_5)_2C{=}C(NO_2)C_6H_5$, which had been synthesized by Kohler and Stone.[13] No other definite product could be isolated from the residual gum. The nitroethylene was further characterized by comparison with some of the authentic substance obtained in a very small yield by treatment of triphenylethylene with nitrous fumes in a manner essentially similar to the procedure described above.[14]

From Diazo-β,β,β-triphenylethane.—When the diazo compound, 1.2 g., dissolved in ether in which was suspended some anhydrous sodium sulfate, was treated with nitrogen oxides prepared as described under the preceding experiment, nitrogen was evolved and the solution became lighter in color. After the diazo compound was decomposed, the mixture was treated in the manner described above and a similar yellow gum was obtained. The latter, when treated with a little glacial acetic acid, yielded slightly impure triphenylnitroethylene, 0.13 g.; this was thrice recrystallized from acetone. Its identity was es-

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(13) Kohler and Stone, THIS JOURNAL, **52**, 766 (1930).

(14) *Cf.* Shilov, *Chem. Abs.*, **24**, 4289 (1930).

tablished by its melting point and that of a mixture with authentic material on hand.

Summary

The synthesis of diazo-β,β,β-triphenylethane is effected by means of a series of steps involving the preparation of ethyl N-nitroso-N-β,β,β-triphenylethyl carbamate derived from β,β,β-triphenylethylamine. This diazo compound is converted into triphenylethylene by rearrangement, when decomposed under a variety of conditions. From either diazo-β,β,β-triphenylethane or β,β,β-triphenylethylamine there is obtained by the action, under specified conditions, of nitrous anhydride, triphenylnitroethylene. The decomposition of the diazo compound in ether or ligroin solutions by acetic acid or benzoic acid leads to the formation, respectively, of benzyldiphenylmethyl acetate or benzoate, hitherto undescribed. The results of the investigation are discussed from the point of view of their bearing upon the mechanism of primary amine nitrite decompositions and the interpretation of certain molecular rearrangements.

BALTIMORE, MARYLAND RECEIVED OCTOBER 20, 1934

[COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Preparation, Alcoholysis and Hydrogenolysis of Nicotinyl Acyl Methanes

BY LEO F. KUICK AND HOMER ADKINS

The literature of organic chemistry contains very little information with respect to the preparation and chemical behavior of 1,3-diketones having a pyridyl or piperidyl group adjacent to one carbonyl.[1] These compounds are of especial interest to us in connection with a study of the relationships of structure to the mode of cleavage of diketones by alcohol,[2] water and hydrogen.[3] The present paper is essentially a presentation of experimental results concerning the preparation, alcoholysis and hydrogenolysis of these nitrogenous diketones.

TABLE I

PREPARATION, PROPERTIES AND ANALYSES OF NICOTINYL ACYL METHANES OR 1,3-DIKETONES $RC(O)CH_2C(O)C_5H_4N$ FROM ETHYL NICOTINATE AND VARIOUS METHYL KETONES

-Nicotinyl (—)- methane	R in $RC(O)CH_3$ is	Yield, %	Phys. constants B. p., °C.	Mm.	M. p. (corr.)	Molecular formula	% N_2 Calcd.	Found	Hydrochloride M. p. (corr.)	% Cl Calcd.	Found
(Acetyl)	Me	63	134–135	6	83.5	$C_9H_9O_2N$	8.59	8.62	154	17.77	17.55
(*n*-Valeryl)	*n*-Bu	46	165–168	8		$C_{12}H_{15}O_2N$	6.83	6.88	122	14.68	14.74
(Isovaleryl)	*i*-Bu	70	134–135	3	44	$C_{12}H_{15}O_2N$	6.83	6.85	128–129	14.68	14.69
(Trimethylacetyl)	*t*-Bu	42	135–136	5	44.5	$C_{12}H_{15}O_2N$	6.83	6.74	173	14.68	14.59
(*n*-Caproyl)	*n*-Amyl	47	150–152	2	29.5	$C_{13}H_{17}O_2N$	6.39	6.45	114	13.87	13.92
(Benzoyl)	Ph	70	198–200	3	121.5	$C_{14}H_{11}O_2N$	6.22	6.19	211	13.56	13.49
(*sym*-Trimethylbenzoyl)	*sym*-Mesityl	60	186–190	1	47.8	$C_{17}H_{17}O_2N$	5.24	5.44	218–219	11.68	11.74
(Nicotinyl)	3-Pyridyl	51			198	$C_{13}H_{10}O_2N_2$	12.39	12.36	240–241	23.72	23.74

Preparation of Diketones.—The nicotinyl acyl methanes were prepared by the condensation of ethyl nicotinate with a suitable monoketone in the presence of sodium ethoxide. The procedure is given in the experimental section and the yields, properties, etc., in Table I.

Eight attempted condensations were unsuccessful, *e. g.*, ethyl nicotinate and methyl tridecyl ketone or *p*-phenylacetophenone; ethyl laurate and methyl nicotinyl ketone or acetophenone, ethyl N-ethylnipecotate and acetone or acetophenone. Ethyl laurate condensed with itself and the nipecotates apparently underwent a similar type of reaction while the nicotinate was recovered unchanged.

Alcoholysis of Diketones.—In preliminary experiments the four possible products of the alcoholysis of nicotinylbenzoylmethane, and of nicotinyltrimethylacetylmethane were identified as being among the reaction products. Two analytical methods were developed and tested for estimating the proportion of the two competing reactions I and II. In the extraction method the basic ketone and ester were extracted

$$RC(O)CH_2C(O)C_5H_9N \begin{cases} \nearrow RC(O)CH_3 + C_5H_4NCO_2Et & \text{I} \\ \searrow RCO_2Et + CH_3C(O)C_5H_9N & \text{II} \end{cases}$$

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(1) Ferenczy, *Monatsh.*, **18**, 673 (1897).

(2) Beckham and Adkins, THIS JOURNAL, **56**, 2676 (1934).

(3) Sprague and Adkins, *ibid.*, **56**, 2669 (1934).