Summary

1. An improved method of making vanadous sulfate, $VSO_4 \cdot 7H_2O$, is described.

2. The oxidation–reduction potential of trivalent–divalent vanadium ions has been determined by potential measurements on cells of the type $\overset{-}{\mathrm{Pt}}$, $^1/_2V_2(SO_4)_3(c_3)$ + $VSO_4(c_2)$ + $H_2SO_4(c_1)$, $H_2SO_4(c_1)$, Hg_2SO_4, $\overset{+}{\mathrm{Hg}}$ at both 25 and 0°.

3. Combining these data with measurements by Harned and Hamer on the cell Pt, H_2, H_2SO_4, Hg_2SO_4, Hg we have estimated the standard potential of the cell dependent on the reaction $V^{++} + H^+ = V^{+++} + {}^1/_2H_2$, and the equilibrium constant of this reaction.

$$_{\mathrm{H}}E_0^{\mathrm{v}} = +0.255 \text{ at } 25°$$
$$_{\mathrm{H}}E_0^{\mathrm{v}} = +0.265 \text{ at } 0°$$
$$K = \alpha_2\alpha_{\mathrm{H}}/\alpha_3 = 4.8 \times 10^5 \text{ at } 25°$$
$$K = \alpha_2\alpha_{\mathrm{H}}/\alpha_3 = 1.3 \times 10^{-5} \text{ at } 0°$$

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Light Absorption and Fluorescence of Triarylmethyl Free Radicals

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The experiments here described had the double purpose (1) of seeking the relation between color and structure in odd molecules and (2) of looking for the "windmill" type of isomerism, which, however, has since been definitely established in the ions of crystal violet and malachite green.[1] Unfortunately, our experimental work was abruptly terminated some years ago so that the interpretation of some of the curves must await further study.

The Absorption and Fluorescence Spectra of Triphenylmethyl.—When the spectrum of triphenylmethyl is observed visually, two sharp absorption bands are seen. The one at higher frequency was found by Anderson[2] to have a double maximum. In order to ascertain whether the several absorption bands represent merely vibrational terms in a single electronic band, we have studied photographically, and with high dispersion, both the absorption and fluorescence of triphenylmethyl. In order to bring out structure both experiments were made at liquid air temperature in the EPA solvent (5 parts ether, 5 parts isopentane and 2 parts ethanol by volume).

When a solution of triphenylmethyl is cooled some fifty degrees below 0° it gradually becomes colorless, owing to almost complete dimerization. On the other hand, when the solution in EPA is suddenly cooled by liquid air it preserves its color indefinitely and under these conditions it is not even photosensitive. Evidently the photochemical process is at least bimolecular and bimolecular reactions cannot occur in rigid media.[3]

Figure 1 is a direct microphotometer tracing of the photograph of the absorption spectrum of triphenylmethyl. Figure 2 gives the corresponding tracing for the fluorescence spectrum. Both spectra prove to be remarkably complex. In Fig. 1 we have indicated seven and in Fig. 2 nine distinct bands which are undoubtedly real since they were confirmed by complete repetition of the photographing and microphotometer tracing.

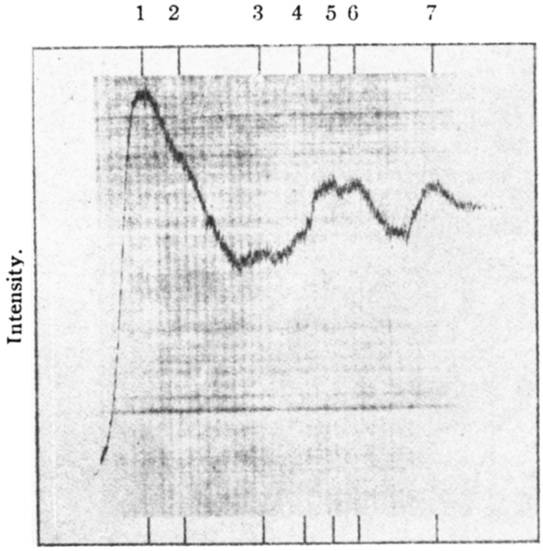

Fig. 1.—Absorption spectrum of triphenylmethyl in EPA at 90°K. There are at least 7 recognizable maxima at the positions marked. The frequencies (cm.$^{-1}$) of the numbered peaks in Figs. 1–5 are given in Table I.

In a molecule so loosely constructed it is most remarkable to find so much resolution of vibrational structure and such narrow individual vibrational bands. In molecules with an even number of electrons, such fine structure is to be found only in tightly bonded structures such as that of perylene.[4]

The extreme sharpness of the bands, especially of the first band, in triphenylmethyl and its alkyl derivatives, shown in later figures, makes it possible to recognize these radicals even in the presence of other colored substances.[3] This sharpness

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[1] Lewis, Magel and Lipkin, THIS JOURNAL, **64**, 1774 (1942).

[2] Anderson, *ibid.*, **57**, 1673 (1935).

[3] Lewis and Lipkin, *ibid.*, **64**, 2801 (1942).

[4] Dadieu, *Z. Elektrochem.*, **35**, 283 (1929).

TABLE I

Band	Fig. 1.		Fig. 2		Fig. 3		Fig. 4		Fig. 5	
	$\bar{\nu}$	$\bar{\nu} - \bar{\nu}_1$	$\bar{\nu}$	$\bar{\nu}_1 - \bar{\nu}$	$\bar{\nu}$	$\bar{\nu} - \bar{\nu}_1$	$\bar{\nu}$	$\bar{\nu} - \bar{\nu}_1$	$\bar{\nu}$	$\bar{\nu} - \bar{\nu}_1$
1	19550		19410		19420		19210		19180	
2	19740	190	19180	230	19560	140	19370	160	19340	160
3	20150	600	18740	670	20070	650	19900	690	19920	740
4	20370	820								
5	20520	970	18440	970						
6	20640	1090	18330	1080	20480	1060	20320	1110	20300	1120
7	21070	1520	17860	1550	20950	1530	20750	1540	20730	1550
8			17560	1850						
9			17200	2210						
10			16900	2510						

is not greatly reduced even at room temperature. Early efforts to determine the degree of dissociation of hexaarylethanes colorimetrically were not very successful, because a spectrophotometer was not ordinarily used, and because of the presence of other colored substances. Since Dr. Taylor and one of the authors[5] first demonstrated the paramagnetism of the free organic radicals, the magnetic method has been highly developed and employed to determine the degree of such dissociations. The accuracy of the method, however, is limited by the very large corrections for diamagnetism. The triarylmethyls prepared by the method that we shall describe show no trace of colored impurities. A spectrophotometric study of absorption as a function of concentration should give dissociation constants of higher precision than can be obtained by other methods.

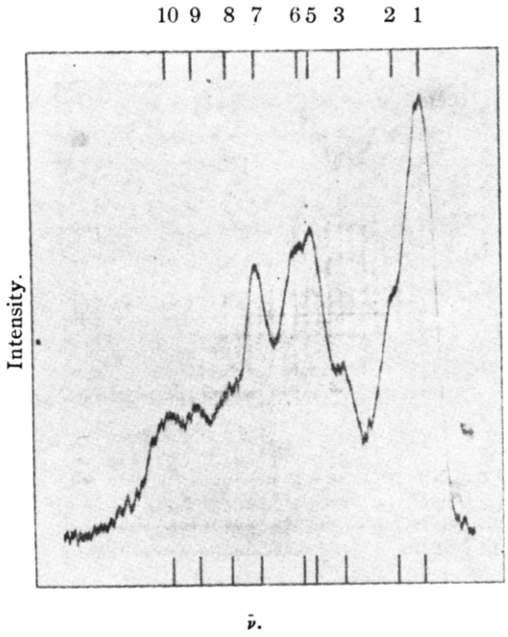

Fig. 2.—Fluorescence spectrum of triphenylmethyl in EPA at 90°K. Nine distinct maxima (or inflections) are recognizable at the points marked.

Lewschin[6] found that curves of absorption and fluorescence appear to be mirror images of each other, with respect to the frequencies of the several maxima. This has been taken to indicate[7] vibrational structure of a single electronic band, the spacing of the vibrational levels being nearly the same in the ground and in the excited states. In no other case has Lewschin's rule been found so nearly true as in the present one, as will be seen from Table I. Here the frequencies of the maxima were read from the curves, without prejudice, and it is evident from the curves that some maxima can be read more accurately than others. These frequencies are listed as well as their separation from the first band. In the next two columns the same thing is done for the fluorescence maxima and their separation (in the opposite direction). Here it is assumed that the fluorescence band corresponding to number four for absorption was not observed. It will be seen that within the limits of error the separations are the same for absorption and fluorescence maxima, thus affording a perfect mirror image with respect to the frequencies of the bands.

We have no idea what the vibrations are that give such a bizarre group of separations, but there can be no doubt that we are dealing with a single electronic band, and that the vibrational separations are almost identical in the excited and unexcited states. That there is very little energy dissipated in the total process absorption-reëmission is shown by the small separation, 140 cm.$^{-1}$, between the first absorption band and the first fluorescence band.

Alkyl-substituted Triphenylmethyls.—Through the kindness of Professor C. S. Marvel of the University of Illinois, we have obtained some of the alkyl-substituted triphenylchloromethanes and have been able to study the free radicals *o*-tolyldiphenylmethyl, and triphenylmethyl with one, two and three para-substituted *t*-butyl groups. The *o*-tolyldiphenylmethyl gave an absorption curve almost identical with that of triphenylmethyl but with the maxima at slightly higher frequencies (50–100 cm.$^{-1}$). On the other hand, the para-substituted radicals that we have investigated gave small shifts toward lower fre-

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[5] Taylor and Lewis, *Proc. Natl. Acad. Sci.*, **11**, 456 (1925).

[6] Lewschin, *Z. Physik*, **72**, 368 (1931).

[7] Hausser, Kuhn and Kuhn, *Z. physik. Chem.*, **29B**, 417 (1935); Lewis, Goldschmid, Magel and Bigeleisen, THIS JOURNAL, **65**, 1150 (1943).

quencies, as shown in Figs. 3, 4 and 5, which give, respectively, the absorption curves of the three *t*-butyl compounds. Even with three *t*-butyl groups the first absorption maximum of triphenylmethyl has been reduced by only 400 cm.$^{-1}$ (an increase of 100 Å. in λ).

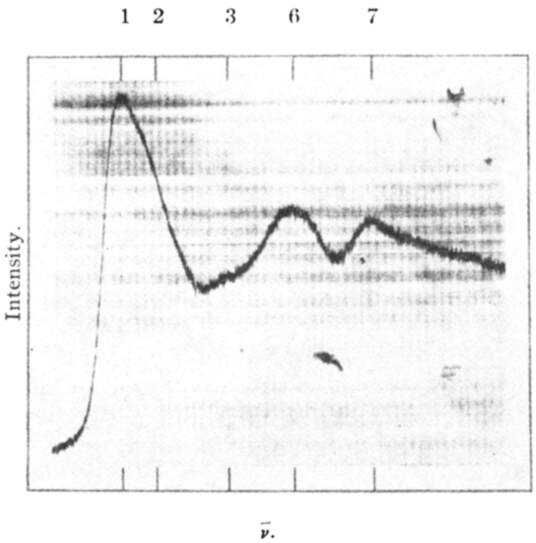

Fig. 3.—The absorption spectrum of diphenyl-*p*-*t*-butylphenylmethyl in EPA at 90°K.

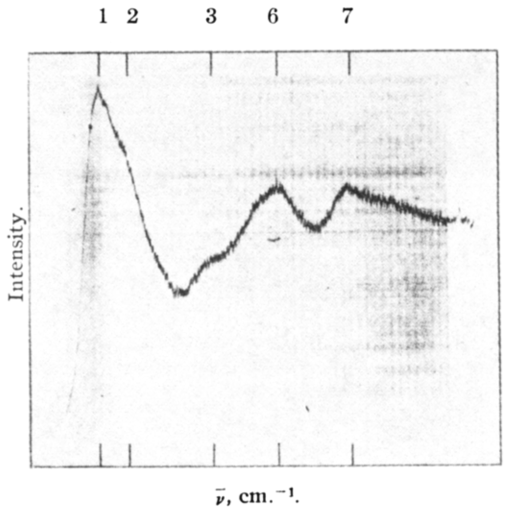

Fig. 4.—The absorption spectrum of bis-(*p*-*t*-butylphenyl)-phenylmethyl in EPA at 90°K.

In spite of these shifts in absorption maxima it is evident that the substituted alkyl groups have had no effect upon the vibrational levels, for the several values of $\bar{\nu} - \bar{\nu}_1$ given in Table I are within the limits of error identical with those obtained with triphenylmethyl. On account of their sharpness the maxima numbered 1 and 7 can be most accurately read, and here the values of $\bar{\nu} - \bar{\nu}_1$ vary only over the range of 30 cm.$^{-1}$. The almost complete identity thus shown between the vibrational levels in the excited state of the several radicals, and between the vibrational levels of the excited and normal states of triphenylmethyl is most remarkable.

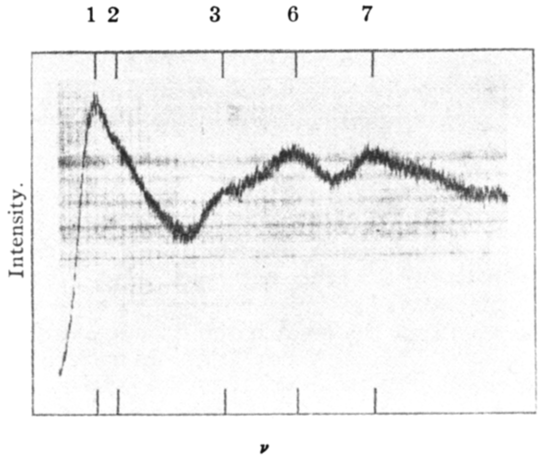

Fig. 5.—The absorption spectrum of tris-(*p*-*t*-butylphenyl)-methyl in EPA at 90°K.

9-Phenylfluorenyl.—Since the effect of a linkage of the phenyls in dyes of the triphenylmethane class has been often discussed[8] it was of interest to find the effect of linking directly together two of the ortho carbons of triphenylmethyl. The radical 9-phenylfluorenyl is almost completely dimerized at room temperature, but the color of the radical appears on heating. We have studied its absorption spectrum in toluene at 93° and in ethyl benzoate at still higher temperatures. The measurements in toluene are given in Fig. 6. Chiefly because of the difficulty of determining the actual concentration of the free

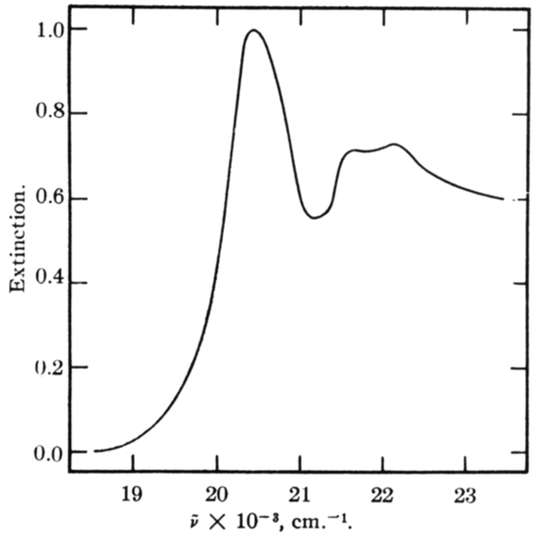

Fig. 6.—Absorption spectrum of 9-phenylfluorenyl in toluene at 93°.

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[8] Wizinger, "Organische Farbstoffe," Ferd. Dümmlers Verlag, Berlin u. Bonn, 1933.

radicals, we give throughout this paper the measured extinction and not the molar extinction coefficients. The curve hardly differs from that of triphenylmethyl at the same temperature except that the bands are shifted to higher frequencies by about 800 cm.$^{-1}$.

α-Naphthyldiphenylmethyl.—The complex spectrum of this radical, which covers the whole visible range, is shown in Fig. 7. We have found that the absorption spectrum does not change much over a wide range of temperature. We make no attempt at present to interpret this spectrum, but point out the great bathochromic effect that the naphthyl group produces in odd molecules as well as in ordinary dyes.

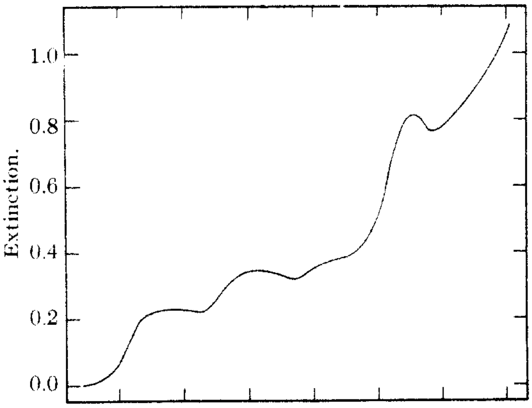

Fig. 7.—Absorption spectrum of α-naphthyldiphenylmethyl in toluene at 27°.

Tri-*p*-xenylmethyl (Tri-*p*-biphenylmethyl).—This free radical when first prepared gives in dilute solution a blue-green which often changes on standing to a violet or red. We were reminded of the claim of Schmidlin[9] that there are two isomers of the free radical, but his results had been shown by Schlenk[10] to be incorrect, and due to faulty preparation of the triarylmethyl halide. Yet the blue radical that we prepared and the red substance which is produced on standing both satisfy the criterion of a free radical, in that the color disappears instantly, even at low temperature, when air is allowed to enter.

We do not believe, however, that the red substance is an isomer, but probably some product of a secondary reaction. The reaction is greatly accelerated by heat and probably by acid, for it is inhibited by small amounts of a base such as triethylamine. In fact, the best way to obtain the pure blue compound is to add a drop or two of triethylamine before reduction of the halide to the free radical.

The blue solution thus prepared and which we take to be pure tri-*p*-xenylmethyl has the absorption curve given in Fig. 8, Curve 1. Such a solution may be kept for months in the dark at room temperature. If it is immersed in ice and illuminated by sunlight the solution rapidly fades, soon becoming entirely colorless.

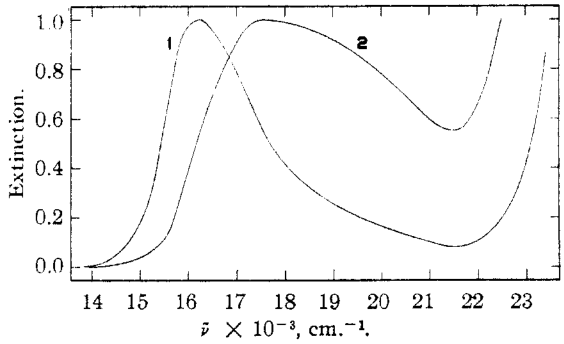

Fig. 8.—Extinction (1) of tri-*p*-xenylmethyl and (2) of the red substance obtained from it on standing; both in toluene at room temperature.

The red substance, on the other hand, is entirely insensitive to light. Thus it was possible from a mixture of the two substances to obtain, by illumination, only the red. The solution thus prepared has the absorption spectrum shown in Fig. 8, Curve 2. This red solution does not change back to the blue on the addition of triethylamine.

Tris-(*p*-nitrophenyl)-methyl.—Gomberg[11] obtained this free radical in impure form, and stated that its solution was violet when hot and blue-green when cold, the color change being completely reversible with changing temperature. We have verified this observation with our pure material. While the color change is pronounced, the change in the measured absorption spectrum is not great. Figure 9, Curve 2, shows the absorption curve of trinitrotriphenylmethyl in chloroform at 20°. At 80° the main peak has shifted about 100 Å. toward higher frequency and there is a little more absorption in the blue region.

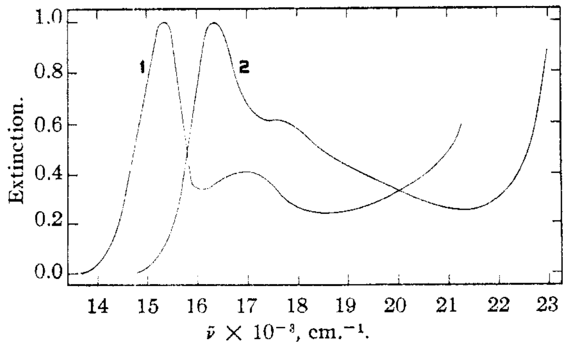

Fig. 9.—Absorption spectrum of tris-(*p*-nitrophenyl)-methyl: (1) in EPA at 90°K.; (2) in chloroform at 20°.

Ths shift in the main maximum continues to low temperatures and at the temperature of liquid air in EPA we obtain Curve 1 of Fig. 9. We have not, however, carried on further experiments to

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(9) Schmidlin, *Ber.*, **45**, 3171 (1912).

(10) Schlenk, *ibid.*, **46**, 1475 (1913).

(11) Gomberg, *ibid.*, **37**, 1640 (1904).

find the cause of this interesting change. It may be noted that this free radical proved to be unexpectedly stable, remaining unchanged on long standing in toluene or chloroform solution, and in the presence of light.

Experimental

Of the chemicals employed, the triphenylchloromethane and the α-naphthyldiphenylchloromethane were prepared from commercial samples by successive recrystallizations. Tri-*p*-biphenylchloromethane (tri-*p*-xenylchloromethane) was prepared by the method of Morton.[12] The 9-phenylfluorenyl was made, with sufficient purity for our purpose, by the simple expedient of preparing a solution of triphenylmethyl in toluene, or ethyl benzoate, and then irradiating with sunlight until there was no more color at room temperature. The other main product of the photochemical reaction, triphenylmethane, is colorless. Tris-(*p*-nitrophenyl)-bromomethane which had been prepared by Gomberg[11] only in impure form, by a complicated method, we found could be made very simply in a pure state by refluxing tris-(*p*-nitrophenyl)-methane with bromine for several hours. After recrystallizing from a mixture of carbon tetrachloride and chlorobenzene, it melted at 189.9–190.9°, cor. Hydrolysis of the product in the presence of silver nitrate solution showed that it contained 17.12% of Br. Theoretical for $(O_2NC_6H_4)_3CBr$ is 17.44% Br.

The preparation of the free radicals from the corresponding halides was carried out on the vacuum bench as indicated in Fig. 10. Mercury, a small piece of silver wire and the halide to be reduced were placed in tube A, which was constricted at C and attached to the line by a ground joint. After exhausting and drying, the tube was surrounded with liquid air and pre-dried solvent from the flask E was distilled in. A was then sealed off at C and allowed to warm. As soon as the mercury melted, the tube was shaken in the dark, and in a few minutes the greater part of the reduction had occurred. The method is not only speedy, but in the case of an unstable radical the whole reduction may be made at a temperature only a little above −40°. In rare cases the silver chloride was so fine that a centrifuge was used to obtain a perfectly clear solution.

When the amalgamated silver was not a sufficiently powerful or rapid reducing agent, thallium amalgam was used. The halide alone was dried in tube A, solvent was distilled in, and before sealing at C the eccentric bulb D, containing thallium amalgam, was rotated about its ground glass joint until a few drops of amalgam fell into the cold solvent. The procedure was then as before. Whichever amalgam was used, it was sometimes convenient to have a side tube, B, which could, if desired, terminate in a flat cell; although many of our measurements were made in round tubes. The side tube had the advantage that a small amount of the liquid from A could be decanted over and then diluted to the desired concentration by distilling the remainder of the solvent from A. We have even succeeded in recrystallizing a radical by decanting most of the liquid into B, then concentrating by distillation of the solvent back to A until crystallization occurred, and then decanting the mother liquor into A, a process that can be continued indefinitely.

Most of the apparatus for studying absorption and emission spectra we have already described.[13] The photographs of the absorption spectra at high dispersion of triphenylmethyl and the *t*-butyl-substituted free radicals were obtained on a large Hilger spectrograph with quartz optics. The dispersion of this instrument was 12.5 Å./mm. at 5000 Å. The absorption spectra shown in Figs. 1, 3, 4 and 5 are direct microphotometer tracings of photographs taken with a tungsten lamp as light source. No plate corrections have been made. Eastman Kodak Co. I-F spectrographic plates were used. The emission spectrum shown in Fig. 2 was obtained with the Steinheil spectrograph on Eastman Kodak Co. I-B ammonia-sensitized spectrographic plates. Here again no plate correction was made. Excitation was by ultraviolet light which passed through such color filters that only the fluorescent light acted upon the plate.

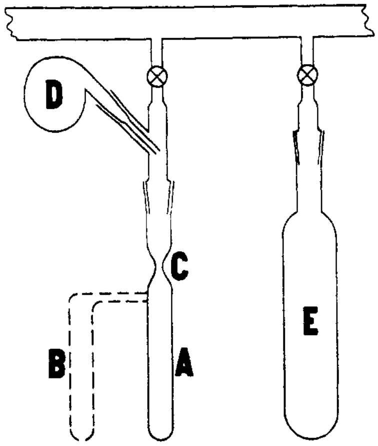

Fig. 10.—Apparatus for producing triarylmethyls from their halides.

Summary

The absorption and fluorescence spectra of triphenylmethyl have been obtained at low temperature and at high dispersion. The subsidiary bands are surprisingly complex and well resolved. A remarkably exact mutual "reflection" of absorption and fluorescence maxima was found. A similarly complex absorption spectrum is found when one, two or three of the *para* hydrogens are replaced by *t*-butyl groups. *o*-Tolyldiphenylmethyl shows an absorption curve nearly identical with that of triphenylmethyl, but was not tried at low temperature and high resolution. A quite similar absorption curve was obtained for 9-phenylfluorenyl.

The absorption spectra, as well as some other properties, were also studied for α-naphthyldiphenylmethyl and tri-*p*-xenylmethyl. The latter, a blue substance, changes irreversibly on standing to a red substance whose absorption spectrum is given.

Pure tris-(*p*-nitrophenyl)-bromomethane was prepared by direct action of bromine upon the corresponding methane. From this the free radical was prepared and Gomberg's observation of a change of color with the temperature was verified. The absorption spectra at different temperatures were determined.

A simple method of making pure triarylmethyls from the corresponding halides is described.

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[12] Morton and Emerson, THIS JOURNAL, **59**, 1947 (1937); Morton and Wood, *ibid.*, **61**, 2902 (1939).

[13] Lewis, Lipkin and Magel, *ibid.*, **63**, 3005 (1941).