methanol bath in a nonsilvered dewar flask which was cooled by circulation of methanol through an external Dry Ice–methanol mixture. The temperature range of the bath was −60 to −68°. The dewar flask was placed in the center of a Rayonet photochemical reactor and irradiated with 8-RUL 3000-Å lamps.

The following results were obtained: *cis*-dihydromayurone[3] in 22 hr gave 16% 7,11,11-trimethylbicyclo[5.4.0]-1-undecan-4-one and 4% *cis*-8,8,9,10-tetramethyldecal-2-one; *trans*-dihydromayurone[3] in 22 hr gave no detectable reaction by glpc; **1c** in 21 hr gave 12% **3c**; **1t** (91% pure) in 21 hr gave no detectable reaction by glpc; **2c** and **2t** (*ca.* 1:1 mixture) in 36 hr, after oxidation with Jones[5] reagent, gave 4% of **4c** and **4t** (1:1). In the case of **2**, the product was isolated and the presence of both **4c** and **4t** shown by the δ 0.97 (**4c**) and 0.79 (**4t**) methyl group nmr singlets. In all the other low temperature irradiations, the percentages were obtained by glpc analysis only.

Quantum Yield Determinations.—Quantum yields were determined according to the procedure of Wagner.[13] Separate solutions of **1c** (0.07 *M*), **1t** (0.07 *M*), **2c** (0.1 *M*), and **2t** (0.1 *M*) in 2-propanol containing octadecane as an internal standard were placed in 1.1-cm Pyrex tubes (each in triplicate), degassed, sealed, and irradiated in parallel at 33° on a merry-go-round using 8-RUL 3000-Å Rayonet lamps. At this concentration, the ketones absorbed >99% of the 300-nm radiation. The amount of ketone that disappeared was measured by glpc analysis (5% Carbowax 20M, 18 ft × $^{1}/_{8}$ in.) by comparing the ketone/standard area ratios before and after irradiation. The quantum yields for disappearance (7–15%) of ketone follow: **1c**, 0.50; **1t** (92% pure, 8% **1c**), 0.74; **2c** 0.45; **2t**, 0.38.

The amount of product formed during the irradiation was measured by comparison of glpc peak height to a graph of peak height *vs.* known concentrations of the respective product, using constant volume injections. The quantum yields for product formation follow: **3c** from **1c**, 0.23; **3c** from **1t**, 0.23; **4c** from **2c**, 0.08; **4t** from **2t**, 0.13.

Two tubes containing 1.0 *M* acetone and 0.20 *M* *cis*-1,3-pentadiene in cyclohexane were irradiated in parallel with the above samples. The average yield (10%) of *trans*-1,3-pentadiene was measured by comparison of glpc (10% UCW 98, 18 ft × $^{1}/_{8}$ in.) peak height to a graph of peak height *vs.* known concentrations of *trans*-1,3-pentadiene in the above solution of *cis*-1,3-pentadiene, acetone, and cyclohexane, using constant volume injections. The quantum yield for the cis to trans isomerization, after being corrected for back reaction, is 0.555.[14]

Acknowledgments.—The author would like to thank W. G. Dauben and A. R. Hochstetler for helpful discussions regarding this research, P. Shubiak for glpc analyses related to the quantum yield determinations, and J. Fischer for excellent technical assistance.

Registry No.—**1c**, 35340-22-8; **1t**, 40447-74-3; **2c**, 40447-75-4; **2t**, 40447-76-5; **3c**, 5523-99-9; **3t**, 40447-78-7; **4c**, 2530-17-8; **4t**, 1197-95-1; 10-methyl-$\Delta^{1,9}$-octal-2-one, 826-56-2; *cis*-10-methyl-$\Delta^{1,9}$-octal-2-ol, 31654-83-8; *trans*-10-methyl-$\Delta^{1,9}$-octal-2-ol, 40447-83-4; *cis*-1,9-methano-10-methyldecal-2-ol, 13903-60-1; *trans*-1,9-methano-10-methyldecal-2-ol, 40447-85-6; $\Delta^{1,9}$-octal-2-one, 1196-55-0; *cis*-$\Delta^{1,9}$-octal-2-ol, 30983-79-0; *trans*-$\Delta^{1,9}$-octal-2-ol, 2763-42-0; *cis*-1,9-methanodecal-2-ol, 40447-89-0; *trans*-1,9-methanodecal-2-ol, 40447-90-3.

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[13] (13) P. J. Wagner and R. W. Spoerke, *J. Amer. Chem. Soc.*, **91**, 4437 (1969).

[14] (14) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

Mono- and Disubstituted Vinyltrialkylammonium Compounds. Synthesis and Stereochemistry

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Methyl propiolate reacts with trimethyl-, triethyl-, tri-*n*-butylammonium, and pyridinium halide salts in water–dioxane to yield *trans*-methoxycarbonylvinyltrialkylammonium salts. Similarly, dimethyl acetylenedicarboxylate adds trimethyl- and triethylammonium halide salts to produce the *cis*-bis(methoxycarbonyl)-vinyltrialkylammonium compounds. Other disubstituted vinyltrimethylammonium salts were prepared by dehydrobromination of 1,1,2-tribromoethyltrimethylammonium bromide and 2-carboxy-1,2-dibromoethyltrimethylammonium bromide to yield the respective (*E*)-dibromovinyltrimethylammonium and (*E*)-1-bromo-2-carboxyvinyltrimethylammonium bromides. The stereochemistry and chemical shift assignment of both the mono- and disubstituted vinylammonium salts were established using the additivity relationship developed by Matter and Tobey, $\delta_{\mathrm{C=CH}} = 5.25 + Z_{\mathrm{gem}} + Z_{\mathrm{cis}} + Z_{\mathrm{trans}}$. The shielding parameters for the trialkylammonium substituent were determined to be $Z_{\mathrm{gem}} = 1.00$, $Z_{\mathrm{cis}} = 0.65$, and $Z_{\mathrm{trans}} = 0.30$. A reinvestigation of the reaction of 1-bromovinyltrimethylammonium bromide with $NaOCH_3$ or KOC_2H_5 revealed that the isomeric *cis*-alkoxyvinyltrimethylammonium bromide is also formed in addition to the reported 1-alkoxyvinyltrimethylammonium bromide.

The synthesis of vinyltrimethylammonium compounds is well documented. In most cases they are prepared by addition of aqueous trimethylamine to acetylene or monosubstituted acetylenic derivatives.[1-3] Until 1969, there were few reports on the synthesis of vinyltrialkylammonium salts containing an alkyl group other than methyl. With ethoxyacetylene, Arens[2] found that aqueous solutions of triethyl- or tri-*n*-butylamine reacted sluggishly or not at all. In an improved modification of Reppe's[1] neurine synthesis, Fisher[4,5] succeeded in preparing a series of *N*-(2-formylvinyl)trialkylammonium salts by treating a mineral acid salt of a tertiary amine with propiolaldehyde. With few exceptions, these and other 2-monosubstituted vinyltrialkylammonium salts have been shown by nmr spectroscopy to possess a trans configuration.[4-7]

Other monosubstituted vinyltrimethylammonium salts have been synthesized either by dehydration[8] or

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[1] (1) W. Reppe, German Patent 860,058 (1949).

[2] (2) J. F. Arens, J. G. Bouman, and D. H. Koerts, *Recl. Trav. Chim. Pays-Bas*, **74**, 1040 (1955).

[3] (3) C. Gardner, V. Kerrigan, J. D. Rose, and D. C. L. Weeden, *J. Chem. Soc.*, 789 (1949).

[4] (4) G. Fisher, *Chem. Ber.*, **102**, 2609 (1969).

[5] (5) G. Fisher, *ibid.*, **103**, 3470 (1970).

[6] (6) J.-M. Lehn and R. Sehr, *Chem. Commun.*, 847 (1966).

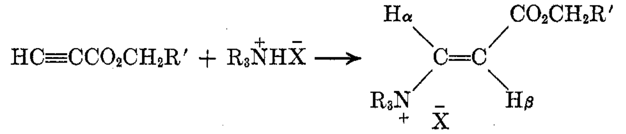
[7] (7) M. Ohtsuru, K. Tori, J.-M. Lehn, and R. Sehr, *J. Amer. Chem. Soc.*, **91**, 1187 (1969).

[8] (8) W. E. Truce and J. A. Simms, *J. Org. Chem.*, **22**, 762 (1957).

dehydrohalogenation[9-11] of 1,2-dihaloethyltrimethylammonium salts. In the latter case, the 1-halovinyltrimethylammonium salts are produced[12] instead of the 2-halo isomers.

Disubstituted vinyltrialkylammonium salts have not been reported. In the course of studying and preparing new monosubstituted vinyltrialkylammonium salts, we also succeeded in synthesizing several of the disubstituted derivatives. In this paper we report our observations on the synthesis and configurational assignments of new mono- and disubstituted vinyltrialkylammonium salts. We also formulate a set of nmr shielding parameters for the trialkylammonium substituent.

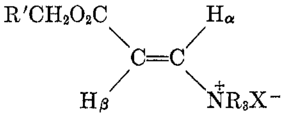
Monosubstituted Ammonium Salts.—When trimethyl-, triethyl-, or tri-*n*-butylammonium bromide was warmed (40°) in a 2:1 (v/v) water–dioxane solution containing an equivalent amount of methyl propiolate for 24 hr, the corresponding *trans*-methoxycarbonylvinyltrialkylammonium salts (**1a–e**) were isolated as crystalline compounds.[14] Similar results were obtained employing the hydrochloride salts or other acetylenic esters (Table I). The stereochemistry of the salts **1** was assigned as trans, since J = 13.8–14.0 Hz for all the alkoxycarbonyl derivatives studied (Table II). The chemical shift of H_α in **1c** and **1d** was shifted to lower field relative to **1b** by 0.25–0.30 ppm. H_β, however, remained invariant to any change in trialkyl substitution. Varying the halide counterion had no effect upon the chemical shifts of the vinyl protons because of minimal ion pairing in water.[16]



1a–e, 2

1a, R = CH_3; R′ = H; X = Cl
b, R = CH_3; R′ = H; X = Br
c, R = C_2H_5; R′ = H; X = Br
1d, R = n-C_4H_9; R′ = H; X = Br
e, R = CH_3; R′ = CH_2Cl; X = Br
2, R_3N = pyridine; R′ = H; X = Cl

TABLE I
PHYSICAL PROPERTIES OF MONOSUBSTITUTED VINYLTRIALKYLAMMONIUM SALTS



No.	R	R′	X	Yield, %[a]	Mp, °C	ν(C=C),[b] cm⁻¹	ν(C=O),[b] cm⁻¹
1a[c]	CH_3	H	Cl	35	179–180	166	1730
1b[c]	CH_3	H	Br	51	164–165	1661	1724
1c[c]	C_2H_5	H	Br	40	165–166	1664	1727
1d[c]	n-C_4H_9	H	Br	33	125–126	1653	1727
1e[c]	CH_3	CH_2Cl	Br	50	136	1661	1715
2[c]	R_3N = pyridine	H	Br	21	105–106	1642	1715

[a] Isolated yield. [b] Nujol mull. [c] Satisfactory analytical data (±0.4% for C, H, N) were provided for this compound: Ed.

In contrast, a pronounced shielding effect was observed for H_α in *trans*-methoxycarbonylvinylpyridinium chloride (**2**), formed in 21% yield from pyridine hydrochloride and methyl propiolate under similar conditions. The absorption of H_α was δ 8.24 compared to the trimethyl analog (**1b**) which appeared at δ 7.50. The change in chemical shift of H_α in the series $CH_3O_2CCH_\beta{=}CH_\alpha NR_3{}^+X^-$ is qualitatively correlated with the polar inductive effect of the substituent R. The δ values decreased in the following order for R: $C_5H_5N > CH_3 > C_2H_5 > n\text{-}C_4H_9$. Pyridinium salts of structure **2** have been long postulated as transient intermediates in the reaction of pyridine with acetylenic esters producing indolizines.[17]

Because of the ambiguity in the literature regarding the structure of 1-bromovinyltrimethylammonium bromide (**3**) and the potential need for configurational assignments of the disubstituted vinyltrialkylammonium salts, a set of shielding increments for a trialkylammonium substituent on the ethylene moiety was determined. Several groups[18,19] using nmr spectroscopy have determined a series of shielding increments Z which, when used in conjunction with the equation $\delta_{C=CH} = 5.25 + Z_{gem} + Z_{cis} + Z_{trans}$, aid in the determination of the stereochemistry of trisubstituted ethylenes. Comparative analysis (see Experimental Section) of the spectrum of neurine bromide and its derivatives with their calculated spectra using the shielding parameters of Matter[18] and Tobey[19] gave the following shielding increments—Z_{gem} = 1.00, Z_{cis} = 0.65, and Z_{trans} = 0.30—for a trialkylammonium substituent. The use of these shielding increments and those reported[18,19] gave calculated values of the chemical shifts for H_α and H_β in good agreement with those observed in this study and those previously reported[6,7] (Table II). The structure of **3** was reconfirmed by comparison of its observed (δ 6.50 and 6.07) *vs.* calculated (δ 6.45 and 5.98) olefinic chemical shifts. A similar analysis was performed for the 1-methoxy- (**4a**) and 1-ethoxyvinyltrimethylammonium bromide (**4b**) derivatives,[20] the latter prepared by two routes.[2,20] In the preparation[20] of **4**, a second isomeric vinyltrimethylammonium ether was observed. This isomer could be removed upon repeated recrystallization from methanol or acetonitrile. Nmr analysis of the product mixture resulting from **3** and $NaOCH_3$-CH_3OH at room temperature (Figure 1) indicated a 3:1 ratio of **4a** to *cis*-methoxyvinyltrimethylammonium bromide (**5a**). The spectrum of the mixture in DMSO-d_6 (or D_2O) showed an AB absorption pattern at δ 4.99 and 4.61 for the vinylic protons with J = 6.5 Hz and single peaks at δ 3.84 and 3.42 for the methoxyl and trimethylammonium

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[9] J. Bode, *Justus Liebigs Ann. Chem.*, **267**, 268 (1890).

[10] K. A. Hofmann and K. Hobald, *Chem. Ber.*, **44**, 1766 (1911).

[11] F. Klages and E. Sierup, *Justus Liebigs Ann. Chem.*, **547**, 65 (1941).

[12] In a recent report[13] the bromovinyltrimethylammonium bromide resulting from dehydrobromination was incorrectly assigned as the 2-bromo isomer.

[13] W. K. Kwok, W. G. Lee, and S. I. Miller, *J. Amer. Chem. Soc.*, **91**, 468 (1969).

[14] After completing this study, we uncovered an observation made by Truce and Brady[15] on the reaction of trimethylammonium chloride and ethyl propiolate in methylene chloride to yield *trans*-ethoxycarbonylvinyltrimethylammonium chloride.

[15] W. E. Truce and W. T. Brady, *J. Org. Chem.*, **31**, 3543 (1966).

[16] A. G. Massey, E. W. Rundull, and D. Shaw, *Spectrochim. Acta*, **20**, 379 (1964); **21**, 263 (1965).

[17] R. M. Acheson in "Advances in Heterocyclic Chemistry," Vol. 1, A. R. Katritzky, Ed., Academic Press, New York, N. Y., 1963, p 125.

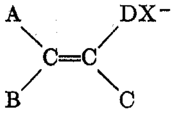
[18] U. E. Matter, C. Pascual, E. Pretsch, A. Pross, W. Simon, and S. Sternhell, *Tetrahedron*, **25**, 691, 2023 (1969); C. Pascual, J. Meier, and W. Simon, *Helv. Chim. Acta*, **49**, 164 (1966).

[19] S. W. Tobey, *J. Org. Chem.*, **34**, 1281 (1969).

[20] F. Klages and E. Drerup, *Justus Liebigs Ann. Chem.*, **547**, 65 (1941).

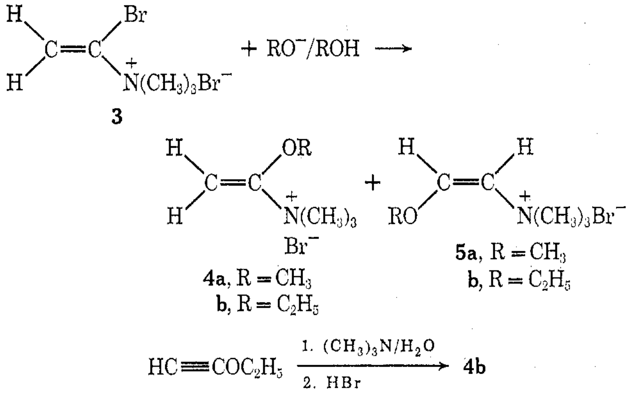
TABLE II

CALCULATED[a] vs. OBSERVED[b] NMR CHEMICAL SHIFTS OF MONOSUBSTITUTED VINYLTRIALKYLAMMONIUM SALTS



No.	A	B	C	D	X	δ_A, obsd	δ_A, calcd	δ_B, obsd	δ_B, calcd	δ_C, obsd	δ_C, calcd	δ_D, obsd
1a	H	CH_3O_2C	H	$N(CH_3)_3$	Cl	6.68	6.70	4.01		7.50	7.43	3.47
1b	H	CH_3O_2C	H	$N(CH_3)_3$	Br	6.63	6.70	3.86		7.47	7.43	3.37
1c	H	CH_3O_2C	H	$N(C_2H_5)_3$	Br	6.61	6.70			7.19	7.43	3.68, 1.31
1d	H	CH_3O_2C	H	$N(C_4H_9)_3$	Br	6.59	6.70			7.22	7.43	
1e	H	$ClCH_2CH_2O_2C$	H	$N(CH_3)_3$	Br	6.67	6.70			7.49	7.43	3.47
2	H	CH_3O_2C	H	NC_5H_5	Cl	6.92	6.70	3.77		8.24	7.43	*c*
3	H	H	Br	$N(CH_3)_3$	Br	6.50	6.45	6.07	6.01			3.54
4a	H	H	CH_3O	$N(CH_3)_3$	Br	4.99	4.69	4.61	4.49	3.84		3.42
4b	H	H	C_2H_5O	$N(CH_3)_3$	Br	4.95	4.69	4.58	4.49	1.37, 4.11		3.52
5a	CH_3O	H	H	$N(CH_3)_3$	Br	3.89		6.56	6.78	5.58	5.04	3.46
5b	C_2H_5O	H	H	$N(CH_3)_3$	Br	1.31, 4.18		6.54	6.78	5.61	5.04	3.52
9	H	HO_2C	H	$N(CH_3)_3$	Cl	6.58	6.90			7.40	7.66	3.42
16	H	HO_2C	H	$N(CH_3)_3$	Br	6.61	6.90			7.49	7.66	3.48
16a	H	HO_2C	H	$N(CH_3)_3$	BF_4	6.52	6.90			7.37	7.66	3.40
d	H	H	Br	$N(CH_3)_3$	BF_4	6.48	6.45	6.03	6.01			3.50
e	H	H	Cl	$N(CH_3)_3$	Br	6.48	6.45	6.03	6.01			3.50
e	H	H	C_6H_5	$N(CH_3)_3$	Br	6.96	7.28	6.75	6.64			

[a] U. E. Matter, C. Pascual, E. Pretsch, A. Pross, W. Simon, and S. Sternhell, *Tetrahedron*, **25**, 691, 2023 (1969); C. Pascual, J. Meier, and W. Simon, *Helv. Chim. Acta*, **49**, 164 (1966); S. W. Tobey, *J. Org. Chem.*, **34**, 1281 (1969); for $^+NR_3$, $Z_{gem} = 1.00$, $Z_{cis} = 0.65$, $Z_{trans} = 0.30$. [b] Measured in D_2O relative to internal standard of 3-(trimethylsilyl)propanesulfonic acid sodium salt. [c] See Experimental Section. [d] Prepared from **3** and Ag_2O followed by acidification with 50% HBF_3. [e] Reference 7.



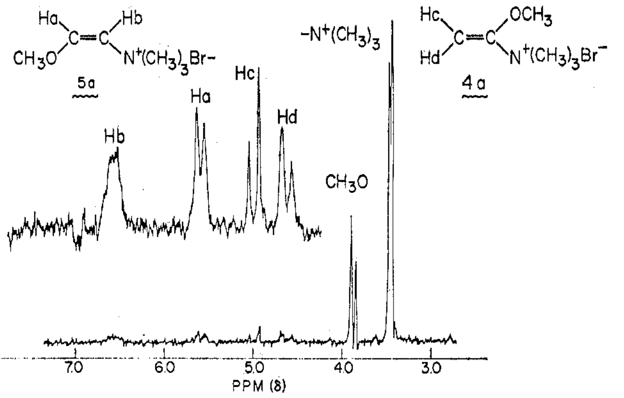


Figure 1.—^1H nmr spectrum of a mixture of **4a** and **5a** in DMSO-d_6 at 35°.

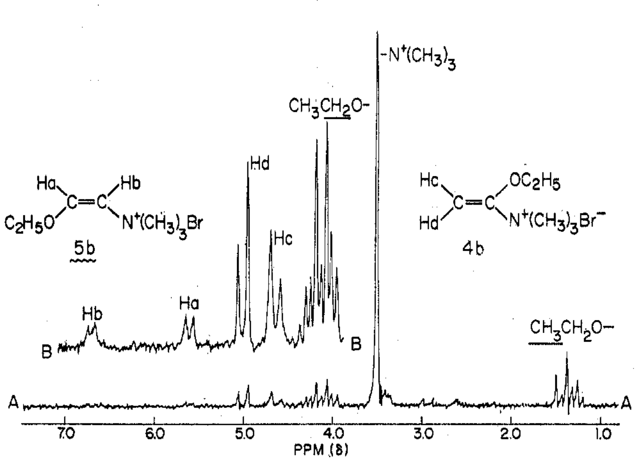
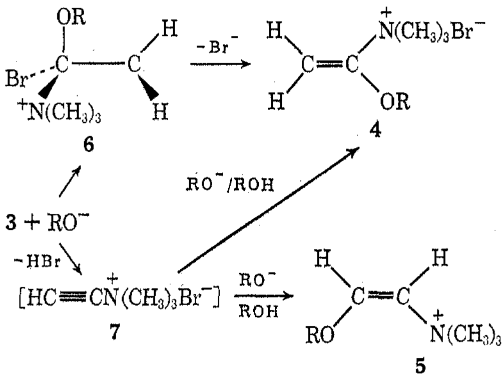


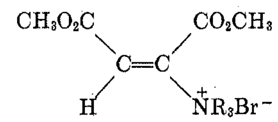
Figure 2.—^1H nmr spectrum of a mixture of **4b** and **5b** in DMSO-d_6 at 35°.

protons. A second AB pattern was observed downfield at δ 5.58 and 6.56 with J = 5.5 Hz. An additional set of peaks at δ 3.89 and 3.46 was also observed for the corresponding methoxyl and trimethylammonium protons. Similar results were obtained when KOH–C_2H_5OH was employed (Figure 2). Attempts to isolate **5a** and **5b** by fractional precipitation employing ethanol–ether or by recrystallization (acetonitrile) gave only **4** as the sole isolable salt. The cis stereochemistry of **5** was assigned on the basis of the vinyl proton coupling (5.5 Hz) and comparison of the observed *vs.* the calculated chemical shifts of the vinylic protons (Table II).

Both **4** and **5** are formed by a competitive substitution–elimination process inherent in many activated ethylenic systems employing alkoxide salts in hydroxylic solvents. Furthermore, isomer **4** can arise by one of two routes. The first involves an addition–elimination process whereby the alkoxide adds to the α carbon to give **6** followed by 60° rotation and rapid elimination of bromide ion, yielding **4**. The alternate and less likely route to **4** would involve dehydrobromination of **3** producing **7**,[21] followed by trans addition (anti-Michael) of alkoxide and a proton. The formation of **5** involves the elimination of hydrogen bromide to produce an intermediate alkynyltrimethylammonium salt (**7**), which then adds alcohol in a trans stereospecific manner.[23,24]



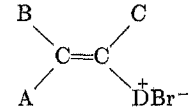
Disubstituted Salts.—When trimethyl- or triethylammonium bromide was treated with dimethyl acetylenedicarboxylate in a 2:1 (v/v) water-dioxane mixture, the corresponding dimethyl trialkylammonium maleates (**8a** and **8b**) were isolated in 60 and 56% yield, respectively. The nmr spectrum of the trimethylammonium derivative **8a** showed only one set of methyl absorptions in addition to the singlet absorption at δ 7.11 for the vinyl proton (Table III). The triethyl derivative **8b** showed an upfield shift for the vinylic proton (δ 7.00) similar to that observed in the methyl propiolate–triethylamine and tri-*n*-butylamine adducts.



8a, R = CH_3
b, R = C_2H_5

TABLE III

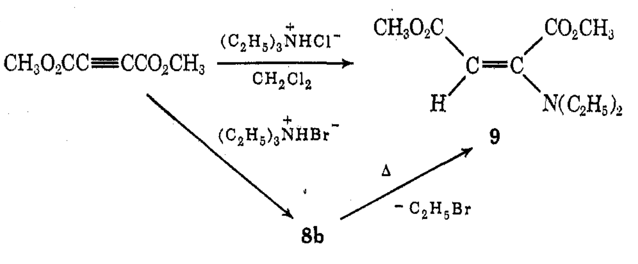
OBSERVED[a] *vs.* CALCULATED[b] NMR CHEMICAL SHIFTS FOR DISUBSTITUTED VINYLTRIALKYLAMMONIUM SALTS



No.	A	B	C	D	Obsd δ_{vinyl}	Calcd δ_{vinyl}
8a	H	CH_3O_2C	CH_3O_2C	$N(CH_3)_3$	7.11	7.00
8b	H	CH_3O_2C	CH_3O_2C	$N(C_2H_5)_3$	7.00	7.00
13	Br	H	Br	$N(CH_3)_3$	8.12	7.08
14	C_2H_5O	H	Br	$N(CH_3)_3$	7.25	7.23
18	HO_2C	Br	H	$N(CH_3)_3$	7.91	7.77

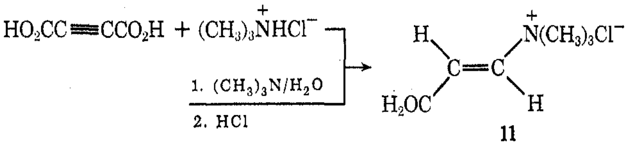
[a] The chemical shifts were measured in D_2O solvent containing internal 3-(trimethylsilyl)propanesulfonic acid sodium salt at 40°. [b] The values were calculated from the equation $\delta_{C-CH} = 5.25 + Z_{gem} + Z_{cis} + Z_{trans}$ using the values of Matter[18] and Toby[19] and $Z_{gem} = 1.00$, $Z_{cis} = 0.65$, and $Z_{trans} = 0.30$ for R_3N^+.

The cis stereochemistry of **8** was supported by comparison of the calculated *vs.* observed chemical shift of the olefinic proton (*i.e.*, δ 7.00 and 7.25 calculated for the cis and trans isomers, respectively) and the presumed similarity in mechanism for the formation of the salts obtained with trialkylammonium halides and methyl propiolate. The reaction of dimethyl acetylenedicarboxylate with triethylammonium chloride in methylene chloride has been reported[25] to yield dimethyl (diethylamino)maleate (**9**) as the sole product. It appears in this case that the chloride salt of **8b** is formed initially and eliminates ethyl chloride producing **9**. When a *solution* of **8b** was refluxed in methylene chloride for 4 hr, the only product isolated was **9** in 93% yield.

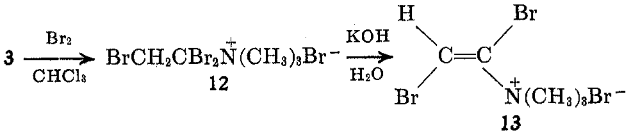


The nmr absorption for the ethylenic proton in **9** at δ 4.52 was in good agreement with that of δ 4.53 reported for dimethyl (dimethylamino)maleate (**10**).[26] The solubility of **8b** in methylene chloride may account for the facile elimination of ethyl chloride, since **10** was not formed when a suspension of insoluble **8a** was refluxed in methylene chloride for 24 hr.

When acetylenedicarboxylic acid reacted with trimethylammonium chloride under conditions similar to those described for the diester, decarboxylation occurred yielding only *trans*-carboxyvinyltrimethylammonium chloride (**11**). Salt **11** was also prepared[27] by the addition of aqueous trimethylamine to methyl propiolate followed by acidification with HCl.



Bromination and Dehydrobromination of Monosubstituted Salts.—Several additional disubstituted vinyltrimethylammonium salts (Table III) were prepared by bromination of the monosubstituted vinyl derivative in chloroform followed by dehydrobromination with base. Bromination of **3** in refluxing chloroform gave 62% yield of 1,1,2-tribromoethyltrimethylammonium bromide (**12**). Dehydrobromination of **12** with aqueous KOH produced (*E*)-1,2-dibromovinyltrimethylammonium bromide (**13**) as the only isolable product.



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[21] The difficult isolation of ethynyltriethylammonium bromide and chloride from dibromoethylene and triethylamine in ether has recently been reported.[22]

[22] R. Tanaka and S. I. Miller, *J. Org. Chem.*, **36**, 3856 (1971).

[23] S. I. Miller, *J. Amer. Chem. Soc.*, **78**, 6091 (1956).

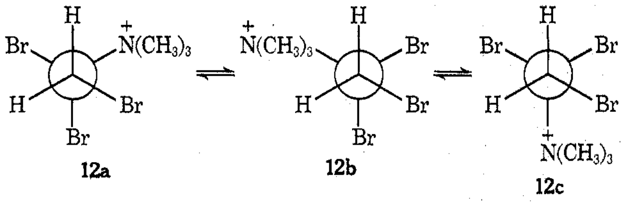
[24] W. E. Truce and J. A. Simms, *ibid.*, **78**, 2756 (1956).

[25] R. J. Alainio and D. G. Farnum, *Can. J. Chem.*, **43**, 700 (1965).

[26] R. Huisgen, K. Herbig, A. Siegl, and H. Huber, *Chem. Ber.*, **99**, 2526 (1966).

[27] Private communication from Professor J.-M. Lehn, Strasbourg. The procedure is similar to that described for ethoxyacetylene and aqueous trimethylamine.[2]

The chemical shift of the vinyl proton in **13** at δ 8.12 exhibited greater shielding than that predicted by the use of the nmr shielding parameters, possibly because of breakdown in the shielding mechanism when one of the substituents is forced out of coplanarity by steric crowding. Assuming trans addition of bromine to **3**, the resulting highly substituted ethane experiences large steric interactions in all three of its conformations. Trans elimination of HBr from **12a** or **12c** would yield (*E*)-**13**, whereas (*Z*)-**13** is expected from **12b**. The infrared spectrum of **13** showed a weak absorption at 1603 cm^{-1} indicative of an *E* configuration. Additional support for the *E* configuration of **13** came from its reaction with a stoichiometric amount of ethanolic KOH, which produced (*E*)-1-bromo-2-ethoxyvinyltrimethylammonium bromide (**14**). Analysis of the calculated chemical shifts for the six possible isomers (Table IV) formed by either an addition–elimination or elimination–addition mechanism indicated the *E* configuration for **14**. The nmr spectrum of **14** exhibited a vinylic proton absorption at δ 7.25 compared to the calculated value of δ 7.23. The *E* configuration of **14** is consistent with an addition–elimination mechanism[28] involving addition of ethoxide ion to the 2-carbon atom producing a ylide-type intermediate (**15**). Clockwise rotation (minimal eclipsing) of **15** followed by fast C–Br bond breaking would yield **14** with retention of configuration. The *Z* isomer of **13** would be expected to undergo a facile elimination of HBr, producing an intermediate bromoethynyltrimethylammonium salt which would add C_2H_5OH to yield products whose calculated olefinic chemical shift would be δ <6.0 ppm (Table IV).



12a **12b** **12c**

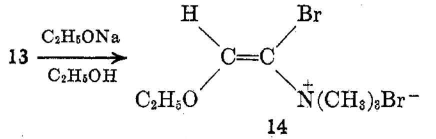


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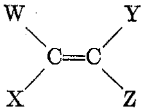
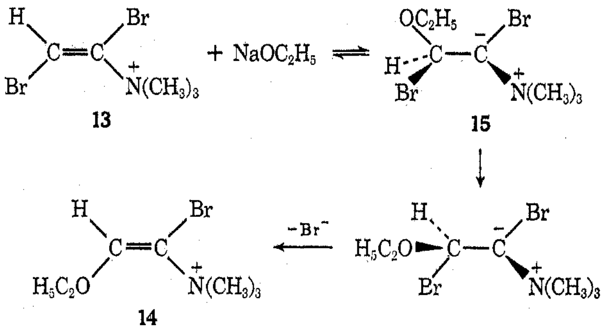
TABLE IV

CALCULATED CHEMICAL SHIFTS

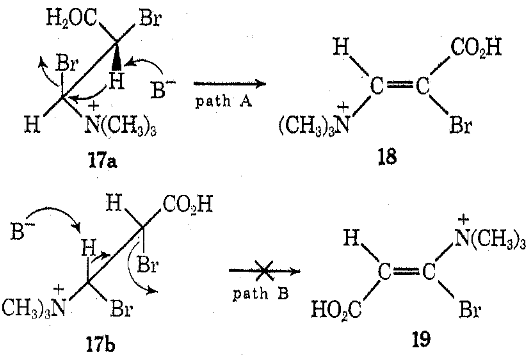


W	X	Y	Z	Calcd δ^a	Obsd δ^b
H	Br	C_2H_5O	$N(CH_3)_3$	5.56	
H	Br	$N(CH_3)_3$	C_2H_5O	5.76	
H	C_2H_5O	Br	$N(CH_3)_3$	7.23	7.25
H	C_2H_5O	$N(CH_3)_3$	Br	7.70	
Br	C_2H_5O	H	$N(CH_3)_3$	5.49	
Br	C_2H_5O	$N(CH_3)_3$	H	5.73	

[a] References 18 and 19 and, for R_3N, $Z_{gem} = 1.00$, $Z_{cis} = 0.65$, and $Z_{trans} = 0.30$. [b] In D_2O.



A second bromine-substituted vinyltrimethylammonium salt was prepared starting from *trans*-$HO_2CCH{=}CHN(CH_3)_3^+Br^-$ (**16**). 2-Carboxy-1,2-dibromoethyltrimethylammonium bromide (**17**) was prepared in 82% yield from **16** and bromine in refluxing chloroform. The use of methanol[9] in place of chloroform yielded surprisingly only the methyl ester of **16** (**1a**). Elimination of HBr with methanolic KOH produced the *E* isomer of 1-bromo-2-carboxyvinyltrimethylammonium bromide (**18**). Decarboxylative debromination to *trans*-bromovinyltrimethylammonium bromide was not observed. Assuming a trans coplanar elimination of HBr by methoxide ion, path A would be favored leading to olefin because of the relative proton acidities of **17a** and **17b**.[29] If there was any contribution by an Elcb mechanism, rotamer **17a** would also be favored to yield olefin because of the enhanced stabilization by the carboxylate ion *vs.* that of an ylide intermediate in **17b**. The observed chemical shift of the vinyl proton in **18** at δ 8.06 was also in good agreement with the calculated value of δ 8.21 compared to that of δ 7.42 for isomer **19**.



Experimental Section

All melting points are uncorrected. Proton nmr spectra were recorded on a Varian Associates A-60 nmr spectrophotometer using D_2O as the solvent, unless noted otherwise. Chemical shifts are expressed in δ (parts per million downfield) from an internal standard of 3-(trimethylsilyl)propanesulfonic acid sodium salt. The infrared spectra were recorded on a Perkin-Elmer 137 infracord and the elemental analyses were performed by the Analytical Laboratories of the Central Research Department, Du Pont Company.

Materials.—Solutions of the trialkylammonium salts were prepared *in situ* by neutralization of an aqueous solution of the corresponding tertiary amine with either 6 *N* HCl or 50% aqueous HBr at 0°.

Dimethyl acetylenedicarboxylate, triethylamine, tri-*n*-butylamine, pyridine hydrochloride, and trimethylamine hydrochloride were obtained from Eastman Organic Chemicals. Methyl propiolate and 25% aqueous trimethylamine were purchased from Aldrich Chemical Co.

Determination of the Shielding Increments for the Trialkyl-

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[28] G. Modina, *Accounts Chem. Res.*, **4**, 73 (1971).

[29] W. von E. Doering and K. C. Schireiber, *J. Amer. Chem. Soc.*, **77**, 514 (1955); W. von E. Doering and A. Kentaro, *ibid.*, **77**, 521 (1955); W. Schlenk and J. Holtz, *Chem. Ber.*, **50**, 274 (1917).

ammonium Group.—The shielding increments for the trialkylammonium group were obtained by first calculating the chemical shift of the vinyl protons in the parent structure using the shielding parameters of Matter[18] and Tobey[19] and subtracting these values from the observed chemical shift of the olefinic protons in the corresponding substituted vinyltrialkylammonium salt. Depending upon the configuration of the proton relative to the trialkylammonium group, a value for a cis, trans, or gem increment was obtained. Eighteen monosubstituted compounds were analyzed in this manner. The average value of these increments was $Z_{\text{gem}} = 1.00 \pm 0.22$, $Z_{\text{trans}} = 0.30 \pm 0.15$, and $Z_{\text{cis}} = 0.65 \pm 0.18$. These values compared favorably with the shielding increments obtained using only ethylene (δ 5.25) and vinyltrimethylammonium bromide.[30] The calculated values using the latter method were $Z_{\text{gem}} = 1.25$, $Z_{\text{trans}} = 0.29$, and $Z_{\text{cis}} = 0.51$.

***trans*-Alkoxycarbonylvinyltrialkylammonium Salts (1a–e). General Method of Preparation.**—A solution of 38 mmol of the trialkylammonium halide salt in 20 ml of water containing 2 drops of the corresponding tertiary amine was treated in one portion at 25° with 46 mmol of the acetylenic ester dissolved in 10 ml of dioxane. An exothermic reaction occurred (ΔT 15–20°). The solution was heated at 35° for 15 hr followed by removal of solvents under vacuum (<40°). The residue was treated with acetonitrile (15 ml) and the product was filtered. Recrystallization from methanol–ether gave pure crystalline salts. The salts prepared by this method are summarized in Table I.

***trans*-Methoxycarbonylvinylpyridinium Chloride (2).**—A mixture consisting of 4.3 g (38 mmol) of pyridine hydrochloride, 2 drops of pyridine, 3.3 g (37 mmol) of methyl propiolate, 20 ml of water, and 10 ml of dioxane was heated at 40–45° for 20 hr. The solvents were removed under vacuum to yield an orange semisolid. Acetonitrile (15 ml) was added and the product was filtered. Recrystallization from acetonitrile yielded 1.6 g (21%) of 2: mp 105–106°; nmr (220 MHz, D_2O) δ 3.77 (s, OCH_3, 3 H), 6.92 (d, β-vinyl H, 1 H), and 8.24 (d, α-vinyl H, 1 H) with J = 14.5 Hz. The aromatic pyridinium protons had δ 8.60 (t, para H, 1H), 8.98 (d, ortho H, 2 H), and 8.11 (overlapping dd, meta H, 2 H).

1-Bromovinyltrimethylammonium Bromide (3) with Methanolic Sodium Methoxide.—Three grams (0.012 mol) of 1-bromovinyltrimethylammonium bromide in 150 ml of methanol was treated with a solution of sodium methoxide (0.66 g in 25 ml of methanol, 0.012 mol) at 25°. After 20 hr, the solution was neutral and a small amount of NaBr was observed. The solvent was removed to yield 3.6 g of a white solid (product and NaBr). After drying *in vacuo* over P_2O_5, the nmr spectrum was recorded in DMSO-d_6. The spectrum was consistent for two isomeric products. There were two closely spaced singlets for the $(CH_3)_3N^+$– group at δ 3.42 and 3.46, and a set of singlet absorptions at δ 3.84 and 3.89 for a CH_3O group. There were two sets of AB patterns for the vinyl protons, the first at δ 4.61 and 4.99 with J = 6.4 Hz, and the second at δ 5.58 and 6.56 with J = 5.0 Hz. The solid was extracted with ethanol and the solvent was removed *in vacuo*. Recrystallization from methanol–ether yielded 2.1 g (87%), mp 170–190°. The spectrum (DMSO-d_6) was similar to that recorded before recrystallization. The elemental analysis indicated two isomeric products.

Anal. Calcd for $C_6H_{14}NOBr$: C, 36.78; H, 7.22; N, 7.15. Found: C, 36.45; H, 6.71; N, 7.07.

The solid was stripped with boiling acetonitrile and an equal volume of ether was added to the filtrate. The precipitate was filtered and dried under vacuum over P_2O_5. The nmr (DMSO-d_6) spectrum indicated a single product attributed to 4a with absorptions at δ 3.45 [s, $(CH_3)_3N^+$, 9 H], 3.85 (s, CH_3O, 3 H), and 4.60 and 4.98 (d, vinyl, 2 H) with J = 6.5 Hz.

1-Bromovinyltrimethylammonium Bromide (3) with Ethanolic Potassium Hydroxide.—A suspension of 15 g (0.061 mol) of 1-bromovinyltrimethylammonium bromide (3) in 350 ml of ethanol was treated dropwise with an ethanolic KOH solution (4.1 g of KOH in 50 ml, 0.061 mol) at 25°. The insoluble KBr was filtered, and an equal volume of ether was added to the filtrate. The product was filtered and purified by mixed solvent recrystallization employing methanol–ether to give 8.0 g (62%) of a mixture consisting of two isomeric products, 1-ethoxyvinyl- (4b) and *cis*-ethoxyvinyltrimethylammonium bromide (5b), ir (Nujol) 1672 cm^{-1} (C=C). The nmr spectrum of the original mixture before purification indicated the isomeric ratio to be *ca.* 3:1. Isomer 4b (major) had δ 1.37 (t, CH_3, 3 H), 4.11 (q, CH_2, 2 H), 3.52 [s, $(CH_3)_3N^+$, 9 H], and an AB pattern at δ 4.99 and 4.61 (d, vinyl, 2 H) with J = 6.5 Hz. Isomer 5b (minor) had δ 1.31 (t, CH_3, 3 H), 4.18 (q, CH_2, 2 H), 3.52 [s, $(CH_3)_3N^+$, 9 H], and an AB pattern at 5.61 and 6.54 (d, vinyl, 2 H) with J = 5.0 Hz.

Anal. Calcd for $C_7H_{16}NBrO$ (mixture): C, 40.02; H, 7.62; Br, 38.09. Found: C, 39.37; H, 7.31; Br, 37.69.

***cis*-1,2-Bis(methoxycarbony)vinyltrimethylammonium Bromide (8a).**—Dimethyl acetylenedicarboxylate (5.4 g, 38.0 mmol) in 10 ml of dioxane was added in one portion at 25° to a solution consisting of 5.3 g (38.0 mmol) of trimethylammonium bromide and 3 drops of triethylamine in 25 ml of water. The temperature rose to 35° and the reaction mixture was subsequently heated at 35° for 15 hr. The solvents were removed *in vacuo* (<40°). The brown, tacky solid was stirred with acetonitrile (35 ml) and the mixture was filtered. Ether was added to the filtrate to produce additional product. Mixed solvent recrystallization using acetonitrile–ether gave 5.9 g (56%) of 8b: mp 108°; ir (Nujol) 3448 (H_2O), 1730 (unsymmetrical doublet, C=O), and 1645 cm^{-1} (C=C); nmr δ 3.85, 3.99 (s, CH_3O_2C, 6 H), 1.35 (t, CH_3, 9 H), 3.73 (q, CH_2, 6 H), and 7.00 (s, vinyl, 1 H).

Anal. Calcd for $C_{12}H_{22}NO_4Br \cdot {}^1/_2H_2O$: C, 43.28; H, 6.96; N, 4.21. Found: C, 43.46; H, 7.39; N, 3.81.

Dimethyl (Diethylamino)maleate (9).—A solution of 1.5 g (4.5 mmol) of 8b in 50 ml of dry methylene chloride was refluxed for 4 hr. The solvent was removed to yield 0.9 g (93%) of a light-yellow oil. Comparison of its ir and nmr spectra with those of an authentic sample prepared from dimethyl acetylenedicarboxylate and diethylamine in methanol indicated identical properties: ir (neat) 1754, 1701 (C=O), and 1587 cm^{-1} (C=C); nmr (CCl_4) δ 6.18, 6.46 (s, CH_3O, 6 H), 3.17 (q, CH_2, 4 H), 1.17 (t, CH_3, 6 H), and 4.52 (s, vinyl, 1 H).

***trans*-Carboxyvinyltrimethylammonium Chloride (11) from Acetylenedicarboxylic Acid.**—A solution consisting of 4.3 g (38 mmol) of acetylenedicarboxylic acid, 3.7 g (37 mmol) of trimethylammonium chloride, 15 ml of dioxane, and 15 ml of water was heated at 45° for 20 hr. The solvents were removed under vacuum to yield an oil. Addition of acetonitrile to the oil yielded a tan solid (2.2 g, 36%). Mixed solvent recrystallization from methanol–ether gave *trans*-carboxyvinyltrimethylammonium chloride (11): mp 173–174° dec; ir (Nujol) 1706 (C=O) and 1667 cm^{-1} (C=C); nmr δ 3.42 [s, $(CH_3)_3N^+$, 9 H], 6.58 and 7.40 (d, vinyl, 2 H) with J = 14.5 Hz.

Anal. Calcd for $C_6H_{12}NO_2Cl$: C, 43.67; H, 7.24; N, 8.46. Found: C, 43.55; H, 7.34; N, 8.37.

1,1,2-Tribromoethyltrimethylammonium Bromide (12).—A mixture of 49 g (0.20 mol) of 3 and 60 g (0.40 mol) of bromine in 320 ml of chloroform was stirred vigorously at 50° for 18 hr. Chloroform and excess bromine were removed on a rotary evaporator to yield a red syrup. The viscous oil was stirred with 200 ml of acetonitrile and filtered (20.7 g). Ether (500 ml) was added to the filtrate to produce 27.8 g of additional product (62% crude product). The crude product was purified by mixed solvent recrystallization from trifluoroacetic acid–ether: mp 154–156°; nmr (CF_3CO_2H) δ 4.72 [s, $(CH_3)_3N^+$, 9 H], and 3.79 (s, CH_2, 2 H).

Anal. Calcd for $C_5H_{11}NBr_4$: C, 14.86; H, 2.74; N, 3.47. Found: C, 14.81; H, 2.65; N, 3.26.

(*E*)-1,2-Dibromovinyltrimethylammonium Bromide (13).—A 50-ml portion of a 1.24 *M* aqueous KOH solution was added dropwise at 25° to a suspension of 25 g (0.062 mol) of 12 in 600 ml of water. The homogeneous solution was evaporated to dryness with dry air over a 2-day period. The residual white crystals were recrystallized from ethanol to yield 13.7 g (70.6%) of 13: mp 138–139°; ir (Nujol) 1603 cm^{-1} (very weak) (trans CBr=CBr); nmr δ 8.12 (s, vinyl 1 H), 3.58 [s, $(CH_3)_3N^+$, 9 H].

Anal. Calcd for $C_5H_{10}NBr_3$: C, 18.53; H, 3.08; N, 4.32. Found: C, 18.50; H, 3.17; N, 4.41.

(*E*)-1-Bromo-2-ethoxyvinyltrimethylammonium Bromide (14).—A suspension of 3 g (9.2 mmol) of 13 in 25 ml of ethanol was treated with 15 ml of a 0.6 *M* ethanolic KOH solution. After 0.5 hr, the KBr was filtered. Ether (25 ml) was added to the filtrate to produce 0.35 g of unreacted 13. The second filtrate was treated with 100 ml of ether to precipitate a leaflike crystalline solid. The product was filtered and dried *in vacuo* over P_2O_5 to yield 1.3 g (50%) of 14: mp 115° dec; ir (Nujol) 1661 cm^{-1} (C=C); nmr (DMSO-d_6) δ 1.42 (t, CH_3, 3 H), 3.50 [s, $(CH_3)_3N^+$, 9 H], 4.96 (q, CH_2, 2 H), and 7.25 (s, vinyl, 1 H).

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(30) M. Ohtsuru and K. Tori, *Chem. Commun.*, 750 (1966).

Anal. Calcd for $C_7H_{15}NOBr_2$: C, 29.08; H, 5.18; N, 4.84. Found: C, 29.26; H, 5.33; N, 4.67.

trans-**Carboxyvinyltrimethylammonium Bromide (16).**—To a stirred mixture of 30 g (0.36 mol) of methyl propiolate in 80 ml of water was added with cooling 90 g of 25% aqueous trimethylamine solution at 25°. The dark mixture was stirred for an additional 3 hr, followed by removal of water and excess trimethylamine under vacuum (30–40° bath). The brown residue was dissolved in 200 ml of 48% aqueous HBr. The water and excess acid were removed on an evaporator. Recrystallization of the dark residue from methanol–ether yielded 44 g (59%) of **16**: mp 120° dec; ir (Nujol) 1724 (C═O) and 1661 cm^{-1} (C═C); uv max (CH_3OH) 208.5 nm (ϵ 2160); nmr (D_2O) δ 3.49 [s, $(CH_3)_3N$, 9 H], 6.61 and 7.49 (d, vinyl, 2 H) with J = 13.8 Hz.

Anal. Calcd for $C_6H_{12}O_2NBr$: C, 34.30; H, 5.72; N, 6.66. Found: C, 34.96; H, 6.09; N, 6.89.

Tetrafluoroborate Salt of 16a.—*trans*-Carboxyvinyltrimethylammonium tetrafluoroborate (**16a**) was prepared in an analogous fashion to that described for the bromide salt. Recrystallization from methanol–ether gave mp 135–136°; ir (Nujol) 1724 (C═O), 1661 (C═C), and 1053 cm^{-1} (BF_4^-); nmr δ 3.20 [s, $(CH_3)_3N^+$, 9 H], 6.41 and 7.22 (d, vinyl, 2 H) with J = 13.8 Hz.

Anal. Calcd for $C_6H_{12}NO_2BF_4$: C, 33.13; H, 5.76; N, 6.45; F, 35.25. Found: C, 33.63; H, 5.27; N, 6.55; F, 34.80.

Bromination of 16 in Methanol.—A solution consisting of 2.2 g (11.0 mmol) of **16** in 100 ml of methanol was treated dropwise with 8 g (50.0 mmol) of bromine in 40 ml of methanol at 35°. After the solution was stirred for 20 hr at 35–40°, the volatiles were removed under water aspirator vacuum. The residual red oil was redissolved in 100 ml of methanol, and an equal volume of ether was added. The precipitated yellow solid was again dissolved in methanol and treated with ether to yield 2.4 g (96%) of *trans*-methoxycarbonylvinyltrimethylammonium bromide (**1a**): mp 164–165°; ir (Nujol) 1658 (C═C) and 1715 cm^{-1} (C═O); nmr δ 3.37 [s, $(CH_3)_3N^+$, CH], 3.86 (s, OCH_3, 3 H), 6.63 and 7.47 (d, vinyl, 2 H) with J = 13.9 Hz.

Anal. Calcd for $C_7H_{14}NO_2Br$: C, 37.51; H, 6.25; N, 5.98; Br, 35.69. Found: C, 37.96; H, 6.40; N, 5.77; Br, 35.79.

2-Carboxy-1,2-dibromoethyltrimethylammonium Bromide (17).—A mixture of 44 g (0.21 mol) of **16** and 50 g (0.33 mol) of bromine in 250 ml of chloroform was stirred vigorously at 45° for 24 hr. The yellow solid was filtered, washed with 200 ml of acetonitrile, and purified by recrystallization from methanol to yield 62 g (82%) of **17**: mp 162–163°; nmr δ 3.58 [s, $(CH_3)_3N^+$, 9 H], 5.86 (d, β-CH, 1 H), and 6.57 (d, α-CH, 1 H) with J = 1.5 Hz.

Anal. Calcd for $C_6H_{12}NO_2Br_3$: C, 19.47; H, 3.26; N, 3.79; Br, 64.82. Found: C, 19.87; H, 3.37; N, 3.87; Br, 65.25.

Dehalogenation of 17 with Potassium Carbonate.—Five grams (0.014 mol) of **17** in 100 ml of water was treated with a potassium carbonate solution (0.94 g in 25 ml of water, 0.0068 mol) at 45–50°. Carbon dioxide was evolved during the addition. The solution was then heated at 60° for 2 hr. The water was removed under vacuum and the residual solid was extracted with ethanol. An equal volume of ether was added to the cooled extract to yield 2.2 g (55%) of (*Z*)-2-bromo-2-carboxyvinyltrimethylammonium bromide (**18**): mp 187° dec; ir (Nujol) 3401 (–OH), 1724 (C═O), and 1631 cm^{-1} (C═C); uv max (CH_3OH) 216 nm; nmr δ 8.06 (s, vinyl, 1 H), and 3.68 [s, $^+N(CH_3)_3$, 9 H].

Anal. Calcd for $C_6H_{11}O_2NBr_2$: C, 24.93; H, 3.81; N, 4.84. Found: C, 24.06; H, 3.58; N, 4.44.

Registry No.—**1a**, 40463-91-0; **1b**, 40463-92-1; **1c**, 40463-93-2; **1d**, 40463-94-3; **1e**, 40463-95-4; **2**, 40463-96-5; **3**, 14800-49-8; **4a**, 40463-98-7; **4b**, 14800-51-2; **5a**, 40464-00-4; **5b**, 40464-01-5; **8a**, 40550-39-8; **8b**, 40464-02-6; **9**, 996-85-0; **11**, 40464-04-8; **12**, 40464-05-9; **13**, 40464-06-0; **14**, 40464-07-1; **16**, 40464-08-2; **16a**, 40464-09-3; **17**, 40464-10-6; **18**, 40464-11-7; methyl propiolate, 922-67-8; 2-chloroethyl propiolate, 40464-12-8; trimethylammonium chloride, 593-81-7; trimethylammonium bromide, 2840-24-6; triethylammonium bromide, 636-70-4; tributylammonium bromide, 37026-85-0; pyridine hydrochloride, 628-13-7; dimethyl acetylenedicarboxylate, 762-42-5; acetylenedicarboxylic acid, 142-45-0; bromine, 7726-95-6; 1-bromovinyltrimethylammonium tetrafluoroborate, 40464-14-0; hydrogen tetrafluoroborate, 16872-11-0.

The Stereochemistry of 1-Alkyl-2-acyl-1,2-dihydroisoquinaldonitriles[1]

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The pmr spectra and in particular the anisochronism (chemical shift differences) of diastereotopic groups (methyl or methylene) in a series of 1-alkyl-2-acyl-1,2-dihydroisoquinaldonitriles (**3** and **4**) have been studied as a function of substituent, temperature, and solvent. On this basis, stereochemical analysis of these systems was accomplished. The amide group configuration is the same in all cases and has been established. The ring configuration is believed to be the one in which the 1-alkyl group is pseudoaxial. In the cases where the 1-alkyl group is isopropyl, only a single conformer about the ring–alkyl bond is observed and on the basis of chemical shift arguments has been assigned. In the cases where the 1-alkyl substituent is either isobutyl or benzyl, more than one such conformer may be present as indicated by spectral temperature dependence; the predominant conformer is tentatively assigned.

Though the preparation of 1-alkyl derivatives of 2-acyl-1,2-dihydroisoquinaldonitriles (Reissert compounds) (**1**) has been well documented,[3-9] only a few examples of these compounds (**3**) have been isolated and characterized.[5-7]

Several interesting stereochemical questions, therefore, remain unanswered for these systems. Among them are those concerning the ring conformation of the 1 substituent, the configuration of the amide moiety, and the conformation about the ring–alkyl bond. Additionally, in recent years there has been much interest in the anisochronism (chemical shift difference) of diastereotopic groups.[10]

In the interest of addressing these questions in the context of the relatively large anisochronisms[1] of the diastereotopic groups, a detailed study of these compounds was undertaken.

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(1) A portion of this work was previously communicated: *Tetrahedron Lett.*, 5549 (1968), and Abstracts, 159th National Meeting of the American Chemical Society, Houston, Tex., Feb 1970, p O-008.

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