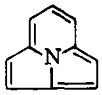
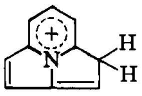
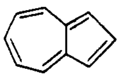
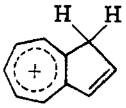
protonates in strong acid to form a conjugate acid II.[5,6] On this basis we have measured rate coefficients for the acid-catalyzed detritiation of I to ascertain whether its behavior will follow that established by trimethoxybenzene,[7] the azulenes,[8] and the methylindoles.[9] In addition we have measured the acidity dependence for the equilibrium protonation of I as well as its thermodynamic ionization constant.


I


II


III


IV

The equilibrium protonation of I was measured spectrophotometrically in aqueous perchloric acid solutions. The data were treated by the method of Long and Paul[10] and the extrapolation to infinite dilution yielded a value of -2.82 ± 0.10 for the pK_a of II at 25°. This is in good agreement with the value obtained by Gerson, *et al.*, for the solvent system methyl alcohol–aqueous perchloric acid (1:4).[5]

This implies that I is a somewhat weaker base than azulene, whose conjugate acid has a pK_a of -1.8. A plot of log indicator ratio *vs.* $-H_0$ for I has a slope of 1.87 ± 0.08. The analogous plot for the equilibrium protonation of azulene, III, has a slope of 1.80 ± 0.12.[8] Thus, within experimental error, the equilibrium protonation of I and III exhibits the same acidity dependence. This implies that the ratio of the activity coefficient of the base to that of the conjugate acid varies in the same manner with changes in medium for both I and III. Both bases are unsubstituted aromatic compounds and should not solvate to a large degree. Thus, their activity coefficients should not vary markedly with changes in medium. The conjugate acids, II and IV, are similar with respect to size, position of protonation, charge dispersal, and acidity of their methylene protons. On these grounds it seems plausible that, with changing medium, the variation in their activity coefficients due to changes in solvation would be similar. If the activity coefficient behavior is as described, the acidity function dependence for the equilibrium protonation of I and III should be similar.

Second-order rate coefficients for the hydrochloric acid-catalyzed detritiation of I were determined at four temperatures.[11] The data are listed in Table I. The activation parameters generated from this data are shown in Table II together with the same data for azulene.[8] The almost identical results suggest that the acid-catalyzed detritiation of I and III occur by similar mechanisms.

TABLE I

VARIATION IN k_{H^+} WITH TEMPERATURE FOR THE HCl-CATALYZED DETRITIATION OF I[a]

Temp., °C.	k_{H^+}, l./mole sec.
5.02	6.60×10^{-3}
14.98	1.81×10^{-2}
24.97	4.80×10^{-2}
34.76	1.18×10^{-1}

[a] $\mu = 0.100$ *via* added sodium chloride.

TABLE II

ACTIVATION PARAMETERS FOR THE HYDRONIUM ION-CATALYZED DETRITIATION OF CYCL[3.2.2]AZINE-1-*t* AND AZULENE-1-*t*[a]

	Cycl[3.2.2]azine-1-*t*	Azulene-1-*t*
E_a, kcal./mole	16.5	16.0
ΔS^*, cal./deg. mole	-11.3	-10.1
ΔF^*, kcal./mole	19.2	19.0

[a] Rate constants used for these calculations had units of liter/mole sec.

The detritiation of I in acetic acid buffers exhibits general acid catalysis. The second-order rate coefficient for acetic acid is 8.48×10^{-5} l./mole sec. at 25° while that for hydronium ion, Table I, is 4.80×10^{-2} l./mole sec. at 25°. For azulene the second-order rate coefficients at 25° for the same species are 2.50×10^{-4} and 0.181 l./mole sec., respectively. The ratio of the second-order rate coefficients, III divided by I, have values of 3.0 and 3.8 for acetic acid and hydronium ion, respectively. This implies similar Brønsted general-acid-catalysis behavior, and is reasonable in view of their similar basicities.

These results indicate that the detritiation of I occurs by the same slow proton-transfer process that has been established for azulene and trimethoxybenzene.

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(5) F. Gerson, E. Heilbronner, N. Joop, and H. Zimmerman, *Helv. Chim. Acta*, **46**, 1940 (1963).

(6) V. Boekelheide, F. Gerson, E. Heilbronner, and D. Mueche, *ibid.*, **46**, 1951 (1963).

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(8) J. Colapietro and F. A. Long, *Chem. Ind.* (London), 1056 (1960); J. Schulze and F. A. Long, *J. Am. Chem. Soc.*, **86**, 331 (1964); R. J. Thomas and F. A. Long, to be published.

(9) B. C. Challis and F. A. Long, *J. Am. Chem. Soc.*, **85**, 2524 (1963). B. C. Challis and F. A. Long, to be published.

(10) F. A. Long and M. A. Paul, *Chem. Rev.*, **57**, 1 (1957).

(11) Tritiated I was prepared by the method of Schulze and Long.[8]

Reactions of Triphenylphosphinalkylimines with Boron Trifluoride[1]

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Triphenylphosphinalkylimines[2] are strong nucleophiles. They readily react with alkyl halides[3-5] hydrogen halides,[2] and nitrosyl chloride.[6] To further test their nucleophilicity they were reacted with boron trifluoride.

Under a perfectly dry nitrogen atmosphere, boron trifluoride reacted with triphenylphosphinalkylimines to give triphenylphosphinalkyliminetrifluoroboron complexes (I, Table I); but in the presence of moisture the only products isolated were the respective alkylamino-

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(1) Presented in part at the International Symposium on Boron–Nitrogen Chemistry, U. S. Army Research Office (Durham), Duke University, Durham, N. C., April, 1963; Abstracts of Papers, p. 216; Advances in Chemistry Series, Vol. 42, R. F. Gould, Ed., American Chemical Society, Washington, D. C., 1964, p. 17.

(2) H. Zimmer and G. Singh, *J. Org. Chem.*, **28**, 483 (1963).

(3) H. Staudinger and E. Hauser, *Helv. Chim. Acta*, **4**, 861 (1921).

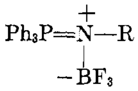
(4) L. Horner and H. Oediger, *Ann.*, **627**, 142 (1959).

(5) R. Appel and A. Hauss, *Z. anorg. allgem. Chem.*, **311**, 290 (1961).

(6) H. Zimmer and G. Singh, *Angew. Chem.*, **75**, 574 (1963); *Angew. Chem., Intern. Ed. Engl.*, **2**, 395 (1963).

Table I

Triphenylphosphinalkyliminetrifluoroborons



$$\mathrm{Ph_3P{=}\overset{+}{N}{-}R}\quad \underset{-\mathrm{BF_3}}{|}$$

No.	R	Formula	M.p., °C.	% yield	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	B–N[a] stretching, cm.$^{-1}$
1	CH_3	$C_{19}H_{18}BF_3NP$	224–226	100	63.55	62.75	5.02	5.01	3.90	3.91	667
2	C_2H_5	$C_{20}H_{20}BF_3NP$	242–243	100	64.40	64.34	5.38	5.38	3.75	3.59	664
3	*i*-C_3H_7	$C_{21}H_{22}BF_3NP$	240	93.8	65.17	64.47	5.68	5.13	...	...	660
4	*t*-C_4H_9	$C_{22}H_{24}BF_3NP$[b]	181–182	64.0	...	...	...	...	...	...	646

[a] Infrared spectra were determined in KBr pellets. [b] When suction was applied it dissociated into $Ph_3P{=}N{-}C(CH_3)_3$ and BF_3. It also decomposed slowly under atmospheric pressure; consequently, no analysis was made.

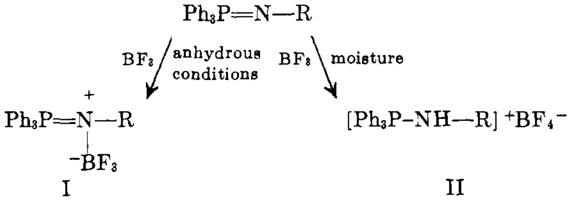
Table II

Alkylaminotriphenylphosphonium Tetrafluoroborates

$[Ph_3P{-}NH{-}R]^+BF_4^-$

No.	R	Formula	M.p., °C.	% yield	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
5	CH_3	$C_{19}H_{10}BF_4NP$	125–126	88.0	60.19	60.10	5.02	5.38	3.70	3.90
6	C_2H_5	$C_{20}H_{21}BF_4NP$	129–131	92.3	61.12	60.54	5.34	5.36	3.56	3.91
7	*i*-C_3H_7	$C_{21}H_{23}BF_4NP$	151–152	85.5	61.96	61.43	5.61	5.61	3.44	3.74
8	*t*-C_4H_9	$C_{22}H_{25}BF_4NP$	169	74.7	62.74	62.85	5.94	6.23	3.33	3.39

triphenylphosphonium tetrafluoroborates (II, Table II).



I II

R = CH_3, C_2H_5, *i*-C_3H_7, and *t*-C_4H_9

When this study was in progress, Appel and Vogt[7] reported the reaction of boron trifluoride with the parent compound of this series, *i.e.*, triphenylphosphinimine, $Ph_3P{=}NH$, and obtained a similar compound. Their results are in agreement with the findings reported here.

The stability of type I complexes depend very much on the steric requirements of the alkyl groups. The methyl and ethyl compounds of this type proved to be quite stable when exposed to the atmosphere, whereas triphenylphosphinisopropyliminetrifluoroboron decomposed slowly to isopropylaminotriphenylphosphonium tetrafluoroborate, but was stable enough to be analyzed. However, triphenylphosphine-*t*-butyliminetrifluoroboron proved to be extremely unstable under these conditions. Upon exposure to the atmosphere for only a few minutes, it decomposed to yield *t*-butylaminotriphenylphosphonium tetrafluoroborate. Obviously, due to steric hindrance,[8] the B–N bond was weakened in this case. Additional proof for this assumption was provided by subjecting triphenylphosphine-*t*-butyliminetrifluoroboron to a slight vacuum. BF_3 was pumped off and triphenylphosphine-*t*-butylimine remained.

Characterization of compounds of types I and II was achieved by C, H, and N analyses, as well as by infrared spectroscopy. All compounds of type II exhibited a sharp absorption peak in the region of 3280–3240 cm.$^{-1}$ corresponding to a N–H stretching frequency; whereas, this absorption, as expected, was absent in compounds of type I. A low-intensity band corresponding to the B–N stretching vibration in the case of type I complexes was observed in the region between 667–646 cm.$^{-1}$.[9] For comparison, the infrared spectra of triphenylphosphine-*t*-butyliminetrifluoroboron (**4**)[10] and *t*-butylaminotriphenylphosphonium tetrafluoroborate (**8**) are compiled in Fig. 1.

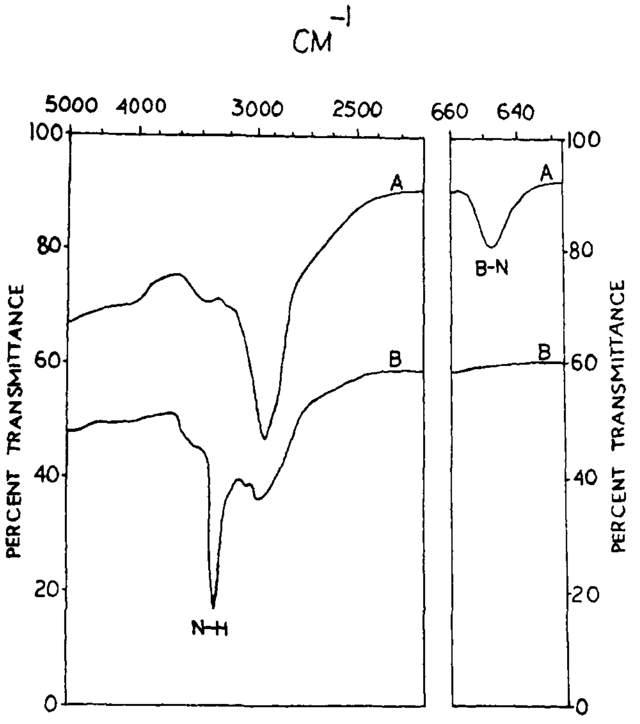


Fig. 1.—Infrared spectra: A, $Ph_3P{=}N^+(BF_3^-)C(CH_3)_3$; B, $[Ph_3P{-}NH{-}C(CH_3)_3]^+BF_4^-$.

Confirmation of structure I was provided by F^{19} nuclear magnetic resonance, measured at a frequency

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[7] R. Appel and F. Vogt, *Ber.*, **95**, 2225 (1962).

[8] H. C. Brown and G. K. Barbara, *J. Am. Chem. Soc.*, **75**, 6 (1953).

[9] R. C. Taylor, Advances in Chemistry Series, Vol. 42, R. F. Gould, Ed., American Chemical Society, Washington, D. C., 1964, p. 59.

[10] Reproducible spectra of compound **4** were obtained by taking them immediately after preparation and isolation of this product.

of 56.4 Mc./sec. with trifluoroacetic acid as an internal reference. Triphenylphosphinemethyliminetrifluoroboron (**1**) showed a single peak at a lower field (3660 c.p.s.), thus confirming the equivalence of the fluorine atoms in the complex. The fluorine chemical shift in methylaminotriphenylphosphonium tetrafluoroborate (**5**) was found to be at 4170 c.p.s.

Experimental[11]

Triphenylphosphinealkyliminetrifluoroboron Complexes.—An appropriate triphenylphosphinalkylimine (0.01 mole) was dissolved in 300 ml. of ether, which had been dried over sodium. The solution was cooled to −72° and boron trifluoride gas (after drying over phosphorus pentoxide) was passed through it at a rate of 2–3 bubbles/sec. The respective triphenylphosphinealkyliminetrifluoroboron complex started to precipitate as a white precipitate. After completion of the reaction the passage of BF_3 was stopped and the reaction mixture was stirred for a few minutes. The precipitate was then collected by suction filtration and dried under vacuum over phosphorus pentoxide. Throughout these operations a dry nitrogen atmosphere was maintained. Analytical samples were prepared by dissolving the compounds in acetone, filtering, and reprecipitating them by adding ether to the filtrate.

Alkylaminotriphenylphosphonium Tetrafluoroborate.—When the above reaction was carried out under ordinary room conditions instead of a dry nitrogen atmosphere, the products isolated were exclusively alkylaminotriphenylphosphonium tetrafluoroborates. They were obtained analytically pure by recrystallization from a chloroform–ethyl acetate mixture.

Acknowledgment.—This work was financially supported by the U. S. Army Research Office, Durham, North Carolina. The authors are grateful to Dr. T. J. Flaut of the Proctor and Gamble Company, Cincinnati, Ohio, for the determination and interpretation of the F^{19} n.m.r. spectra.

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[11] Melting points are uncorrected. Microanalysis was by A. Bernhardt, Mulheim/Ruhr, Germany, and by Galbraith Laboratories, Knoxville, Tenn.

The Reaction of Silver 2-Bromo-3-methyl-2-butenoate with 1,1-Diphenylethylene

H. D. HARTZLER

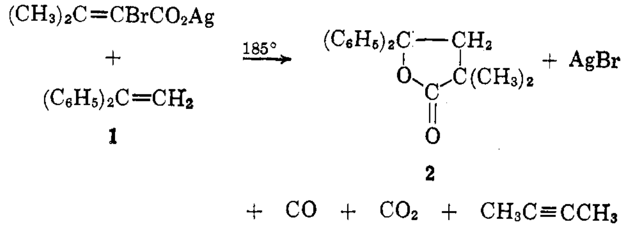
Contribution No. 982 from the Central Research Department, Experimental Station, E. I. duPont de Nemours and Company, Wilmington, Delaware

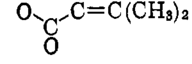
Received May 11, 1964

In the course of examining reactions intended to generate methylene carbenes[1] we briefly investigated the thermal decomposition of some silver salts of α-bromo-α,β-unsaturated acids. Analogous salt decompositions have been useful in the generation of benzyne,[2] carbon dichloride,[3] and carbon difluoride.[4]

The silver salts of 2-bromo-3-methyl-2-butenoic acid, 2-bromo-3,3-diphenylacrylic acid, and 2-bromo-3-biphenyleneacrylic acid were prepared. All decomposed in the range 185–205° with gas evolution and formation of silver bromide. Thermal decomposition of these salts suspended in olefins gave complex mixtures. Hydrocarbons were minor reaction products and methylenecyclopropanes were not found.

The decomposition of silver 2-bromo-3-methyl-2-butenoate (**1**) in 1,1-diphenylethylene gave a peculiar result. 2,2-Dimethyl-4,4-diphenyl-γ-butyrolactone (**2**) was formed consistently in yields of 20–25%. Silver bromide was formed in 98% yield. The gaseous products were carbon monoxide (35%), carbon dioxide (12%), and traces of 2-butyne. Repeated attempts to prove that the lactone was the unsaturated lactone **3** failed; so recourse was made to proving structure **2**.

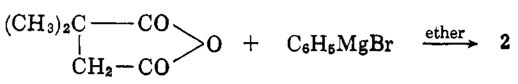




3

The n.m.r. spectrum of **2** showed the resonances of the methyl groups (singlet) at τ 8.90, the methylene (singlet) at 7.08, and the phenyl at 2.6. The intensities were the expected 3:1:5. The benzhydrilic lactone was readily hydrogenolyzed with palladium catalyst to give 2,2-dimethyl-4,4-diphenylbutyric acid in 95% yield. The n.m.r. spectrum of this acid showed the resonances of the methyl groups (singlet) at τ 8.83, the methylene (doublet) centered at 7.50, the methine (triplet) centered at 5.83, the aromatic hydrogens at 2.6, and the carboxylic acid hydrogen at −1.76. The intensity ratios were 6:2:1:10:1, respectively.

The lactone **2** was synthesized independently by the addition of phenylmagnesium bromide to unsymmetrical dimethylsuccinic anhydride. There is ample precedent for this type of reaction of anhydrides.[5] In this case, addition proceeds cleanly at the sterically unhindered carbonyl. No isomeric 3,3-dimethyl-4,4-diphenyl-γ-butyrolactone was found in the reaction product. This synthesis gave lactone **2** in 23% yield which was identical in all respects with that obtained from the salt decomposition. The mechanism of the formation of **2** was not investigated.



Experimental[6]

Silver 2-Bromo-3-methyl-2-butenoate.—2-Bromo-3-methyl-2-butenoic acid[7] (26 g., 0.15 mole) was stirred in 200 ml. of water and was dissolved by the addition of ammonium hydroxide. The silver salt was precipitated by the addition of a solution of 25.5 g. of silver nitrate in 25 ml. of water. The solid was filtered and

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[1] H. D. Hartzler, *J. Am. Chem. Soc.*, **86**, 526 (1964).

[2] H. E. Simmons, *J. Org. Chem.*, **25**, 691 (1960).

[3] W. M. Wagner, *Proc. Chem. Soc.*, 229 (1959).

[4] J. M. Birchall, G. W. Cross, and R. N. Haszeldine, *ibid.*, 81 (1960).

[5] M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall Co., Inc., New York, N. Y., 1954, pp. 846-869.

[6] Melting points are uncorrected. N.m.r. spectra were obtained in deuteriochloroform solutions on a Varian A-60 spectrometer. Infrared spectra were obtained on a Perkin-Elmer Model 21 spectrometer.

[7] L. N. Owen and M. V. S. Sultanbawa, *J. Chem. Soc.*, 3089 (1949).