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 = C₂H₅) 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 chromato-

graphic analysis. The data are more consistent with structures V and VI than with other combinations.

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 C₁₈H₃₀O₆: 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
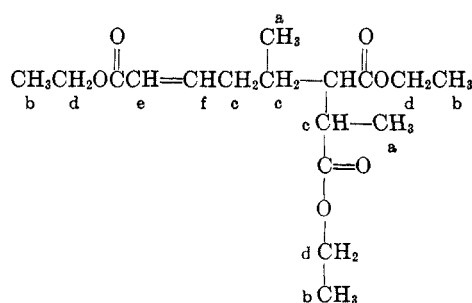
Chemical shifts[a]	Assignment	Multiplicity	Protons Calcd	Protons Found[b]
9.14	a	Doublet	6	5.7
8.79 and 8.77	b	2 triplets	9 (22[c])	9.0 (22.8)
8.5–7.5	c	Multiplet	7	8.1
5.96 and 5.92	d	2 quartets	6	5.9
5.27	e	Doublet	1	1.0
3.22	f	2 triplets	1	1.0

[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.

The Proton Magnetic Resonance Spectrum of Diphenyliodonium Salts[1]

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

TABLE I

NMR DATA FOR THE ETHYL 3-BUTENOATE DIMERS

Chemical shifts[a]	Assignment	Calcd contribution to spectrum	Integrated area	Calcd contribution/ integrated area
~9.02 t	a	2.31		
~8.70 t	c	4.62 (8.31)	10.0	0.83
~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.

(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.

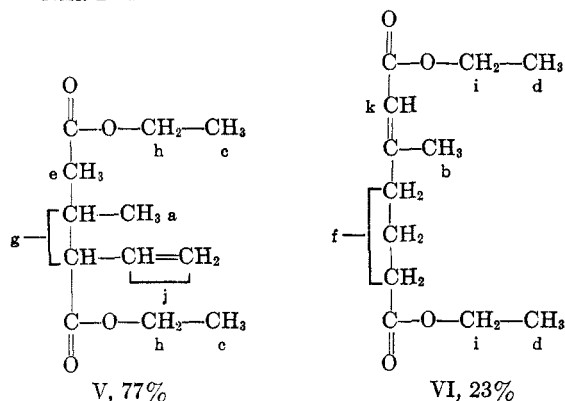(2) National Institute of Health Postdoctoral Fellow, 1963–1965.

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(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).

TABLE I

PROTON NMR PEAKS (τ), SHIELDING PARAMETERS (d), ELECTRON DENSITIES (ρ), AND SUBSTITUENT CONSTANTS (σ)[a]

Anion	Solvent	ortho hydrogens			meta hydrogens				para hydrogens			
		τ	d_o	ρ_o	τ	d_m	ρ_m	σ_m	τ	d_p	ρ_p	σ_p
					The Diphenyliodonium Cation							
Cl⁻	CH₂Cl₂	2.01	−0.72	0.933[b]	2.65	−0.08	0.992[b]	+0.53	2.49	−0.24	0.978[b]	+0.68
	CH₃OH	1.84	−0.89	0.917[b]	2.52	−0.21	0.980[b]	+0.81	2.36	−0.37	0.965[b]	+0.88
	D₂O	1.96	−0.77	0.928[b]	2.60	−0.13	0.988[b]	+0.64	2.42	−0.31	0.971[b]	+0.79
NO₃⁻	CH₂Cl₂	2.03	−0.70		2.58	−0.15			2.42	−0.31		
	CH₃OH	1.84	−0.89		2.52	−0.21			2.34	−0.39		
	D₂O	1.97	−0.76		2.59	−0.14			2.43	−0.30		
AcO⁻	CH₂Cl₂	2.09	−0.64		2.67	−0.06			2.52	−0.21		
	CH₃OH	1.85	−0.88		2.52	−0.21			2.34	−0.39		
	D₂O	1.94	−0.79		2.58	−0.15			2.42	−0.31		
					Iodobenzene							
	CH₂Cl₂[c]	2.37	−0.36	0.966[b]	2.99	+0.26	1.024[b]	+0.28[d]	2.80	+0.07	1.006[b]	+0.35
	CH₃OH	2.39	−0.34		3.01	+0.28			2.82	+0.09		
			−0.363[e]			+0.265[e]				+0.07[e]		
			−0.40[f]		g	+0.25[f]				+0.03[f]		

[a] Values for τ and d are given in parts per million. The notations d, ρ, and σ refer respectively to chemical shifts relative to benzene, electron density, and substituent constants. [b] The values for ρ are not corrected for the magnetic anisotropy of the substituents. [c] Identical results were obtained in CCl₄. [d] Values taken from ref 25. [e] Shielding parameters in cyclohexane, extrapolated to infinite dilution, given in ref 12. [f] Shielding parameters in cyclohexane, 5 mole %, given in ref 10.

polarographic reduction,[7] and crystallographic structure.[8] This article reports on the proton magnetic resonance spectrum of the diphenyliodonium cation, while a following paper reports on the spectra of methyl-substituted diphenyliodonium cations.

The nmr spectra of substituted benzenes has been studied extensively.[9–14] Correlation of the proton,[9–12] fluorine,[13] and carbon[10,13e,14] chemical shifts with the σ_m and σ_p Hammett substituent constants has been attempted by several authors. Early interpretations were complicated by the low resolutions obtained at 40 Mc/sec, but with better resolution at 60 Mc/sec and with the aid of deuterium labeling[10a] reliable band assignments have been made. After much study of the effects of solvent[13,15] and concentration,[9b] chemical shifts with substituent constants have been obtained.

Several attempts have also been made to correlate the chemical shifts with the charge densities at different positions of an aromatic system.[13e,16–21] Recently

it was shown that a linear correlation exists between proton resonance chemical shifts and electron density on the attached carbon.[18–20] This relationship was applied to a variety of aromatic molecules, and fairly good correspondence between the electron densities inferred from the chemical shifts and those obtained from simple MO calculations have been obtained.

The proton chemical shifts, relative to benzene, of diphenyliodonium chloride, nitrate, and acetate in methylene chloride, methanol, and deuterium oxide have now been determined and are summarized in Table I. From the shielding parameters (d) substituent constants (σ) have been calculated[12] for the phenyliodonio group ($C_6H_5I^+$), and charge densities (ρ) have been calculated[21] for the three unsubstituted positions of the diphenyliodonium ion.

Experimental Section

Diphenyliodonium chloride,[5b] nitrate,[5a] and acetate[22] were prepared according to described procedures. Spectra were run on a Varian HR-60 high-resolution nmr spectrometer and on a Varian A-60 nmr spectrometer. When the concentration of diphenyliodonium chloride in D₂O and in CH₃OH was varied from 2 mole % (6.32 mg/ml) to 20 mole %, the τ values were found to be constant within ±0.03 ppm. Extrapolation to infinite dilution was therefore not necessary, and it is assumed that in this concentration range the measured chemical shifts approach that of an "isolated molecule." Owing to its low solubility in CH₂Cl₂, the maximum concentration of diphenyliodonium chloride was about 2 mole %. In CH₂Cl₂ and in CH₃OH tetramethylsilane (TMS) was used as internal reference, while in D₂O acetonitrile was used as internal reference (τ 1.98).[23]

In iodobenzene, an A₂B₂C system, band assignments were made in 1961[10a] with the aid of deuterium labeling. As the spectral pattern of iodobenzene and the diphenyliodonium ion are similar, band assignments for the latter have been made by analogy. To facilitate comparison, nmr spectra and chemical shifts of iodobenzene and the iodonium salts were determined in methylene chloride, carbon tetrachloride, and methanol at the same concentrations. The shielding parameters for iodobenzene in the first two solvents are identical and correspond exactly with those reported by Martin and Dailey,[12] which are included in Table I.

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TABLE II
DIPHENYLIODONIUM SALTS AND IODOBENZENE CHEMICAL SHIFTS RELATIVE TO *meta* POSITION

Solvent	Anion	Diphenyliodonium salt			Iodobenzene		
		ortho	*meta*	*para*	*ortho*	*meta*	*para*
CH_2Cl_2	Cl^-	-0.64	0	-0.16	-0.62	0	-0.19
	NO_3^-	-0.55	0	-0.16			
	AcO^-	-0.58	0	-0.15			.
MeOH	Cl^-	-0.68	0	-0.16	-0.62	0	-0.19
	NO_3^-	-0.68	0	-0.18			
	AcO^-	-0.67	0	-0.18			
D_2O	Cl^-	-0.64	0	-0.18			
	NO_3^-	-0.62	0	-0.16			
	AcO^-	-0.64	0	-0.16			
Av		-0.63 ± 0.05	0	-0.16 ± 0.02	-0.62	0	-0.19

TABLE III
A COMPARISON OF σ VALUES FOR POSITIVELY CHARGED SUBSTITUENTS

Substituent	Compounds	Solvent	σ_m	σ_p	$\sigma_m - \sigma_p$	Ref
$(CH_3)_3N^+$	Benzoic acids[a]	50% EtOH	+1.02	+0.88	+0.14	b
	Anilinium ions[a]	H_2O	+0.85	+0.75	+0.10	b
	Dimethylanilinium[a]	H_2O	+0.67	+0.65	+0.02	b
	Phenols[a]	H_2O	+0.83	+0.70	+0.13	b
	Thiophenols[a]	48% EtOH	+0.86	+0.78	+0.08	b
	2,6-Di-*t*-butylphenols[a]		+0.85	+0.77	+0.08	b
	c	75% CH_3OH	$+0.93^d$	$+0.86^e$	+0.07	13c, f
$(CH_3)_2S^+$	Benzoic acids[a]	H_2O	+1.00	+0.90	+0.10	b
	Phenols[a]	H_2O	+1.00	+1.16	-0.16	b
$C_6H_5I^+$	Benzoic acids[a]	CH_3CN-H_2O	+0.85	...	...	6
	Phenols[a]	43% EtOH	...	+0.71	...	6
	Anilinium ions[g]		+0.98	+1.06	-0.08	6
	c	CH_2Cl_2	+0.53	+0.68	-0.15	h
	c	CH_3OH	+0.81	+0.88	-0.07	h
	c	D_2O	+0.64	+0.79	-0.15	h
N_2^+	Phenols	H_2O		+3.04		25
$(C_6H_5)_2C^+$	c	F_3CCO_2H		$+2.48^i$		21

[a] Titration. [b] F. G. Bordwell and P. J. Boutan, *J. Am. Chem. Soc.*, **78**, 87 (1956); S. Oae and C. C. Price, *ibid.*, **80**, 3425, 4938 (1958). [c] Nmr spectroscopy. [d] Determination from *meta*-substituted fluorobenzenes; $\sigma_m = \sigma_I.^{13c}$ [e] Determined from *para*-substituted fluorobenzenes; $\sigma_p = \sigma_I + \sigma_R$: L. A. Cohen and W. M. Jones, *J. Am. Chem. Soc.*, **85**, 3402 (1963). [f] R. W. Taft, Jr., *ibid.*, **79**, 1045 (1957). [g] Ultraviolet spectroscopy. [h] Present work. [i] Value calculated from the proton chemical shift data given in ref 21.

Discussion

For the diphenyliodonium cation the chemical shifts relative to benzene (d) are greater in methanol than in methylene chloride (Table I). This is in accord with the reasonable assumption that diphenyliodonium chloride is more dissociated in methanol than in methylene chloride, approaching the free ion. The influence of the positive charge, felt most by the *ortho* hydrogens, is diminished in methylene chloride, presumably because the effect of the charge is partially neutralized by the counterion (chloride). The crystal structure of diphenyliodonium chloride[8] seems to allow some covalency in the I–Cl bond: the chlorine is almost in the C–I–C plane, the C–I–Cl angle is about 87°, the I–Cl distance is 3.08 A, and the over-all structure is that of a trivalent iodine with a modified T structure. In deuterium oxide the free diphenyliodonium ion may exist in a solvated form, in which the oriented oxygen atoms of the solvent partially neutralize the positive charge.

Fraenkel[24] has demonstrated that in *p*-chloroanilinium chloride in dimethyl sulfoxide the effect of the positive charge is neutralized by ion-pair formation, so that the chemical shifts of the ring protons are those of chlorobenzene. However, in the more hindered N,N,N-trimethyl-*p*-chloroanilinium salt close approach of the

(24) G. Fraenkel, *J. Chem. Phys.*, **39**, 1641 (1963).

chloride ion is prevented, and the effect of the positive charge is greatest on the *ortho* hydrogens, as is found in the present study.

When we focus attention on the relative positions of the *meta* hydrogens in iodobenzene and in the diphenyliodonium cation, we see that the hydrogens on the cation are moved downfield (deshielded) by τ 0.38–0.41 in methylene chloride and by τ 0.46–0.56 in methanol. In Table II are collected the chemical shifts (all downfield) of the *ortho* and *para* hydrogens *relative to the meta hydrogens in the same molecules*. We see that in both cases the sequence is (downfield) *o*-H, *p*-H, *m*-H (upfield). Indeed, rather surprisingly, the magnitudes of the chemical shifts are similar in iodobenzene and in the diphenyliodonium cation.

To explain the downfield position of the *para* hydrogens relative to the *meta* hydrogens, we can invoke deshielding by conjugative electron withdrawal into d or f orbitals of iodine; the presence or absence of a positive charge on iodine apparently has a negligible effect on the magnitude of this withdrawal. Such conjugative electron withdrawal from the *para* position has been used to explain the lowered basicity of the 4-aminodiphenyliodonium ion as compared to the 3-aminodiphenyliodonium ion.[3,6]

One might say that the still greater shift downfield of the *ortho* hydrogens reflects the addition of inductive electron withdrawal to conjugative electron with-

drawal. This unlikely "explanation" requires that the magnitude of inductive electron withdrawal be unaffected by the presence or absence of a positive charge on iodine. Alternatively, one may say that iodine withdraws electrons conjugatively more from the *ortho* position than from the *para* position in both iodobenzene and the diphenyliodonium ion.

As for electrostatic effect of the positively charged iodine, we can perhaps ascribe to it the whole shift downfield of the hydrogens in the diphenyliodonium cation relative to those in iodobenzene, but we cannot use it to explain the relative chemical shifts of the hydrogens within the diphenyliodonium cation.

It has been shown[10,13] that shielding parameters for substituents *para* to H[1], C[13], and F[19] are well correlated by Hammett's σ constants. In the present work σ_p for the phenyliodonio group has been calculated from the equation obtained for the straight-line plot of Ham-

$$d^x{}_p = -0.658\sigma_p + 0.21$$

mett's substituent constants[25] σ_p against the shielding parameters $d^x{}_p$ of the various substituents (x) obtained by Martin and Dailey.[12] The values for $d^x{}_p$ given by Spiesecke and Schneider[10a] give slightly lower values for σ_p for the phenyliodonio group.
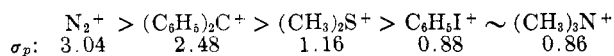
The correlation between σ_m and $d^x{}_m$ is not as good as for σ_p and $d^x{}_p$ since the differences in the shielding at this position are small and give scattered points on a graph. This has also been observed in the C[13] studies.[10a,13e] In the F[19] studies there seems to be a better correlation for certain *meta* substituents only, with Taft's σ_I values.[13c–e] The poor correlation with σ_m has been attributed, although inconclusively, to anisotropy[26] of the substituents (effect should be small on this position), to specific solvent interactions and to small "field effects" due to polar groups. While a plot of the $d^x{}_m$ values given by Martin and Dailey[12] vs. σ_m values[25] shows widely scattered points, the best line drawn through the two extremes of the scale, NH$_2$ and NO$_2$, gives a value for σ_m for the phenyliodonio group (C$_6$H$_5$I$^+$) which is in good agreement with previously found values. The equation of this line is given by

$$d^x{}_m = -0.47\sigma_m + 0.17$$

These values are included in Table I. It can be seen that in methanol, where ionization is almost complete, σ_m and σ_p are indeed very close ($\sigma_p - \sigma_m = 0.07$).

Table III summarizes the above constants of the phenyliodonio, trimethylammonio, dimethylsulfonio, diphenylcarbonio, and diazonio groups. It is seen that values obtained by nmr agree fairly well with those obtained by other methods.

From the available data the order of decreasing tendency for electron withdrawal appears to be as follows.

$$\text{N}_2{}^+ > (\text{C}_6\text{H}_5)_2\text{C}^+ > (\text{CH}_3)_2\text{S}^+ > \text{C}_6\text{H}_5\text{I}^+ \sim (\text{CH}_3)_3\text{N}^+$$
$$\sigma_p:\quad 3.04 \qquad 2.48 \qquad\quad 1.16 \qquad\quad 0.88 \qquad\quad 0.86$$

Buckingham[16] has shown that the change in the proton screening constant Δd^x of a C–X bond when subjected to an electric field E, arising from polar groups in other parts of the molecule, is given by

$$\Delta d^x = -2 \times 10^{-12}E_z - 10^{-18}E^2$$

(25) H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

(26) The correction for anisotropy of iodine was determined from C[13] nmr studies: G. S. Reddy and J. H. Goldstein, *J. Chem. Phys.*, **38**, 2736 (1963).

where E_z is the component of E in the bond direction. Recently Musher[20] showed that for most intramolecular fields the E^2 term is negligible and the nuclear magnetic shielding can be considered as varying linearly with the electric field.

Shaefer and Schneider[21] applied this linear relationship to several aromatic compounds and found a generally good agreement with values by simple MO calculations. Difficulties arise from the magnetic anisotropies of the substituents, affecting mostly the *ortho* positions. The following equation was derived[21] where

$$d^x = k\Delta\rho$$

d^x is the proton chemical shift in the x-substituted benzene relative to benzene (shielding parameter); $\Delta\rho$ is the "excess" local charge on the carbon atom in the aromatic system. In benzene the π-electron density ρ at each carbon atom is unity ($\Delta\rho = 0$). The constant k is found from the slope of the line when the proton chemical shifts d^x (with appropriate corrections for ring size) in the six π-electron system C$_5$H$_5{}^-$, C$_6$H$_6$, and C$_7$H$_7{}^+$ were plotted against $\Delta\rho$. The value of 10.7 ppm/electron thus obtained is in good agreement with previous values.[19,20] With this value for k, the electron densities ρ for the phenyliodonio group and iodobenzene were calculated and are included in Table I.
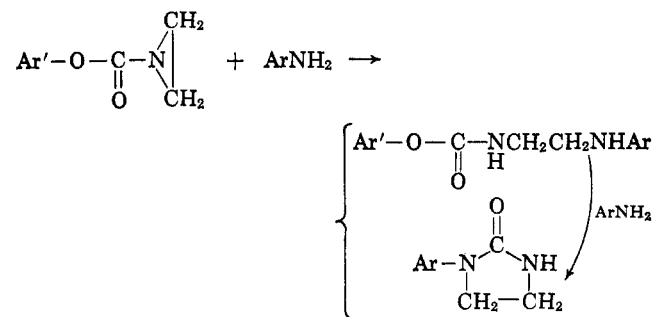

Reaction of 1-(p-Chlorophenyloxycarbonyl)-azetidine with Aromatic Amines

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In a previous paper,[1] it has been reported that the reaction of 1-(aryloxycarbonyl)aziridines with aromatic amines gives 1-aryl-1,3-imidazolidin-2-ones along with 2-arylaminoethylcarbamic acid aryl esters at comparatively low temperatures.

Further, it has been shown that the imidazolidinones are formed from the ring-opened products in the presence of amines.

Now the study was extended to an azetidine derivative, 1-(p-chlorophenyloxycarbonyl)azetidine (I). I was prepard by the interfacial condensation reaction of p-chlorophenyl chloroformate with azetidine. Reactions of I with arylamines (II) were carried out at several temperatures. In contrast to the results with aziridine

(1) Y. Iwakura and A. Nabeya, *J. Org. Chem.*, **25**, 1118 (1960).