

square and 2 mm. thick while kept under benzene in a beaker) were dropped through the condenser over a period of one-half hour. After twelve hours of refluxing the mixture was decomposed with water, the benzene layer was evaporated to 30 ml. and the carbinol precipitated with petroleum ether. The crude carbinol was then recrystallized either from xylene or alcohol after treatment with decolorizing carbon. Three experiments by this method gave 48, 48 and 47% yields, respectively, and a fourth, for some unexplained reason, gave 55%. Use of sodium sand instead of chips gave only 31%. Pieces of sodium 2-3 mm. in diameter and 2 cm. long produced only 39%. Activation of the chips with a little amyl alcohol before dropping through the condenser lowered the yield to 37%. Freshly distilled and excess diethyl carbonate did not improve the results.

**4-Bromo-4'-dimethylbiphenyl.**—Methylation of 4-amino-4'-bromobiphenyl (from reduction of the corresponding nitro compound by the method of García-Banús and Medrano<sup>9</sup>) was carried out in sealed tubes using 10 g. of the amino compound, 9 g. of methanol and 3 g. of concentrated hydrochloric acid. The tubes were heated to 140-150° for twelve hours and the products isolated in

(9) García-Banús and Medrano, *Añales soc. españ. fis. quím.*, **20**, 475 (1922); *C. A.*, **17**, 2574 (1923).

the conventional manner. The first two runs were made in Carius tubes about 66 cm. in length and gave yields of 0 and 9%. In the next three runs two of the tubes were only 43 cm., while a third was 66 cm. long. The batches were combined and gave an over-all yield of 28%. The final runs were therefore made in tubes only 36 cm. long and gave yields of 42, 44, 45, 42, and 45%. The length of the tube is limited by the volume of the reagent used. Seals of the short tubes must be well annealed in a luminous flame to prevent bursting at reaction temperatures.

### Summary

4'-Dimethylaminobiphenyl has been prepared, its failure to have any properties resembling a dye noted, and the absence of any carbonium salt color until neutralization of the basic nitrogen atom observed. These results are not in accord with those predicted from the carbenium theory of triphenylmethane dyes.

Improved conditions for triarylcannabinol formation and for sealed tube methylation of an amine compound have been recorded.

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RECEIVED JULY 18, 1939

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 202]

## Triarylcannabinols. VIII. Occurrence of Color with Trikenylcarbonium Salts

BY AVERY A. MORTON AND L. F. MCKENNEY

When trikenylcannabinol is dissolved in nearly dry acetic acid and the solution saturated with dry hydrogen chloride only a slight color is discernible. Upon adding a few drops of water a pronounced red color appears. By adding anhydrous calcium sulfate to the colored solution, the color gradually fades as would be expected if water were removed by the desiccant. It is apparent that water has played a definite part in production of color. Nor is the phenomenon limited to one reagent. Nitromethane, acetone, formamide, urea, methanol, benzamide and many other compounds intensify color in the same way. In all cases intensity of color goes through a maximum as the quantity of agent is increased.

Formation instead of destruction of color with water is remarkable. The action is suggestive of complex formation though efforts to crystallize a complex from the strongly colored solution yielded the carbinol only and the position of the maximum absorption band was not displaced in the case of agents with which the color was intense.

The very weak acid, acetic, will not form a color with the carbinol unless the solution is heated. Nitric acid in acetic acid will produce a color with a few drops of nitromethane but not with water. With still stronger acids, sulfuric and perchloric, colored crystalline salts were obtained. In particular trikenylcarbonium perchlorate,  $(C_6H_5C_6H_4)_3CClO_4 \cdot HClO_4$ , was a very stable compound, easily crystallized and purified. Upon electrolyzing a solution of this carbonium salt in nitromethane, nitrobenzene, or glacial acetic acid, the cathode rather than the anode portion became colorless. The same phenomenon was observed with an acetic acid solution of trikenylcannabinol to which a little sulfuric acid had been added, with a nitromethane solution of triphenylcarbonium perchlorate,  $(C_6H_5)_3CClO_4$ , and with nitromethane solutions of trikenylcarbonium sulfate, nitrate, and chloride. Furthermore, when a very dilute and colorless solution of trikenylcarbonium perchlorate in nitrobenzene was electrolyzed it was about the anode rather than the cathode that color reappeared.

Absence of color at the cathode cannot be due to a chemical reaction such as reduction since pure triphenyl- and triphenylcarbinols were recovered from the cathode compartment after electrolysis of the perchlorate salts in nitromethane. Were reaction at the cathode involved, there would of necessity have been decoloration at the anode due to migration of the supposedly colored cation away from that region. In spite of absence of color at the cathode it was found, in tests with the two perchlorate salts, that the bulk of the triarylcarbinol was isolated from that region. The whole behavior is in agreement with a view that the triarylcarbonium ion, or triarylcarbinol, is not capable of being colored if the perchlorate ion is removed by electrolysis and will appear colored once more when the ion is added.

The above phenomena were differentiated from those of the dye, crystal violet. Electrolysis was carried out in aqueous solution since conductance of this salt in nitromethane proved to be very poor. In this case the cation remained colored. It was deposited and reduced on the platinum anode. The reduced material was recovered and oxidized to reform the dye. Electrolysis of this material was typical of what might be expected. The ammonium ion, carrying the quinoid nucleus, was colored and was conveyed to the cathode compartment where it was reduced. The anode compartment became less colored from migration of the colored cations toward the cathode.

### Experiments

**Color Formation with Water.**—The acetic acid was Mallinckrodt reagent grade which was found to have a melting point of 16.45° corresponding to about 0.1% water by weight. Triphenylcarbinol 0.115 g. (0.00024 mole) was dissolved in 200 ml. of acetic acid and the solution saturated with hydrochloric acid, prepared either from concentrated sulfuric acid and sodium chloride without any drying precautions or from aqueous concentrated hydrochloric acid dropped onto concentrated sulfuric acid, followed by drying over anhydrous aluminum chloride suspended on glass wool. In both cases the resulting acetic acid solution of the carbinol was faintly tinted. Addition of a few drops of water to such a solution caused it to become an intense red color. Samples for color analysis were made up by adding water to 25-ml. portions of the above solution. To maintain a constant volume, enough additional acetic acid was added to each sample to make the total volume equal to 30 ml. The intensity and position of the color band was determined in the Hardy color analyzer using the coordinates which correspond to absorption spectra measurements. The results are given in the table below. The quantity of water is corrected for the amount present in the acetic acid.

TABLE I

Water added, ml.	Acetic acid added, ml.	Total water present, mole	Color intensity <sup>a</sup> <i>D</i> at 542 m $\mu$
0	5.0	0.0014	0.060
0.25	4.75	.0153	.140
0.50	4.50	.0292	.270
1.0	4.0	.0569	.325
2.0	3.0	.1124	.580
3.0	2.0	.1669	.260
4.0	1.0	.2234	.135

<sup>a</sup> *D* = density, *T* = transmitted light,  $D = \log 1/T$ .

The quantity of water plotted against the color intensity is a straight line up to maximum absorption. Beyond that point hydrolysis and precipitation occurred. The maximum absorption was at 542 m $\mu$ , a value agreeing well with that, 544, obtained by Burawoy,<sup>1</sup> who used a spectroscope with solutions of triphenylcarbinol and sulfuric acid in acetic acid.

**Fading of Color with Calcium Sulfate.**—A colored solution formed by dissolving triphenylcarbinol in glacial acetic acid, saturating with hydrogen chloride, and adding a few drops of water, was allowed to remain in contact with anhydrous calcium sulfate (the commercial grade known as Drierite was used). After eighteen hours the color had faded to a very light tint while an identical solution without calcium sulfate remained intensely colored. Addition of two drops of water to the solution which had stood over the drying agent restored the original red color. Tests with magnesium perchlorate and phosphorus pentoxide as desiccants were unsatisfactory because the soluble perchlorate and phosphoric acid themselves developed a color with the carbinol in absence of hydrochloric acid. Sodium sulfate was ineffective as a bleaching agent. The drying action of this last agent is known to be very considerably less than that of calcium sulfate.

**Agents Producing Color.**—Other compounds besides water have been found to cause a red color in the carbinol-hydrochloric acid-acetic acid solution. In Table II a list of these substances is given. The compounds are arranged in order of descending intensity of color. In the case of agents which imparted approximately equal intensity, the order is based on the moles of reagent required.

Ammonium acetate (ammonia), tetrachloroethane, ethyl iodide, iodobenzene, bromobenzene, phenol, anisole, phenetole, diphenyl ether, acetone, crotonaldehyde, ethyl benzoate, *sym*-trinitrobenzene, and nitrobenzene produced no color under the above conditions. Although small quantities of phenol and tetrachloroethane had no effect, addition of 0.002 g. of the carbinol to phenol or to tetrachloroethane as solvents caused an intense red color to appear.

**Crystallization of the Carbinol from the Colored Solution.**—The solubility of triphenylcarbinol in glacial acetic acid at room temperature was found to be 2.60 g. per liter. A solution of 0.4888 g. of the carbinol in 200 ml. of nearly dry acetic acid was saturated with dry hydrochloric acid and water added to produce a color. Upon standing crystals of carbinol precipitated from the strongly colored solution. Similar tests were made a number of times with identical results. The crystals were filtered, washed with anhydrous ether, and dried. The melting point varied from

(1) Burawoy, *Ber.*, **64**, 1635 (1931); **66**, 228 (1933).

TABLE II

Compound	Color	Quantity needed to produce maximum color, mole
Nitromethane	Very intense	0.037
Water	Intense	.005
Acetonitrile	Intense	.019
Formamide	Intense	.025
Formanilide	Strong <sup>a</sup>	.0008
Acetanilide	Strong	.0011
Urea	Strong <sup>b</sup>	.0017
Methanol	Strong	.013
Dichlorodiethyl ether	Strong	.035
Propionamide	Medium	.0014
<i>m</i> -Dinitrobenzene	Medium	.0015
Benzamide	Medium	.0041
Acetamide	Medium	.0042
Acetoacetic ester	Medium	.040
Diphenylamine	Light	.003
Ethanol	Light	.017
Benzophenone	Light salmon	.0014
Mesityl oxide	Light salmon <sup>c</sup>	.0022
Acetaldehyde	Light salmon <sup>d</sup>	.018
Iodine (dilute solution in acetic acid)	Light salmon	

<sup>a</sup> Salmon colored instead of red. <sup>b</sup> Color faded in five minutes and a precipitate formed. <sup>c</sup> Color rapidly changed to brown. <sup>d</sup> Color slowly changed to brown.

200 to 201° as compared with the pure carbinol which melts at 206.5–207°.

**Solutions of Trixenylichloromethane in Anhydrous Acetic Acid.**—Trixenylichloromethane was prepared from the carbinol by reaction with acetyl chloride. The product was recrystallized from dry benzene until it was colorless. Its melting point was 193.0–193.5° with some decomposition. Dry acetic acid was prepared in four different ways to ensure that the color formed with trixenylichloromethane was not due to some impurity. By the first method 400 g. of reagent glacial acetic acid was kept over 50 g. of phosphorus pentoxide for twenty-four hours. It was then distilled through a 20-turn Davis column, all joints being of glass. The portion coming over at 118.4° was again treated with 50 g. more of the pentoxide after which it was distilled through the same column. By the second method, 700 g. of the acid (m. p. 15.65°) was refluxed with 28.3 g. of acetic anhydride and 14 g. of chromic oxide according to the method of Orton and Bradfield.<sup>2</sup> The acid was then distilled through the Davis column mentioned above. The fraction (200 ml.) boiling from 117.6 to 117.7° at 748 mm. was collected. Since both of the above fractions showed a pronounced red color when the chloro compound was dissolved in them, the refluxing with acetic anhydride was repeated in the absence of the chromic acid to ensure that no volatile chromyl compound had been formed. Glacial acetic acid, 700 g., was refluxed for twenty-four hours with 28 g. of acetic anhydride. The fraction which distilled at 118.4 to 118.6° was collected. To ensure further the absence of any inorganic compounds which might produce the color, a physical method of drying was employed. Reagent glacial acetic acid, 200 ml., and 200 ml. of anhydrous thiophene-free benzene were carefully

fractionated through the column. A fraction, 100 ml., boiling at 117.8° (750 mm.) was collected and used. With all four samples of acetic acid a light to medium color was obtained when 0.002 g. of trixenylichloromethane was dissolved in 10 ml. of the acid.

**Effect of Acetic Acid.**—Trixenylicarbinol dissolved in glacial acetic acid was colorless when cold but strongly colored upon heating. The color disappeared when the solution was cooled.

**Effect of Nitric Acid.**—Trixenylicarbinol, 0.003 g., was dissolved in 15 ml. of glacial acetic acid. To this solution was added 6 drops of red fuming nitric acid (sp. gr. 1.6). No color developed. To 5-ml. portions of this solution were added, respectively, up to 10 drops of water and 1 ml. of nitromethane. The first caused no color while the second produced an intense red solution. Addition of 0.002 g. of the carbinol to concentrated nitric acid produced an intense red color.

**Salts of Trixenyl- and Triphenylcarbinols.**—Trixenylicarbinol, 1.1 g., was dissolved in 20 ml. of hot acetic anhydride and treated, a drop at a time, with 4 ml. of 60% perchloric acid. Beautiful green plate crystals separated immediately. The solution was cooled in an ice-bath, filtered, and the solid dried for twenty-four hours in an oven at 50–55° or until the analysis for acid content was constant. The yield varied from 80–86%. The analysis was carried out by boiling with standard caustic solution for ten minutes, followed by titration of the excess alkali. The organic matter recovered after this treatment was shown to be pure trixenylicarbinol by its melting point, 206.5–207°. The calculated for  $(C_6H_5C_6H_4)_3CClO_4 \cdot HClO_4$  is 29.5% perchloric acid; found 29.6 and 29.7%. The crystals were stable in air and melted sharply at 219.5–220°. They dissolved slightly in benzene, forming colorless solutions which became colored on heating and colorless again on cooling.

Dark red crystals with green iridescence of trixenylicarbinol sulfate could be prepared by a similar reaction. They also could be obtained by cooling a hot solution of trixenylicarbinol in concentrated sulfuric acid. They were spread upon a tile and dried in a vacuum desiccator over solid sodium hydroxide. Because of their hygroscopic nature and the low volatility of sulfuric acid, the analysis was very unsatisfactory: calcd. for  $(C_6H_5C_6H_4)_3CHSO_4 \cdot H_2SO_4$ , 29.4% sulfuric acid, found 34 and 36%. Pure trixenylicarbinol was recovered as the organic portion from the analysis.

The nitrate was prepared by adding 1 g. of the carbinol to 20 ml. of fuming nitric acid, sp. gr. 1.6. After a half minute it was diluted with an equal volume of water and heated on a steam-bath. The red oil which rose to the top was removed. On cooling, it solidified to a red amorphous mass which reached a constant acid value of 21.3 and 21.4% nitric acid when kept in a vacuum desiccator over caustic. The theoretical for  $(C_6H_5C_6H_4)_3NO_3 \cdot HNO_3$  is 21.2%. No nitration of the carbinol had occurred as shown by the melting point of the recovered material. From one preparation a few green (red by transmitted light) needle-shaped crystals of the nitrate salt were obtained which decomposed to a brown oil at 110°. The dark brown triphenylcarbonium perchlorate, prepared in the manner described for the trixenylmethyl compound,

(2) Orton and Bradfield, *J. Chem. Soc.*, 983 (1927).

analyzed within 0.1% of the theoretical for  $(C_6H_5)_3CClO_4$  and showed all of the properties already reported by Hofmann<sup>3</sup> and co-workers.

**Electrolysis of Triphenylcarbonium Perchlorate and other Salts.**—Qualitative observations were made in a V-shaped 11 mm. i. d. tube with platinum electrodes. Solutions of the perchlorate salt were made by addition of a few crystals to anhydrous acetic acid, nitromethane, and nitrobenzene. Upon electrolysis of the resulting colored solutions the cathode compartment became colorless. For analysis of the two compartments a larger cell was made from 23 mm. i. d. tubing with vertical arms 24 cm. apart and 17 cm. high, and provided with a 20-mm. stopcock in the center and smaller cocks for draining the contents from around the platinum electrodes. The perchlorate salt, 150 mg., was dissolved in 130 ml. of Eastman Kodak Company pure nitromethane which had been twice redistilled to yield a fraction boiling at 101°. The current at the start was 14 ma. It rose rapidly to 18 and dropped slowly to 2 within two hundred and twenty minutes. The cathode compartment by that time was entirely colorless. The central stopcock was closed and 15 ml. each drawn off from around the cathode and the anode. The analysis was carried out by adding 5-ml. samples to 0.1 N alkali, extracting with ether and reextracting the ether layer with water to ensure removal of all of the perchlorate ions. Attempts to titrate the acid portion gave uncertain results because of the presence of traces of nitromethane. The ether layer was evaporated in a weighed beaker and dried to constant weight in an oven at 50-55°. The results are tabulated below.

Triphenylcarbinol	Milligrams per 5 ml. in samples 1 and 2		Average
From cathode compartment	7.3	7.5	7.4
From anode compartment	2.0	2.2	2.1
In original solution	4.0	4.4	4.2

Although the gain, 3.2 mg. around the cathode, was greater than the loss, 2.1 mg. about the anode, the evidence of transference of the carbinol toward the cathode is well beyond experimental error. The triarylcarbinol recovered from either compartment had a melting point of 206.5-207° identical with that of our purest samples. A mixed melting point showed no depression. When examined under the microscope the recovered crystals appeared to be entirely of one kind and identical with triphenylcarbinol.

A solution of 150 mg. of the perchlorate salt in 100 ml. of nitrobenzene had a strong purplish-red color. Upon dilution to one-fifth of this strength the color first appeared red and then turned colorless after a time. Upon electrolysis of this dilute solution a red color reappeared at the anode while the cathode portion remained colorless.

Similar disappearances of color, possibly due to hydrolysis, were noted upon dilution of solutions in nitromethane and acetic acid.

Nitromethane solutions of the sulfate (1 mg. per 5 ml.), the chloride (6 mg. per 5 ml.), and the nitrate (12 mg. per 5 ml.) were electrolyzed in the V-shaped cell. In each case the cathode compartment became colorless.

Triphenyl- or triphenylcarbinol was electrolyzed in a solution of commercial glacial acetic acid, Mallinckrodt reagent grade, to which 3-4 drops of concentrated sulfuric acid were added. In both cases the solution became entirely colorless around the cathode.

**Electrolysis of Triphenylcarbonium Perchlorate.**—When the brown solution of 160 mg. of the perchlorate salt in 140 ml. of nitromethane was electrolyzed the cathode compartment became colorless as in the case of the triphenyl compound. The analysis was carried out in a similar manner and is recorded below.

Triphenylcarbinol	Milligrams per 5 ml. in samples 1 and 2		Average
From cathode compartment	6.9	6.1	6.5
From anode compartment	3.1	3.6	3.4
In original solution	4.0	4.4	4.2

The triphenylcarbinol recovered from the anode and the cathode was shown to be identical with an authentic sample by melting point, mixed melting point, and microscopic examination.

**Electrolysis of Crystal Violet.**—Solutions of crystal violet—approximately 2.5 mg. per 50 ml. of water—were electrolyzed in the large cell. After ten hours the cathode region was almost colorless and the anode section showed a considerable decrease in color intensity. Some colorless solid material which had been deposited on the platinum cathode was dissolved in hydrochloric acid and treated with lead dioxide. The blue color of crystal violet reappeared.

## Summary

Addition of small amounts of water and some other compounds to a solution of triphenylcarbinol in glacial acetic acid saturated with hydrochloric acid causes formation of an intense red color.

Triphenylcarbonium perchlorate and triphenylcarbonium perchlorate have been prepared. Solutions of the former salt when subjected to electrolysis in organic solvents show disappearance of color around the cathode rather than in the anode compartment.

(3) Hofmann, Kirmreuther and Thal, *Ber.*, **43**, 183 (1910).