test[12] for unreacted phosphorus was negative. *Caution: White phosphorus is highly poisonous and ignites when exposed to the air.*[13]

Reaction Temperature.—A dispersion of white phosphorus (6.2 g, 0.2 g-atom) in anhydrous ethanol (276 g, 6.0 moles) was prepared by warming the mixture to 45° in a 1-l. Morton flask and dispersing the phosphorus when molten with a high-speed stirrer. The dispersion was cooled to −10° and chlorinated with a 1:1 mixture of chlorine and nitrogen at −10 to 0° until a test for unreacted phosphorus was negative (3 hr). Constant stirring was required, as the phosphorus tended to settle out when the stirring was stopped. Occasional flashing was observed. The reaction mixture, which was greenish black in color, was allowed to warm to room temperature, stripped of solvent under reduced pressure, and distilled, giving 15.6 g (43%) of **triethyl phosphate**,[11] bp 66–68° (2 mm), n^{23}_{D} 1.4050.

Anal. Calcd for $C_6H_{15}O_4P$: P, 17.0. Found: P, 16.7.

The infrared spectrum of the product showed no diethyl ethylphosphonate. A gas chromatographic analysis gave its purity as 99.7%, with 0.2% of ethanol and 0.1% of another impurity.

The effect of higher reaction temperatures on the yield of triethyl phosphate is shown in Table I. The experimental procedure was the same including the 3-hr reaction time, except for the use of a regular mechanical stirrer in place of the high-speed stirrer in the last two experiments. The product of the 45–50° experiment, which gave the highest yield (85%), was a colorless liquid, bp 69° (1–2 mm), n^{23}_{D} 1.4048.

Anal. Calcd for $C_6H_{15}O_4P$: P, 17.0; Cl, nil. Found: P, 16.9; Cl, 0.8.

Ethanol:Phosphorus Ratio.—A slurry of 37.2 g (1.2 g-atoms) of white phosphorus, 276 g (6.0 moles) of anhydrous ethanol, and 600 g of benzene was chlorinated with 218 g (3.1 moles) of chlorine over a 1.5-hr period at 45–50°. Hydrogen chloride evolution was brisk. The resulting solution, which gave a negative test for unreacted phosphorus, was purged with nitrogen and split into four equal portions.

One portion was worked up in the preferred manner, by stripping carefully under vacuum at temperatures not exceeding 40°. Distillation gave 46.1 g (84%) of product, bp 60–63° (0.7 mm), n^{24}_{D} 1.4074, which was high in acidity and hydrolyzable chlorine (P, 16.8; acidity, 41.9 ml of 0.1 *N* NaOH/g, of which one-third was accounted for by chlorine: 13.9 ml of 0.1 *N* $AgNO_3$/g, or Cl, 4.9).

Another portion was stripped of solvent at atmospheric pressure. The product, 24.9 g, bp 60–63° (0.7 mm), n^{24}_{D} 1.4038, now showed an analysis of almost pure triethyl phosphate (P, 17.1; Cl, 0.05; acidity, 1.3 ml of 0.1 *N* NaOH/g), but the yield had dropped to 45% and a large undistilled residue remained. It appeared that the chlorine-containing by-product was destroyed at the expense of some of the triethyl phosphate.

Reduced Pressure.—An experiment was carried out in an apparatus modified to accommodate a vacuum of 200 mm in order to have the ethanol at reflux. The vapor pressure of ethanol is 174.0 mm at 45° and 222.2 mm at 50°.[14] The chlorine and nitrogen were premixed and admitted through a capillary tube extending under the surface of the alcohol. Vacuum was applied by means of a water aspirator. The chlorination of 6.2 g (0.2 g-atom) of white phosphorus in 276 g (6.0 moles) of anhydrous ethanol under these conditions required 1 hr at 45–50° (200 mm). The resulting solution was purged with nitrogen, analyzed for hydrolyzable chlorine and acidity, and stripped of excess ethanol under reduced pressure. Distillation of the product gave 32.0 g (88%) of triethyl phosphate, bp 70–80° (1.5 mm), n^{26}_{D} 1.4041.

Analysis of the purged solution before stripping gave 33.71 ml of 0.1 *N* $AgNO_3$/g and 34.62 ml of 0.1 *N* NaOH/g, corresponding to 1.02 moles of HCl and 1.06 moles of total acidity (HCl and P-OH). The theoretical value is 0.80 mole of acid, all as HCl.

Scale-Up.—A large-scale laboratory run was made without difficulty, employing 155 g (5.0 g-atoms) of white phosphorus and 4600 g (100 moles) of anhydrous ethanol in a 12-l. flask. The chlorination took 6.5 hr at 45–50° and required 1200 g of chlorine, *vs.* the calculated 887.5 g (12.5 moles). Distillation of the product remaining after stripping off the excess ethanol gave a small forecut (45 g, n^{24}_{D} 1.4219) followed by 740 g (81%) of triethyl phosphate, bp 77° (1.0 mm), n^{24}_{D} 1.4049.

Anal. Calcd for $C_6H_{15}O_4P$: P, 17.0. Found: P, 16.7.

The undistilled residue was a brown, viscous oil, 110 g, n^{24}_{D} 1.4042, with a phosphorus content (P, 26.1) approaching that of diethyl pyrophosphate (P, 26.5).

Other Alcohols.—Several other trialkyl phosphates were prepared by the chlorination of white phosphorus in the appropriate alcohol at 45–50°, the actual experimental conditions being modified to suit the alcohol.

Trimethyl phosphate,[11] bp 51–52° (2 mm), n^{24}_{D} 1.3956, was prepared in 34% yield following the procedure used for the ethyl ester in Table I, *i.e.*, a 3-hr reaction time at 45–50° with a 30:1 ratio of methanol:phosphorus.

Anal. Calcd for $C_3H_9O_4P$: P, 22.1. Found: P, 22.1.

A faster chlorination time (1.5 hr) improved the yield of trimethyl phosphate to 61%. No dimethyl methylphosphonate was detected in either product (infrared).

Tributyl phosphate,[11] bp 88–90° (0.005 mm), n^{24}_{D} 1.4238, was also prepared by the procedure used for the ethyl ester in Table I. The yield was quantitative.

The preparation of **tristearyl phosphate**[15] required more extensive modification, since the alcohol itself was a solid. A solution of 1.0 g (0.032 g-atom) of white phosphorus, 64.8 g (0.24 mole) of stearyl alcohol, and 250 ml of benzene was chlorinated over a 25-min period at 45–50°, filtered, and stripped of volatiles under vacuum. The residue, which was partly solid, was triturated in a mortar under acetone, filtered, washed with acetone, and dried, giving 35.7 g (98%) of product, mp 55.5–57.5° after recrystallization from ethanol. The product was found to be a 1:1 adduct of tristearyl phosphate and stearyl alcohol.

Anal. Calcd for $C_{72}H_{149}O_5P$: C, 76.80; H, 13.34; P, 2.75. Found: C, 76.61; H, 13.31; P, 2.74.

The presence of stearyl alcohol in the product was verified by gas chromatographic analysis (calcd, 24.0; found, 24.0).

Acknowledgment.—We are indebted to Mr. Leon A. Zengierski for capable technical assistance, to Mr. Rex A. Schad and Mr. William L. Schall for some of the starting materials, and to the members of our analytical and spectral laboratories under the direction of Mr. Richard L. McCullough and Mr. Abram Davis for their cooperation.

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[12] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VIII, Longmans, Green and Co., London, 1961, p 793.

[13] For proper handling, see "Phosphorus and Its Compounds," Vol. II, J. R. Van Wazer, Ed., Interscience Publishers, Inc., New York, N. Y., 1961, p 1202.

[14] "International Critical Tables," Vol. III, E. W. Washburn, Ed., McGraw-Hill Book Co., Inc., New York, N.Y., 1928, p 217.

[15] W. Davey, *Ind. Eng. Chem.*, **42**, 1841 (1950), gave mp 72° for tristearyl phosphate.

Electrolytic Reductive Coupling. X.[1] Reactions of Allylic Tautomers of Activated Olefins

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Received October 4, 1965

Electrolysis of the allylic tautomers of activated olefins under conditions similar to those used in the electrolytic reductive coupling of the activated olefins themselves[1] promises to provide a new tool for investigating the problems associated with the "three-carbon shift." We report here the results of a limited experimental study in this area.

The base-catalyzed equilibration of β,γ–α,β-unsaturated systems (I, II, and III, where X = an electron-attracting group) has been studied extensively.[2] At

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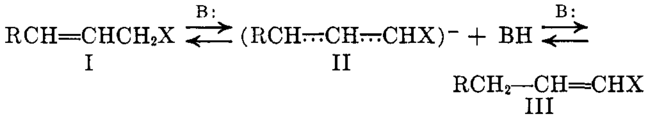
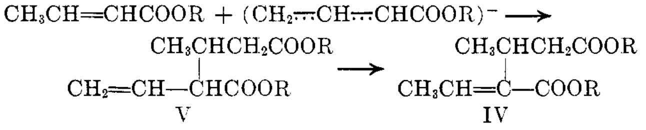
[1] Paper IX: M. M. Baizer and J. D. Anderson, *J. Org. Chem.*, **30**, 3138 (1965).

[2] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp 562–556.



$$\underset{\mathrm{I}}{\mathrm{RCH{=}CHCH_2X}} \overset{B:}{\rightleftarrows} \underset{\mathrm{II}}{(\mathrm{RCH{\cdots}CH{\cdots}CHX})^-} + \mathrm{BH} \overset{B:}{\rightleftarrows} \underset{\mathrm{III}}{\mathrm{RCH_2{-}CH{=}CHX}}$$

any given time the predominance of I or III is determined by both kinetic and thermodynamic factors. In general when R = H the *equilibrium* involving the addition of II to a proton lines far in the direction of the more thermodynamically stable III.[3] Michael adduction, however, of the allyl cyanide–crotononitrile anion (II, R = H; X = CN) to acrylonitrile yields ultimately the product formally derived from I.[5] The dimerization of ethyl crotonate in ether with an equimolar quantity of sodium ethoxide[6] probably involves the addition of the carbanion II (R = H; X = $COOC_2H_5$) to III (R = H; X = $COOC_2H_5$) to yield 2-ethylidene-3-methylglutaric acid ("dicrotonic acid," IV, R = H) *via* 2-vinyl-3-methylglutaric acid[7] (V, R = H). A



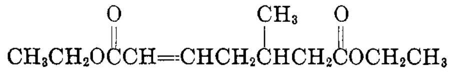
$$\mathrm{CH_3CH{=}CHCOOR} + (\mathrm{CH_2{\cdots}CH{\cdots}CHCOOR})^- \longrightarrow$$

$$\underset{\mathrm{V}}{\mathrm{CH_2{=}CH{-}\overset{\substack{CH_3CHCH_2COOR\\|}}{C}HCOOR}} \longrightarrow \underset{\mathrm{IV}}{\mathrm{CH_3CH{=}\overset{\substack{CH_3CHCH_2COOR\\|}}{C}{-}COOR}}$$

similar sequence appears to be involved in the formation of dicrotononitrile from allyl cyanide and a catalytic quantity of Triton B.[8]

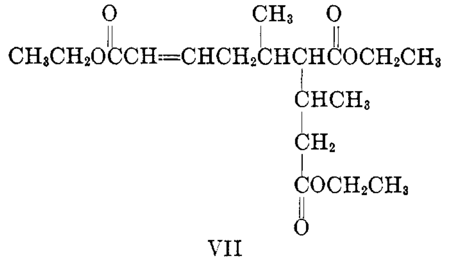
Electrolysis under our usual conditions[9] of allyl cyanide containing *ca.* 10% crotononitrile (by vpc analysis) gave a quantitative yield[10] of a single isomer of 3,4-dimethyladiponitrile, identical with that obtained from crotononitrile. The recovered monomer fraction contained both allyl cyanide and crotononitrile.

Ethyl 3-butenoate[11] (1.6% ethyl crotonate) formed diethyl 3,4-dimethyladipate[12] in approximately the same yield as was obtained from ethyl crotonate. The recovered monomer was *exclusively* ethyl crotonate (by vpc analysis). In addition three minor by-products were obtained: two *dimers* (mol wt 228 by mass spectrometry) in the ratio 77:23 and a trimer. Analysis of the nmr spectrum of the dimer fraction suggested that it was a mixture of V (R = C_2H_5) and VI, the latter having arisen by addition of the γ-carbanion to ethyl crotonate. The nmr spectrum of the trimer was consistent with VII[13] but not with alternate formulations.



$$\mathrm{CH_3CH_2O\overset{\substack{O\\\|}}{C}CH{=}CHCH_2\overset{\substack{CH_3\\|}}{C}HCH_2\overset{\substack{O\\\|}}{C}OCH_2CH_3}$$

VI



$$\mathrm{CH_3CH_2O\overset{\substack{O\\\|}}{C}CH{=}CHCH_2\overset{\substack{CH_3\\|}}{C}H\underset{\substack{|\\CHCH_3\\|\\CH_2\\|\\COCH_2CH_3\\\|\\O}}{C}H\overset{\substack{O\\\|}}{C}OCH_2CH_3}$$

VII

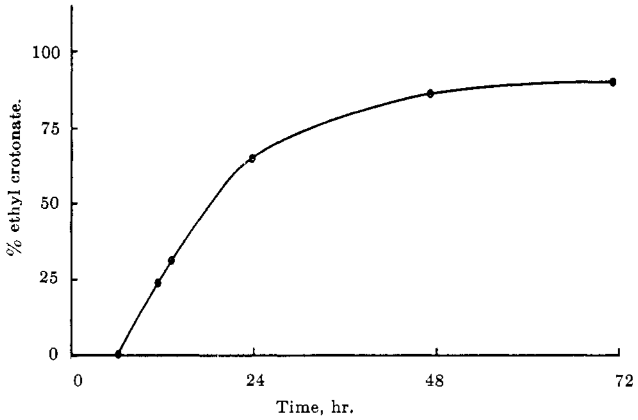


Figure 1.—The isomerization of ethyl 3-butenoate to ethyl crotonate, catalyzed by tetraethylammonium hydroxide. The reaction mixture was 0.1 mole of ethyl 3-butenoate, 10.8 g of dimethylformamide, 7.6 g of tetraethylammonium *p*-toluenesulfonate, and 1.9 g of water. Tetraethylammonium hydroxide (10% in water) (1-ml portions) was added at 1.5, 2.9, 4.4, 6.1, and 11.1 hr.

The electrolysis of the ethyl 3-butenoate had taken 5.5 hr and the *bulk* of the catholyte had been kept at a pH of 8–10. It was interesting to compare the *complete* isomerization which had been observed under these conditions with the base-catalyzed isomerization under nonelectrolytic conditions. Figure 1 demonstrates that even at pH 12–14 equilibration of the ester yielded only 90% of the crotonate after 72 hr. This difference suggests that during electrolyses in aqueous media a zone near the cathode is available for very effective basic catalysis even though the bulk of the solution may be neutral.[14]

The results of these experiments demonstrate that in *bulk* electrolyses compounds that are not polarographically reducible[15] became reducible if *in situ* tautomerization leads to a conjugated system.

Experimental Section[16]

The apparatus and general procedure have been described previously.[17] The cathode area was about 55 cm², and the cathode was mercury.

Allyl cyanide was purchased material,[18] n^{24}D 1.4049. Vpc analyses indicated 7–11% crotononitrile content. Ethyl 3-butenoate, bp 122°, n^{25}D 1.4077, was prepared in 67.5% yield.[11] Vpc analysis indicated a 1.6% ethyl crotonate content.

Electrolysis of Allyl Cyanide.—The catholyte contained 90.0 g of allyl cyanide, 59 g of recrystallized tetraethylammonium *p*-toluenesulfonate, and 19 g of water. The anolyte was a concentrated solution of the quaternary salt. Electrolysis proceeded at 25° and 2.5 amp for a total of 9.0 amp hr. The pH was controlled at *ca.* 8–9 by dropwise addition of acetic acid as usual. The cathode voltage (*vs.* sce) was −2.01 to −2.04 v. Acetoni-

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[3] When R = alkyl the equilibrium may be shifted to the left.[2,4]

[4] D. E. O'Connor and C. D. Broaddus, *J. Am. Chem. Soc.*, **86**, 2267 (1964), and references cited therein.

[5] H. A. Bruson, *Org. Reactions*, **5**, 106 (1949); E. D. Bergmann, D. Ginsburg, and R. Pappo, *ibid.*, **10**, 186 (1959).

[6] H. von Pechmann, *Ber.*, **33**, 3323 (1900).

[7] The structure of the isomeric "isodicrotonic acid" was not determined.[6]

[8] H. A. Bruson and T. W. Riener, *J. Am. Chem. Soc.*, **65**, 22 (1943).

[9] M. M. Baizer and J. D. Anderson, *J. Electrochem. Soc.*, **111**, 223 (1964).

[10] Based upon current input.

[11] J. D. R. Thomas and A. B. Watson, *J. Chem. Soc.*, 3958 (1956).

[12] I. L. Knunyants and N. S. Vyazankin, *Dokl. Akad. Nauk SSSR*, **113**, 112 (1957); *Chem. Abstr.*, **51**, 14635 (1957).

[13] VII is apparently the product of VI and ethyl crotonate *via* a Michael addition.

[14] A referee has pointed out the possibility that, under the unusual conditions in the proximity of the cathode, the ester is not equilibrated rapidly by an exceptionally active catalytic medium, but may be subject to an unusual kinetically controlled predominant formation of the more stable isomer.

[15] O. H. Müller, *Chem. Rev.*, **24**, 110 (1939).

[16] Boiling points are uncorrected. For the vpc procedure an F & M Model 300 (analytical) or Model 770 was used. The nmr spectra were obtained on a Varian A-60 spectrometer.

[17] M. M. Baizer, *J. Electrochem. Soc.*, **111**, 215 (1964).

[18] Aldrich Chemical Co., Inc.

trile (total 40 ml) had to be added from time to time toward the end of the reaction in order to maintain homogeneity. The catholyte was then diluted with an equal volume of water, the mercury was separated, and the mixture was extracted with four 100-ml portions of methylene chloride. The extracts were washed with water, dilute acetic acid, and water, and then dried over Drierite. The filtered solution was fractionated at atmospheric pressure through a 2-ft jacketed Vigreux column. The recovered material (bp to 118°) was found by vpc analysis to contain both crotononitrile and allyl cyanide. The higher boiling residue, 23.1 g (theory 22.8 g) boiled entirely at 130 (3.0 mm) to 136° (3.3 mm), $n^{24}{}_D$ 1.4500. Vpc examination on a column of 1% silver nitrate and 18% Carbowax 20M on 35–40 mesh Chromosorb W showed the product to be identical with the one isomer of **3,4-dimethyladiponitrile** previously obtained from crotononitrile.[9]

Diethyl 3,4-Dimethyladipate. A. From Ethyl Crotonate.—The catholyte contained 50.0 g of ethyl crotonate, 80.0 g of the above salt, 20 g of water, and 50 g of acetonitrile. Electrolysis proceeded at 2.0 amp for 3 hr at a cathode voltage (*vs.* sce) of −2.00 ± 0.02 v. Control and work-up were as above. The product, bp 103° (1.5 mm), $n^{25}{}_D$ 1.4324, weighed 18.3 g (72.5%[10]) and contained only one component (vpc). There was no distillation residue.

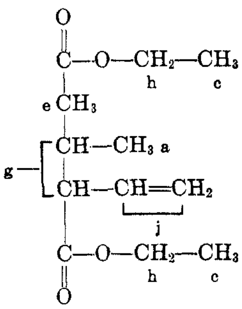
B. From Ethyl 3-Butenoate.—The catholyte contained 60.0 g of ester, 40.0 g of quaternary salt, 10.0 g of water, and 57.0 g of dimethylformamide. Electrolysis at 33 ± 2° was run at 1.0 amp for the first 4 hr and 2.0 amp for the remaining 1.5 hr. The cathode voltage (*vs.* sce) was −2.05 ± 0.05 v. Work-up was as above. The products obtained by fractional distillation were (i) 17.7 g of ethyl crotonate; (ii) a mixture of hydro dimer and *ca.* 2.4 g of V (R = C_2H_5) and VI, bp 97–99° (1.4 mm); (iii) 23.4 g of diethyl 3,4-dimethyladipate; and (iv) 4.1 g of VII, bp bp 133–135° (0.1 mm), $n^{25}{}_D$ 1.4585.

The components of fraction ii were separated by preparative vpc. The *dimers* obtained were further separated by vpc connected to a rapid-scan mass spectrometer for molecular weight determination.

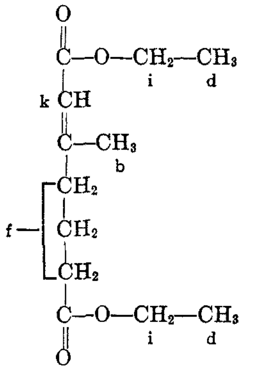
The nmr data for compounds V and VI are summarized in Table I. The contribution of the protons in each compound to the spectrum was calculated according to the gas chromatographic analysis. The data are more consistent with structures V and VI than with other combinations.

TABLE I

NMR DATA FOR THE ETHYL 3-BUTENOATE DIMERS



V, 77%



VI, 23%

Chemical shifts[a]	Assignment	Calcd contribution to spectrum		Integrated area	Calcd contribution/ integrated area
~9.02 t	a	2.31	8.31	10.0	0.83
~8.70 t	c	4.62			
~8.70 t	d	1.38			
~8.14 d[b]	b	0.69		0.8	0.86
~7.50 m	e + f	2.92	4.46	4.8	0.93
~7.00 m	g	1.54			
~5.87 q	h	3.08	4.00	4.4	0.91
~5.87 q	i	0.92			
~4.50 m	j	2.31	2.54	2.9	0.89
~4.50 m	k	0.23			

[a] Chemical shifts are expressed in τ values in parts per million with reference to tetramethylsilane. [b] The doublet for the methyl assigned b is probably due to *cis–trans* isomers; d = doublet, t = triplet, q = quartet, m = multiplet.

The trimer fraction (iv) was shown by vpc to contain three components. The major product comprised 92% and the two minor products totaled 8% of the sample.

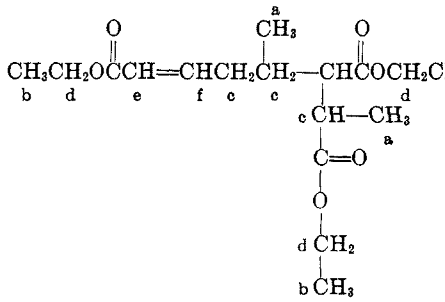
Anal. Calcd for $C_{18}H_{30}O_6$: C, 63.13; H, 8.84; mol wt, 342. Found: C, 63.41; H, 8.97; mol wt, 329 (ebullioscopic).

In the mass spectrum of the ethyl 3-butenoate trimer (iv) no parent ion was observed. However a fragmentation ion was observed at *m/e* 297. Assuming an ethoxy group was lost from the parent ion, the molecular weight would be 342.

The nmr data for compound VII are summarized in Table II. The data are more consistent with structure VII, the *trans*-olefin than with other possible structures.

TABLE II

NMR DATA FOR THE ETHYL 3-BUTENOATE TRIMER



Chemical shfts[a]	Assignment	Multiplicity	Protons Calcd		Protons Found[b]	
9.14	a	Doublet	6	22[c]	5.7	22.8
8.79 and 8.77	b	2 triplets	9		9.0	
8.5–7.5	c	Multiplet	7		8.1	
5.96 and 5.92	d	2 quartets	6		5.9	
5.27	e	Doublet	1		1.0	
3.22	f	2 triplets	1		1.0	

[a] Chemical shifts are expressed in τ values in parts per million with reference to tetramethylsilane. [b] Found values calculated on the basis of integrated area for ester methyls equal to theory. [c] The peaks in this region were not well separated.

Acknowledgment.—We wish to thank Mr. Robert Anderson and Mr. Donald Bauer for obtaining and interpreting the nmr spectra and Mr. M. T. Jackson for obtaining and interpreting the mass spectra.

The Proton Magnetic Resonance Spectrum of Diphenyliodonium Salts[1]

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Received July 16, 1965

The physical properties and behavior of diaryliodonium salts previously reported include ultraviolet[3] and infrared[4] spectra, ion association,[5] acidity and basicity,[6]

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(1) This research was supported in part by a fellowship from the National Cancer Institute, Public Health Service, National Institutes of Health, No. 1 F2 CA-19, 690-02. It is publication XXVI in the series on diaryliodonium salts.

(2) National Institute of Health Postdoctoral Fellow, 1963–1965.

(3) F. M. Beringer and I. Lillien, *J. Am. Chem. Soc.*, **82**, 5153 (1960).

(4) I. Lillien, *J. Chem. Soc.*, 4498 (1962).

(5) (a) F. M. Beringer and E. M. Gindler, *J. Am. Chem. Soc.*, **77**, 3203 (1955); (b) F. M. Beringer, E. J. Geering, I. Kuntz, and M. Mausner, *J. Phys. Chem.*, **60**, 141 (1956); (c) F. M. Beringer and M. Mausner, *J. Am. Chem. Soc.*, **80**, 4535 (1958).

(6) F. M. Beringer and I. Lillien, *ibid.*, **82**, 5141 (1960).