

which resisted crystallization from several organic solvents was obtained. This oil showed an ultraviolet absorption maximum in 95% ethanol at 282 $m\mu$ ($\log \epsilon$, 3.17), but in ethanol which was 0.1 M in potassium hydroxide, this maximum was shifted to 300 $m\mu$ ($\log \epsilon$, 3.39). This characteristic¹¹ shift in the B-band absorption to longer wavelength and increased intensity in the phenoxide ion as compared to the un-ionized phenol clearly demonstrated that the oil was the desired ether cleavage product, 4-(2,6-dimethyl-3-hydroxyphenyl)-butanol. The yield was 6.2 g. (51%).

An adjusted yield of 80% was obtained when the ethereal solution extracted from the basic solution was shown to contain 5.5 g. of unchanged starting material.

p-Toluenesulfonyl chloride (8.0 g.) was added in one portion to a solution prepared from 5.58 g. of 4-(2,6-dimethyl-3-hydroxyphenyl)-butanol in 55 ml. of dry pyridine which had been cooled to -5° . The reaction mixture was allowed to stand for 2 hr. at 0° , and 6 ml. of water was added in the following portions at 5 minute intervals: 0.6 ml., 0.6 ml., 0.6 ml., 1.2 ml. and 3 ml. The reaction mixture then was diluted with 60 ml. of water and extracted with three 60-ml. portions of chloroform. The combined chloroform extracts were washed successively with cold dilute sulfuric acid, water and 5% aqueous sodium bicarbonate and dried over anhydrous sodium sulfate. Evaporation of the solvent under reduced pressure gave 8.2 g. of a gummy residue.

Although this material could not be recrystallized from a number of organic solvents, its infrared spectrum showed absorption bands at 7.35, 8.41 and 8.50 μ , which are characteristic of the *p*-toluenesulfonate group.¹² Chromatography of the oil on alumina gave only a liquid major fraction, but this material showed infrared absorption bands of exactly the same position and intensity as those of the crude material. This finding demonstrated that the major portion of the crude oil was the desired tosylate VII. The yield of VII was 70%.

Solvolysis of 4-(2,6-Dimethyl-3-hydroxyphenyl)-butyl-*p*-toluenesulfonate (VII).—To a solution of 0.81 g. of potassium in 500 ml. of anhydrous *t*-butanol was added 6.0 g. of

VII in 75 ml. of anhydrous *t*-butanol (all alcohol used was dried by reflux over sodium followed by distillation). After 15 hr. reflux the solution was cooled, diluted with 700 ml. of water and extracted with three 250-ml. portions of ether. After the ethereal solution had been dried and the solvent evaporated, chromatography of the residue obtained on alumina (Bio-Rad, Basic Alumina, AG10), eluting with 500 ml. of pure pentane followed by 500 ml. of 2% ether in pentane, gave after evaporation of the solvent 0.48 g. of the *o*-dienone II as an almost colorless oil; $\lambda_{\text{max}}^{\text{EtOH}}$ 328 $m\mu$ ($\log \epsilon$ 3.55); $\lambda_{\text{inf}}^{\text{CHCl}_3}$ 6.00 μ , $\lambda_{\text{inf}}^{\text{CHCl}_3}$ 6.12 and 6.38 μ .

The 2,4-dinitrophenylhydrazone of II was prepared from 100 mg. of the dienone, 120 mg. of 2,4-dinitrophenylhydrazone, 8 ml. of absolute methanol and two drops of concentrated hydrochloric acid, with a 2.5 hr. reflux period. This derivative when recrystallized from absolute methanol melted at 129.5–131°.

Anal. Calcd. for $\text{C}_{18}\text{H}_{20}\text{N}_4\text{O}_4$: C, 60.66; H, 5.66; N, 15.72. Found: C, 60.12; H, 5.78; N, 16.00.

Continued elution of the chromatographic column with 500 ml. of 10% ether in pentane gave 0.17 g. of a light yellow oil which from its infrared and ultraviolet spectrum appeared to be composed of about equal quantities of the dienone II and the crossed-conjugated dienone XV.

Finally, by eluting the column with 500 ml. of 15% ether in pentane, 0.18 g. of the pure *p*-cyclohexadienone XV was obtained; $\lambda_{\text{max}}^{\text{EtOH}}$ 238 $m\mu$ ($\log \epsilon$ 3.92) and 265 $m\mu$ ($\log \epsilon$ 3.72) (inflection); $\lambda_{\text{inf}}^{\text{CHCl}_3}$ 6.01 μ ; $\lambda_{\text{inf}}^{\text{CHCl}_3}$ 6.14 and 6.21 μ . The reported³ values for XV are $\lambda_{\text{max}}^{\text{EtOH}}$ 241 $m\mu$ ($\log \epsilon$ 3.95) and 265 $m\mu$ ($\log \epsilon$ 3.74) (inflection); $\lambda_{\text{inf}}^{\text{CHCl}_3}$ 6.0 μ , $\lambda_{\text{inf}}^{\text{CHCl}_3}$ 6.11 and 6.195 μ .

The 2,4-dinitrophenylhydrazone of XV was prepared in almost quantitative yield when a mixture of 30 mg. of the dienone, XV, 30 mg. of 2,4-dinitrophenylhydrazone, 3 ml. of absolute ethanol and 3 drops of concentrated sulfuric acid was allowed to stand overnight at room temperature. This material recrystallized as deep red scales from *i*-butanol, m.p. 224–230° (reported³ 232–234°). It had $\lambda_{\text{max}}^{\text{CHCl}_3}$ 259 $m\mu$ ($\log \epsilon$ 4.08), 313 $m\mu$ ($\log \epsilon$ 3.63) and 407 $m\mu$ ($\log \epsilon$ 4.40), which are very close to those reported.³

The total weight of the three chromatographic fractions obtained was 0.84 g., which amounted to a 27% yield of the dienones II and XV.

(11) L. Doub and J. M. Vandenberg, *J. Am. Chem. Soc.*, **69**, 2714 (1947).

(12) R. S. Tipson, *ibid.*, **74**, 1354 (1952).

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY, EAST LANSING, MICH].

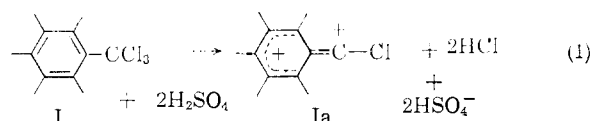
Multicharged Carbonium Ions. III. Long-lived Ions from Trichloromethylpolymethylbenzenes¹⁻³

BY HAROLD HART AND RICHARD W. FISH⁴

RECEIVED MAY 25, 1961

Mesitylene is converted to trichloromethylmesitylene (II) with carbon tetrachloride and aluminum chloride. Under similar conditions, rearrangement occurs with durene, the product being trichloromethylprehnitene (III). Both II and III ionize in 100% sulfuric acid in a fashion analogous to trichloromethylpentamethylbenzene (I), giving long-lived dipositive carbonium ions. The evidence is based on cryoscopy, stoichiometry, conductance measurements, visible, ultraviolet and nuclear magnetic resonance spectroscopy. Ultraviolet spectra of trichloromethylpolymethylbenzenes support the contention that these molecules are strained. Pentamethylbenzoic trifluoroacetic anhydride has been prepared from the dipositive ion Ia.

It was recently shown¹ that trichloromethylpentamethylbenzene (I) ionizes in sulfuric acid with the formation of the deep red pentamethylphenylchlorodicarbonium ion (Ia).



(1) For previous papers, see H. Hart and R. W. Fish, *J. Am. Chem. Soc.*, **80**, 5894 (1958); **82**, 5419 (1960).

(2) Presented, in part, before the Organic Chemistry Division of the A.C.S., Symposium on Carbonium Ions, St. Louis, Mo., March 27, 1961.

(3) This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of said fund.

(4) Petroleum Research Fund Fellow, 1958–1960. This paper is taken from part of the Ph.D. thesis submitted by R. W. F. to Michigan State University, 1960.

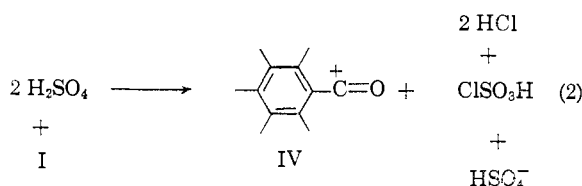
Evidence included the fivefold freezing point depression, quantitative and rapid sweep of two and only two moles of hydrogen chloride from such solutions (the remaining solution showing a threefold freezing point depression), conductance measurements consistent with the production of two bisulfate ions, and quantitative hydrolysis to pentamethylbenzoic acid (PMBA). Spectra (visi-

ble, ultraviolet and n.m.r.) supported structure Ia.⁵

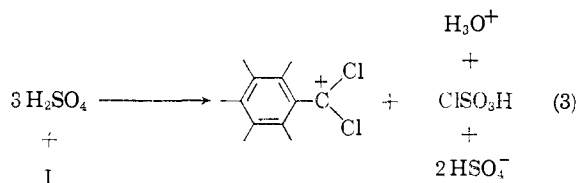
There are many structural factors one might want to evaluate concerning the formation and reactivity of this type of dicarbonium ion. Among these are the kind and number of ring substituents, the possible leaving groups and the contribution of the remaining un-ionized group (in Ia, chlorine). In this paper we report two more examples of dication formation from less methylated homologs of I.

Trichloromethylation of Mesitylene and Durene.—Both mesitylene and durene gave trichloromethyl derivatives in good yield when treated in a manner similar to pentamethylbenzene¹ with carbon tetrachloride and aluminum chloride. The product from mesitylene was a liquid, distillable at reduced pressure without decomposition. In the freezer, most of the product crystallized, and low temperature trituration with pentane left a crystalline product which, though liquid at room temperature, was quantitatively hydrolyzed to mesitoic acid. It was therefore trichloromethylmesitylene (II)

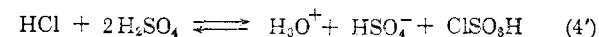
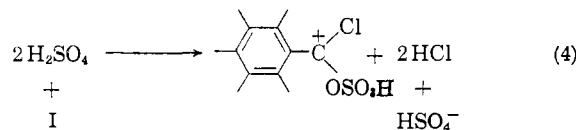
(5) Alternative, but rejected, explanations of the data had been considered but were not discussed in our previous paper (ref. 1). But because our attention has on several occasions been called to them, they are perhaps worthy of brief mention here. Equation 2 fits the cryoscopic, stoichiometric and n.m.r. data, but is inconsistent with the ultraviolet and visible spectra (see particularly footnote 13, which rules



out the presence of the pentamethylbenzoyl ion) and with the conductance measurements. Equation 3, while it fits the cryoscopy and conductance measurements, is not consistent with the sweeping of two moles of hydrogen chloride without change in spectrum. Modi-

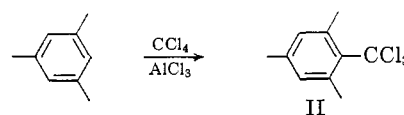


fications of eq. 1 in which Ia is covalently bound to sulfate are possible. Perhaps the best of these is a combination of 4 and 4', which, if the latter were a mobile equilibrium with an equilibrium constant of 1, would



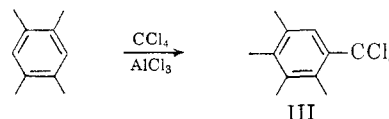
explain the cryoscopy and would furnish 1.5 HCl and 1.5 HSO₄⁻, close (but in our view, well outside the limits of error) to the observed values of 2 for each of these (based on stoichiometry and conductance). But if this were correct, the conductance should decrease to only one bisulfate after sweeping the hydrogen chloride; in fact, the conductance was unaffected by the sweeping (see Tables III and V of ref. 1). Furthermore, in independent experiments, 4' was approached from the right; even after several hours, the theoretical amount of hydrogen chloride could not be swept from solutions of chlorosulfonic acid in slightly aqueous sulfuric acid.

We have enjoyed the benefit of stimulating discussions with Professor R. J. Gillespie concerning these alternatives.



formed without migration of methyl groups. It is likely that some of the oily material which did not crystallize contained isomeric trichloromethyltrimethylbenzenes, but these were not investigated.

The crystalline product, m.p. 90–91.5°, from durene proved to be trichloromethylprehnitene (III), a result of methyl migration. The structure was established by analysis, by hydrolysis to 2,3,4,5-tetramethylbenzoic acid, m.p. 168–169°,^{6a}



and different (m.p. and m.m.p.) from 2,3,5,6-tetramethylbenzoic acid, m.p. 178–179°⁷ (the latter prepared by carbonation of the Grignard reagent from bromodurene). Methanolysis of III, or esterification (diazomethane) of the acid obtained by hydrolysis of III, gave a methyl ester, m.p. 35–36°,^{6b} different from the authentic methyl ester of durene carboxylic acid, m.p. 58°.^{6a} Finally, copper-quinoline decarboxylation of the acid obtained from III gave prehnitene, whose infrared spectrum was identical with that of an authentic sample.⁸

The formation of rearranged product III in this reaction is interesting, and may proceed by formation and rearrangement of trichloromethyldurene. But several attempts to isolate the latter, either by lowering the reaction temperature or by altering the amount of aluminum chloride, were unsuccessful. The rearrangement has analogies in the Jacobsen rearrangement⁹ and in the conversion of acetyldurene to acetylprehnitene in 80% yield with excess aluminum chloride,¹⁰ and may be the result of size, electronegativity, or both, of the substituent other than methyls.

Properties of Sulfuric Acid Solutions of II and III.—Both II and III gave deep red, stable solutions in sulfuric acid; these solutions were immediately decolorized when poured onto ice or cold methanol, and gave the corresponding acids or esters in nearly quantitative yield.

In order to determine the generality of ionization according to eq. 1, these sulfuric acid solutions were subjected to the same series of physical measurements described previously.¹ The freezing point data, electrical conductance and quantitative determination of hydrogen chloride are summarized in Tables I, II and III. It is clear from these data that the behavior of II and III parallels in detail that of trichloromethylpentamethylbenzene (I); the ionization of II and III

(6) (a) V. Meyer and L. Wöhler, *Ber.*, **29**, 2569 (1896); (b) V. Meyer and W. Moiz, *ibid.*, **30**, 1277 (1897).

(7) O. Jacobsen, *ibid.*, **22**, 1215 (1889).

(8) L. I. Smith and O. W. Cass, *J. Am. Chem. Soc.*, **54**, 1609 (1932).

(9) See L. I. Smith, *Org. Reactions*, **1**, 370 (1942).

(10) G. Baddeley and A. G. Pendleton, *J. Chem. Soc.*, 807 (1952).

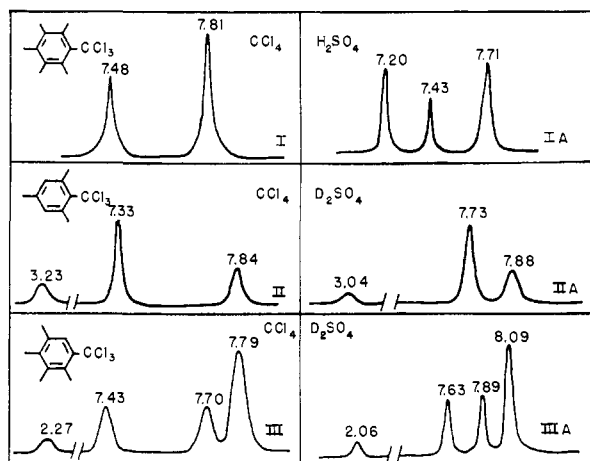
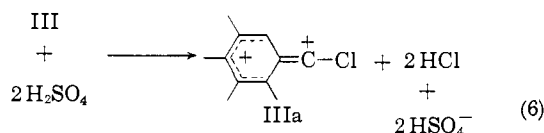
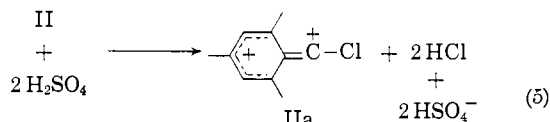


Fig. 1.—Nuclear magnetic resonance spectra (60 Mc.) of three trichloromethylpolymethylbenzenes in carbon tetrachloride (un-ionized) and in sulfuric acid (dicarbonium ions). Numbers over peaks are τ -values. Horizontal scale is not identical for the various spectra.

in sulfuric acid is therefore best represented as in eq. 5 and 6.



The n.m.r. spectra of I in carbon tetrachloride and in sulfuric acid were cited¹ as being consistent with ionization to a dicarbonium ion (eq. 1), but an unequivocal assignment of bands was not possible through lack of proper reference compounds. These spectra are reproduced here (Fig. 1), now with τ -values,¹¹ for comparison with similar spectra of II, IIa, III and IIIa. The spectra of II and IIa are particularly cogent in that they confirm the previous assignments¹ for I and Ia. The 7.48 and 7.81 τ bands in I, with relative areas 2:3, were assigned to the *ortho* and (*meta* + *para*) methyls, respectively. In II the relative areas of these bands (7.33 and 7.84 τ) are 2:1, consistent with the view that the less shielded protons are on the two methyls *ortho* to the trichloromethyl group. In sulfuric acid, II shows two bands with the same relative areas (2:1) but much closer (7.73 and 7.88 τ ¹²). This is consistent with the structure assigned to the ion IIa, where each of the aromatic carbons holding a methyl group may carry a formal positive charge. The *o*-methyls are again at low field, verifying the previous assignment¹ in Ia of

(11) For definition, see L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 47.

(12) Absolute comparisons are not possible, because of the very great difference in solvents (CCl_4 vs. H_2SO_4); in the latter, the reference compound (tetramethylsilane) was present as a second phase.

TABLE I
CRYOSCOPIC DATA^a

Compound	Wt., g.	H ₂ SO ₄ , g.	T ₁ , °C. ^b	ΔT , °C.	i^c	ν^d
I ^e	0.2369	95.3	9.950	0.302	5.27	
	.2384 ^f			.613	5.33	
	.2377 ^f			.882	5.12	5
	.2510	95.0	9.990	.299	4.91	
II	.2409 ^f			.591	4.95	
	.2106 ^f			.819	4.80 ^g	
	.1250	46.50	10.360	.356	5.14 ⁱ	
	.2471	51.30	10.315	.631	5.09 ⁱ	5
	.1974	52.20	10.402	.328	5.20	
III	.2718	114.3	10.098	.300	5.18	
	.2868 ^f			.615	5.16	
	.3095	94.2	9.904	.402	5.04	5
	.3100 ^f			.798	5.00	
	.2540 ^h	45.85	10.421	.394	2.93	
	.1300 ^h	45.85	10.418	.190	2.76	3
VII	.2048	107.80	10.361	.179	5.64 ^j	6
	.2157	87.62	10.065	.240	5.83 ^k	

^a Data for I and the first four values under III were obtained by Robert R. Rafos. ^b For values below 10.36°, water was purposely added to eliminate corrections arising from self-ionization of sulfuric acid. ^c Calculated from $i = \Delta T/6.12m_s$, where m_s is the molality of the solute. ^d The number of particles produced per molecule of solute; see R. J. Gillespie, *Rev. Pure Appl. Chem.*, 9, 1 (1959). ^e These new data supplement those of ref. 1; the need was felt for additional data with large values of ΔT , taken on the water side of sulfuric acid. ^f These are successive additions of solute to a single sulfuric acid sample; the ΔT values are additive and the i -values cumulative. ^g After 2, 4 and 9 hours, this value increased to 4.85, 4.89 and 5.00, respectively. ^h Hydrogen chloride was swept from these solutions prior to cryoscopic measurements; see Table III for additional data. ⁱ These values increased markedly after several hours, possibly due to sulfonation. ^j After 12 hours, this value was 6.08. ^k After 12 hours, this value was 5.96.

TABLE II

MOLAR CONDUCTIVITIES^a IN 100% SULFURIC ACID AT 25°

M	I ^b	II	III
0.05	307	303	308
.10	212	198	212
.20	156	162	152

^a Rounded off with regard to molarity; for actual data on II and III see Table VI and on I see ref. 1. ^b For evidence that these values represent production of two bisulfates per mole of solute, see Table III of ref. 1. In summary, these values are very like those of *o*-phenylenediamine (two bisulfates) and very different from those of potassium bisulfate (one bisulfate).

TABLE III

STOICHIOMETRY WITH RESPECT TO HYDROGEN CHLORIDE

Compound	Wt., g. ^a	t , min.	AgNO ₃ , ml.	Moles Cl ⁻ /mole solute
II	0.3652	30	29.75 ^b	1.910
	.4054	120	44.59 ^b	2.026
III ^c	.2540	30	23.76 ^c	2.088
	.1300	15	11.93 ^c	2.048 ^d

^a Sample was dissolved in 25 ml. of 100% sulfuric acid and swept with dry nitrogen for the time shown. ^b 0.1078 N. ^c 0.0888 N. ^d No additional chloride after 12 hours of sweep. ^e A solution containing 0.4621 g. of III in 25 ml. of 100% H₂SO₄ was swept free of hydrogen chloride, hydrolyzed, the organic acid extracted, the sulfate of the aqueous layer removed by barium hydroxide precipitation and the remaining chloride determined gravimetrically. There was obtained 0.95 mole of Cl⁻/mole of III. A similar experiment, with 0.3195 g. of III, gave 0.82 mole Cl⁻/mole of III, using the Fajans method.

the 7.20 τ band to the *o*-methyl protons and the 7.71 τ band to the *m*-methyl protons (from its relative intensity, the assignment of the 7.43 τ band to the *p*-methyl protons is unequivocal). Finally, attention is called to the relatively unexceptional positions of the aromatic hydrogens (3.23 and 3.04 τ in II and IIa, respectively).

Assignments in the n.m.r. spectra of III and IIIa cannot yet be made with certainty, but the spectra show several features of interest. First is the very low field (2.27 and 2.06 τ in III and IIIa, respectively) for the single aromatic hydrogen. This is strong confirmatory evidence that the species are prehnitene, rather than durene derivatives, with the aromatic hydrogen adjacent either to the strongly electron-withdrawing trichloromethyl group (in III) or high positive charge density (in IIIa). The low field 7.43 τ band in III is undoubtedly due to the three hydrogens on the *o*-methyl; the area confirms the presence of a single methyl *ortho* to the CCl₃ group. The bands at 7.70 and 7.79 τ , relative areas 1:2, are probably due to the methyl *para* and the two methyls *meta* to the CCl₃ group, but this assignment is by no means certain. Its plausibility is enhanced by the greater (0.20 *vs.* 0.09 τ) separation between these bands in IIIa.

The visible and ultraviolet spectra of the three dicarbonium ions (Ia, IIa, IIIa) are compared in Fig. 2, and the data are summarized in Table IV. The

TABLE IV
SPECTRA OF THREE DICARBONIUM IONS IN SULFURIC ACID

Ion	Wave length, $m\mu$		Molar absorptivity index (ϵ)
	λ_{max}	λ_{min}	
Ia		710	260
	545		2370
		485	1550
	393		34,600 ^a
		387	32,200
	385		32,600
		327	1000
	265		7300
		250	5820
		235	9160
IIa		700	115
	485		2110
		472	2090
	372		20,650
		304	1315
	281		5670
		258	2420
IIIa	239		7860
		705	40
	515		1340
		465	1100
	398 ^c		21,380
	387		22,050 ^b
		318	910
	285		7300
	261	3110	
	239	9040	

^a After standing 24 hours in a glass-stoppered flask, this value was 34,500. ^b After 24 hours, 21,870. ^c Infection.

general similarity in shape suggests common structural features; the decrease in the longest wave length maximum from 545 to 515 to 485 $m\mu$ with

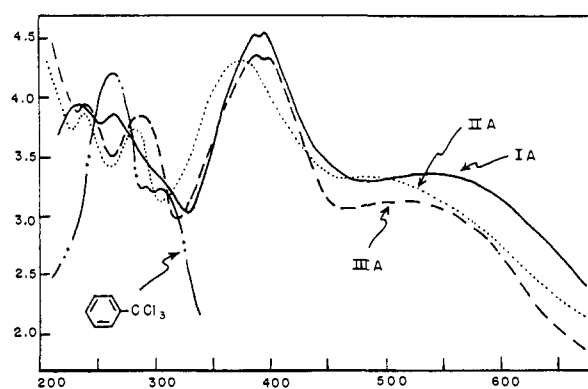
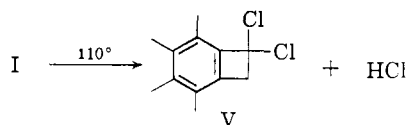


Fig. 2.—Visible and ultraviolet absorption spectra of three dicarbonium ions Ia, IIa and IIIa and of benzotrichloride, all in 100% sulfuric acid. For data, see Table IV.

decreasing number of methyl groups suggests that this band arises from a transition in which positive charge must be distributed on the aromatic ring. Benzotrichloride is not very soluble in 100% sulfuric acid, but on standing a sufficient quantity eventually dissolves (reacts?) to permit an ultraviolet spectrum to be observed. Although it is not known what species this spectrum represents, it is included in Fig. 2 to show the striking difference between it and its methylated homologs.¹³

Spectra of the Trichloromethyl Compounds in a Non-ionizing Solvent.—The strain in molecules which have a trichloromethyl group *ortho* to one or two methyls must be large indeed, as demonstrated by the facile *thermal* transformation of I to the benzocyclobutene (V).¹⁴ Compound V, despite the four-membered ring, is presumably thermodynamically more stable than I.



The spectral consequence of this strain in polychlorinated toluenes and xylenes has been discussed recently by Ballester.¹⁵ As hydrogens in the methyl groups of the side-chain were successively replaced by chlorine, a bathochromic shift and loss in spectral detail were observed; pentachloro-(ring)-toluene absorbed at 293 $m\mu$, whereas perchlorotoluene absorbed at 319 $m\mu$, and perchloro-*p*-xylene was a yellow solid, λ_{max} 365 $m\mu$. The strain in the latter two compounds was estimated, from these spectral shifts, to be 6–15 kcal./mole (minimum values). A likely maximum value is

(13) The spectra eliminate eq. 2 for the ionization. The spectrum of PMBA (presumably the pentamethylbenzoyl ion IV) in sulfuric acid shows a very intense maximum, ϵ 57,900, at 293 $m\mu$. At this same wave length solutions of I in sulfuric acid (presumably the spectrum of Ia) had ϵ 1500. The maximum concentration of IV in these solutions is therefore about 2.6%; in fact, the value must be much less than this for two reasons. First, Ia could hardly be expected to have zero absorptivity index in this region and, second, purposeful addition of 5% of PMBA to solutions of I in sulfuric acid resulted in a sharp and easily detectable rise in the absorptivity index at 293 $m\mu$ (to >2500). The amount of IV present in sulfuric acid solutions of I is negligible.

(14) H. Hart and R. W. Fish, *J. Am. Chem. Soc.*, **82**, 749 (1960).

(15) M. Ballester and J. Castañer, *ibid.*, **82**, 4259 (1960).

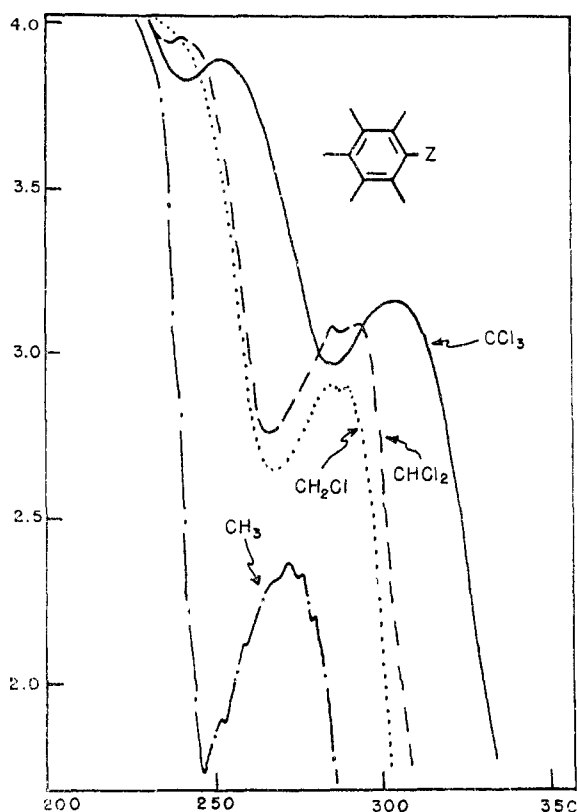


Fig. 3.—Effect of successive replacement of hydrogen by chlorine in one of the methyl groups of hexamethylbenzene on the ultraviolet absorption spectrum (in cyclohexane). For data, see Table V.

24 kcal./mole estimated by Brown¹⁶ for the homomorphous complex of trimethylboron with 2,6-lutidine. The trichloromethylpolymethylbenzenes behave similarly. In Fig. 3 (see Table V for data) are the spectra of four pentamethylbenzenes substituted in the sixth ring position with CH_3 , CH_2Cl , CHCl_2 , CCl_3 . The bathochromic shift and broadening of the bands, especially for the last of these (I) is consistent with the increased strain. A comparison of the spectra of I, II and III (Fig. 4, data in Table V) again shows the marked strain in I, where the ring is completely substituted and bond bending or rotation allows no conformation which relieves strain. The spectra of II and III, where the methyl groups are not entirely buttressed, show greater detail and absorption at lower wave lengths than I. Their behavior in sulfuric acid shows that they are strained, but presumably not as much as I.

Miscellaneous Experiments with the Pentamethylphenylchlorodicarbonium Ion (Ia).—Methods other than solution in sulfuric acid have been investigated for preparing dicarbonium ions, partly for identification purposes, and also in order to carry out subsequent organic reactions with them. One successful method and reaction sequence will be described here. When boron trifluoride is bubbled into a suspension of I in trifluoroacetic acid (containing a little anhydride) a

(16) H. C. Brown, D. Gintis and L. Domash, *J. Am. Chem. Soc.*, **78**, 5387 (1956).

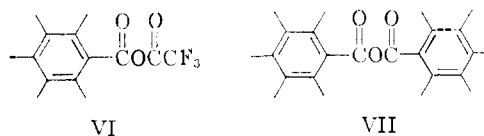
TABLE V
SPECTRA OF SOME CHLORINATED POLYMETHYLBENZENES IN HEXANE

Compound	Wave length, $m\mu$ λ_{max}	λ_{min}	Molar absorptivity index (ϵ)
I	302		1560
		283	920
	250		7680
II		239	6440
	282		2160
		280	1325
	277		1620
III		275	1525
	272		1825
		255	985
	230		4510
	289		1040
		287	1034
Dichloromethylpenta-methylbenzene ^b		270	825
		232	8175
	292		7820
	285		1210
Chloromethylpenta-methylbenzene ^b		287	1155
		266	545
	285		1170
		239	8910
		235	8525
	288		780
Chloromethylpenta-methylbenzene ^b		285	765
	283		775
		268	430
	238 ^a		8450

^a Inflection. ^b The preparation of these compounds will be described in a separate paper. The first has not been reported previously; the m.p., and probably the method of preparation, of the second (ref. 23) are in error.

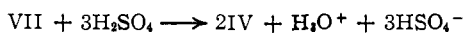
deep red solution is formed which shows the same visible, ultraviolet and n.m.r. spectrum as Ia.¹⁷ Evaporation to dryness *in vacuo* gave a dark red solid, insoluble in aromatic and aliphatic hydrocarbons and carbon tetrachloride, slightly soluble in chloroform and readily soluble in ether. Hydrolysis of the solid gave PMBA in 90–95% yield.

It seems fairly certain that the solid is a salt of dicarbonium ion Ia. Attempts to obtain analytically pure samples without vacuum line techniques were not successful, probably because of hydrolysis. The nature of the anion is not certain; it may be CF_3CO_2^- , $[\text{BF}_3\text{CF}_3\text{CO}_2]^-$ or some similar species. That trifluoroacetate is still present is certain from the following results. The dark red residue was distilled under reduced pressure, giving in good yield a colorless liquid which rapidly crystallized in the receiver, m.p. 180–185°. This reacted readily with base; it consumed the correct amount for the mixed anhydride of pentamethylbenzoic and trifluoroacetic acids (VI) and gave these acids on acidification.



(17) Details may be found in ref. 4, p. 104.

Attempts to recrystallize VI from anhydrous ether gave a new compound, m.p. 212–214°, which proved to be pentamethylbenzoic anhydride (VII). Identification of VII was based on analysis, twin carbonyl bands at 5.56 and 5.75 μ , lack of reactivity with alkali, an *i*-factor of 6 in sulfuric acid (see Table I) and reduction in high yield with lithium aluminum hydride to pentamethylbenzyl alcohol.



Studies on the scope of multicharged carbonium ion formation and reactions are continuing.

Acknowledgment.—We are indebted to John Fleming for running the n.m.r. spectra of II, IIa, III and IIIa, to Robert R. Rafos for some of the cryoscopic measurements, and to Norman Roobol for preparing analytically pure trichloromethylmesitylene (II).

Experimental¹⁸

Trichloromethylmesitylene (II).—The procedure was analogous to that used¹ to prepare the pentamethyl homolog. To a stirred suspension of 67 g. (0.5 mole) of anhydrous powdered aluminum chloride and 100 ml. of carbon tetrachloride there was slowly added (1.5 hours) 30 g. (0.25 mole) of mesitylene in 50 ml. of carbon tetrachloride. The slurry became dark red and hydrogen chloride evolved immediately. The mixture was maintained at 37–42° by occasional heating for 3 hours (HCl evolution ceased). The mixture was poured into a well stirred ice–5% hydrochloric acid solution. The organic layer was washed with water, dried (CaCl₂) and distilled *in vacuo*, yielding 48.3 g. (81.7%) of II, b.p. 126–126.5° (5 mm.), n_D^{25} 1.5640. On standing in the freezing compartment of a refrigerator, most of this material crystallized; the crystals were triturated with cold pentane. Redistillation gave pure II.

Anal. Calcd. for C₁₀H₁₁Cl₃: C, 50.56; H, 4.67; Cl, 44.77. Found: C, 50.63; H, 4.77; Cl, 44.70.

A solution of 5 g. of II in 50 ml. of 50% aqueous acetone was refluxed 12 hours, then poured into ice-water. The white solid was collected on a filter. The filtrate was distilled under vacuum to remove most of the acetone, extracted with ether (3 × 25 ml.) and the solvent removed. The combined white solid products, on recrystallization from methanol, gave 3.28 g. (95.0%) of 2,4,6-trimethylbenzoic acid, m.p. 153–154° (lit. value¹⁹ 153.2–154.0°).

A solution of 1.462 g. of II in 10 ml. of 100% sulfuric acid was dark red; when poured onto crushed ice a gelatinous white precipitate, difficult to filter, was obtained. The product was isolated by extraction with ether, washing with water, and drying (CaCl₂). Recrystallization from methanol gave 0.98 g. (97.0%) of 2,4,6-trimethylbenzoic acid, m.p. 153–154°.

A solution of 10 g. of II in 25 ml. of cold 100% sulfuric acid was carefully poured, at 0°, into 100 ml. of absolute methanol. Work-up was according to a procedure described in detail by Newman.²⁰ There was obtained 6.91 g. (91.2%) of methyl mesitoate, b.p. 80–86° (2 mm.), n_D^{20} 1.5058 (lit. values¹⁹ 130–131° (23 mm.), n_D^{20} 1.5076). The infrared spectrum and refractive index were identical with those of a sample prepared by the reaction of diazomethane with mesitoic acid.

Trichloromethylprehnitene (III).—The procedure was completely analogous to that described above for II, with the use of durene (Shell or Eastman) in place of mesitylene. The product was purified either by distillation, by successive recrystallizations from pentane, or both, and was obtained in about 75% yield, m.p. 90–91.5°.

Anal. Calcd. for C₁₁H₁₃Cl₃: C, 52.51; H, 5.21; Cl, 42.28. Found: C, 52.39; H, 5.13; Cl, 42.34.

A solution of 2.0 g. of III in 50 ml. of 50% aqueous acetone was refluxed for 10 hours, the acetone removed by vacuum

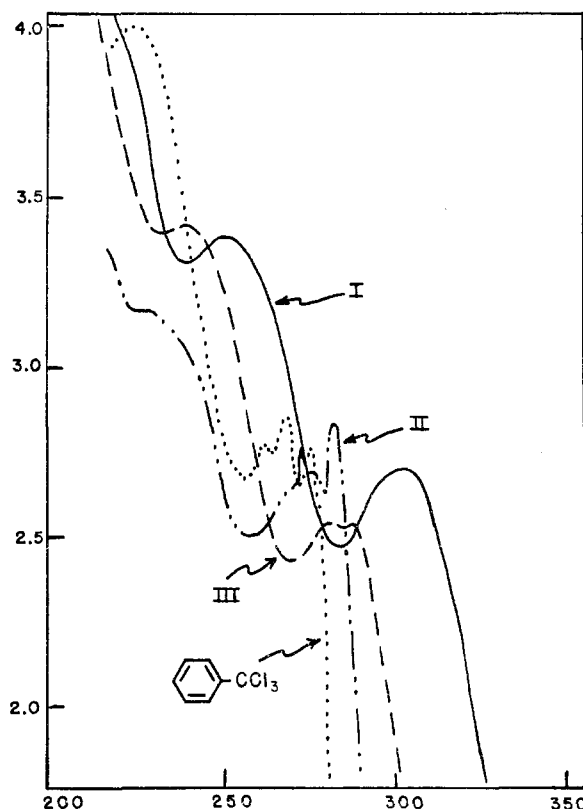


Fig. 4.—Ultraviolet absorption spectra of several trichloromethylbenzenes in cyclohexane.

distillation, 50 ml. of water added and the solid collected. Recrystallization from aqueous methanol gave 1.31 g. (91.8%) of 2,3,4,5-tetramethylbenzoic acid, m.p. 169–170° (lit. value⁹ 168–169°). The same acid (m.p., m.m.p., infrared spectrum) was obtained in 88.7% yield by hydrolysis of the dark red solution of 1.0 g. of III in 10 ml. of 100% sulfuric acid.

A solution of 5.0 g. of III in 25 ml. of absolute methanol was refluxed 10 hours. Removal of the excess methanol with a Rinco evaporator left a yellow-white residue which, on recrystallization from aqueous methanol, gave 3.41 g. (89.3%) of methyl 2,3,4,5-tetramethylbenzoate, m.p. 35–36° (lit. value^{6b} 35–36°). The same ester (m.p., m.m.p., infrared spectrum) was obtained by methanolysis of a sulfuric acid solution of III or by reaction of the hydrolysis product of III with diazomethane.

Comparison of the acid or methyl ester obtained from III with authentic 2,3,5,6-tetramethylbenzoic acid,²¹ m.p. 176–177°, or its methyl ester, m.p. 56–57°, prepared from the acid and diazomethane, showed both pairs to be distinctly different (m.p., infrared).

The acid (2,3,4,5-tetramethylbenzoic acid) obtained by aqueous acetone hydrolysis of III (*vide supra*) was decarboxylated as follows. A mixture of 5 g. of the acid, 20 g. of quinoline and 0.5 g. of cupric sulfate was heated just under reflux for 1 hour, then slowly distilled. After removal of the quinoline by acid extraction, the neutral product was purified by vapor phase chromatography. The product (2.1 g.) had the same retention time, refractive index and infrared spectrum as an authentic sample^{6,22} of prehnitene.

Physical Measurements.—Details of the experimental procedure for the cryoscopic and conductance measurements, and for the quantitative determination of hydrogen chloride, were given in ref. 1 and will not be repeated here. The data are summarized in Tables I, II and III. The detailed conductance data are in Table VI.

(21) M. S. Newman and H. A. Lloyd, *ibid.*, **74**, 2672 (1952).

(22) P. J. Launer and D. A. McCaulay, *Anal. Chem.*, **23**, 1875 (1951).

(18) All analyses by Spang Microanalytical Laboratory, P. O. Box 1111, Ann Arbor, Mich.

(19) M. S. Newman, H. G. Kuivila and A. B. Garrett, *J. Am. Chem. Soc.*, **67**, 704 (1945).

(20) M. S. Newman, *ibid.*, **63**, 3382 (1941).

TABLE VI
CONDUCTANCE DATA IN 100% SULFURIC ACID, 25.000°

Solute	M	A	Solute	M	A
II	0.0491	308.4	III	0.0522	308.0
	.0992	197.5		.0520	306.9
	.1118	200.1		.0988	203.7
	.2017	162.2		.0991	212.3
				.1920	149.2
				.1933	151.8

Ultraviolet and visible spectra were determined in 1-cm. ground glass stoppered quartz cells using a Beckman DK2 or DU spectrophotometer; n.m.r. spectra were obtained on a Varian Associates 60 Mc instrument.

Reaction of Trichloromethylpentamethylbenzene (I) with Boron Trifluoride-Trifluoroacetic Acid.—A deep red solution was obtained when 2.65 g. (0.01 mole) of I was treated with 20 ml. of trifluoroacetic acid, 2 ml. of trifluoroacetic anhydride and excess boron trifluoride, all well protected from atmospheric moisture. Removal of the solvent and BF_3 *in vacuo* left a dark red residue which, on hydrolysis, gave a 95% yield of pentamethylbenzoic acid.

Experiments on other samples of this red solid showed it to be insoluble in benzene, hexane, carbon tetrachloride, slightly soluble in chloroform and readily soluble in ether. Its visible and n.m.r. spectra in trifluoroacetic acid containing a little trifluoroacetic anhydride were nearly identical with solutions of I in 100% sulfuric acid.

A sample of this red solid, prepared from 5.0 g. of I, was heated *in vacuo*, whereupon a colorless liquid, b.p. 130–142° (5 mm.), which solidified in the receiver was obtained, m.p. 180–185°, 3.28 g. Recrystallization from anhydrous ether gave 1.97 g. (57.1%) of white crystals, m.p. 212–214°, of what was shown to be pentamethylbenzoic anhydride (VII). The ether filtrate had a strong odor of trifluoroacetic acid.

Anal. Calcd. for $\text{C}_{24}\text{H}_{30}\text{O}_3$: C, 78.65; H, 8.25; mol. wt., 366.5. Found: C, 78.75; H, 8.40; mol. wt. (Rast, camphor), 350, 360.

The white solid, m.p. 180–185°, was easily hydrolyzed. In a separate experiment, 1.000 g. of this solid, dissolved in 25 ml. of acetone and 50 ml. of 0.2159 *N* sodium hydroxide, was heated on the steam-bath for 15 minutes. After cooling, the excess alkali was titrated (24.37 ml. of 0.1953 *N* hydrochloric acid required for phenolphthalein end-point). The solution consumed 6.04 meq. of sodium hydroxide (theory for the mixed pentamethylbenzoic trifluoroacetic anhydride (VI) is 6.4 meq.).

Pentamethylbenzoic anhydride (VII) was very resistant to alkaline hydrolysis (only an insignificant amount of base was consumed when an alkaline aqueous acetone solution was refluxed for 3 hours). Reduction with lithium aluminum hydride in tetrahydrofuran, by standard techniques, gave pentamethylbenzyl alcohol, m.p. 159–160° (lit. value⁷ 160.5°), in 51% yield. Its m.p. and infrared spectrum were identical to samples prepared by hydrolysis of chloromethylpentamethylbenzene and by lithium aluminum hydride reduction of pentamethylbenzoic acid.

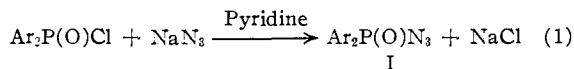
COMMUNICATIONS TO THE EDITOR

PREPARATION AND REACTIONS OF DIARYLPHOSPHONYL AZIDES

Sir:

In view of the recently reported reaction of sodium azide with trivalent phosphorus compounds to yield phosphinic nitrides¹ and the reaction of lithium azide with chlorobis(perfluoromethyl)phosphine to yield the sometimes stable azidobis(perfluoromethyl)phosphine,² we wish to report the synthesis and reactions of a series of new diarylphosphonyl azides having surprising thermal stability.

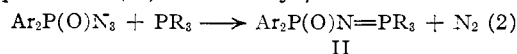
We have found that sodium azide reacts smoothly with diarylphosphonyl chlorides in anhydrous solvents such as pyridine, benzene, or acetonitrile to give the corresponding diarylphosphonyl azides (I) in good yields (Equation 1).



These azides have been found to be surprisingly stable to heat and shock. In a typical experiment, 6.99 g. (0.0297 mole) of diphenylphosphonyl chloride and 2.09 g. (0.032 mole) of sodium azide in 20 ml. of pyridine (distilled from calcium hydride) were heated under reflux with stirring for 18 hr. The solids were removed from the reaction mixture by filtration under argon and the solvent was removed from the filtrate at reduced pressure. The residual dark oil was distilled in a simple bulb-to-bulb apparatus at about 0.05 mm. to yield

6.31 g. (87.4% yield) of colorless diphenylphosphonyl azide boiling at 137–140°. A small amount of decomposition was indicated by a slight pressure increase. *Anal.* Calcd. for $\text{C}_{12}\text{H}_{10}\text{N}_3\text{OP}$: N, 17.28; P, 12.74; mol. wt., 243. Found: N, 17.2; P, 12.88; mol. wt., 247. In a similar manner, bis-*p*-tolylphosphonyl, bis-*p*-chlorophenylphosphonyl, and diphenylthiophosphonyl azides have been prepared and characterized by elemental analysis and molecular weight. The infrared spectra showed strong azide absorption at about 4.65 μ .³ The diphenylphosphonyl azide was characterized further by solvolytic conversion to diphenylphosphonic acid, isopropyl diphenylphosphonate, and diphenylphosphonamide, and by the reactions here described.

The diarylphosphonyl azides were found to react with a variety of tertiary phosphorus compounds, such as triphenylphosphine, phenyldimethylphosphine, and trimethylphosphite in an easily controlled liberation of one mole of nitrogen⁴ (Equation 2). The resulting diarylphosphonimidophosphoranes (II) are readily purified white solids



and have been found to be rather stable to hydrolysis with dilute hydrochloric acid and with dilute ammonium hydroxide solution. In a typical experiment, 1.38 g. (0.00526 mole) of triphenyl-

(3) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 230.

(1) D. L. Herring, *Chem. and Ind.* (London), 717 (1960).
(2) G. Thal, C. P. Haber and C. M. Douglas, *Proc. Chem. Soc.*, 219 (1960).

(4) The similar reaction of arylsulfonyl azides with trialkyl- and triarylphosphites has appeared recently, J. Goardier and H. Ullmann, *Ber.*, 94, 1067 (1961).