

The subject will be continued, and it is hoped that perhaps larger quantities of tetraphenylmethane will be obtained by the action of triphenyliodomethane upon mercury-diphenyl.

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HYDRAZO- AND AZO-DERIVATIVES OF TRIPHENYL-METHANE.¹

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ONE of us has recently² described a method by which small quantities of tetraphenylmethane were obtained. The method involved the synthesis of triphenylmethaneazobenzene, which was obtained by the oxidation of the corresponding hydrazo-derivative. The azo-body, on being heated to 110°–120° C., loses nitrogen, and furnishes, among other products, tetraphenylmethane.

The present work was undertaken with the hope of obtaining substitution derivatives of tetraphenylmethane, by subjecting substituted azo-compounds of triphenylmethane to the same treatment as the simple azo-compound itself. For the present, we shall only give a description of the hydrazo- and azo-bodies, which have been prepared by us in connection with this work.

The number of mixed azo-bodies, *i. e.*, those containing an aliphatic and an aromatic radical, is quite limited. A few have been prepared by E. Fischer and Ehrhard,³ and Tafel⁴ by the oxidation of the corresponding hydrazo-derivatives. The principal method of preparation is, however, by combining aromatic diazo-salts with aliphatic compounds. This reaction, first worked out by V. Meyer⁵ on nitroethane, has since been extended to a large number of such aliphatic compounds, as contain a (CH₂)-group linked to some negative groups. Nitro-compounds, malonic ester, aceto-acetic ester, etc., give such bodies. The constitution of all these so-called azo-bodies has, however, recently been called into question by the work of Japp

¹ Read at the Boston meeting of the American Chemical Society, August, 1898.

² *Ber. d. chem. Ges.*, 30, 2043; *This Journal*, 20, 773.

³ *Ann. Chem. (Liebig)*, 199, 328, 1879; *Ber. d. chem. Ges.*, 29, 793, 1896.

⁴ *Ber. d. chem. Ges.*, 18, 1742, 1885.

⁵ *Ber. d. chem. Ges.*, 8, 751, 1875; 18, 1742, 1885.

and Klingmann,¹ and others,² who have shown, for many compounds, the identity of the azo-formula, $R.N : N.CH$, with that of the hydrazo-formula, $R.NHN : C$. This has opened the question, as to whether all the mixed azo-compounds, obtained by the above reaction, are not after all hydrazones. An intramolecular change of this nature can, of course, take place only in such compounds as contain a (CH)- or (CH₂)-group. If this view be correct, then the number of mixed azo-bodies is indeed very small. The phenylazoisovaleric acid of Prentice³ might be mentioned in this connection as being a true mixed azo-compound.

We have found that the reaction of phenylhydrazine with triphenylbrommethane is of general application. All hydrazines, so far as tried, react very readily with this bromine compound, and give hydrazo-bodies, which furnish, on oxidation, with more or less readiness, the desired azo-derivatives. The following hydrazines have been tried: Paratoluyldiazine, orthonitrophenylhydrazine, metanitrophenylhydrazine, paranitrophenylhydrazine, metachlorophenylhydrazine, parachlorophenylhydrazine, metabromphenylhydrazine, and α -naphthylhydrazine.

These hydrazo-bodies are well crystallized; they are colorless, with the exception of those containing the nitro-group, which are colored yellow to reddish-brown. They are soluble in benzene, chloroform, less soluble in ether and alcohol, and very sparingly soluble in ligroïn. They oxidize very readily on exposure to the air, thus resembling more the aromatic than the purely fatty hydrazo-bodies. They are weak bases and form salts with dry hydrochloric, oxalic, picric, and other acids.

The azo-derivatives are also well crystallized compounds, colored from yellow to orange. They are very soluble in benzene and chloroform, less soluble in ether, alcohol, and acetic acid, and only sparingly soluble in ligroïn. They all give off their

¹ *Ber. d. chem. Ges.*, 20, 3398, 1887; *Ann. Chem.* (Liebig), 247, 190.

² R. Meyer: *Ber. d. chem. Ges.*, 21, 118, 1888; 24, 1241, 1891; V. Meyer, 1888: *Ber. d. chem. Ges.*, 21, 11; Baeyer and Claisen: *Ibid.*, 1697; 25, 746, 1892; v. Fehmann, 1892: *Ber. d. chem. Ges.*, 25, 3190.

³ *Ann. Chem.* (Liebig), 292, 272.

nitrogen on being heated, thus resembling the simple triphenylmethaneazobenzene. The liberation of nitrogen is quantitative, and takes place at temperatures ranging from 103.5° to 118.5° C. The relative position of the chlorine or the nitro-group seems to exert no particular influence upon the temperature at which the azo-body decomposes.

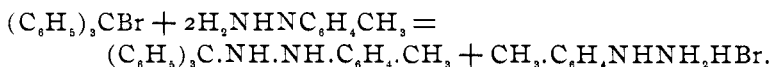
Molecular weight determinations show them to be monomolecular.

When dissolved in chloroform and treated with bromine, they form crystalline perbromides. These have not yet been analyzed.

EXPERIMENTAL PART.

ACTION OF PARATOLUYLHYDRAZINE.

Triphenylmethanehydrazoparatoluene, $(C_6H_5)_3C.NH.NH.C_6H_4.CH_3$.—Paratoluyllhydrazine¹ (two molecules) was dissolved in dry ether and slowly added, with stirring, to a cold ethereal solution of triphenylbrommethane (one molecule). The solution was allowed to stand protected from the air until the precipitate of toluylhydrazine hydrobromide separated out. The reaction is represented by the following equation :



Upon filtering off the precipitate of toluylhydrazine hydrobromide and concentrating the ethereal solution, white crystals of the hydrazo-body were obtained. They were recrystallized from ether and analyzed with the following results :

0.212 gram gave 15 cc. nitrogen at 20° and 736.6 mm.

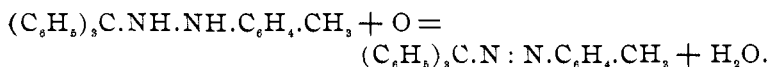
	Calculated for $C_{26}H_{27}N_2$.	Found.
N	7.69	8.02

This hydrazo-derivative is readily oxidized on exposure to the air, especially in an alcoholic solution. It is a weak base, forming salts with dry hydrochloric, oxalic, picric, and other acids. It is soluble in benzene, chloroform, less soluble in alcohol and ether, and insoluble in water and ligroin. It melts with decomposition at 157° C.

Triphenylmethaneazoparatoluene, $(C_6H_5)_3C.N:N.C_6H_4.CH_3$.—After trying numerous oxidizing agents, such as potassium per-

¹ E. Fischer, 1876: *Ber. d. chem. Ges.*, 9, 890.

manganate, ferric chloride, mercuric oxide, and amyl nitrite, the last named reagent was found to give the best results.¹ The hydrazo-body was suspended in ether and the calculated quantity of amyl nitrite added. A drop of acetyl chloride was sufficient to start the action. The hydrazo-body was gradually changed to the azo, which dissolving in the ether produced a deep yellow solution. Upon concentration, long yellow needles of the azo-compound separated. The reaction is as follows:



Recrystallized from methyl alcohol the compound gave the following results upon analysis:

0.1505 gram gave 0.4725 gram carbon dioxide + 0.083 gram of water.

0.263 gram gave 18 cc. nitrogen at 21° and 731.5 mm. when heated to 150° C.

	Calculated for $C_{26}H_{22}N_2$.	Found.
C.....	86.18	85.79
H.....	6.07	6.15
N.....	7.73	7.70

The molecular weight determination furnished the following results:

Triphenylmethaneazoparatoluene, $C_{26}H_{22}N_2 = 362$.

Solvent: Benzene.

Grams solvent.	Grams substance.	Observed depression.	Molecular weight found.
18.589	0.4563	0.42°	292

The azo-compound is soluble in benzene, chloroform, ether, less soluble in alcohol, and only sparingly soluble in ligroin. It melts at 103.5° C. with evolution of nitrogen. An attempt has been made to determine the products of decomposition. The substance was mixed with copper-bronze, to facilitate decomposition, and heated to 120° C. The reaction which took place was apparently a complicated one, and as yet satisfactory results have not been obtained.

ACTION OF NITROHYDRAZINES.

Triphenylmethanehydrazoorthonitrobenzene, $(C_6H_5)_3C.NH.NH.-$

¹ Recent experiments show that nitrous acid gas, passed into an ethereal solution of the hydrazo-derivatives of triphenylmethane, gives the best results in oxidizing them to the corresponding azo-compounds. This Journal, 20, 775.

$C_6H_4NO_2(o)$.—Orthonitrophenylhydrazine¹ was allowed to react with triphenylbrommethane under conditions similar to those in the preparation of triphenylmethanehydrazoparatoluene. Upon concentrating the ethereal solution brownish crystals of triphenylmethanehydrazoorthonitrobenzene separated. The yield is quantitative. Recrystallized from ether it was analyzed with results as follows :

0.1816 gram gave 17.4 cc. nitrogen at 22.5° and 741.7 mm.

	Calculated for $C_{25}H_{21}N_3O_2$.	Found.
N	10.63	10.86

This hydrazo-compound is soluble in benzene, chloroform, less soluble in ether and alcohol, and is insoluble in ligroïn. It forms salts with dry acids, melting-point 168° C. It oxidizes partially to the azo-compound on exposure to the air.

Triphenylmethaneazoorthonitrobenzene, $(C_6H_5)_3C.N:N.C_6H_4NO_2(o)$.—This compound is prepared from the corresponding hydrazo-body by oxidation with amyl nitrite or nitrous acid gas in an ethereal solution. Recrystallized from methyl alcohol it is obtained in bright canary-yellow needles, perfectly pure.

0.261 gram gave 0.7273 gram carbon dioxide + 0.1201 gram of water.

0.1437 gram gave 13.5 cc. nitrogen at 22° and 739 mm.

	Calculated for $C_{25}H_{19}N_3O_2$.	Found.
C	76.33	75.98
H	4.83	5.11
N	10.67	10.62

The compound is soluble in benzene, chloroform, ether, less soluble in alcohol, and sparingly soluble in ligroïn. Melting-point 116° C. It forms a crystalline perbromide.

Molecular weight determination :

Triphenylmethaneazonitrobenzene, $C_{25}H_{19}N_3O_2 = 393$.

Solvent: Benzene.

Grams solvent.	Grams substance.	Observed depression.	Molecular weight found.
18 598	0.6245	0.49°	338

Triphenylmethanehydrazometanitrobenzene, $(C_6H_5)_3C.NH.NH.C_6H_4NO_2(m)$.—Metanitrophenylhydrazine² is treated with triphenylbrommethane, as in the case of the corresponding ortho-

¹ Bischler, 1889 : *Ber. d. chem. Ges.*, 22, 2801.

² Bischler and Brodsky, 1889 : *Ber. d. chem. Ges.*, 22, 2809.

body. The hydrazo-compound crystallizes out on concentrating the solution in reddish-brown crystals. Recrystallized from ether it gave the following results:

0.2374 gram gave 0.6528 gram carbon dioxide + 0.1151 gram of water.

0.2342 gram gave 22.6 cc. nitrogen at 22° and 741.7 mm.

	Calculated for $C_{25}H_{21}N_3O_2$.	Found.
C	75.37	75.11
H	5.28	5.34
N	10.63	10.96

The body is soluble in benzene, chloroform, less soluble in ether and alcohol, and very sparingly soluble in ligroïn, melting-point 165° C. Yield quantitative.

Triphenylmethaneazometanitrobenzene, $(C_6H_5)_3C.N:N.C_6H_4NO_2$ -*(m)*, is prepared by oxidation of the corresponding hydrazo-body. Recrystallized from methyl alcohol it forms canary-yellow needles.

0.2535 gram gave 22.5 cc. nitrogen at 23.5° and 734 mm.

	Calculated for $C_{25}H_{19}N_3O_2$.	Found.
N	10.67	9.98

The azo-compound is soluble in ether, benzene, less soluble in alcohol, and sparingly soluble in ligroïn, melting-point 111°-112° C. It forms a crystalline perbromide.

Triphenylmethaneazonitrobenzene, $C_{25}H_{19}N_3O_2 = 393$.

Solvent: Benzene.

Grams solvent.	Grams substance.	Observed depression.	Molecular weight found.
16.874	0.556	0.46°	361

Triphenylmethanehydrazoparanitrobenzene, $(C_6H_5)_3C.NH.NH.C_6H_4NO_2$ (*p*).—Paranitrophenylhydrazine¹ was allowed to act on triphenylbrommethane as in previous instances. The ethereal solution was evaporated nearly to dryness, when the hydrazo body crystallized in large reddish needles. Yield almost quantitative. Recrystallized from ether it gave the following figures:

0.2163 gram gave 21.8 cc. nitrogen at 22° and 730 mm.

	Calculated for $C_{25}H_{21}N_3O_2$.	Found.
N	10.63	11.15

Triphenylmethanehydrazoparanitrobenzene is very soluble in

¹ *Ber. d. chem. Ges.* 25, 119, Ref.

benzene, chloroform and ether, less soluble in alcohol, and sparingly soluble in ligroin. Melting-point 170° C. It is a weak base and forms salts with dry acids.

Triphenylmethaneazoparanitrobenzene, $(C_6H_5)_3C.N:N.C_6H_4NO_2$ -*(p)*.—This body results from the oxidation of the corresponding hydrazo-compound with amyl nitrite or nitrous acid gas, and crystallizes from methyl alcohol in large reddish needles. It was analyzed with the following results :

0.1763 gram gave 17 cc. nitrogen at 24° and 736.4 mm.	Calculated for $C_{26}H_{18}N_2O_2$.	Found.
N.....	10.67	10.76

The compound is very soluble in benzene, chloroform, ether, less soluble in alcohol, and very sparingly in ligroin. Melting-point 118.5° C. The determination of the molecular weight shows it to be monomolecular.

Triphenylmethaneazonitrobenzene, $C_{26}H_{18}N_2O_2 = 393$.

Solvent : Benzene.

Grams solvent.	Grams substance.	Observed depression	Molecular weight found.
16.698	1.0965	0.855°	381

ACTION OF CHLORHYDRAZINES.

Metachlorphenylhydrazine, $ClC_6H_4.NHNH_2$.—Ten grams of metachloraniline were dissolved in ten times its weight of concentrated hydrochloric acid and cooled with ice. The calculated quantity of sodium nitrite, dissolved in twice its weight of water, was added. The diazo-solution was then reduced with the calculated quantity of stannous chloride dissolved in strong hydrochloric acid. A white precipitate of the double hydrochloride of tin and chlorphenylhydrazine separated out. This was redissolved in boiling water, decomposed with potassium hydroxide and the free base extracted with ether. The yield is about eighty-five per cent. of the theoretical quantity. Fractionated in a vacuum, it is obtained as a colorless liquid boiling at 165° C. at 23 mm. It remains liquid at -15° C. It gave the following figures on analysis :

0.2717 gram gave 0.2700 gram silver chloride.

0.1559 gram gave 27.7 cc. nitrogen at 23° and 739 mm.

	Calculated for $C_6H_7N_2Cl$.	Found.
Cl.....	24.91	24.55
N.....	19.65	20.19

Triphenylmethanehydrazometachlorbenzene, $(C_6H_5)_3C.NH.NH.C_6H_4Cl(m)$.—The preparation is similar to that of the preceding hydrazo-bodies. Recrystallized from ether it gave the following results on analysis :

0.3665 gram gave 23.8 cc. nitrogen at 21.5° and 737 mm.

	Calculated for $C_{25}H_{21}N_2Cl$.	Found.
N	7.28	7.36

It is colorless when pure, but turns yellow on exposure, due to partial oxidation. It is soluble in benzene, chloroform, less soluble in ether and alcohol, and very sparingly soluble in ligroin. It melts at $150^\circ C$.

Triphenylmethaneazometachlorbenzene, $(C_6H_5)_3C.N : N.C_6H_4Cl(m)$.—This body is prepared in the same way as the previous azo-bodies. Recrystallized from methyl alcohol it forms bright yellow needles.

0.2607 gram gave 0.0632 gram silver chloride.

0.2463 gram gave 17 cc. nitrogen at 19° and 736.6 mm.

	Calculated for $C_{25}H_{19}N_2Cl$.	Found.
Cl	9.32	9.85
N	7.32	7.83

It is soluble in benzene, chloroform, less soluble in ether and alcohol, and is slightly soluble in ligroin. It melts at $109^\circ C$. The following molecular weight determination shows it to be monomolecular.

Triphenylmethaneazochlorbenzene, $C_{28}H_{19}N_2Cl = 382.5$.

Solvent : Benzene.

Grams solvent.	Grams substance.	Observed depression.	Molecular weight found.
20.700	0.6452	0.475°	330

Triphenylmethanehydrazoparachlorbenzene, $(C_6H_5)_3C.NH.NH.C_6H_4Cl(p)$.—This is obtained by the action of parachlorhydrazine on triphenylbrommethane. Analysis gave the following figures :

0.1593 gram gave 0.0715 gram silver chloride.

0.3458 gram gave 24.2 cc. nitrogen at 24° and 741.7 mm.

	Calculated for $C_{28}H_{21}N_2Cl$.	Found.
Cl	9.44	9.95
N	7.28	7.89

It melts at $145^\circ C$., and in other properties resembles the corresponding chlor-derivatives closely.

Triphenylmethaneazoparachlorbenzene, $(C_6H_5)_3C.N:N.C_6H_4Cl$ (*p*).—The preparation and properties of this body are similar to those of the corresponding chlorazo-body. It melts at $107^\circ C$.

0.142 gram heated to $130^\circ C$. gave 8.8 cc. nitrogen at 23.5° and 734 mm.

	Calculated for $C_{25}H_{15}N_2Cl$.	Found.
N	7.32	6.92

ACTION OF METABROMPHENYLHYDRAZINE.

Metabromphenylhydrazine, $C_6H_4Br.NHNH_2$.—This compound was prepared in the same way as the corresponding chlorhydrazine. It is a colorless liquid. Analyzed it gave the following results:

0.2672 gram gave 0.3687 gram carbon dioxide + 0.0942 gram of water.

0.1887 gram gave 25 cc. nitrogen at 21° and 746.8 mm.

0.4513 gram gave 58.4 cc. nitrogen at 18.5° and 727.7 mm.

	Calculated for $C_6H_7N_2Br$.	Found.	
		I.	II.
C	38.50	38.29
H	3.74	3.91
N	14.97	14.54	15.12

When the base is treated with hydrochloric acid a chloride containing one molecule of the acid is formed.

Triphenylmethanehydrazometabrombenzene, $(C_6H_5)_3C.NH.NH.C_6H_4Br$ (*m*).—Mode of preparation and properties similar to those of the corresponding chlor-compound; melting-point $149^\circ C$.

0.3017 gram gave 0.7693 gram carbon dioxide + 0.1336 gram of water.

0.3000 gram gave 18.8 cc. nitrogen at 19° and 741.7 mm.

0.2533 gram gave 16 cc. nitrogen at 22° and 734 mm.

	Calculated for $C_{25}H_{21}N_2Br$.	Found.	
		I.	II.
C	69.93	69.55
H	4.89	4.92
N	6.52	6.84	7.09

Triphenylmethaneazometabrombenzene, $(C_6H_5)_3C.N:N.C_6H_4Br$ (*m*).—Preparation and properties similar to those of the corresponding chlor-compound; melting-point $110^\circ C$. Analysis gave the following results:

0.2273 gram gave 0.5860 gram carbon dioxide + 0.1030 gram of water.

0.2606 gram gave 16.4 cc. nitrogen at 22° and 746 mm.

	Calculated for $C_{25}H_{19}N_2Br$.	Found.
C	70.25	70.31
H	4.45	4.85
N	6.55	6.92

Molecular weight determination :

Triphenylmethaneazobrombenzene, $C_{25}H_{19}N_2Br = 427$.

Solvent : Benzene.

Grams solvent.	Grams substance.	Observed depression.	Molecular weight found.
20.800	1.1020	0.70°	378

ACTION OF α -NAPHTHYLHYDRAZINE.

Triphenylmethanehydrazo- α -naphthalene, $(C_6H_5)_3C.NH.NH.C_{10}H_7$, is produced when triphenylbrommethane is treated with the α -naphthylhydrazine.¹ The ethereal solution should be evaporated in absence of air, and the crystalline residue rapidly dried, as this hydrazo-compound is very prone to oxidation, giving a dark-brown mass. The pure hydrazo-compound crystallizes in small white cubes.

0.2650 gram gave 18.2 cc. nitrogen at 21.5° and 734 mm.

	Calculated for $C_{29}H_{24}N_2$.	Found.
N	7.00	7.68

It is very soluble in ether, benzene, chloroform, less soluble in alcohol, and only slightly in ligroïn.

Triphenylmethaneazo- α -naphthalene, $(C_6H_5)_3C.N:N.C_{10}H_7(\alpha)$. — This azo-compound could not be obtained when amyl nitrite was employed. But upon careful oxidation of the hydrazo-derivative, suspended in a mixture of ether and ligroïn, with nitrous acid gas, the azo-body separates out in bright yellow needles, mixed with reddish-yellow cubes. Both forms of the crystals give the same melting-point, 114° C.

0.1995 gram gave 13.6 cc. nitrogen at 22° and 730 mm.

	Calculated for $C_{29}H_{22}N_2$.	Found.
N	7.03	7.61

In its general properties and solubility it resembles the other azo-derivatives of triphenylmethane.

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¹ *Ann. Chem.* (Liebig), 232, 236.