experiments: one of stainless steel, the other of Monel with a stainless steel head. The autoclave was approximately two-thirds filled with active carbon (Cliffchar No. 6 or CXA) granules (60–100 g.) and pretreated with anhydrous hydrogen fluoride (5–10 g.) at 225–350° for 8 hr. to convert silicate into silicon tetrafluoride and remove moisture and any impurities in the ash content of the carbon which might react with carbonyl fluoride. The volatile products from the pretreatment were removed *in vacuo*.

A reaction temperature of 400–450° with a pressure of >100 atm. was found suitable for the preparation of dichlorodifluoromethane. In a typical experiment, carbonyl fluoride (0.13 mole) and phosgene (0.36 mole) were condensed into the pretreated autoclave which was then heated in a salt-bath at 425° for 17 hr. The weight of crude product, obtained by venting the autoclave while still at 250°, then pumping out the hot autoclave, amounted to 90% of that of the reactants. Spectroscopic examination of a sample of the crude product revealed the presence of all the chlorofluoromethanes, CF_4, CCl_4, COFCl, CO_2 and unchanged reactants (10–15%). The crude product was washed with 15% aqueous sodium hydroxide to leave CF_2Cl_2 (56% conversion), CF_3Cl (12% conversion), $CFCl_3$ (23% conversion) and smaller amounts of CF_4 (some of which gets lost during the washing process) and CCl_4. Conversions are based on carbonyl fluoride taken.

A similar experiment with a reaction time of 8 hr. gave the following conversions based on carbonyl fluoride taken: CF_2Cl_2, 43%; CF_3Cl, 21%; $CFCl_3$, 4%; CF_4, 8%; and a 27% conversion to CCl_4 based on phosgene.

In a further experiment, a 0.1-l. stainless steel autoclave containing 63 g. of an activated carbon catalyst which had been used in an earlier experiment and was impregnated with 26–27% of ferric chloride was charged with carbonyl fluoride (0.13 mole), phosgene (0.33 mole) and chlorine (3 g.). Reaction at 425° for 6 hr. gave CF_2Cl_2 (34% conversion), CF_3Cl (21%), $CFCl_3$ (25%), CF_4 (5%) and CCl_4 (11%).

Pyrolysis of Carbonyl Chlorofluoride.—Carbonyl chlorofluoride (30.5 g.), heated to 420° for 8.5 hr. in a 0.1 l. stainless steel autoclave, gave gaseous products (27.5 g.) which were washed with 15% aqueous potassium hydroxide in the usual way. Infrared spectroscopic analysis revealed dichlorodifluoromethane (3% conversion) and chlorotrifluoromethane (1% conversion).

In a second experiment carbonyl chlorofluoride (30 g.) was heated to 425° for 19 hr. in presence of a silicate-free activated carbon catalyst (60 g.), impregnated with 27% ferric chloride. The conversions, calculated on the basis that two moles of carbonyl chlorofluoride yield one mole of chlorofluoromethanes, were: CF_2Cl_2, 13%; CF_3Cl, 38%; CF_4, 13%.

Reaction of Phosgene with Hydrogen Fluoride.—Phosgene (60 g.), anhydrous hydrogen fluoride (12.5 g.) and chlorine (7.5 g.) were heated at 425° for 17 hr. in a 0.3 l. Monel autoclave containing pretreated activated carbon catalyst (102 g.), impregnated with 27% ferric chloride. The conversions (based on $COCl_2$ taken) were: CF_2Cl_2, 14%; CF_3Cl, 54%; and CF_4, 4%.

The above experiment, repeated at 350° for 6 hr., gave: CF_2Cl_2, 47%; CF_3Cl, 13%; $CFCl_3$, 7%; and CCl_4, 7%.

In a third experiment phosgene (0.5 mole), hydrogen fluoride (0.45 mole) and chlorine (0.1 mole) were heated as above at 340° for 6.25 hr. The conversions were: CF_2Cl_2, 34%; CF_3Cl, 20%; $CFCl_3$, 10%; CF_4, 4%.

Disproportionation of Dichlorodifluoromethane.—The activated carbon catalyst (100 g., CXA carbon) was prepared *in situ* in a 0.3 l. nickel autoclave by treatment with anhydrous hydrogen fluoride (30 g.) at 350° for 1.5 hr. The autoclave was then pumped out while maintained at 350° for 1.5 hr. The catalyst was used for a reaction between phosgene and anhydrous hydrogen fluoride as described earlier, after which it was heated at 350° *in vacuo* for 1.5 hr. before further use. Dichlorodifluoromethane (152 g.) was next condensed into the autoclave which was heated to 350° for 6 hr. The autoclave was cooled and the gaseous products collected in a cooled trap. Heating the catalyst at 300° *in vacuo* for an hour yielded further product by desorption from the carbon. Distillation and analysis gave CF_2Cl_2 (79.0 g.), CF_3Cl (17.3 g.), $CFCl_3$ (18.0 g.), CCl_4 (14.8 g.) and a small amount of CF_4. Using these figures, 1 mole of CF_2Cl_2 would give 0.52 mole CF_2Cl_2, 0.13 mole CF_3Cl, 0.10 mole $CFCl_3$ and 0.076 mole CCl_4.

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Carbonium Ions. VI. σ^+-Parameters[1]

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A comparison is made between independently determined σ^+-values. A combination of literature data and more extensive work on arylmethanol–arylmethyl cation equilibria permitted the evaluation of σ^+-parameters for a total of nineteen substituents. All nineteen were *p*-substituents and the σ- and σ^+-values in each case were markedly different.

Although Pearson[2] and ourselves[3] had published a few σ^+-values, it was Brown and Okamoto[4,5] who evaluated a total of ten such parameters and critically tested their applicability. These authors found nineteen reaction series in which the log k/k_0 *vs.* σ plots were more linear with σ^+-values than with the usual values of σ. These authors also reviewed the development of this field.

The most critical test of the generality of σ^+-values is whether values independently calculated from different reaction series are invariant. We have found only four reaction series in which σ^+-values can be independently determined. A comparison of these values is presented in Table I and the agreement is encouraging although it is by no means within experimental precision. Of these four series, only the solvolysis of α,α-dimethylbenzyl chlorides[4] has a sufficient number of points, ten, to firmly establish the value of ρ[6] for the series. Rho for the other three series were based on two to four points (listed in Table I) which would be sufficient due to the wide range of σ-values encompassed if complete reliance could be placed on these few points.

Since the value of ρ for the arylmethanol arylmethyl cation equilibria was based on only four points, we have decided to recompute ρ for this

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[1] Grateful acknowledgment is made to the National Science Foundation for support of this work.

[2] D. E. Pearson, J. F. Baxter and J. C. Martin, *J. Org. Chem.*, **17**, 1511 (1952).

[3] N. Deno and A. Schriesheim, THIS JOURNAL, **77**, 3051 (1955).

[4] H. C. Brown and Y. Okamoto, *ibid.*, **79**, 1913 (1957).

[5] Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957).

[6] For the definitions of σ and ρ, see refs. 2–5, and L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, Chapter VII.

TABLE I

COMPARISON OF σ^+-VALUES INDEPENDENTLY COMPUTED

Para substituent	$ArC(CH_3)_2Cl + H_2O$ (ref. 4)	$ArCH(C_6H_5)Cl$[a] + ROH	$ArC(C_6H_5)_2CCl$[b] + H_2O	Arylmethylcation equil.[c]		
				Ar_3C^+	Ar_2CH^+	$ArCH(C_6H_5)^+$
Methoxy	−0.76	−0.82	−0.77	− 0.64	− 0.65	−0.65
Phenoxy		− .39			− .28	
Methyl	− .31	− .32	− .24	− .24	− .23	− .23
Ethyl	− .29	− .35				− .22
Isopropyl	− .28					− .21
t-Butyl	− .25					− .21
3,4-C_4H_4	− .17		− .08			
Fluoro	− .07		.05			.00
Chloro	.11	.12	.20	.11	.08	.09
Bromo	.15	.14	.22		.10	
Iodo	.13		.19		.11	
ρ	−4.62	−3.72	−2.52	−11.91	−11.39	−5.55

[a] Calcd. from the data of J. F. Norris and co-workers, THIS JOURNAL, **50**, 1804, 1808 (1928). [b] Calcd. from the data of A. C. Dixon and G. E. K. Branch, *ibid.*, **58**, 492 (1936). [c] These values, although obtained from three different series, all depend on the ρ calculated from the triarylmethyl cation series and are thus interdependent (ref. 3). Part of the data appear in ref. 3 and part in Table III of this paper.

TABLE II

NEW VALUES OF σ^+

Para substituent	σ^{+a}			
	Ar_3C^+	Ar_2CH^+	$ArSi(CH_3)_3 + H^+$ (ref. 8)	$ArH + Cl_2$ (ref. 9)
Dimethylamino	− 1.49	− 1.87	− 1.79	− 1.52
Anilino	− 1.35			
Amino	− 1.33			
Hydroxy	− 0.82		−- 0.96	− .093
Acetylamino[b]	− .48			− .72
Benzoylamino[b]	− .44			− .72
Phenoxy		− 0.35		− .63
Phenyl			− .12	
Fluoro		− .03	.05	
Chloro	.05	.07	.23	.01
Bromo		.09	.26	.03
Iodo		.10		
ρ	−11.07	−10.02	− 4.14	−13.05

[a] σ^+ was calculated from the relation: $\log k/k_0 = (\sigma)(\rho)$. Rho was determined for each series by a least squares treatment of a selected series of $\log k/k_0$ values. Data for the following substituents were selected. All four series used 4-methoxy and 4-methyl. The first series (column 1) also used data for 3-methyl, 3-chloro and 4-nitro. The second series (column 2) also used data for 3-chloro. The third series (column 3) also used data for 4-ethyl, 4-isopropyl, 4-*t*-butyl and 3-methyl. The fourth series (column 4) also used data for 4-*t*-butyl. For the 3-chloro, 3-methyl and 4-nitro substituents, the normal σ-values were used while for the other substituents, σ^+-values from ref. 4 (Table I) were used. In all four reaction series, additional points for the *p*-halogen substituents could have been used in evaluating ρ. This was not done because the σ^+-values independently determined in Table I do not show good agreement for the halogens. Also, regardless of the method of computing ρ for the four series in Table II, the σ^+-values for the *p*-halogens show poor agreement. [b] There is an uncertainty in the experimental data for these two substituents which may be the cause of the discrepancy. The difficulties with these two substituents in the triarylmethanol–triarylmethyl cation equilibria is discussed in the text. In the chlorination of substituted benzenes, it is possible that N-chlorination affects the kinetics although not appearing as a final product.

series using in addition to the above four points, two additional points (4-methoxy and 4-methyl) for which Brown and Okamoto[4,5] have published σ^+-values. This procedure[7] increased the average deviation of the original four points from 0.020 to 0.027 and had the advantage of bringing the two sets of σ^+-values in closer agreement. This procedure also was used for the diarylmethanol–diarylmethyl cation equilibria as well as two other reaction series, the protonolysis of aryltrimethylsilanes[8] and the chlorination of substituted benzenes.[9]

With the value of ρ established for these series by the procedure described above, values of σ^+ can be computed for six new substituents. A comparison of the values so calculated are presented in Table II.

Reaction series for which σ^+-values seem to be applicable have ρ values ranging from −0.62 to −11.35.[5] In searching for some criterion for the applicability of σ^+-values, the following facts were clear. A resonance interaction or charge delocalization must take place directly between substituent and reaction center, a view that has been discussed by a number of authors and needs no further elaboration. The amount of positive charge to be delocalized varies. It is nearly a full +1 in the solvolysis of α,α-dimethylbenzyl chlorides while it is perhaps only $+^1/_3$ in the triarylmethyl cations, where a full +1 charge is delocalized into three identical substituents. In some of the reaction series, such as the Diels–Alder reaction listed,[5] the charge may be much less than even $^1/_3$. In contrast, some reaction series which must have close to a full +1 charge to delocalize (at least with certain substituents) as well as a large negative value of ρ, fail to give linear plots with either σ^+ or σ. Notable examples of this type are the solvolysis of benzyl tosylates[10] and the brominolysis of benzeneboronic acids.[11]

These facts become consistent if the hypothesis is accepted that it is not so important how much charge is delocalized into the substituent, but that the amount remain *constant* throughout the reaction series. This is illustrated by the arylmethyl cation equilibria where triaryl and diarylmethyl cation equilibria give good linear plots with σ^+. The amount of charge delocalized per substituent varies from $^1/_3$ for the triaryls to $^1/_2$ for the diaryls, but the fraction remains constant in each series.

The new data on arylmethanol–arylmethyl cation equilibria appear in Table III. These data were obtained as previously described[12] by measuring the concentration of arylmethyl cation spectrophotometrically. The absorption spectra of the new arylmethyl cations are briefly summarized in Table IV.

It was assumed that the added arylmethanol either remained unchanged or was converted to

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[7] Suggested by Dr. H. C. Brown.

[8] C. Eaborn, *J. Chem. Soc.*, 4858 (1956).

[9] P. B. de la Mare, *ibid.*, 4451 (1954).

[10] J. K. Kochi and G. S. Hammond, THIS JOURNAL, **75**, 3445 (1953).

[11] H. G. Kuivila and co workers, *ibid.*, **77**, 4834 (1955); **74**, 5068 (1952).

[12] N. Deno, J. Jaruzelski and A. Schriesheim, *ibid.*, **77**, 3044 (1955).

TABLE III

DETERMINATION OF VALUES OF pK_{R^+} FROM LOG (c_{R^+}/c_{ROH}) DATA

H_2SO_4, %	log (c_{R^+}/c_{ROH})[a]	pK_{R^+} C_0 + log (c_{R^+}/c_{ROH})
4,4'-Difluorodiphenylmethanol[b]		
78	0.692	−12.91
77	.365	−12.99
76	.052	−13.03
75	− .240	−13.06
74	− .548	−13.01
73	− .862	−13.16
	Best value	−13.03
4,4'-Dibromodiphenylmethanol[b]		
82	0.577	−14.06
81	.218	−14.16
80	.108	−14.00
79	− .382	−14.24
78	− .652	−14.25
77	− .927	−14.27
	Best value	−14.16
4,4'-Diphenoxydiphenylmethanol		
69	1.33	− 9.93
68	1.14	− 9.86
67	0.646	− 9.79
66	.712	− 9.77
65	.334	− 9.89
	Best value	− 9.85
4,4'-Diiododiphenylmethanol[b]		
85	0.940	−14.48
84	.764	−14.40
83	.572	−14.33
82	.360	−14.28
81	.126	−14.25
80	− .130	−14.25
79	− .393	−14.25
78	− .599	−14.20
77	− .811	−14.15
	Best value	−14.26
Xanthenol		
19	0.865	− 0.94
17	.708	− .88
15	.468	− .86
13	.263	− .85
11	.000	− .85
9	− .190	− .82
7	− .440	− .81
5	− .746	− .82
	Best value	− .84

pH	log (c_{R^+}/c_{ROH})	pK_{R^+} pH + log (c_{R^+}/c_{ROH})
4,4',4''-Trihydroxytriphenylmethanol		
1.19	0.799	1.99
1.49	.411	1.97
2.02	− .176	1.84
2.30	− .348	1.95
2.62	− .741	1.97
	Best value	1.97
4,4',4''-Trianilinotriphenylmethanol		
6.36	1.076	7.44
7.17	0.596	7.77
7.50	.255	7.79
7.78	.102	7.88
	Best value	7.78

H_2SO_4, %	log (c_{R^+}/c_{ROH})	pK_{R^+} H_0 + log (a_{H_2O}) + log (c_{R^+}/c_{ROH})
4,4',4''-Triacetylaminotriphenylmethanol		
20	−0.91	− 1.86
25	− .49	− 1.80
30	− .07	− 1.73
35	.34	− 1.74
40	.75	− 1.77
	Best value	− 1.78
4,4',4''-Tribenzoylaminotriphenylmethanol		
20	−1.33	− 2.28
25	−0.76	− 2.07
30	− .49	− 2.15
35	− .23	− 2.31
40	.04	− 2.4
45	.32	− 2.5
50	.86	− 2.7
	Best value	− 2.30

[a] The ratio (c_{R^+}/c_{ROH}) was equal to ($e/e_{R^+} - e$) where e is the measured extinction coefficient at a particular acid concentration and e_{R^+} is the extinction coefficient of the arylmethyl cation. The extinction coefficient of the free alcohol was negligible at the wave lengths used and e_{R^+} showed a negligible variation with acid concentration in the region adjacent to the one in which e was measured. [b] The optical density was not constant with time so that a short extrapolation was necessary to determine the value of the extinction coefficient at zero time. [c] This value is in agreement with the value 2.00 reported in ref. 14.

TABLE IV

ABSORPTION SPECTRA FOR ARYLMETHYL CATIONS[a]

Cation	Wave length of max., mμ	log e	H_2SO_4, %
4,4'-Difluorodiphenylmethyl	452	4.87	98
4,4'-Dibromodiphenylmethyl	504	5.04	98
4,4'-Diiododiphenylmethyl	560	4.99	98
4,4'-Diphenoxydiphenylmethyl	515	5.03	73
Xanthenyl	375	4.60	25
4,4',4''-Trianilinotriphenylmethyl	590	4.59	[c]
4,4',4''-Trihydroxytriphenylmethyl	480	4.88	7
4,4',4''-Triacetylaminotriphenylmethyl	525	4.33	55
4,4',4''-Tribenzoylaminotriphenylmethyl	510–545	4.95	60

[a] The spectra are reported in greater detail in the Ph.D. Thesis of W. L. Evans, Pennsylvania State Univ., 1957. [b] The spectra were recorded in sulfuric acid of the concentration listed in this column. [c] The spectra were measured in a buffer at pH 1.19.

arylmethyl cation. This assumption needs justification for the 4-amino, 4-hydroxy, 4-anilino, 4-acetylamino and 4-benzoylamino substituents, all of which can conceivably exist in quininoid forms derived from the arylmethanols by loss of water. Goldacre and Phillips[13] have shown that with 4,4',4''-triaminotriphenylmethanol, the amount of dehydrated quininoid form is negligible. Likewise a similar result was shown for 4,4',4''-trihydroxytriphenylmethanol by the work of Bodforss and Hansson.[14]

In the case of the 4-acetylamino and 4-benzoylamino substituents, three observations indicated that no significant fraction existed in the quininoid form. At 10% sulfuric acid where the concentration of arylmethyl cation was negligible, no absorption was detected above 320 mμ in 10^{-4} M solutions. Absorption would have been expected if quininoid form were present. Also the arylmethanol form and not the quininoid form precipitates from aqueous solution. Thirdly, analogous compounds have been found to exist solely in the arylmethanol form. The extensive work of Adams and co-workers[15] on quinonedibenzimides has shown that these compounds readily add alcohols, water and even acetic acid. Further indirect evidence that the quininoid forms are not significant is that a sensitive search for any dehydrated quininoid form of 4,4',4''-trimethyltriphenylmethanol failed.[16]

The interpretation of the data in the case of the 4-acetylamino and 4-benzoylamino substituents presented unexpected difficulties. Unlike other arylmethanol–arylmethyl cation equilibria that

(13) R. J. Goldacre and J. H. Phillips, *J. Chem. Soc.*, 1724 (1949).

(14) S. Bodforss and H. G. Hansson, *Kgl. Fysiograf. Sällskap. Lund Förh.*, **24**, No. 10, 1 (1954); *C. A.*, **49**, 14559 (1955).

(15) R. Adams and co-workers, THIS JOURNAL, **74**, 3657, 5872 (1952); **72**, 4603 (1950).

(16) N. Deno and W. L. Evans, *ibid.*, **78**, 582 (1956).

have been studied,[12] the data did not fit eq. 1.

$$d \log (c_{R^+}/c_{ROH}) = -d\, C_0 \qquad (1)$$

We offer the following interpretation as most likely and will omit discussions of other possibilities.

Let R′OH represent 4,4′,4″-triacetylamino- or tribenzoylaminotriphenylmethanol, ROH represent the arylmethanols used to evaluate the C_0 acidity function[12] and B the bases used by Hammett to evaluate the H_0 acidity function. Equation 2 follows directly from the R′OH/R′$^+$ equilibrium constant expression.

$$(pK_{R^+}) - \log (c_{R^+}/c_{R'OH}) = -\log (a_{H^+}) + \log (a_{H_2O}) + \log (f_{R'}/f_{R'OH}) \qquad (2)$$

If log (f'_{R^+}) were to equal log (f_{BH^+}) instead of log (f_{R^+}),[17] eq. 3 can be derived using the definition of H_0. The experimental data fit this equation approximately as demonstrated in Table III. The values of σ^+ in Table II for these two substituents were derived from $pK_{R'+}$ values obtained by the use of eq. 3.

$$(pK_{R'^+}) - \log (c_{R'^+}/c_{R'OH}) = H_0 + \log (a_{H_2O}) \qquad (3)$$

It was again found that diarylmethyl cations of the type Ar_2CH^+, although stable in 97% sulfuric acid, were not chemically stable in acid concentrations where they coexisted with comparable concentrations of the free diarylmethanol. This result suggested that reaction occurs between the free alcohol and its cation. Two such reactions definitely occur. The first, represented by eq. 4, is being studied by Bartlett and co-workers.[18] The second, represented by eq. 5, was shown to occur with 4,4′-dichlorodiphenylmethanol, since on diluting a sulfuric acid solution of 4,4′-dichlorodiphenylmethyl cation with water, the ether was isolated.[19] It has now been shown to occur also with diphenylmethanol. When a nearly 1/1 equilibrium mixture of the alcohol and its cation stood for two weeks at 25° in 76% sulfuric acid, a 14% yield of the ether was isolated.

$$R_2CHOH + R_2CH^+ = R_2CH_2 + R_2CO + H^+ \qquad (4)$$

$$R_2CHOH + R_2CH^+ = R_2CH\text{–}O\text{–}CHR_2 + H^+ \qquad (5)$$

The equilibrium in the case of 4,4′,4″-triacetylaminotriphenylmethanol was also unstable possibly due to hydrolysis of the amide group.

Experimental

The methods for determining the concentrations of arylmethanol and arylmethyl cation have been previously presented. In this work, method C of ref. 12 was used throughout. The preparation of the alcohols is described below.

4,4′-Difluorodiphenylmethanol.—4,4′-Difluorobenzophenone was prepared from fluorobenzene, carbon tetrachloride and aluminum chloride in carbon disulfide.[20] The ketone was reduced to the alcohol with zinc dust, alcohol and sodium hydroxide.[21] The m.p. of 4,4′-difluorodiphenylmethanol has been reported as 91°[20] and 48°.[21] Since we obtained material melting at 91° by the method that had been reported to give 48° melting material, it seems clear that it is only a matter of two crystalline forms.

4,4′-Dibromodiphenylmethanol.—4,4′-Dibromobenzophenone was prepared by the same method as used with the fluoro analog.[20] Although the ketone was reduced with lithium aluminum hydride in ether, this method offers no advantages over the aluminum isopropylate reduction previously employed.[20]

4,4′-Diiododiphenylmethanol.—4,4′-Diaminobenzophenone,[22] was diazotized at 0–5° in 20% hydrochloric acid. A large excess of saturated potassium iodide solution was added. After standing overnight, sodium hydrogen sulfite solution was added to remove iodine and the remaining yellow solid was filtered and recrystallized from 2-propanol. The yield of white crystals, m.p. 235–237°, was 52%. This method seems to be preferable to the aluminum chloride-catalyzed reaction of 4-iodobenzoyl chloride and iodobenzene which was reported to give an 18% yield of ketone.[23]

The ketone was reduced by refluxing 1.9 g. with 12 g. of aluminum isopropylate and 125 ml. of 2-propanol until acetone evolution ceased. After hydrolysis with 20% hydrochloric acid, the water-insoluble solid was recrystallized four times from 2-propanol. The yield of yellow needles of 4,4′-diiododiphenylmethanol was 0.8 g. (42%), m.p. 130.5–131.5°.

Anal. Calcd. for $C_{13}H_{10}OI_2$: C, 35.81; H, 2.49. Found: C, 36.46; H, 2.48.

4,4′-Diphenoxydiphenylmethanol.—4,4′-Diphenoxybenzophenone was prepared from diphenyl ether, carbon tetrachloride and aluminum chloride in carbon disulfide at 25°. The product was purified with difficulty by repeated recrystallizations from benzene–pentane. The yield of pure product, m.p. 128–130°, was only 6%. This ketone had previously been prepared in 70% yield from 4.4′-dibromobenzophenone and potassium phenoxide (m.p. 147°)[24] and by chromic acid oxidation of 1,1-bis-(4-phenoxyphenyl)-propene (m.p. of product was 139°).[25]

The ketone was reduced with lithium aluminum hydride in ether. The product after hydrolysis was recrystallized several times from pentane to give a 24% yield of white crystals of 4,4′-diphenoxydiphenylmethanol, m.p. 88–91°.

Anal. Calcd. for $C_{25}H_{20}O_3$: C, 81.50; H, 5.47. Found: C, 81.72; H, 5.94.

4,4′,4″-Trianilinotriphenylmethanol.—This compound was prepared from diphenylamine and oxalic acid.[26] A 10% yield of the red-brown triarylmethyl salt was obtained which melted at 240–243° (reported 237–238°).

4,4′,4″-Triacetylaminotriphenylmethanol.—Pararosaniline (free base) was acetylated by dissolving 10 g. in 100 ml. of acetic anhydride containing 2.5 g. of sodium acetate. After one day, water was added and the precipitated solid was triturated with water at 100°. The solid was refluxed for several minutes with 2-propanol containing a slight excess of sodium hydroxide. The remaining solid was recrystallized many times from a mixture of ethanol and 2-propanol. The eventual yield was 0.4 g. (3%) of white solid, m.p. 182° dec. (reported[27] 192°). We were unable to obtain the product when the acetylation was conducted in refluxing acetic anhydride as had been reported.[27]

4,4′,4″-Tribenzoylaminotriphenylmethanol.—A mixture of 15 g. of pararosaniline and 100 ml. of benzoyl chloride was heated on the steam-bath for 8 hr. The mixture was added to ice and after one day the solid was triturated with 200 ml. of methanol. The green residue was recrystallized a number of times from methanol containing a slight excess of sodium hydroxide. The yield of white crystals, m.p. 191.5–193°, was 2.8 g. (9%).

Anal. Calcd. for $C_{40}H_{31}O_4N_3$: C, 77.78; H, 5.06; N, 6.80. Found: C, 77.50; H, 5.24; N, 6.59.

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[17] This postulate is plausible. The cation, R′$^+$, differs from the usual triarylmethyl cations in having a nitrogen substituent upon which most of the positive charge may be localized. It would thus resemble BH$^+$ more in charge distribution which is a critical factor in determining activity coefficient behavior (N. Deno and C. Perizzolo, THIS JOURNAL, **79**, 1345 (1957)). The other nitrogen substituted triarylmethanols have all been studied in the *p*H range where differences between d log (f_{R^+}) and d log (f_{BH^+}) vanish.

[18] P. D. Bartlett and J. D. McColum, *ibid.*, **78**, 1441 (1956).

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