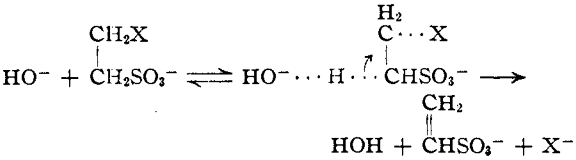
molecule. Hydroxide ions are attracted to this point and form the transition state by attracting an already activated hydrogen. In the next step the electron pair partially released in the first step shifts toward the other carbon (now most electrophilic) permitting the solvolytic ionization of the halogen and the formation of the olefin. The first reaction is rate controlling and is responsible for the measured energy of activation. This formulation is at present probably indistinguishable from the postulation that only one transition state is involved as shown.



$$\mathrm{HO^-} + \underset{\mathrm{CH_2SO_3^-}}{\overset{\mathrm{CH_2X}}{|}} \rightleftharpoons \mathrm{HO^-\cdots H\cdots} \underset{\mathrm{CHSO_3^-}}{\overset{\overset{\mathrm{H_2}}{\mathrm{C\cdots X}}}{|}} \longrightarrow \mathrm{HOH} + \underset{\mathrm{CHSO_3^-}}{\overset{\mathrm{CH_2}}{\|}} + \mathrm{X^-}$$

However, the complete independence of the energy of activation on the halogen present would seem to exclude the activation of the carbon–X bond in the transition state complex.

It is obvious that either variation of this mechanism would account for a bimolecular elimination reaction (points 1 and 2). Point 3 is explained, as already indicated, by the negative inductive effect of the sulfonate ion which facilitates the release of the proton to the hydroxide ion. It appears that this step which consumes all the energy of activation is consequently independent of the halogen present on the other carbon. The lower frequency factors (point 4) here observed would be expected if it were necessary for the transition state to be in a *trans* configuration as shown, for steric hindrance would make such a configuration less probable than in the other cases. Moreover, the greater attraction (inductive field effect) of bromine than chlorine for the sulfonate group may be responsible for the more frequent occurrence of the *trans* configuration in the bromo compound and hence the larger frequency factor.

Acknowledgment.—We wish to thank the Armstrong Cork Company of Lancaster, Pa., for their support in the investigation, and Dr. P. O. Powers and Professor C. C. Price for their helpful suggestions.

Summary

Rate measurements on the reaction of sodium 2-haloethanesulfonates with hydroxide ions in water medium at several temperatures show the reaction to be second order. The rate constants are given by the expressions:

$$k_{\mathrm{Cl}} = 1.26 \times 10^9 e^{-17400/RT}$$
$$k_{\mathrm{Br}} = 7.8 \times 10^9 e^{-17400/RT}$$

The nucleophilic elimination mechanism postulated accounts for the observed features of the reaction and the major differences between these reactions and the corresponding reactions of some alkyl halides.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY]

Aliphatic Diazo Compounds.[1] Investigation of α-Diazo-γ,γ,γ-triphenylpropane, in Relation to Molecular Rearrangements and Stability[2]

BY LESLIE HELLERMAN AND R. L. GARNER

Our interest in the aliphatic diazo series, and particularly the phenylated derivatives such as diazo-β,β,β-triphenylethane and α-diazo-γ,γ,γ-triphenylpropane, has centered in problems concerned with the relationship of their structure to stability and their relative tendency to undergo intramolecular rearrangements, as well as with the bearing of their properties upon the mechanism of the action of nitrous acid upon primary amines[1a] and the amino acids. We have described[1c] the thermal rearrangement of diazo-β,β,β-triphenylethane, $(C_6H_5)_3CCH(N_2)$, to yield triphenylethylene as the major product, with triphenylacetaldazine in small amount; and, the conditions under which the decomposition of this diazo compound yields, in the presence of certain organic acids, esters related to benzyldiphenylcarbinol, and in the presence of nitrogen trioxide, triphenylnitroethylene. There has been discussed the theory of these actions, and it has been shown that the decomposition of the nitrite of β,β,β-triphenylethylamine, yields rearrangement products analogous to those obtained from the above-named diazo compound derived from this amine.

In contrast, it now is demonstrated that the homolog, α-diazo-γ,γ,γ-triphenylpropane, $(C_6H_5)_3CCH_2CH(N_2)$, generally possesses greater "stability" than the diazoethane, and indeed many of the diazoalkanes that have been described, and shows little tendency to undergo rearrangements under conditions that invariably promote such reactions in the case of the more

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[1] Antecedent papers in this series: (a) Hellerman, Cohn and Hoen, THIS JOURNAL, **50**, 1716–1729 (1928); (b) Hellerman and Newman, *ibid.*, **54**, 2859 (1932), and (c) Hellerman and Garner, *ibid.*, **57**, 139–143 (1935).

[2] Submission of this paper for publication has been delayed for some years. We appreciate the courtesy of F. G. Cottrell, former Chief of the Fixed Nitrogen Investigations Unit, Bureau of Chemistry and Soils, and of the late Julius Stieglitz, former Director of the George Herbert Jones Chemical Laboratory, The University of Chicago, for the use of certain facilities in connection with a portion of this work.

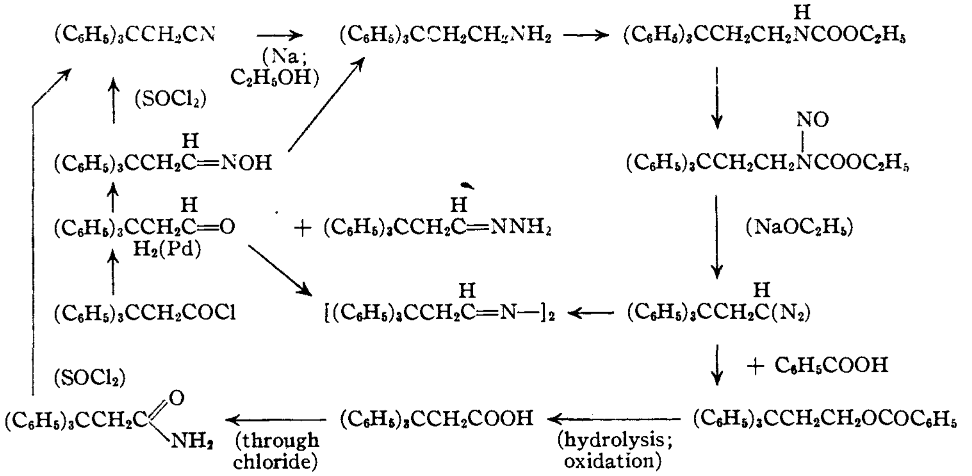
sensitive diazoethane. Under these conditions, α-diazo-γ,γ,γ-triphenylpropane was found indeed to decompose, but the products were characteristically those to be anticipated from intermolecular rather than intramolecular transformations. Unlike the lower homolog, α-diazo-γ,γ,γ-triphenylpropane afforded, on thermal decomposition, *principally* γ,γ,γ-triphenylpropionaldazine, and by the action in ether solution of benzoic and acetic acids, the *normal* esters, γ,γ,γ-triphenylpropyl benzoate and acetate, respectively. Furthermore the diazopropane reacted stoichiometrically with iodine.

This contrast in behavior lends added emphasis to the preference for stabilization through intramolecular changes in the configuration, $(\mathrm{R}{:})_3\mathrm{C}{:}\overset{\mathrm{H}}{\ddot{\mathrm{C}}}{:}$ or $(\mathrm{R}{:})_3\mathrm{C}{:}\overset{\mathrm{H}}{\ddot{\mathrm{C}}}{:}\mathrm{H}$, where the R groups are alkyl, or especially aryl, and the residues themselves represent transitorily existing decomposition intermediates.[3] Equally pointed is the suggestion from these observations, and from experiments to be cited in another paper, that the β,β,β-triphenylethyl group as a whole appears to possess the stability that would be anticipated if the electron-attracting phenyl groups were presumed to exert a significant deactivating influence upon the vicinal $-\mathrm{CH_2}-$ grouping in the diazopropane and structurally related compounds to be discussed elsewhere. This would imply a strengthening of certain bond linkages militating, for example, against the spontaneous rearrangement of the groups, $(\mathrm{C_6H_5}{:})_3\mathrm{C}{:}$ or $\mathrm{H}{:}$ to the terminal carbon atom with incomplete octet in a fragment, $(\mathrm{C_6H_5})_3\mathrm{C}{:}\underset{\mathrm{H}}{\overset{\mathrm{H}}{\ddot{\mathrm{C}}}}{:}\overset{\mathrm{H}}{\ddot{\mathrm{C}}}{:}$ or $(\mathrm{C_6H_5})_3\mathrm{C}{:}\underset{\mathrm{H}}{\overset{\mathrm{H}}{\ddot{\mathrm{C}}}}{:}\overset{\mathrm{H}}{\ddot{\mathrm{C}}}{:}\mathrm{H}$, if such were formed intermediately[3] on thermal or acidic decomposition of α-diazo-γ,γ,γ-triphenylpropane.

It is of some interest that the products obtained by decomposition of the latter diazo compound under certain conditions, resemble the materials obtained after thermal decomposition of the nitrite of γ,γ,γ-triphenylpropylamine. These are difficultly crystallizable, possible polymeric products.

The proof of non-rearrangement, *i. e.*, persistence of the carbon skeleton, in certain transformations involving α-diazo-γ,γ,γ-triphenylpropane, as well as of the identity of the diazo compound itself, has necessitated a considerable amount of synthetic work which is presented in the experimental part. Therein are treated also advances in certain of the preparative procedures.

The flow-sheet schematizes the interrelationships among most of the compounds described.



Experimental

Preparation of β,β,β-Triphenylpropionitrile,[4] $(\mathrm{C_6H_5})_3\mathrm{CCH_2CN}$.—β,β,β-Triphenylpropionamide,[5] 30 g., and pure thionyl chloride, 30 ml., were refluxed together for seven hours, moisture being excluded. The reaction melt was treated with crushed ice; the resulting solid was collected, triturated with dilute alkali, washed with water, and dried thoroughly in a vacuum. The product was extracted with a *little* hot 95% ethanol to remove a gummy impurity, after which it was crystallized fractionally from 95% ethanol, care being taken to work with concentrated solutions and to *avoid sharp cooling*. The recrystallized product consisted of white tablets, melting at 139.5-140°; yield 15 to 25 g. Some nitrile was recoverable from the filtrates. Yields were improved in preparations on a larger scale.

Anal. Calcd. for $\mathrm{C_{21}H_{17}N}$: N, 4.94. Found: N (Dumas), 5.08.

Formation of β,β,β-Triphenylpropionitrile from β,β,β-Triphenylpropionaldoxime (see below).—The importance of the nitrile as an intermediate in various syntheses

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[3] The theory is discussed briefly in ref. 1c.

[4] The preparation of this nitrile by the action of thionyl chloride and β,β,β-triphenylpropionamide, its reduction to γ,γ,γ-triphenylpropylamine, as well as the preparation of several derivatives of the amine were previously carried out by L. Hellerman and J. R. Sudzuki (unpublished, Sudzuki, Masters Dissertation, The University of Chicago Libraries, 1928). Their directions are reproduced and expanded here for the sake of completion. β,β,β-Triphenylpropionitrile, prepared both from triphenylpropionamide and triphenylpropionaldoxime and completely characterized by Hellerman and Sudzuki and the present authors, evidently is identical with the compound "A" described by Fosse, *Compt. rend.*, **145**, 198 (1907); *cf.* Fosse, *Bull. Soc. Chim.*, [4] **49**, 159 (1931). This nitrile was prepared also by Bergmann and Wolff, *Ber.*, **63**, 1176 (1930).

[5] Hellerman, THIS JOURNAL, **49**, 1738 (1927).

required its characterization[4] by preparation through an independent method.

When 0.15 g. of β,β,β-triphenylpropionaldoxime was refluxed with 2 ml. of thionyl chloride for one hour, and the mixture poured upon ice, there was obtained a yellow-brown solid which was crystallized from ethanol, m. p. 140°, melting point of a mixture with β,β,β-triphenylpropionitrile prepared from β,β,β-triphenylpropionamide, 140°.

Stability of β,β,β-Triphenylpropionitrile toward Oxidation: Hydrolysis of the Nitrile.—Some of the nitrile was heated for several hours with glacial acetic acid and chromic anhydride, at the boiling point, after which the mixture was treated with water and the product collected, dried and crystallized from ethanol. The product was identified as unchanged nitrile.

After a portion of the nitrile was refluxed for fourteen hours in an ethanolic potassium hydroxide solution (40%), there was recovered, in addition to unchanged nitrile, a small amount of β,β,β-triphenylpropionamide, m. p. 192°, which was identified by comparison with an authentic sample.[5] Separation of the amide and parent nitrile was effected by fractional crystallization from ethanol, the nitrile being the slightly more soluble compound.

Preparation of γ,γ,γ-Triphenylpropylamine and its Hydrochloride, $(C_6H_5)_3CCH_2CH_2NH_3Cl$.—To β,β,β-triphenylpropionitrile, 15 g., dissolved in 150 ml. of absolute ethanol (under reflux, protected from moisture) was added in several large portions 16.5 g. of clean sodium The reaction was permitted to proceed briskly; for its completion, the mixture was heated on a water-bath until all of the sodium had dissolved. A little ethanol was added and the solution was diluted somewhat with water. Concentrated hydrochloric acid was added until the mixture was strongly acid. Most of the ethanol then was removed in a vacuum leaving suspended in the residual aqueous solution the amine hydrochloride; this was collected, dried and crystallized from absolute ethanol and ether; yield 17 g.; dec. pt. 248–249°, in a bath preheated to 240°.

Anal. Calcd. for $C_{21}H_{22}NCl$: N, 4.32. Found: N (Dumas), 4.21.

When the hydrochloride was dissolved in hot water and an excess of concentrated ammonium hydroxide added, a white solid precipitated. This was collected, washed with water and dried on a porous plate, m. p. 96°, m. p. of the product crystallized from ligroin, 96°.

Anal. Calcd. for $C_{21}H_{21}N$: N, 4.88. Found: N (Dumas), 5.06.

After the amine was permitted to stand in a desiccator over phosphoric anhydride for several days the melting point was found to be 65°. However, a mixture of this material with freshly prepared amine was found to melt at 94–96°. When the lower-melting modification was dissolved in hydrochloric acid and reprecipitated with ammonia, the product melted at 94–96°.

Formation of γ,γ,γ-Triphenylpropylamine from β,β,β-Triphenylpropionaldoxime (see below).—After this oxime was reduced with sodium similarly to the procedure outlined above there was isolated a product found to be identical with γ,γ,γ-triphenylpropylamine hydrochloride previously prepared from β,β,β-triphenylpropionitrile The amine derived from this preparation exhibited the peculiar melting point behavior described in the foregoing, and was identical in all respects with the amine previously prepared.

γ,γ,γ-Triphenylpropylammonium Chloroplatinate.—The chloroplatinate precipitated in orange crystals when a small excess of chloroplatinic acid was added to a cold, concentrated solution of γ,γ,γ-triphenylpropylamine hydrochloride in absolute ethanol. The salt was collected and washed with cold ethanol until the filtrate was colorless, after which it was dried to a constant weight in a vacuum desiccator.

Anal. Calcd. for $C_{42}H_{44}N_2PtCl_6$: Pt, 19.8. Found: Pt, 19.5.

γ,γ,γ-Triphenylpropylammonium Nitrate.—Colorless crystals of the nitrate precipitated when to a solution of 1 g. of γ,γ,γ-triphenylpropylamine hydrochloride in 200 cc. of water was added an excess of dilute nitric acid. The product was collected, washed with ice-cold water, and dried over phosphoric anhydride. The nitrate is only slightly soluble in water; it decomposed at 193–196° in a bath preheated to 190°.

Anal. Calcd. for $C_{21}H_{22}O_3N_2$: N, 8.0. Found: N (Dumas), 7.7.

γ,γ,γ-Triphenylpropylammonium Nitrite.—The hydrochloride,[6] 1 g., dissolved in 200 ml. of water, was treated with a small excess of a concentrated solution of sodium nitrite. A white precipitate formed, was collected, washed with iced water until chloride ion was removed, and dried over phosphoric anhydride; practically insoluble in water, dec. pt. 118–119°.

Anal. Calcd. for $C_{21}H_{22}O_2N_2$: N, 8.4. Found: N (Dumas), 8.0.

Ethyl N-γ,γ,γ-Triphenylpropyl Carbamate, $(C_6H_5)_3CCH_2CH_2NHCOOC_2H_5$. — γ,γ,γ-Triphenylpropylamine hydrochloride, 20 g., in an aqueous suspension, was shaken with 9 g. of ethylchlorocarbonate and 10 g. of sodium carbonate. The product was maintained in a finely-divided form by means of several triturations in a mortar. The solid product was collected, washed with warm hydrochloric acid to *remove traces of amine*, with water until free from acid, and dried over phosphoric anhydride. It was recrystallized from a mixture of 20 parts ligroin (b. p. 60–90°) and one part of chloroform; yield, practically quantitative; m. p. 126°.

Anal. Calcd. for $C_{24}H_{25}NO_2$: C, 80.2, H, 7.0; N, 3.9; mol. wt., 359.2. Found: C, 80.2; H, 7.1; N (Dumas), 4.0; mol. wt. (Rast),[7] 357.

Preparation of Ethyl N-Nitroso-N-γ,γ,γ-triphenylpropyl Carbamate, $(C_6H_5)_3CCH_2CH_2N(NO)COOC_2H_5$.—Pure ethyl N-γ,γ,γ-triphenylpropyl carbamate, 15 g., was placed in a three-necked flask fitted with an oil-sealed stirrer and appropriate inlet and outlet tubes, and protected from moisture. Anhydrous (freshly heated) sodium sulfate, 15 g., and 250 ml. of dry ether were added and the flask cooled in an ice–salt-bath. The gases prepared by the action of 80% sulfuric acid upon sodium nitrite and dried by passage through two towers of calcium chloride were conducted into the vigorously stirred solution. When the mixture had become deep green [one hour], sodium sulfate was removed by filtration, and the filtrate concentrated in a stream of dry air. A pale yellow, glistening nitroso-urethan crystallized. When one-third of the original volume of ether remained, the product was collected, washed with a little cold ether and dried in a vacuum desiccator containing beakers of phosphorus pentoxide, chipped paraffin and sodium hydroxide; it thus was obtained directly in a pure state. Any nitroso-urethane admixed with residual sodium sulfate (see above) was recovered by dissolving the salt in warm water, and promptly collecting and drying the residue. The yield was 9.7 g.; dec. pt. 120–120.5° (cor.), when the bath was preheated to 110°.

Anal. Calcd. for $C_{24}H_{24}N_2O_3$: N, 7.2. Found: N (Dumas), 7.3.

Preparation of α-Diazo-γ,γ,γ-triphenylpropane, $(C_6H_5)_3CCH_2CH(N_2)$.—To 7.1 g. of ethyl N-nitroso-N-γ,γ,γ-triphenylpropylcarbamate dissolved in 100 ml. dry ether, contained in a small flask protected from moisture and cooled in an ice–salt-bath, was added a solution of sodium ethylate prepared from 0.7 g. of pure sodium and 12 cc. of absolute ethanol. After several hours during which the solution had deepened in color, the solvent was evaporated in a stream of dry air. Concentration was carried out at 0°; complete drying of the residue was accomplished when the flask and contents were allowed to stand for twelve hours in a vacuum desiccator charged with paraffin and phosphoric anhydride. The crude product was triturated

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(6) *Cf.* Hellerman, Cohn and Hoen, This Journal, **50**, 1716 (1928).

(7) Molecular weight determination by Robert Broh-Kahn.

with ice cold water, collected, washed with ice water, and dried over phosphorus pentoxide; yield of nearly pure diazo compound, 5.3 g. Purification was effected by means of recrystallization from ether with the aid of an alcohol–carbon dioxide bath, the product being obtained as orange-yellow, elongated plates which decomposed at 105.5–106° (cor.) in a bath preheated to 100°. The pure, dry substance was stable at 0° for many months, and decomposed only slowly at room temperature.

Anal. Calcd. for $C_{21}H_{18}N_2$: N, 9.4. Found: N (Dumas), 9.4; N(diazo),[10] 9.2, 9.0.

Titration with Standard Iodine (in chloroform).—The diazo compound in chloroform solution was titrated with iodine in chloroform; a faint pink end-point developed as the evolution of nitrogen ceased.

Diazo compound, 1.2728 g., required 53.75 ml. of iodine–chloroform solution (1.00 ml. ≈ 0.0205 g. iodine), corresponding to 1.2730 g. on the basis of mole for mole equivalence.

Decomposition of α-Diazo-γ,γ,γ-triphenylpropane

No decomposition was observed during storage of the substance at 10° for six months. However, there occurred gradual decomposition of a sample exposed to the atmosphere of the laboratory. The only definite product isolated was identified as β,β,β-triphenylpropionaldazine (described below).[8]

When powdered copper was added to an ether solution of the diazo compound, a slow decomposition took place. Evaporation of the ether yielded a gummy product and some β,β,β-triphenylpropionaldazine, m. p. 187°, and unchanged by admixture with an authentic sample.

Thermal Decomposition of α-Diazo-γ,γ,γ-triphenylpropane in Aqueous Suspension: β,β,β-Triphenylpropionaldazine, $[(C_6H_5)_3CCH_2CH{=}N{-}]_2$.—When a suspension of 1 g. of the diazo compound in 50 ml. of water was heated, rapid decomposition took place at approximately 85°. The reaction was completed at 100° until evolution of nitrogen had ceased. The mixture was cooled, and the reaction product, a brittle "glass" was removed, pulverized and dried; weight 0.88 g. It was treated repeatedly with boiling ether in which it was only slightly soluble, after which the white residue was recrystallized from benzene; the m. p. rose from 170 to 184°. The product did not depress the melting point of β,β,β-triphenylpropionaldazine, prepared from triphenylpropionaldehyde by the method to be outlined presently, and it did depress the melting points of other similar aldazines.

Anal. Calcd. for $C_{42}H_{36}N_2$: N, 4.9. Found: N (Dumas), 5.1.

Decomposition of α-Diazo-γ,γ,γ-triphenylpropane in the Presence of Acids

With Acetic Acid: Formation of γ,γ,γ-Triphenylpropyl Acetate, $(C_6H_5)_3CCH_2CH_2OCOCH_3$.—When α-diazo-γ,γ,γ-triphenylpropane, 1.5 g., was treated with 2.5 ml. of glacial acetic acid a violent reaction resulted. From the reaction mixture excess acetic acid was removed in a vacuum desiccator charged with flaked sodium hydroxide. The product was washed with petroleum ether and the residual solid recrystallized from isopropyl ether; yield 0.48 g.; m. p. 118° (cor.).[9]

Anal. Calcd. for $C_{23}H_{22}O_2$: C, 83.7; H, 6.7; mol. wt., 330.2. Found: C, 84.1, 84.3; H, 7.0, 7.0; mol. wt. (Rast), 320.

From the washings of crude product a gum was obtained which appeared to be similar to the material obtained from the experiments with formic acid and sulfuric acid described below.

Similar results were obtained when the diazo compound in ether solution was treated with acetic acid.

With Benzoic Acid: Formation of γ,γ,γ-Triphenylpropyl Benzoate, $(C_6H_5)_3CCH_2CH_2OCOC_6H_5$.—When 3.0 g. of α-diazo-γ,γ,γ-triphenylpropane in ether solution (100 ml.) was treated with 3.4 g. of benzoic acid dissolved in 50 ml. of ether, there resulted a vigorous evolution of nitrogen. The ether solution of reaction products was washed with sodium carbonate solution, and with water, after which it was dried with anhydrous sodium sulfate, and concentrated in a stream of dry air. The resulting solid was recrystallized from methyl ethyl ketone; m. p. 138–138.5° (cor.).

Anal. Calcd. for $C_{28}H_{24}O_2$: C, 85.67; H, 6.17. Found: C, 85.60, 85.65; H, 6.32, 6.35.

The structure was verified as follows: some of the product was added to a methanolic potassium hydroxide solution (15%) and the mixture refluxed for two hours. The solvent was removed, and the residue washed with water and then treated with ether. The aqueous washings were acidified, yielding benzoic acid. From the ether solution triphenylpropanol was obtained by removal of the solvent and oxidized as follows. Of the solid alcohol, 0.3 g. was treated with 5.0 ml. of acetic acid and 0.15 g. of chromic anhydride. The mixture was heated for half an hour at 100°. The green solution was treated with 25 ml. of water, cooled, and neutralized by the addition of concentrated potassium hydroxide. When hydrochloric acid was added cautiously, there was obtained a precipitate which was collected, washed with water and dried; yield more than 0.2 g.; m. p. 175°. The acid was recrystallized from ethanol; m. p. 180°, and melting point of a mixture with authentic β,β,β-triphenylpropionic acid,[5] 180°.

With Sulfuric or Formic Acid.—Treatment of the diazo compound with hot 25% sulfuric acid or with 90% formic acid, yielded a dark resinous gum from which no definite pure product has been obtained. The products resembled those obtained when γ,γ,γ-triphenylpropylammonium nitrite was decomposed thermally or when the parent amine was treated with nitrous anhydride. The materials were almost nitrogen free and probably contained polymerization products. The product from sulfuric acid treatment was sulfur-free. The gums could be fractionated partially by treatment with ethanol; they "solidified" when dried intensively. Analysis of one of the less soluble fractions gave the following figures: C, 80.6; H, 6.8; N, 1.5. The more soluble fraction had the composition: C, 88.4, 88.5; H, 6.4, 6.4. For comparison, the calculated values for triphenylpropanol, $C_{21}H_{20}O$, which was sought and not found in these products is: C, 88.1; H, 6.3. The analyses indicate obvious possibilities regarding the structure of polymeric products, but the absence of supplementary data renders speculation unprofitable.

β,β,β-Triphenylpropionaldehyde and Derivatives

Preparation of β,β,β-Triphenylpropionaldehyde, $(C_6H_5)_3CCH_2CHO$.—This aldehyde was synthesized by the catalytic reduction of triphenylpropionyl chloride[5] with hydrogen. The catalyst[10] used was prepared as follows. Freshly precipitated barium sulfate, 20 g., was washed, and suspended in 150 cc. of water. Palladium chloride, 0.5 g., was added and the mixture heated to boiling. A solution of 10 g. of sodium carbonate in 200 cc. of water was added slowly and the suspension was boiled gently for ten minutes. The light brown solid was collected and washed sparingly with water until the filtrate gave no test for chloride ion. The catalyst was dried in a vacuum desiccator.

Triphenylpropionyl chloride,[5] 20 g., was placed in a two-necked round-bottomed flask, fitted with an appropriate hydrogen inlet tube reaching to the bottom of the flask, and with a reflux condenser protected with a calcium chloride tube. Catalyst, 12 g., and 100 ml. of sodium-dried xylene were added and the cork fittings of the flasks carefully sealed. The mixture was heated to the boiling point in an oil-bath, and hydrogen gas (washed with alkaline permanganate and with sulfuric acid and passed through

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[8] Triphenylacetaldazine was erroneously designated β,β,β-triphenylacetaldazine in ref. 1c.

[9] Wooster, Segool and Allan, Jr., THIS JOURNAL, **60**, 1666 (1938), record m. p. 114–115° for γ,γ,γ-triphenylpropyl acetate, prepared by another method.

[10] German Patent 256,500; Busche and Stove, *Ber.*, **49**, 1064 (1916).

calcium chloride) was passed in for four hours. After filtration from the catalyst, the xylene was distilled in a vacuum; the residual product was obtained in the form of a pale yellow oil which solidified when stirred. The aldehyde, washed with a little low-boiling petroleum ether, was obtained in the form of fine, white needles melting at 101°; yield 16.5 g. When the product was recrystallized from methyl alcohol, the melting point was unchanged. The compound is soluble in most of the organic solvents; recrystallization from alcohol is wasteful. The product gave a positive aldehyde test with Schiff reagent. It was further characterized by analysis and preparation of the oxime and hydrazone.

Anal. Calcd. for $C_{21}H_{18}O$: C, 88.1; H, 6.3. Found: C, 87.9; H, 6.4.

β,β,β-Triphenylpropionaldoxime.—Triphenylpropionaldehyde, 5 g., hydroxylamine hydrochloride, 4 g., and sodium bicarbonate, 5 g., were added to 50 ml. of 95% alcohol and 8 ml. of water and the mixture was refluxed. After an hour the hot solution was filtered and diluted with boiling water to faint turbidity. A white crystalline precipitate formed, which was collected, washed with warm water and dried in a vacuum desiccator; yield 4.6 g., recrystallized from ethanol, m. p., 190.5–191° (cor.).

Anal. Calcd. for $C_{21}H_{19}NO$: N, 4.64. Found: N (Dumas), 4.75.

Triphenylpropionaldehyde Hydrazone.—A mixture of 5.7 g. of triphenylpropionaldehyde, 5 g. of recently fused and powdered barium oxide, 6 g. of hydrazine hydrate (90%) and 25 ml. of absolute ethanol was refluxed for ten hours. The alcohol was removed by distillation in a vacuum. The residue was extracted with ether and the latter evaporated in a stream of dry air. A white crystalline solid remained; yield 4.2 g. The hydrazone was found to be soluble in the usual organic solvents. It was best purified by means of fractional crystallization from ether; m. p., 92°.

Anal. Calcd. for $C_{21}H_{20}N_2$: N, 9.3. Found: N (Dumas), 9.4.

When the hydrazone in benzene solution at 5° was shaken with yellow mercuric oxide for several hours, there resulted, after filtration and removal of the solvent, a pale yellow oil which solidified gradually. The product was extracted with ether and a small amount of white, insoluble material remained; m. p. 189–192°. This was identified as triphenylpropionaldazine by comparison with an authentic sample of the latter. The crude reaction products from this and other similar experiments were found by test to contain no diazo compound. No definite product other than the aldazine was isolated.

Synthesis of β,β,β-Triphenylpropionaldazine.—When β,β,β-triphenylpropionaldehyde hydrazone, 0.45 g., and triphenylpropionaldehyde, 0.43 g., were refluxed in ether solution for an hour, a white solid precipitated from the solution. This was collected, washed thoroughly with boiling ether, and dried; m. p. 190–191°.

Anal. Calcd. for $C_{42}H_{36}N_2$: N, 4.9. Found: N (Dumas), 5.1.

Summary

Decompositions of α-diazo-γ,γ,γ-triphenylpropane are found to result in the formation of products to be anticipated from intermolecular rather than intramolecular transformations. This is in contrast to the behavior of the lower homolog, diazo-β,β,β-triphenylethane. The thermal decomposition of the diazopropane yields, principally, β,β,β-triphenylpropionaldehyde azine, and its decomposition in the presence of acetic or benzoic acid gives, respectively, γ,γ,γ-triphenylpropyl acetate or benzoate. It is recognized that some of the evidence may not exclude absolutely the possibility of intramolecular rearrangement but none of the observations appears definitely to support such a conclusion. Reference is made to structural factors affecting the stability of certain compounds containing the β,β,β-triphenylethyl group.

There is described a feasible method for the preparation of β,β,β-triphenylpropionitrile; there are presented syntheses of γ,γ,γ-triphenylpropylamine its hydrochloride, chloroplatinate, nitrate and nitrite; of ethyl N-γ,γ,γ-triphenylpropyl carbamate, the corresponding crystalline nitrosocarbamate, and α-diazo-γ,γ,γ-triphenylpropane; and of β,β,β-triphenylpropionaldehyde, its oxime, hydrazone and azine. Evidence is cited for the persistence of the carbon skeleton in certain transformations involving the diazo compound.

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The Action of Grignard Reagents upon β,β,β-Triphenylpropionitrile. Stability of the Triphenylethyl Grouping[1]

BY R. L. GARNER AND LESLIE HELLERMAN

The properties of certain compounds containing as a substituent the β,β,β-triphenylethyl grouping afford presumptive evidence regarding a rather remarkable degree of stability or non-reactivity in this configuration. The pertinent observations are considered to be related to the inductive effect of the unsymmetrically substituted, electron-attracting phenyl groups, connoting a significant degree of "deactivation"[2] in the methylene grouping vicinal to the triphenylmethyl group. Cumulative evidence includes (1) certain reactions of α-diazo-γ,γ,γ-triphenylpropane, leading to non-rearranged products of its decomposition[2]; and (2) marked resistance to the action of powerful oxidizing reagents (*e. g.*, hot chromic acid) of α,α,α-triphenylethane, β,β,β-triphenylpropionic acid and β,β,β-triphenylpropionitrile.[3] In addition, β,β,β-triphenylethylamine is much less readily attacked by oxidizing reagents under various conditions[4] than are such amines as benzylamine and benzohydrylamine.[5] Most convincing, however, are the clear-cut observations recorded

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[1] Submission of this paper has been delayed for some years; compare ref. 2.

[2] Hellerman and Garner, THIS JOURNAL, **68**, 819 (1946).

[3] Ref. 2, p. 819; Kuntze-Fechner, *Ber.*, **36**, 473 (1903).

[4] Hellerman, THIS JOURNAL, **68**, 825 (1946).

[5] Hellerman and Sanders, *ibid.*, **59**, 1742 (1927).