The product was dried at 100° for 6 hr. under vacuum and then analyzed.

Anal. Cacld. for $C_8H_9B_2NO_4$: C, 46.91; H, 4.42. Found: C, 47.23; H, 4.72.

A suspension of 210 mg. of this acetamido compound in 3 ml. of ammoniacal silver nitrate[15] was warmed on a hot-plate to effect solution. After standing for several minutes, a solid product began to crystallize, admixed with finely divided silver. The crystalline material was dissolved by warming, and the solution was treated with charcoal, filtered and cooled. The mixture was filtered, washed and dried, yielding 50 mg. of material, m.p. 110–112°. A mixed melting point of this product with acetanilide showed no depression.

2-Ureidobenzene-1,4-diboronic Acid Monoanhydride.—A suspension of 4.0 g. of 2-nitrobenzene-1,4-diboronic acid and 100 mg. of platinum oxide in a solution of 30 ml. of glacial acetic acid and 30 ml. of water was reduced catalytically. After the uptake of hydrogen was completed, the solution was filtered to remove the catalyst and the amine was converted to the urea without prior isolation of the amine. To the acetic acid solution 3.3 g. of potassium cyanate in 10 ml. of water was added. The solution was stirred, warmed to 40° and allowed to stand for 0.5 hour. The mixture was cooled, filtered, washed and dried to yield 2.1 g. of a white crystalline solid, m.p. >350°. A sample for analysis was obtained by recrystallization twice from methanol–water.

Anal. Calcd. for $C_7H_8B_2N_2O_4$: C, 40.85; H, 3.91. Found: C, 40.99; H, 4.16.

A solution of 300 mg. of the ureido compound in 5 ml. of ammoniacal silver nitrate[15] was prepared by warming the mixture on a hot-plate. The solution was heated for 10 min., treated with charcoal, filtered and cooled. A precipitate of 77 mg. was obtained which showed no melting point depression with phenylurea.

2-Acetamidobenzeneboronic Acid Anhydride.—A suspension of 5 g. of *o*-nitrobenzeneboronic acid in 50 ml. of 50% acetic acid was reduced catalytically in the presence of 200 mg. of platinum oxide. After the absorption of hydrogen was complete, the solution was filtered and concentrated under reduced pressure with frequent additions of water in order to remove the acetic acid. The concentrated aqueous solution upon cooling yielded 2.5 g. of a white crystalline solid, m.p. 298–300°. A sample for analysis was successively recrystallized from methanol–water; m.p. 300–301°.

Anal. Calcd. for $C_8H_8BNO_2$: C, 59.68; H, 5.01. Found: C, 59.14; H, 5.48.

A suspension of 200 mg. of *o*-acetamidobenzeneboronic acid anhydride in 3 ml. of 10% ammoniacal silver nitrate[15] was warmed until the solid completely dissolved. The solution was filtered while hot to remove any finely divided silver. Upon crystallization, 77 mg. of acetanilide was obtained.

Acknowledgments.—The author is very grateful to Dr. William H. Sweet, Associate Professor in Surgery at the Harvard Medical School, for his interest and encouragement. The technical assistance of Mr. Pal Szabady is acknowledged. The author wishes to thank Mr. E. Nyilas for determining the ultraviolet absorption spectra of the diborimidazoline.

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[15] One gram of silver nitrate was dissolved in 8 ml. of water and this was diluted to 10 ml. with 28% aqueous ammonia.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

The Formation of Trianisylmethylcarbonium Ion by the Interaction of Tetraanisylethylene with Electron Acceptors[1]

BY ROBERT E. BUCKLES, RONALD E. ERICKSON,[2] JOHN D. SNYDER[3] AND WILLIS B. PERSON

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When tetraanisylethylene (I) interacted with various electron acceptors, a characteristic blue (λ_{max} around 575 mμ) solution was usually observed. On standing, dilute solutions (10^{-3} M or less) of this blue complex gradually turned yellow (λ_{max} around 490 mμ). The yellow absorbing species in these solutions has been identified as trianisylmethylcarbonium ion (II) on the basis of its visible absorption spectrum. When a relatively large volume of a solution (5 × 10^{-3} M) of I in ethylene chloride was allowed to react with an equimolar amount of chlorine for two days a 22% yield of 4′-methoxy-2,2,2-trianisylacetophenone (III) could be isolated. This pinacolone on interaction with electron acceptors also gave solutions of II. These solutions could be prepared with higher concentrations than those possible starting with I. With these more concentrated solutions identification of II by means of infrared absorption spectroscopy was possible. The relative intensities of ten absorption bands in the infrared spectra of various model compounds and in the infrared spectra of the solutions under investigation were compared in order to establish the identification.

An earlier report[4] described in detail the changes in the ultraviolet and visible absorption spectrum observed when tetraanisylethylene (tetrakis-(*p*-methoxyphenyl)-ethylene) (I) interacted with bromine in ethylene chloride. In the present investigation the same general behavior was observed when Compound I interacted with a number of other electron acceptors. First a blue solution with a broad absorption peak around 575 mμ was observed. On standing, this blue solution slowly turned yellow if the concentration of I was of the order of 10^{-3} M or less. This yellow solution was characterized by an absorption peak around 490 mμ. In more concentrated solutions either the change to the yellow solution was incomplete or side reactions such as halogenation became important so that the yellow absorbing species was still formed only in relatively low concentrations.

Representative electron acceptors which were observed to give this interaction with I are listed in Table I along with the wave length characteristic of the absorption peak of the final yellow solution. In each case except for that of iodine in ethylene chloride the electron acceptor interacted with I to give a blue solution (λ_{max} around 575 mμ), which slowly turned yellow on standing. The molar absorbancy index (molar extinction coefficient) of the peak near 490 mμ, based on the initial concentration of I, was found to be as high as 5 × 10^4 in some experiments involving iodine chloride,

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[2] Monsanto Predoctoral Fellow, 1957–1958.

[3] Du Pont Predoctoral Fellow, 1957–1958.

[4] R. E. Buckles and W. D. Womer, THIS JOURNAL, **80**, 5055 (1958).

TABLE I

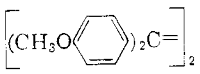
THE FORMATION OF TRIANISYLMETHYLCARBONIUM ION (II) FROM THE INTERACTION OF TETRAANISYLETHYLENE (I) WITH VARIOUS ELECTRON ACCEPTORS

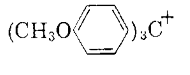
Acceptor	Approx. concn. of I, *M*	Mole ratio of acceptor to 1	Solvent	λ, mμ of peak
Br_2	10^{-5}	1	$(CH_2Cl)_2$	490
ICl	10^{-5}	1	$(CH_2Cl)_2$	491
IBr	10^{-5}	1	$(CH_2Cl)_2$	489
I_2[a]	10^{-4}	5	$(CH_2Cl)_2$	492
Cl_2	10^{-3}	1	$(CH_2Cl)_2$	489
H_2SO_4	10^{-3}	100	HOAc	484
CF_3COOH	10^{-3}	100	CCl_4	488
CCl_3COOH	10^{-3}	100	CCl_4	484
Phenol	10^{-1}	10	CCl_4	488
BF_3	10^{-5}	4	CH_2Cl_2	488
PCl_5	10^{-3}	1	CCl_4	494
PCl_3	10^{-3}	10^3	CCl_4	490
BzCl	10^{-3}	10^4	CCl_4	490

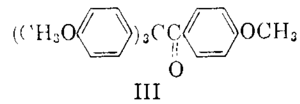
[a] The interaction of iodine with I in ethylene chloride did not give the peak at 575 mμ characteristic of the blue solutions; in acetonitrile, however, this peak was observed.

trichloroacetic acid or trifluoroacetic acid as electron acceptors.

In each case where the absorption peak was not complicated by other absorption, an inflection point was observed around 460 mμ as well as the peak itself, near 490 mμ. These characteristics of the absorption spectra are consistent with the assumption that the yellow species was the trianisylmethylcarbonium ion (tris-(*p*-methoxyphenyl)-methylcarbonium ion) (II). The perchlorate of II was found to have an approximate molar absorbancy index of 10^5 in ethylene chloride and in methylene chloride at 490 mμ. In each of these solvents the inflection point of 460 mμ was also observed. In sulfuric acid the peak for II has been reported[5] with this same intensity at 483 mμ. The production of II by the interaction of I with electron acceptors in dilute solution was thus observed in yields as high as 50% with iodine chloride, trichloroacetic acid and trifluoroacetic acid.


I


II


III

In an experiment on amounts large enough to allow product isolation, 1.97 × 10^{-3} mole of I with a slight excess of chlorine in 400 *m*l. of ethylene chloride reacted until the solution was somewhat yellow. From this solution it was possible to isolate a 22% yield (4.3 × 10^{-4} mole) of 4′-methoxy-2,2,2-trianisylacetophenone (4′-methoxy-2,2,2-tris-(*p*-methoxyphenyl)-acetophenone) (III) by evaporation and treatment of the residue with absolute ethyl alcohol. The production of this product requires the presence of water, but for this yield only 7.8 mg. of water would be necessary and such amounts would be available in the solvent or on the walls of the vessel.

In another experiment the pinacolone III was detected as a product of the interaction of I with trichloroacetic acid in carbon tetrachloride. The identification was based on the infrared absorption spectrum of the reaction mixture after the acid was neutralized by aqueous base. This spectrum showed a doublet at 1166 and 1183 cm.$^{-1}$, which was specifically characteristic of III, as well as the less definitive carbonyl stretching frequency at 1680 cm.$^{-1}$. Also the bands characteristic of many of the anisyl derivatives as shown in Table II were observed.

The pinacolone III was found to interact with electron acceptors to give the yellow absorbing species with the same spectral characteristics as those shown by trianisylmethylcarbonium perchlorate. In Table III are listed data showing the extent of the formation of II from III on interaction with various electron acceptors in dilute solutions.

In one series of experiments the pinacolone III (4.36 × 10^{-5} *M*) was allowed to react with a large excess of iodine (1.73 × 10^{-3} *M*) in ethylene chloride. When kept in the dark for several hours the solution had a spectrum characteristic of the two components absorbing independently. After illumination for several hours the characteristic absorption peaks of the carbonium ion II (490 mμ) and the triiodide ion (295 and 365 mμ)[6] began to appear. After several days of illumination these peaks reached their maximum intensities. Although it was impossible to correct for the absorption of other, unknown species, which must be present, an estimate of the concentration of the carbonium ion II could be made after correction for the absorption by excess iodine. This concentration was 2.4 × 10^{-5} *M* which is 55% of the original concentration of III. The absorption peaks observed for triiodide ion were intense enough to account for this concentration and a reasonable background of absorption from other species.

When tetraanisylethylene I and excess iodine were allowed to react in a similar fashion only small amounts of II and triiodide ion could be detected after several days of illumination. Extensive spectral changes were observed on long illumination, but they were mostly caused by unidentified reactions.

Similar experiments with bromine and with iodine chloride were unsuccessful. The absorption peak characteristic of tribromide ion (273 mμ)[7] was obscured by other absorbing species in the solutions. With iodine chloride the trihalide ion expected would be the iododichloride ion (dichloroiodate (I) ion). The absorption peak of low intensity (340 mμ)[8] which is characteristic of this ion was obscured by the absorption of other species and the characteristic peak of high intensity (227 mμ)[8] was outside the range of transparency of the solvent.

The production of II from III appeared to be more efficient than the production from I. This fact was especially evident when more concentrated solutions than those possible with I were used.

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(5) C. G. Swain, L. Kaiser and T. Knee, THIS JOURNAL, **77**, 4681 (1955).

(6) R. E. Buckles J. P. Yuk and A. I. Popov, *ibid.*, **74**, 4379 (1952).

(7) R. E. Buckles and J. P. Yuk, *ibid.*, **75**, 5048 (1953).

(8) R. E. Buckles and J. F. Mills, *ibid.*, **76**, 4845 (1954).

TABLE II

CHARACTERISTIC INFRARED ABSORPTION BANDS[a] USED IN THE IDENTIFICATION OF TRIANISYLMETHYLCARBONIUM ION (II)

Compound	Apparent molar absorbancy indices (10^{-3}) at Characteristic wave numbers[b] 1610	1585	1515	1366	1302	1250	1215	1177	1166	1035
Tetraanisylethylene (I)	0.70	0.12	0.80	..	0.41	1.38	..	0.90	..	0.53
4′-Methoxy-2,2,2-trianisylacetophenone (III)[c]	.80	.24	1.07	..	.49	0.88	0.75	.88[d]	0.88	.58
Dianisylmethane	.08	.03	0.34	..	.08	.37	.20[e]	.15	..	.16
4,4′-Dimethoxybenzophenone[f]	.91	.18	.20	..	.38	.84	.19[e]	.15	.65[g]	.30
Anisole	.16	..	.23	..	.07	.28	09[e]	06	..	.13[h]
1,1,2,2-Tetraanisyl-1,2-ethanediol	.46	.23	1.16	..	.78[e,i]	1.48[j]	1.06	.58[e]	.79[k]	.70
Trianisylcarbinol	.35	.18	0.75	..	.84[e,i]	1.28[j]	1.21	.81	..	.58
Perchlorate of II[l]	..	5.27	..	2.73	1.30[m]	3.20[n]	1.83	..	6.02	.85[o]
III + excess ICl[c]	.92	3.04	.41	1.83	0.84[m]	2.33[n]	0.75	.75[d,e]	3.26	.88[o] .35[e]
III + ICl (1:1)[c]	.94	1.92	1.00	0.78	.48[m]	1.07[n]	.60	0.65[d]	2.39	.49[o] .54
III + Br_2 (1:1)[c,p]	.89	0.83	1.02	0.23	.39[m]	0.66	.51	0.69[d]	1.26	.33[o] .54
III + excess CCl_3COOH[c]	.70	2.61	.88	1.61	1.04[m]	2.18	1.61	1.16[d,e]	3.06	.85[o] .42[e]

[a] The spectrum of each model compound was measured in at least two solvents. The composite spectrum was then used for the estimation of intensities in each case. Solvents used were chloroform, methylene chloride, ethylene chloride, carbon tetrachloride and carbon disulfide. [b] Apparent molar absorbancy index (a) for each of the absorption bands was calculated from the absorbance or optical density (A), concentration (c) and cell thickness (b) by means of the equation: $abc = A = \log (I_0/I)$. The units are l. mole^{-1} cm.$^{-1}$. [c] The pinacolone also had its characteristic carbonyl stretching frequency at 1680 cm.$^{-1}$. This band was also present in the solutions of III with electron acceptors, but the intensity was greatly decreased. [d] Maximum absorbance at 1183 cm.$^{-1}$. [e] This value was for an inflection point. [f] The benzophenone also had its characteristic carbonyl stretching frequency at 1650 cm.$^{-1}$. [g] Another band of molar absorbancy index 0.18 was observed at 1150 cm.$^{-1}$. [h] Maximum absorbance at 1040 cm.$^{-1}$. [i] Maximum absorbance at 1280 cm.$^{-1}$. [j] Maximum absorbance at 1241 cm.$^{-1}$. [k] Maximum absorbance at 1170 cm.$^{-1}$. [l] The band at 1090 cm.$^{-1}$ in the spectrum of this compound is characteristic of the perchlorate ion (see footnote 9, p. 575). [m] Maximum absorbance at 1312 cm.$^{-1}$. [n] Maximum absorbance at 1260 cm.$^{-1}$. [o] Maximum absorbance at 1015 cm.$^{-1}$. [p] With excess bromine there was extensive evolution of hydrogen bromide so that no quantitative measurements could be made.

TABLE III

THE FORMATION OF TRIANISYLMETHYLCARBONIUM ION (II) FROM THE REACTION OF ELECTRON ACCEPTORS WITH 4′-METHOXY-2,2,2-TRIANISYLACETOPHENONE (III) IN ETHYLENE CHLORIDE

Concn. III, $M \times 10^5$	Acceptor	Concn. acceptor, $M \times 10^4$	A at max.[a]	Yield of II,[b] %
0.61	CF_3COOH	4.3	0.39	64
3.1	I_2	1.9	0.68	22
4.36	I_2	17.3	2.40[c]	55
1.5	Br_2	1.27	0.37	25
1.5	Br_2	2.53	.58	39
1.5	Br_2	3.83	.71	47
1.5	Br_2	5.06	.78	52
1.5	Br_2	6.33	.82	55
0.61	ICl	0.60	.61	100
1.5	ICl	1.29	1.48	99[d]
1.5	ICl	2.58	1.49	99[d]
1.5	ICl	3.88	1.48	99[d]
1.5	ICl	5.17	1.47	98[d]
1.5	ICl	6.46	1.48	99[d]

[a] The absorbance or optical density (A) was measured at λ_{max} (around 490 mμ) after the solution had aged for 24 hours at 26°. Each value was corrected for the absorption of the excess electron acceptor. [b] The yield was calculated on the basis of a molar absorbancy index of 10^5 for II. [c] This value was obtained by dilution of the original solution and correction for the absorbance of the excess iodine. [d] These values had dropped to an average value of 97% after the solutions were aged for 10 days.

It was possible to prepare solutions of II of concentrations large enough for semi-quantitative determinations of the infrared spectra. In Table II are summarized data on ten characteristic infrared absorption bands used in identifying II in the reaction mixtures. Included are the most pertinent model compounds studied, as well as the solutions of III with electron acceptors. The ten bands given in Table II include all of the intense characteristic bands associated with the model compounds between 1000 and 1610 cm.$^{-1}$. Besides these bands the carbonyl compounds showed characteristic carbonyl frequencies, and all of the samples showed absorption bands in the carbon–hydrogen stretching region around 3000 cm.$^{-1}$ when a suitable solvent was used. Relatively minor absorption bands and inflection points have not been included in Table II unless they were significant in the comparisons made.

The identification of the yellow absorbing species as the carbonium ion II was definitely established by the relative apparent intensities of the bands which were characteristic of most of the model compounds, the shift in position of some of the bands, and the characteristic band shapes. Associated with the formation of II was the appearance of the band at 1366 cm.$^{-1}$. This band was not observed in the spectrum of any of the other model compounds. The increases in apparent intensities of the bands at 1585, 1302, 1250, 1215 and 1166 cm.$^{-1}$ were also characteristic of the formation of II. The band at 1302 cm.$^{-1}$ was shifted to 1312 cm.$^{-1}$ in the spectrum of II. The band at 1250 cm.$^{-1}$ was shifted to 1260 cm.$^{-1}$ in the spectrum of the perchlorate of II and in some of the solutions of III with electron acceptors. It was a broad band so that the location of the exact frequency of the peak absorption was difficult to determine. The shift of the band at 1035 to 1015 cm.$^{-1}$ was particularly significant because in the case of the interactions of II with electron acceptors where some III remained unchanged the band at 1035 cm.$^{-1}$ as well as the one at 1015 cm.$^{-1}$ was observed, at least as an inflection point.

The frequencies considered in the identification of II can be tentatively assigned[9] as follows: 1610 and 1505 cm.$^{-1}$, ring vibrations; 1515 cm.$^{-1}$, ring vibration characteristic of *p*-substitution; and 1250 and 1035 cm.$^{-1}$, C–O–C stretching frequencies of aromatic ethers. The bands at 1166 and 1176 cm.$^{-1}$ also seem to be associated with the methoxy group in these compounds. They appear to be sensitive to the amount of conjugation of the methoxy group with an electronically deficient center. The band at 1366 cm.$^{-1}$ was observed only for the perchlorate of II among the model compounds studied. It seems to be associated with the presence of a positive center conjugated with the methoxy group in the *para* position.

From the data given in Table II it is apparent that in no case was the pinacolone III converted to the carbonium ion II quantitatively as was observed in dilute solutions with iodine chloride. The intensities of the peaks characteristic of II were always considerably lower than those observed for the perchlorate of II. In fact in the more concentrated solutions the maximum yield of II observed was of the order of 60%. In these more concentrated solutions competing side reactions such as halogenation become more important than they are in dilute solutions.

In the earlier report[4] on the interaction of I with bromine, copper powder was found to remove the blue absorbing species characterized by the absorption peak at 575 mμ and to give essentially 100% recovery of I in solution. This result was verified in the present work. Complexes with halogens were destroyed by copper powder and complexes with proton donors were destroyed by aqueous base. In either case compound I was detected unchanged in solution by spectrophotometric methods. Also in the earlier investigation[4] the yellow species formed by I with bromine was found to be removed by copper powder and to be quantitatively regenerated when more bromine was added. This removal of the yellow species II by copper followed by its regeneration when halogen was added to the solution was qualitatively verified in the present work, but the regeneration was not quantitative. The report[4] that Compound I was formed from II by the action of copper could not be verified, however. It is possible that the solutions in the earlier work which contained the carbonium ion II also contained I or the blue complex so that treatment with copper powder gave a solution which had a spectrum close enough to that of I to be misleading.

In the light of the present identification of the yellow species as II, its removal by copper powder must involve the formation of the covalent trianisylmethyl halide. This result could be accomplished either by the destruction by copper of the trihalide ion accompanying II or by the interaction of copper halide with II. The covalent halide would be expected[10] to be only slightly ionized in a solvent such as ethylene chloride. The regeneration of II from the covalent halide on the addition of halogen would involve formation of trihalide ion. Such an enhancement of the ionization of triphenylmethyl chloride by iodine chloride has been observed.[11]

$$Ar_3CX + X_2 \rightleftarrows Ar_3C^+X_3^-$$

The more concentrated solutions of II available from the interaction of III with iodine chloride were treated with copper powder. Those from the interaction of III with trichloroacetic acid were treated with aqueous bicarbonate. In the latter case particularly a comparison of relative intensities and shapes of the characteristic infrared absorption bands which are listed in Table II identified the main species present after the destruction of II as trianisylmethanol. Very nearly the same spectrum was obtained between 1000 and 1610 cm.$^{-1}$ for the solution resulting from the reaction of copper with the solutions of II prepared from III and iodine chloride. It would be expected that the infrared absorption spectra of the trianisylmethyl halides would be very similar to that of the carbinol in this region. In all cases some III (or possibly halogenated derivative of III) was found to be still present in the solutions on the basis of the carbonyl stretching frequency at 1680 cm.$^{-1}$ and the characteristic doublet at 1183 and 1166 cm.$^{-1}$ which was partially obscured by other absorption but which still showed up clearly enough to be significant.

The results of the interaction of three other pinacolones with iodine chloride in ethylene chloride are summarized in Table IV. The triphenylmethylcarbonium ion from benzopinacolone had the characteristic double absorption peak which is observed[10,11] in 98% sulfuric acid, but the absorption was only about one-tenth as intense. The spectra of dianisylphenylmethylcarbonium ion and of dianisyl-(*p*-bromophenyl)-methylcarbonium ion formed from the corresponding pina-

TABLE IV

ABSORPTION SPECTRA PEAKS OF THE TRIARYLMETHYLCARBONIUM IONS FORMED BY INTERACTION WITH IODINE CHLORIDE IN ETHYLENE CHLORIDE

Compound	Concn., $M \times 10^4$	ICl concn., $M \times 10^2$	λ_{max}, mμ	*A*s
Benzopinacolone	3.4	3.2	437	1.01
			414	1.00
2,2-Dianisyl-2-phenylacetophenone	0.25	0.32	505	1.90
			417	0.81
2,2-Dianisyl-2-(*p*-bromophenyl)-4′-bromoacetophenone	.30	.64	512	1.37
			433	0.76
1,2-Dianisyl-1,2-diphenylethylene	.23	.32	510	.87
			430	.41

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[9] R. N. Jones and C. Sandorfy in W. West (Editor), "Techniques of Organic Chemistry, Vol. 9, Chemical Applications of Spectroscopy," Interscience Publishers, Inc., New York, N. Y., 1956, Chapter 4.

(10) A. G. Evans, A. Price and J. Thomas, *Trans. Faraday Soc.*, **51**, 481 (1955); A. Bently, A. G. Evans and J. Halpern, *ibid.*, **47**, 711 (1951).

(11) R. E. Buckles and J. D. Snyder, unpublished work.

colones were not verified, but the dual peaks in their spectra were consistent with those found for other unsymmetrical triarylmethylcarbonium ions.[12]

A number of tetraarylethylenes other than I were reinvestigated in the light of the present results. Of the rather extensive list of compounds used in the earlier investigation[4] only 1,2-dianisyl-1,2-diphenylethylene showed spectral changes parallel to those of I on interaction with iodine chloride. The triarylmethylcarbonium ion which was formed may have been partially halogenated, however. It would be expected to be the same as that formed from 2,2-dianisyl-2-phenylacetophenone if the anisyl group underwent the expected[13] preferential migration, but it was not the same (see Table IV).

At present there is not enough evidence available to establish a mechanism for the formation of II either from I or from III. The formation of II from I and in some cases even the formation of the blue complex from I was accelerated by illumination. These results would imply that the mechanism of formation of II might involve some free radical intermediates. In connection with these results it should be noted that there have been recent reports[14] of free radical character associated with the highly colored complexes of iodine with aromatic hydrocarbons having condensed ring systems.

In any event the formation of II from I would involve complexing with the electron donor and the migration of an anisyl group followed by a dissociation step. Similarly III would be expected to interact with the electron donor at the carbonyl group followed by a dissociation step. No products other than the carbonium ion II, the pinacolone III and unchanged tetraanisylethylene I have been detected in any of the reaction mixtures even though a good deal of effort was expended on the attempted detection of other products—especially derivatives of anisic acid or anisaldehyde from the interaction of III with various electron acceptors. The formation of the pinacolone III from I requires an oxidizing agent. Molecular halogen can act as an oxidizing agent, but when the electron acceptor is a proton, oxygen or some other oxidizing agent must be involved.

The interaction of III at the carbonyl group seems reasonable since 4,4′-dimethoxybenzophenone reacted with iodine chloride or trichloroacetic acid to give solutions in which the intensity of the carbonyl frequency at 1650 cm.$^{-1}$ was considerably depressed while bands at other frequencies, which are given in Table II, were somewhat intensified. Removal of the iodine chloride by copper powder or of the trichloroacetic acid by aqueous bicarbonate gave rise to the spectrum of the benzophenone unchanged.

Experimental Part

Solvents.—Commercial ethylene chloride was boiled with concentrated sulfuric acid under reflux for two days and then was separated from the bulk of the acid by distillation. The distillate was washed three times with concentrated sulfuric acid, twice with water, twice with aqueous sodium bicarbonate and finally four to six times with water. After preliminary drying over anhydrous magnesium sulfate the solvent was boiled with phosphorus pentoxide under reflux for 24 hours. It was then distilled twice from fresh phosphorus pentoxide through an efficient fractionating column. Ethylene chloride purified by this method was of consistent quality. It was transparent down to 240 mμ and it was stable to the halogens used in this investigation. No impurities could be detected by gas chromatography. The difficulties encountered in earlier investigations[4,7,15] with this solvent seem to have been overcome by this method.

Commercial methylene chloride was purified as described in an earlier report.[16] Carbon tetrachloride, chloroform and carbon disulfide were Reagent Grade, used without further purification.

Chemicals.—Most of the chemicals used were available either from commercial sources or from the synthetic methods used in the previous investigations[4,16] on tetraarylethylenes. Trianisylmethylcarbonium perchlorate and trianisylmethanol were kindly supplied by Mr. Robert Duty of this Laboratory.

Iodine Chloride.—To a tared flask was added 63.5 g. (0.25 mole) of iodine. Dry chlorine was passed into the flask until the gain of weight was 17.8 g. (0.25 mole of chlorine). The mixture was purified by fractional crystallization until its melting point was constant (27.1–27.3°).

Iodine Bromide.—Ten grams (0.039 mole) of iodine was dissolved in 20 ml. (58.6 g., 0.37 mole) of bromine in a crystallizing dish. The excess bromine was allowed to evaporate. The dark residue was placed in a glass-stoppered brown bottle. On standing, iodine bromide sublimed onto the walls of the bottle. These freshly sublimed crystals were used for making stock solutions.

4′-Methoxy-2,2,2-trianisylacetophenone (III).—A solution of 10.0 g. of 4,4′-dimethoxybenzophenone in 1 l. of isopropyl alcohol containing a drop of glacial acetic acid was left in a location exposed to sunlight for two months. From the reaction mixture 8.0 g. of crude yellow product was obtained. Crystallization from benzene gave 1,1,2,2-tetraanisyl-1,2-ethanediol, m.p. 178°, reported[17] m.p. 182.°

A solution of 7.0 g. of this pinacol and 0.05 g. of iodine in 30 ml. of glacial acetic acid was boiled for 10 minutes. The mixture was poured over 80 g. of ice. The precipitate was crystallized from ethyl alcohol–benzene to give 4′-methoxy-2,2,2-trianisylacetophenone, m.p. 136–137° which is that reported.[18]

2,2-Dianisyl-2-phenylacetophenone.—A solution of 10.0 g. of 4-methoxybenzophenone in 250 ml. of isopropyl alcohol containing one drop of glacial acetic acid was left in a location exposed to sunlight for one week. The reaction mixture yielded 8.0 g. of crude product. Crystallization from absolute ethyl alcohol yielded 1,2-dianisyl-1,2-diphenyl-1,2-ethanediol, m.p. 157–159°. The m.p reported[18] is 170–171°, but this may be a diastereomer since the pinacolone checks.

A solution of 3.5 g. of this pinacol and a small crystal of iodine in 20 ml. of glacial acetic acid was boiled under reflux for an hour. The mixture was poured onto ice to give an oily solid product. Crystallization from absolute alcohol gave 2.5 g. of 1,2-dianisyl-2-phenylacetophenone, m.p. 124–125° which compares favorably with that reported[18] (125–126°).

2,2-Dianisyl-2-(*p*-bromophenyl)-4′-bromoacetophenone.—A solution of 12.0 g. of 4-bromo-4′-methoxybenzophenone in 1 l. of isopropyl alcohol containing a drop of glacial acetic acid was left in a location exposed to sunlight for one month. From the reaction mixture was obtained 5.0 g. of crude product, m.p. 168–170°, which was presumably 1,2-bis-(*p*-bromophenyl)-1,2-dianisyl-1,2-ethanediol.

A solution of 11.0 g. of this crude pinacol and 0.05 g. of iodine in 250 ml. of glacial acetic acid was boiled for 15 minutes. Steam distillation yielded 9.5 g. of crude product. Crystallization from ethyl alcohol and then benzene yielded 2,2-dianisyl-2-(*p*-bromophenyl)-4′-bromoacetophenone, m.p 164–165°.

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Anal. Calcd. for $C_{30}H_{22}Br_2O_8$: C, 58.3; H, 3.84. Found: C, 58.8; H, 4.04.

4′-Methoxy-2,2,2-trianisylacetophenone (III) from the Interaction of Tetraanisylethylene (I) with Chlorine.—An ethylene chloride solution containing 0.893 g. (1.97×10^{-3} mole) of I and 2.3×10^{-3} mole of chlorine was allowed to stand in diffuse daylight for two days. The yellow solution was concentrated by distillation under reduced pressure to give an orange residue. Crystallization from ethyl alcohol-benzene and then from absolute ethyl alcohol gave 0.20 g. (22%) of III, m.p. 138–140°. Further crystallization sharpened the m.p. to 139–140°. A mixed m.p. with authentic III showed no depression.

Many other similar experiments with other electron acceptors and I were tried but no product other than I could be isolated.

Spectrophotometric Measurements.—Visible and ultraviolet absorption spectra were determined using a Cary model 11 recording spectrophotometer. A set of matched silica cells of path length 1.00 ± 0.01 cm. were used to determine the spectra. Some measurements were made in cells of longer path length of comparable precision.

All infrared spectra were obtained using a Perkin–Elmer model 21 infrared spectrophotometer equipped with a sodium chloride prism. Many of the measurements were made using matched pairs of fixed liquid cells of 0.025-, 0.10- and 1.0-mm. path length. Two special cells containing no metal parts in contact with the solution were also used.[19]

Solutions of model compounds of satisfactory concentrations were made up in suitable solvents. Concentrations ranging from 10^{-3} to 10^{-5} M were used for most measurements in the visible and ultraviolet region. Concentrations from about 1 to 10^{-2} M were used in the infrared region. In the studies on the complexes and the reaction mixtures stock solutions were prepared for convenience in mixing solutions of various compositions. In some experiments the measurements had to be made on freshly prepared solutions; for others aging of the solutions was necessary. For the experiments requiring the removal of the electron acceptor at some stage excess copper bronze was used to remove halogens and aqueous bicarbonate was used to remove proton donors. In all of these experiments a wide latitude of operations was possible. After each removal of reagent or addition of reagent it was possible to measure spectra in whichever region desired for the purpose of identifying species present in the solution.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO]

Solvation Effects and Relative Rates. II. Some Benzyl Chlorides in Methanol[1]

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A general analysis of solvation effects and relative rates, with particular attention to the problem of the effect of structure upon reactivity, is presented and is applied to the solvolysis reactions of some benzyl chlorides in methanol. Data for the analysis are presented, being obtained from measurements of the rates of solvolyses of benzyl, *p*-methylbenzyl and *p*-*t*-butylbenzyl chlorides, of the vapor pressures of the pure chlorides, and of the Henry's law constants for the chlorides in solution, all at 25.06°. It is observed that the relative reactivities of the *p*-methylbenzyl and *p*-*t*-butylbenzyl chlorides lie in the Baker–Nathan sequence, but it is pointed out that differential solvation effects make ambiguous any interpretation of this sequence in terms of "intrinsic" reactivity.

Introduction

Most reactions of interest to organic chemists occur in solution. In such reactions solute–solvent interactions (solvation effects) are inherent in the reacting systems and in the values of the specific rate constants observed. If one is concerned with an interpretation of the effect of structure or of reaction medium upon the rate of a reaction, these solvation effects introduce serious complications, for they operate both with the reactants and with the critical complex and need not be identical for different structures or media. For the purpose of isolating solvation effects from "intrinsic" reaction rates, it is useful to analyze rate data in terms of idealized gas-phase reactions where intermolecular interactions are at a minimum. An analysis appropriate to our studies of solvation effects and relative rates is outlined here for the usual situation where all reactants are incorporated in the critical complex.

The energetics of interest in defining the rate of a reaction may be represented schematically as in Fig. 1 which is similar to the representation of Winstein and Fainberg.[2] The free energies of activation, ΔF_s^* and ΔF_g^*, are differences in standard free energies and represent the changes in free energies associated with the transfer from the ground states to the transition states of the moles of reactants necessary for the formation of one mole of critical complex, all species being in their standard states of concentration. Specific rate constants in solution and in the gas phase depend upon these free energies and are given, according to the absolute rate equation,[3] by equations 1 and 2, respectively. The magnitudes of the specific rate

$$k_s = (kT/h)e^{-\Delta F^*_s/RT} \qquad (1)$$

$$k_g = (kT/h)e^{-\Delta F^*_g/RT} \qquad (2)$$

constants and of the free energies of activation depend upon the choice of standard states. These are defined, implicitly, as hypothetical unit concentrations in the concentration dimensions of the specific rate constants. Thus, the standard states represented by the energy levels in Fig. 1 are normally defined by the values (and dimensions) of the specific rate constants as experimentally determined.[4] Where desirable, however, alternative

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(1) For the previous paper in this series see, R. A. Clement and M. R. Rice, THIS JOURNAL, **81**, 326 (1959); for a preliminary report of some of this work, see R. A. Clement and J. N. Naghizadeh, *ibid.*, **81**, 3154 (1959).

(2) S. Winstein and A. H. Fainberg, *ibid.*, **79**, 5937 (1957).

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(4) For unimolecular reactions, specific rate constants have no concentration dimensions and are, as are the associated free energies of activation, independent of the choice of standard states. In these cases, the standard states represented by the energy levels in Fig. 1 must be defined, explicitly.