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Syntheses of Arylcyanotriazenes and Related Compounds[1)]

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1-Aryl-3-cyanotriazene potassium salts (IIa—j) were synthesized by treating the corresponding arylazides (Ia—j) with potassium cyanide.

When IIa—j were treated with dimethyl sulfate in the presence of dicyclohexyl-18-crown ether-6 (18-crown-6), methylation occurred at N^1 and N^3 of the triazeno group. The resulting two isomers, 1-aryl-3-cyano-1-methyltriazenes (IIIa—j) and 1-aryl-3-cyano-3-methyltriazenes (IVa—f) were all separable by means of chromatography on silica gel. However, several of the 3-isomers (IVg—j) were not isolated. On the other hand, the direct alkylation of arylcyanotriazene potassium salts (IIa, c, e) with dimethyl sulfate in methanol gave only the 1-methyl derivatives, 1-aryl-3-cyano-1-methyltriazenes (IIIa, c, e). The alkylated positions in these products were determined by chemical and spectral studies.

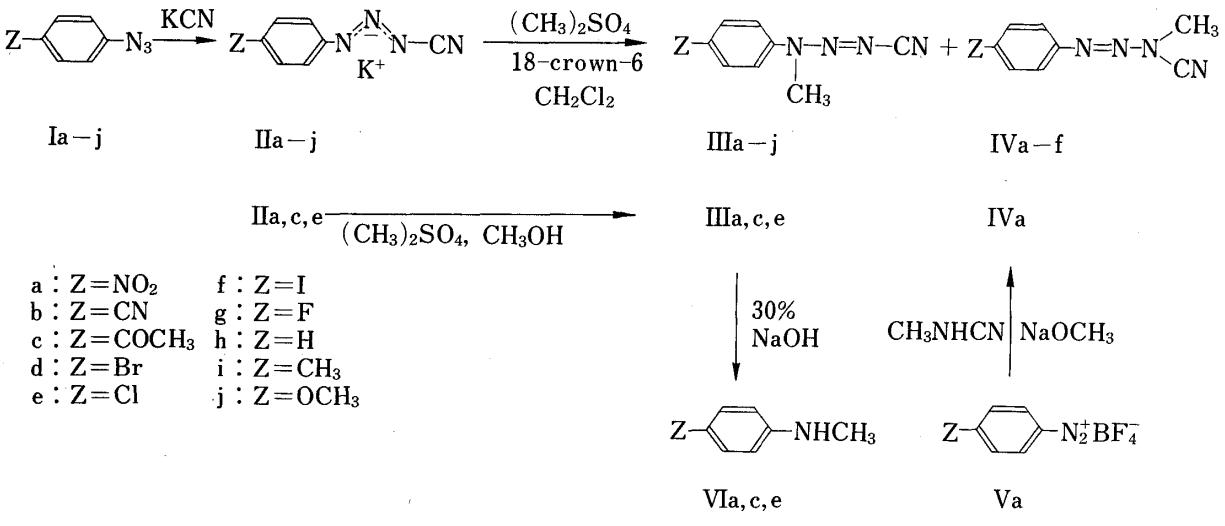
A clear correlation between the Hammett constants and the ^{13}C-nuclear magnetic resonance (^{13}C-NMR) chemical shifts of the nitrile carbons of (1-aryl-3-cyano)methyltriazenes (IIIa—j, IVa—f) was obtained.

Keywords——triazenes; cyanotriazenes; cyanotriazene potassium salts; nitriles; 18-crown-6; methylation; ^{13}C-NMR; the selective proton decoupling; Hammett constants

We reported the synthesis of heterocyclic triazene derivatives by using cyanotriazene potassium salts which could be readily prepared by the reaction of azides and potassium cyanide.[2,3)] Triazenes have recently received much attention because of their biological effects, including carcinogenic and antitumor activities.[4)]

This paper describes the syntheses of 1-aryl-3-cyanotriazenes and related compounds. ^{13}C-Nuclear magnetic resonance (^{13}C-NMR) and infrared (IR) spectroscopies were applied for the structural assignment of these compounds.

1-(*p*-Nitrophenyl)- (IIa), 1-(*p*-cyanophenyl)- (IIb), 1-(*p*-acetylphenyl)- (IIc), 1-(*p*-bromophenyl)- (IId), 1-(*p*-chlorophenyl)- (IIe), 1-(*p*-iodophenyl)- (IIf), 1-(*p*-fluorophenyl)- (IIg), 1-phenyl- (IIh), 1-(*p*-tolyl)- (IIi) and 1-(*p*-methoxyphenyl)-3-cyanotriazene potassium salt



Ia—j IIa—j IIIa—j IVa—f IIIa, c, e IVa VIa, c, e Va

Chart 1

(IIj) were synthesized in 40—98% yields by heating the corresponding arylazides (Ia—j) and potassium cyanide in aqueous methanol (Chart 1). The 1-aryl-3-cyanotriazenes having electron-withdrawing groups at the 4-position of the phenyl ring are stable, but those having electron-releasing groups partially decomposed on recrystallization because of their instability. Their IR spectra in Nujol showed a cyano group absorption at 2075—2160 cm^{-1}. As described later the position of the cyano group bound to the azides was chemically elucidated to be the terminal nitrogen of the azide group by the reaction of *p*-nitrobenzene diazonium tetrafluoroborate with methylcyanamide to give the corresponding 3-cyano-3-methyltriazene. The structure of 4-(3-cyano-1-triazeno)pyridine 1-oxide potassium salt, in which the cyano group is present at the terminal position, has already been determined by X-ray structure analysis.[5]

The phase-transfer alkylation of these cyanotriazene potassium salt was examined (Chart 1). Treatment of IIa—f with dimethyl sulfate in the presence of dicyclohexyl-18-crown ether-6 (18-crown-6) in dichloromethane gave a mixture of the positional isomers, 1-aryl-3-cyano-1-methyltriazenes (IIIa—f) and 1-aryl-3-cyano-3-methyltriazenes (IVa—f). These

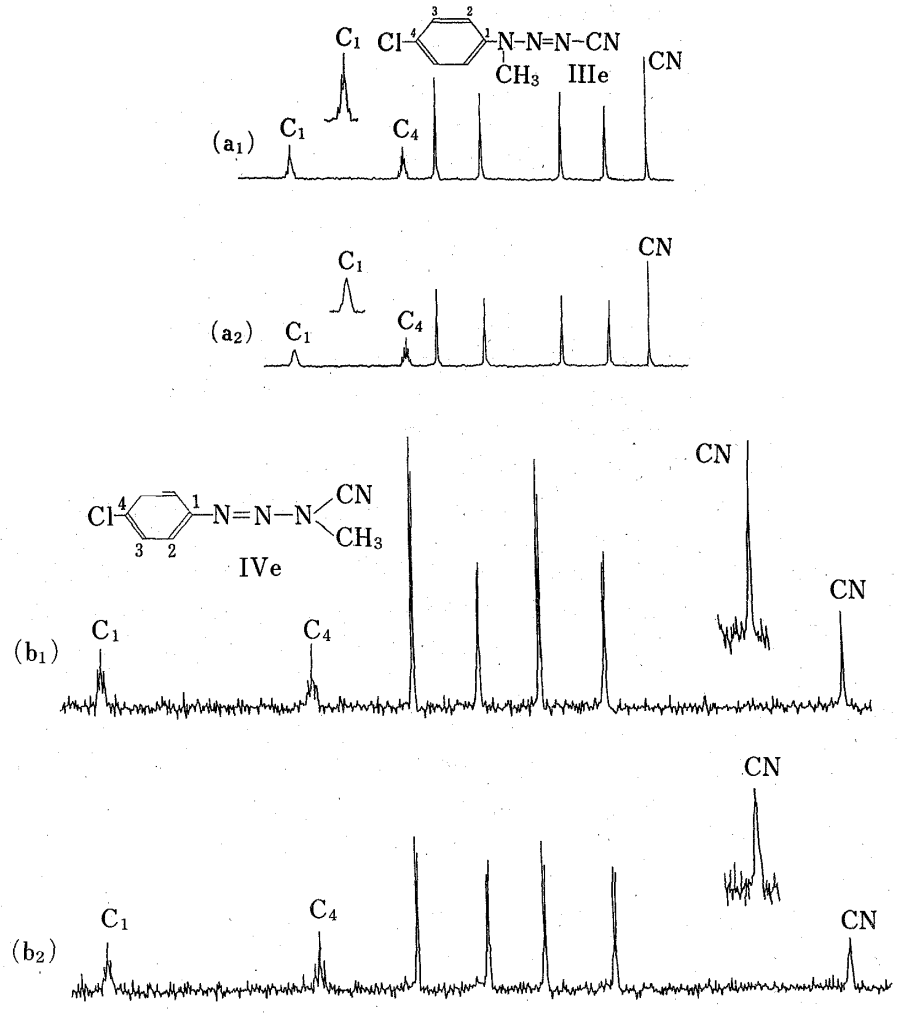


Fig. 1. The Selective Proton Decoupling ^{13}C-NMR Spectra[12] of 1-(*p*-Chlorophenyl)-3-cyano-1-methyltriazene (IIIe) and Its 3-Methyl Isomer (IVe) in $CDCl_3$

When the methyl protons of IIIe were irradiated, the signal of C^1-carbon changed from a broad peak to a quintet (from the spectrum a_2 to a_1), while the signal of the CN-carbon changed from a broad singlet to a sharp one (from the spectrum b_2 to b_1) in IVe.

The irradiated frequencies were as follows: a_1: 57.0 518 MHz; a_2: 56.0000 MHz; b_1: 57.0257 MHz; b_2: 56.000 MHz.

isomers were all separated by means of column chromatography on silica gel with a mixture of *n*-hexane and diethyl ether as an eluting solvent. As shown in Table I, the N^1-methyl products (IIIa—f) were obtained in 36—39% yields, and the N^3-methyl products (IVa—f) in 28—42% yields. On the other hand, similar alkylation of IIg—j gave only the N^1-methyl products (IIIg—j) in 30—43% yields.

A direct alkylation of these cyanotriazene potassium salts was then tried. When IIa,c,e were treated with dimethyl sulfate in methanol, the corresponding N^1-methyl derivatives (IIIa, IIIc and IIIe) were obtained in 76, 88 and 45% yields, respectively, but the corresponding N^3-isomers (IVa,c,e) were not obtained. The facts that IIIa and IIIc were produced in such high yields, and that formation of the N^3-isomers could not be detected by thin layer chromatography (TLC) during the reaction, suggested that no N^3-methylation occurred in this type of methylation. Consequently, in the direct methylation of the arylcyanotriazene potassium salts having electron-withdrawing groups such as NO_2 and CH_3CO in methanol, the reaction should proceed with the contribution of a localized form, Ar–$\bar{N}$–N=N–CN, whereas that in the

TABLE I. Yields and Physical Data of 1-Aryl-3-cyanotriazene Potassium Salts (IIa—j), 1-Aryl-3-cyano-1-methyltriazenes (IIIa—j) and 1-Aryl-3-cyano-3-methyltriazenes(IVa—f)

Compd. No.	Yield[a] (%)	mp (℃)	Recryst. solvent	IR[b] ν_{max} cm^{-1} CN	UV[c] λ_{max} nm (log ε)	Formula	Analysis (%) Calcd (Found) C	H	N
IIa	92	>300	EtOH	2137	248 396 (4.27) (4.39)	$C_7H_4KN_4O_2$	36.67 (36.28	1.76 1.84	30.54 30.23)
IIb	90	>300	EtOH-H_2O	2160 (2220)	235 346 (4.05) (4.44)	$C_8H_4KN_5\cdot 1/2H_2O$	43.90 (43.73	2.30 2.21	32.00 32.41)
IIc	89	>300	MeOH	2145	238 357 (4.04) (4.41)	$C_9H_7KN_4O$	47.78 (47.63	3.12 3.06	24.76 24.62)
IId	98	>300	EtOH-H_2O	2090 2147	227 328 (3.98) (4.32)	$C_7H_4BrKN_4\cdot H_2O$	29.90 (29.74	2.15 2.22	19.93 19.85)
IIe	70	>300	MeOH-H_2O	2148	227 324 (3.95) (4.28)	$C_7H_4ClKN_4\cdot H_2O$	35.51 (35.40	2.55 2.40	23.67 23.52)
IIf	71	>300	EtOH-H_2O	2135 2120	232 332 (3.96) (4.33)	$C_7H_4IKN_4\cdot 1/2H_2O$	26.34 (26.13	1.58 1.60	17.56 17.45)
IIg	86	>300	EtOH-H_2O	2152	232 320 (3.85) (4.17)	$C_7H_4FKN_4\cdot H_2O$	38.17 (38.12	2.75 2.58	25.44 25.44)
IIh	40	>300	EtOH-ether	2120	225 320 (3.92) (4.23)	$C_7H_5KN_4$	43.50 (43.22	3.13 3.10	29.00 29.05)
IIi	60	>300	EtOH-H_2O	2140	228 322 (3.84) (4.14)	$C_8H_7KN_4\cdot 1.7H_2O$[e]	41.97 (41.96	4.58 4.38	24.48 24.58)
IIj	45	>300	EtOH-ether	2075 2120	223 305 330 (3.88) (4.04) (4.09)	$C_8H_7KN_4O\cdot 1/2H_2O$	43.03 (42.79	3.61 3.60	25.09 25.08)
IIIa	38 (76)	110—111	MeOH	2197	238 335 (3.76) (4.40)	$C_8H_7N_5O_2$	46.83 (46.78	3.44 3.53	34.12 34.20)
IIIb	39	144—145	MeOH	2197 (2227)	238 318 (3.75) (4.29)	$C_9H_7N_5$	58.37 (58.07	3.81 3.84	37.82 37.74)
IIIc	38 (88)	106—107	MeOH	2198	243 262[sh] 324 (3.63) (3.69) (4.29)	$C_{10}H_{10}N_4O$	59.39 (59.19	4.98 4.91	27.71 27.49)
IIId	35	77—78	MeOH-ether	2197	238 320 (3.85) (4.24)	$C_8H_7BrN_4$	40.19 (40.01	2.95 2.98	23.44 23.45)
IIIe	38 (45)	76—77	MeOH-ether	2198	240 319 (3.84) (4.23)	$C_8H_7ClN_4$	49.37 (49.24	3.62 3.81	28.79 29.06)
IIIf	36	105—106	MeOH	2197	241 323 (3.92) (4.25)	$C_8H_7IN_4$	33.58 (33.56	2.47 2.45	19.59 19.61)
IIIg	36	54—55[d]	EtOH	2198	233 313 (3.85) (4.12)	$C_8H_7FN_4$	53.93 (53.99	3.96 3.84	31.45 31.42)
IIIh	30	66—67	MeOH	2197	240 313 (3.65) (4.19)	$C_8H_8N_4$	59.98 (59.99	5.03 4.93	34.98 34.54)
IIIi	43	58—59	MeOH	2195	242 319 (3.74) (4.19)	$C_9H_{10}N_4$	62.05 (61.85	5.79 5.72	32.17 32.07)
IIIj	30	56—57	MeOH	2197	243 330 (3.83) (4.16)	$C_9H_{10}N_4O$	56.83 (56.77	5.30 5.25	29.42 29.06)
IVa	42	101—102[d]	Ether	2238	312 (4.27)	$C_8H_7N_5O_2$	46.83 (46.60	3.44 3.43	34.12 34.47)
IVb	37	115—116	Ether	2240 (2230)[sh]	294 (4.27)	$C_9H_7N_5$	58.37 (58.37	3.81 3.92	37.82 37.75)
IVc	32	104—105[d]	Ether	2236	298 (4.28)	$C_{10}H_{10}N_4O$	59.39 (59.31	4.98 4.88	27.71 27.43)
IVd	31	76—77	Ether-hexane	2234	293 (4.25)	$C_8H_7BrN_4\cdot 1/3H_2O$[e]	39.20 (39.71	3.01 2.86	22.86 22.85)
IVe	31	70—71	Ether	2236	291 (4.09)	$C_8H_7ClN_4$	49.37 (49.13	3.63 3.61	28.79 29.01)
IVf	28	80—81	Ether-hexane	2235	308 (4.20)	$C_8H_7IN_4$	33.58 (33.53	2.47 2.52	19.59 19.65)

a) Yields of IIIa—j and IVa—f are those obtained from the reaction of IIa—j with Me_2SO_4 in the presence of 18-crown-6. Yields in parentheses are those in the reaction without crown ether in MeOH
b) IIa—j were measured in nujol, while IIIa—j and IVa—f were done in $CHCl_3$. Frequencies in parentheses are CN stretching vibration in the aromatic ring. sh: shoulder.
c) IIa—j were measured in 95% EtOH, while IIIa—j and IVa—f were done in $CHCl_3$. sh: shoulder.
d) Decomposition point.
e) Hygroscopic.

presence of 18-crown-6 occurs preferentially through a delocalized form, $[Ar-\overline{N}=N=\overset{+}{N}=C\equiv N]^-$, probably due to the formation of a complex of potassium ion-crown ether.

1-(*p*-Nitrophenyl)-3-cyano-3-methyltriazene (IVa) could be synthesized by the reaction of *p*-nitrobenzene diazonium tetrafluoroborate (Va) with methylcyanamide (Chart 1). However, since similar attempts to obtain other cyanomethyltriazenes (IVb—j) were unsuccessful, the methylated position of both isomers was determined by comparing their spectral data with those of the *p*-nitro compounds (IIIa, IVa), whose structures were confirmed by synthesis. The results obtained from selective proton decoupling experiments were also valuable to clarify the methylated position in these cyanomethyltriazenes.

Fig. 1 shows the selective proton decoupling ^{13}C-NMR spectra of 1-(*p*-chlorophenyl)-3-cyano-1-methyltriazene (IIIe) and its 3-methyl isomer (IVe). When the protons of the methyl group of IIIe were irradiated, only the broad signal at 148.8 ppm, which was assigned to the C^1-position of the phenyl, changed. Thus, it could be determined that the methyl group of IIIe was attached to the N^1-position of the cyanotrizene moiety. On the other hand, when the protons of the methyl group of IVe were irradiated, the signal of the nitrile carbon at 110.9 ppm changed from a broad peak to a sharp singlet, and IVe was proved to have an N^3-methyl structure.

It seems reasonable that, when the N^1-methyl isomers (IIIa,c,e) were heated in a mixture of aqueous 30% sodium hydroxide solution and methanol for 30 min, the corresponding *N*-methylanilines (VIa,c,e) were obtained in 83—94% yields (Chart 1). The N^3-methyl isomers (IVa,c,e) reacted with 2-naphthol to produce the red azo compounds,[2,3] whereas the N^1-methyl isomers (IIIa,c,e) were largely recovered (more than 90%) unchanged.

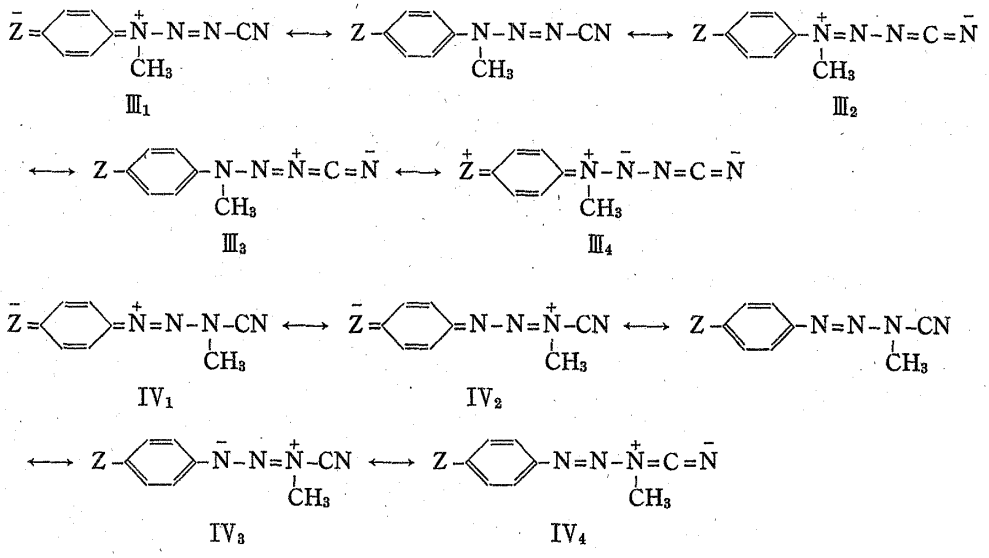
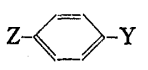


Chart 2

The IR spectra of 1-aryl-3-cyano-1-methyltriazenes (IIIa—j) and their 3-methyl isomers (IVa—f) in chloroform or in nujol showed characteristic strong absorptions of nitrile stertching vibration at 2195—2198 and 2234—2240 cm^{-1}, respectively (Table I). The 1-methyl derivatives seem to have formally the character of a resonance hybrid[6] of III_{2-4} as shown in Chart 2, whereas in the 3-methyl isomers the contribution of the carbodiimide type IV_4 is expected to be diminished due to the inductive effect (—I effect) of the methyl group. Thus, the nitrile bands of the 1-methyl derivatives appeared at clearly frequencies than those of the 3-methyl isomers.

In addition, the absorption maxima in the ultraviolet (UV) spectra of the 1-methyl derivatives in chloroform were usually observed at longer wavelength than those of the 3-methyl derivatives (Table I).

TABLE II. ^{13}C Chemical Shifts[12] of 1-Aryl-3-cyanotriazene Potassium Salts (IIa—j), 1-Aryl-3-cyano-1-methyltriazenes (IIIa—j) and 1-Aryl-3-cyano-3-methyltriazenes (IVa—g)[a]



IIa—j: Y = [N=N=N-CN]$^-K^+$
IIIa—j: Y = N(CH_3)-N=N-CN
IVa—f: Y = N=N-N(CH_3)-CN

Compd.	C-1	C-2	C-3	C-4	N-CN	N-CH_3	Others (Z)
IIa	156.6	122.1	126.3	146.2	127.1		
IIb	155.1	122.1	134.5	108.3	126.9		120.8(CN)
IIc	155.1	121.7	131.0	135.2	127.9		203.1(CO), 27.4(CH_3)
IId	150.7	124.0	133.7	120.9	128.8		
IIe	149.9	123.3	130.4	132.6	128.7		
IIf	150.9	123.6	138.8	91.9	128.0		
IIg[b]	147.7	123.1	116.7	162.2	128.7		
IIh	151.9	121.8	130.2	138.1	128.9		
IIi	149.1	121.9	131.2	138.5	129.5		21.6(CH_3)
IIj	145.2	122.4	115.3	158.6	128.6		56.4(OCH_3)
IIIa	147.0	119.4	125.2	146.4	115.3	35.1	
IIIb	145.5	119.5	133.6	111.1	115.5	35.1	117.6(CN)
IIIc	145.6	119.0	129.7	135.8	115.7	35.2	195.7(CO), 26.3(CH_3)
IIId	141.6	121.0	132.5	121.4	116.2	35.7	
IIIe	141.8	120.7	129.5	133.5	116.1	35.7	
IIIf	142.3	121.1	138.5	92.5	116.2	35.6	
IIIg[c]	138.9	121.6	116.3	161.7	116.4	36.3	
IIIh	142.6	119.6	129.4	127.8	116.5	35.9	
IIIi	140.4	119.5	130.0	138.0	116.8	36.0	20.7(CH_3)
IIIj	136.1	121.2	114.6	159.2	116.9	36.4	55.5(OCH_3)
IVa	151.1	123.0	124.9	148.2	110.2	37.0	
IVb	149.6	122.8	133.2	113.1	110.3	36.8	117.9(CN)
IVc	150.0	122.4	129.5	137.8	110.7	36.6	196.9(CO), 26.6(CH_3)
IVd	145.8	123.7	132.3	123.9	110.9	36.3	
IVe	145.4	123.4	129.3	135.7	110.9	36.3	
IVf	146.4	123.8	138.5	95.8	110.9	36.4	
IVg[d]	143.4	124.0	116.0	163.3	110.9	36.3	

a) Data for IIa—j were obtained in DMSO-d_6–D_2O (1:3) solution. Data for IIIa—j and IVa—g were obtained in $CDCl_3$ solution.
b) J_{F-C^1}=4.8 Hz; J_{F-C^2}=8.5 Hz; J_{F-C^3}=21.9 Hz; J_{F-C^4}=242.0 Hz.
c) J_{F-C^1}=2.3 Hz; J_{F-C^2}=8.5 Hz; J_{F-C^3}=23.1 Hz; J_{F-C^4}=247.9 Hz.
d) Data are for the mixture of IIIg and IVg, since IVg was too unstable to isolate. J_{F-C^1}=3.9 Hz: J_{F-C^2}=8.5 Hz; J_{F-C^3}=23.0 Hz; J_{F-C^4}=249.4 Hz.

In the ^{13}C-NMR spectra of the cyanotriazenes (Table II) the chemical shifts of the nitrile carbons were at 115—117 ppm for the 1-methyl derivatives (IIIa—j) and at 110—111 ppm for the 3-methyl isomers (IVa—f), but at 127—130 ppm for the potassium salts (IIa—j). It is interesting that the chemical shifts of the nitrile carbons of IVa—f appear at higher field, particularly at 110.2 ppm for IVa, as compared with those of common nitriles at 112—116 ppm[7-9]

The signals for the nitrile carbons of these methylcyanotriazenes (IIId—j, IVd—f) having electron-releasing or weakly electron-withdrawing groups were shifted to lower field than those of the derivatives (IIIa—c, IVa—c) having strongly electron-withdrawing groups. The nitrile carbons (δ-position) of the methylcyanotriazenes, even though separated from the benzene nucleus through the three nitrogen atoms, appear to be influenced by substituent effects.

It was recently reported that the chemical shifts for the nitrile carbon atoms located at the γ-position to the aromatic ring of benzylidene malononitriles showed a Hammett-type correlation.[10] Thus, we evaluated the correlation between Hammett constants and the ^{13}C-chemical shifts of the nitrile group located at the δ-position to the aromatic ring in arylcyano-

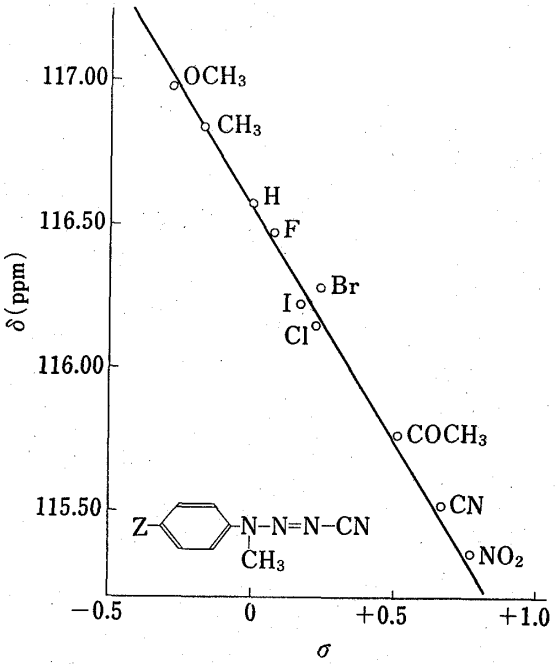


Fig. 2. Hammett Plot for Nitrile Carbons of Arylcyanomethyltriazenes (IIIa—j)

methyltriazenes. When the chemical shifts of the nitrile carbon of the 1-methyl derivatives (IIIa—j) were plotted as a function of σ and σ^+ substituent constants,[11] a straight line was obtained with correlation coefficients of $r=0.999$ for σ and $r=0.960$ for σ^+. A similar analysis for the 3-methyl isomers (IVa—f) gave correlation coefficients of $r=0.969$ for σ and $r=0.958$ for σ^+. These data showed a better correlation with σ than with σ^+ (Fig. 2). The ρ values for the nitrile carbon in the 1-methylcyanotriazenes and 3-methyl derivatives are negative, as given in Table III. These results should be considered as reflecting the contribution of carbodiimide-type structure (*e.g.* III_{2-4} and IV_4) to the overall structure, as shown in Chart 2, since the carbodiimide carbons are deshielded relative to the nitrile carbons.[7] Comparison of the slope ($\rho=-1.56$) obtained from IIIa—j with the slope ($\rho=-1.25$) from IVa—f suggests that the nitrile carbons in IIIa—j are more susceptible to substituent effect than those of IVa—f.

Table III. Correlation Results using σ and σ^+ Constants

System	Constants	n	ρ	i	s	r
IIIa—j	σ	10	−1.56	116.5	0.03	−0.999
	σ^+	10	−1.12	116.3	0.17	−0.960
IVa—f	σ	6	−1.25	111.2	0.08	−0.969
	σ^+	6	−1.07	111.1	0.08	−0.958

n, number of data points; ρ, slope as determined by the least-squares method; i, calculated intercept; s, standard deviation; r, correlation coefficient

Antitumor activities of these newly synthesized arylcyanomethyltriazenes are under investigation by means of our first screening system.

Experimental[12]

All melting points are uncorrected. IR spectra were measured on a JASCO A-102 spectrophotometer and UV spectra on a Shimadzu UV-240 spectrophotometer. ^{13}C-NMR spectra were measured with a JEOL FX-200 spectrometer with tetramethylsilane as an internal standard.

Arylazides (Ia—j)——A typical experiment is described here for Ic. *p*-Acetylphenylazide (Ic): A solution of $NaNO_2$ (5.1 g, 0.077 mol) in water was added dropwise to a solution of *p*-aminoacetophenone (10.5 g, 0.077 mol) in 10% HCl (120 ml) at 0—5°C with vigorous stirring. The mixture was kept below 5°C for 30 min, and then a solution of NaN_3 (5.5 g, 0.085 mol) in water (100 ml) was added dropwise while the temperature was kept below 5°C. After being stirred for 1 h, the reaction mixture was allowed to reach at room temperature, then it was extracted with ether. The extract was dried over anhyd. Na_2SO_4, and the solvent was evaporated off. The residue was recrystallized from isopropyl ether to give *p*-acetylphenylazide (Ic), yellow prisms, mp 42.5—43.5°C (dec.). Yield, 10.5 g (84%). IR ν_{max}^{Nujol} cm^{-1}: 2075 (N_3). *Anal.* Calcd for $C_8H_7N_3O$: C, 59.62; H, 4.38; N, 26.07. Found: C, 59.48; H, 4.27; N, 25.89. Other arylazides were prepared similarly.

p-Nitrophenylazide (Ia): Brownish-yellow prisms (from isopropyl ether), mp 71.5—72.5°C (dec.) (lit.,[13] mp 71—73°C). Yield, 83%. IR ν_{max}^{Nujol} cm^{-1}: 2085 (N_3). *Anal.* Calcd for $C_7H_4N_4$: C, 58.33; H, 2.80; N, 38.87. Found: C, 58.02; H, 2.71; N, 38.61.

p-Bromophenylazide (Id): bp 71—72°C (2 mmHg) [lit.,[14] bp 69°C (2.1 mmHg)].

p-Chlorophenylazide (Ie): bp 65—66°C (5 mmHg) [lit.,[15] bp 44—46°C (1.0 mmHg)].

p-Iodophenylazide (If): Pale yellow prisms (from EtOH), mp 33.5—34.5°C (lit.,[16] mp 36°C). Yield, 90%. IR ν_{max}^{Nujol} cm^{-1}: 2090 (N_3).

p-Fluorophenylazide (Ig): bp 26—27°C (2 mmHg). IR ν_{max}^{neat} cm^{-1}: 2100 (N_3).

Phenylazide (Ih): bp 35—36°C (4 mmHg) [lit.,[17] bp 49—50°C (5 mmHg)]. *p*-Tolylazide (Ii): bp 66—67°C (4 mmHg) [lit.,[15] bp 55—56°C (4.5 mmHg)].

p-Methoxyphenylazide (Ij): bp 67—68°C (2.5 mmHg). IR ν_{max}^{neat} cm^{-1}: 2100 (N_3).

Arylcyanotriazene Potassium Salts (IIa—j)——A typical experiment is described here for IIc. 1-(*p*-Acetylphenyl)-3-cyanotriazene potassium salt (IIc): A solution of potassium cyanide (1.4 g, 0.02 mol) in water (10 ml) was added to a solution of Ic (3.2 g, 0.02 mol) in MeOH (20 ml) with stirring at 60°C. After being stirred for 3 h, the reaction mixture was allowed to stand at room temperature, and the separated crystals were filtered off, and recrystallized from MeOH. Yellow needles, mp >300°C. Yield, 4.0 g (89%). Other arylcyanotriazene potassium salts (IIa, b, d—j) were similarly obtained. Their physical and analytical data are shown in Table I. The ^{13}C-NMR spectral data are presented in Table II.

Alkylation of the Potassium Salts (IIa—j) with Dimethyl Sulfate in the Presence of Dicyclohexyl-18-Crown Ether-6 in Dichloromethane——A typical experiment is described here for IIIc. 18-Crown-6 (380 mg, 0.001 mol) was added to a suspension of finely powdered IIc (2.3 g, 0.01 mol) in CH_2Cl_2 (100 ml). The mixture was stirred for 15 min, then Me_2SO_4 (1.3 g, 0.01 mol) was added, while the temperature was kept below 5°C. The mixture was stirred for 3 h, and then allowed to stand overnight at room temperature. It was concentrated under reduced pressure, and extracted with ether. The solvent was evaporated off, and the residue was chromatographed on a silica gel column. A small amount of unidentified material was eluted in the first fraction with hexane–ether (4: 1). The second fraction, eluted with hexane–ether (2: 1), gave 1-(*p*-acetylphenyl)-3-cyano-3-methyltriazene (IVc). Yellow needles (from ether), mp 104—105°C. Yield, 650 mg (32%). The third fraction, eluted with ether, gave 1-(*p*-acetylphenyl)-3-cyano-1-methyltriazene (IIIc). Yellow needles (from MeOH), mp 106—107°C. Yield, 780 mg (38%). The alkylation of other potassium salts (IIa, b, d—j) with Me_2SO_4 in the presence of crown ether was similarly carried out, and arylmethylcyanotriazenes (IIIa—j, IVa—e) were obtained. However, IVg—j were not obtained. The physical and analytical data of these compounds are presented in Table I and Table II.

Alkylation of the Potassium Salts (IIa, c, e) with Dimethyl Sulfate in Methanol——1-(*p*-Acetylphenyl)-3-cyano-1-methyltriazene (IIIc): A solution of Me_2SO_4 (140 mg, 0.001 mol) in MeOH (10 ml) was added to a solution of IIc (230 mg, 0.001 mol) in MeOH (70 ml), and the reaction mixture was allowed to stand overnight at room temperature. The solvent was distilled off under reduced pressure, and the residue was extracted with $CHCl_3$. The solvent was evaporated off, and the residue was chromatographed on a column of silica gel with hexane–ether (1: 1). A small amount of acetophenone was eluted in the first fraction, and the second fraction gave IIIc (200 mg, 88%), which was identified by comparing it with the material prepared in the presence of crown ether. Compounds IIIa and IIIe were also obtained by a similar method in 76 and 45% yields, respectively. In the case of IIIa the first fraction gave a small amount of nitrobenzene, while in the case of IIIe an unknown material was obtained. The physical and analytical data for IIIa, c, e are shown in Table I.

Synthesis of 1-(*p*-Nitrophenyl)-3-cyano-3-methyltriazene (IVa) from *p*-Nitrobenzene Diazonium Salt——A solution of cyanamide (450 mg, 0.01 mol) in anhyd. MeOH (25 ml) was added to a solution of NaOMe (600 mg, 0.01 mol) in anhyd. MeOH (50 ml), and the mixture was allowed to stand for 30 min at room temperature, then Me_2SO_4 (1.3 g, 0.01 mol) was added (formation of monomethylcyanamide).[18] The reaction mixture was allowed to stand overnight, then *p*-nitrobenzene diazonium tetrafluoroborate (2.5 g, 0.01 mol) was added. The reaction mixture was stirred for 3 h at 5°C, and filtered. The filtrate was concentrated to dryness under reduced pressure, and the residue was chromatographed on a column of silica gel using hexane–ether (1: 2). The first fraction gave a small amount of nitrobenzene, and the second fraction gave IIIa (250 mg, 12%) which was identical with an authentic sample.

Decomposition of Arylcyanomethyltriazenes (IIIa, c, e) in 30% Sodium Hydroxide Solution——A typical experiment is described here for IIIc. A solution of 1-(*p*-acetylphenyl)-3-cyano-1-methyltriazene (IIIc) (21 mg, 0.0001 mol) in MeOH (20 ml) was added to 30% NaOH solution (10 ml), and the mixture was heated in a water bath for 30 min. The reaction mixture was extracted with CH_2Cl_2. The solvent was evaporated off, and the residue was chromatographed on a column of silica gel using a mixture of benzene and ethyl acetate (3: 7). The eluate gave 13 mg (85%) of *p*-acetyl-*N*-methylaniline, mp 108—109°C (from ether) (lit.,[19] mp 108—109°C).

Compounds IIIa and IIIe also gave *p*-nitro-*N*-methylaniline [bp 65°C (8 mmHg); lit.,[19] bp 57°C (6 mmHg)] and *p*-chloro-*N*-methylaniline [mp 155—156°C (from ether–MeOH); lit.,[19] mp 152°C] in 83% and 94% yields. However, the 3-methyltriazene isomers (IVa, c, e) did not give *N*-methylaniline derivatives in the reaction with 30% NaOH solution.

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References and Notes

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