amorphous, glassy mass, m.p. about 40°. The product showed a strong NCO absorption at 4.68 μ.

Anal. Calcd. for $C_{20}H_{15}AsN_2O_2$: As, 19.22; N, 7.19. Found: As, 19.06; N, 7.20.

1,3,5-Tri-*n*-butyltin-*s*-triazine-2,4,6-trione (VIII).—In a flask deeply immersed in an oil bath and equipped with a Dean–Stark receiver, a stirred mixture of 180 g. (0.3 mole) of bis(tri-*n*-butyltin) oxide and 25.8 g. (0.2 mole) of powdered cyanuric acid was heated to 100°, at which point water was evolved. The temperature was slowly raised to 160°, and finally reduced pressure was applied in order to remove quantitatively the water of reaction from the liquid reaction product. After 1 hr., 5.4 ml. (0.3 mole) of water was collected in the cooled receiver. A small amount of unreacted cyanuric acid (0.6 g.) was removed by filtration. Traces of unreacted bis(tri-*n*-butyltin) oxide were removed by heating the reaction product to 200° at 0.2 mm. Colorless liquid compound VIII was obtained in almost quantitative yield (200 g.), $n^{22}D$ 1.5099, infrared absorptions at 5.98 and 6.2 μ. Attempts to crystallize or to distil VIII failed. No solidification occurred at −30°, and no distillation took place at 240° (0.03 mm.). From these experiments (bath temperature 280°) VIII was recovered unchanged.

Anal. Calcd. for $C_{39}H_{81}N_3O_3Sn_3$: C, 47.02; H, 8.14; N, 4.22; Sn, 35.78. Found: C, 46.94; H, 7.95; N, 4.28; Sn, 35.33.

1,3,5-Triphenyltin-*s*-triazine-2,4,6-trione (IX).—Triphenyltin hydroxide (11 g., 0.03 mole, m.p. 93°) was thoroughly mixed with cyanuric acid (1.3 g., 0.01 mole). Upon heating to 150° complete fusion occurred, which was followed by solidification after 15 min. Approximately 0.5 ml. (about 0.03 mole) of water was collected in a trap. Colorless reaction product IX did not melt or decompose at 340°.

Anal. Calcd. for $C_{57}H_{45}N_3O_3Sn_3$: N, 3.58; Sn, 30.4. Found: N, 3.61; Sn, 30.1.

$[(C_4H_9)_4Sn_2(NCO)_2O]_n$ (X).—The finely powdered mixture of 248.7 g. (1 mole) of dibutyltin oxide and 60.1 g. (1 mole) of urea was slowly heated to 175° with agitation. Ammonia (1 mole) and water (0.5 mole) were evolved, and the mixture melted to a clear, viscous oil. It was kept at 195° for 2 hr. The colorless product solidified on cooling to a wax-like material. It had a melting range from 195–215°, good solubility in warm alcohols and acetone, and strong NCO absorption at 4.6 μ.

Anal. Calcd. for $C_{18}H_{36}N_2O_3Sn_2$: N, 4.96; Sn, 41.94. Found: N, 5.12; Sn, 41.8.

Studies on Geometric Isomerism by Nuclear Magnetic Resonance. I. Stereochemistry of α-Cyano-β-alkoxy-β-alkylacrylic Esters[1]

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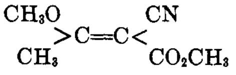
The n.m.r. technique has been applied to the determination of the geometric configurations of a series of α-cyano-β-alkoxy-β-alkylacrylic esters and the spectra have been discussed on the basis of the assumption that the resonance peak of the β-methyl protons is more deshielded in the *cis* configuration than in the *trans*. It is found that these esters are more stable in the *cis* configuration, except for methyl α-cyano-β-methoxy-β-*t*-butylacrylate.

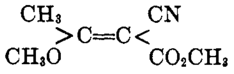
In connection with other work, a series of α-cyano-β-alkoxy-β-alkylacrylic esters have been prepared by alkylation of acylcyanoacetic esters. These esters, which possess an ethylenic bond substituted by four different groups, occur in two isomeric forms.[2] Some of them have been isolated pure, but their geometric configurations are still open to question.[3] In the case of these esters there are no infrared bands which can be reliably correlated with configurations, and ultraviolet spectra as well as dipole moment cannot be used to make a definite assignment of configuration.

Jackman[4,5] and other several authors[6-8] demonstrated that, provided both isomers of a pair are available, n.m.r. spectroscopy can be used to establish the geometric configurations of some α,β-unsaturated esters. This method is based on the fact that the protons of a *cis*-β-methyl group are more deshielded than those of a *trans*-β-methyl group. However, in the type of compound shown below, it is difficult to decide which of the protons of the two β-methyl groups is more deshielded, since these protons might experience a long-range shielding effect of the cyano group, in addition to the effect of the methoxycarbonyl group. The present paper, therefore, discusses the geometric configurations of α-cyano-β-alkoxy-β-alkylacrylic esters on the basis of some assumption.



$$\begin{matrix}CH_3O & & CN\\ & >C{=}C< & \\ CH_3 & & CO_2CH_3\end{matrix}$$

cis ester



$$\begin{matrix}CH_3 & & CN\\ & >C{=}C< & \\ CH_3O & & CO_2CH_3\end{matrix}$$

trans ester

Results and Discussion

The esters studied in this work are listed in Table I, together with the chemical shifts (p.p.m. downfield from internal tetramethylsilane). With samples obtained only in a stereoisomeric mixture, the percentage of the isomeric composition, determined from the relative peak areas, has also been given in Table I. Representative n.m.r. spectra of the esters are shown in Figures 1 and 2.

The resonance signals at 3.78 p.p.m. in Figure 1A and at 3.75 p.p.m. in Figure 1B were assigned to the methoxycarbonyl protons, since the spectrum of the corresponding ethyl ester (IIa) lacks a signal in this region; the signals at 4.01 p.p.m. in Figure 1A and at 4.04 p.p.m. in Figure 1B were assigned to the methoxy group by comparison with the spectrum of the corresponding ethoxy ester (IIIa). The remaining signals at 2.62 p.p.m. in

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(1) Presented at the 3rd Symposium on N.m.r., Osaka, Japan, Nov 1963.

(2) The isomeric forms of a series of the esters are denoted as (i) *cis* (in which the alkyl and alkoxycarbonyl groups are on the same side of the C=C double bond) and (ii) *trans* (in which these groups are on opposite sides). These notations are opposite to those used by Eistert and Merkel [*Chem. Ber.*, **86**, 895 (1953)].

(3) F. Arndt, H. Scholz, and E. Frobel, *Ann.*, **521**, 95 (1935).

(4) L. M. Jackman and R. H. Wiley, *Proc. Chem. Soc.*, 196 (1958).

(5) (a) L. M. Jackman and R. H. Wiley, *J. Chem. Soc.*, 2881 (1960); (b) *ibid.*, 2886 (1960).

(6) J. W. K. Burrcel, L. M. Jackman, and B. C. L. Weedon, *Proc. Chem. Soc.*, 233 (1959).

(7) (a) R. Morris, C. A. Vernon, and R. F. M. White, *ibid.*, 304 (1958); (b) D. E. Jones, R. O. Morris, C. A. Vernon, and R. F. M. White, *J. Chem. Soc.*, 2349 (1960).

(8) S. Fujiwara, H. Shimizu, Y. Arata, and S. Akabori, *Bull. Chem. Soc. Japan*, **33**, 428 (1960).

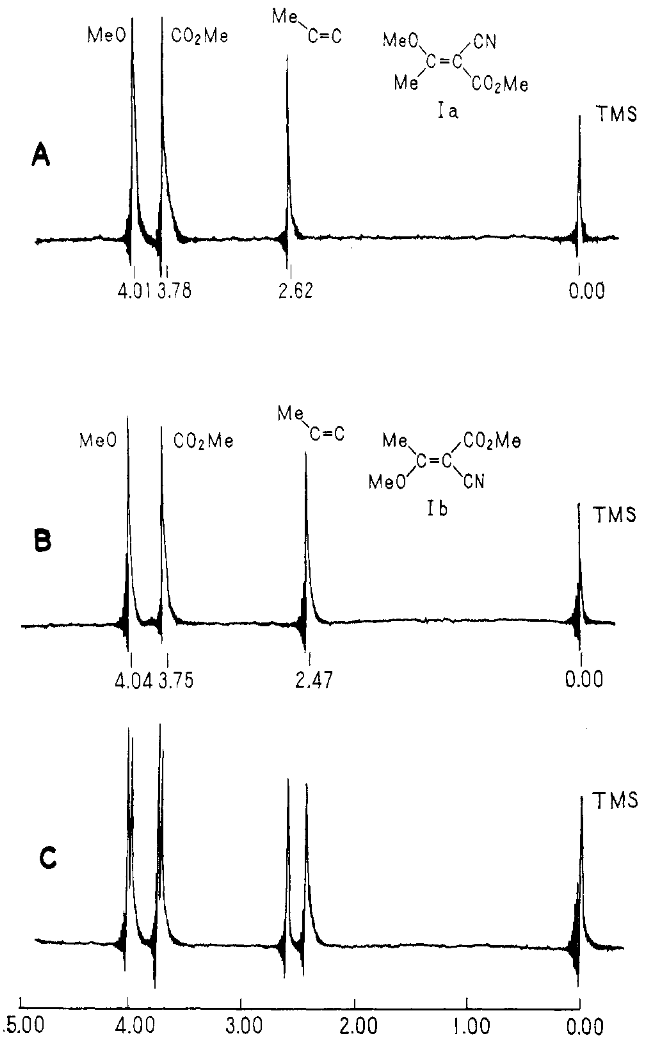

Figure 1.—A, n.m.r. spectra of Ia (40 Mc.); B, of Ib (40 Mc.); C, of a mixture of Ia and Ib in the approximate ratio of 1:1.

Figure 1A and at 2.45 p.p.m. in Figure 1B are evidently due to the β-methyl protons.

In all the spectra studied, the resonance position for the methoxycarbonyl group appears constantly in the range 3.74–3.80 p.p.m., and that for the methyl protons and for the methylene protons in the ethoxycarbonyl group, respectively, in the ranges 1.31–1.35 and 4.22–4.30 p.p.m. Replacement of the methoxycarbonyl group by the ethoxycarbonyl group has practically no effect on the chemical shift of the β-methyl group in the corresponding ester. The differential shifts of the β-methoxy protons between the *cis* and *trans* isomers are much smaller than those of the β-methyl protons. This fact may be explained by assuming that the conformation is preferred in which the methoxy protons are located apart far from the alkoxycarbonyl and cyano groups.

The differential shifts in the β-methyl protons between *cis* and *trans* isomers (0.17 p.p.m.) are large enough to use for the assignment of configuration. However, it was necessary to decide which of the resonance lines is due to *trans* isomer and which is due to *cis* one. Thus, assignment of each of two signals of individual protons to the correct stereoisomer had to be based on some assumption.

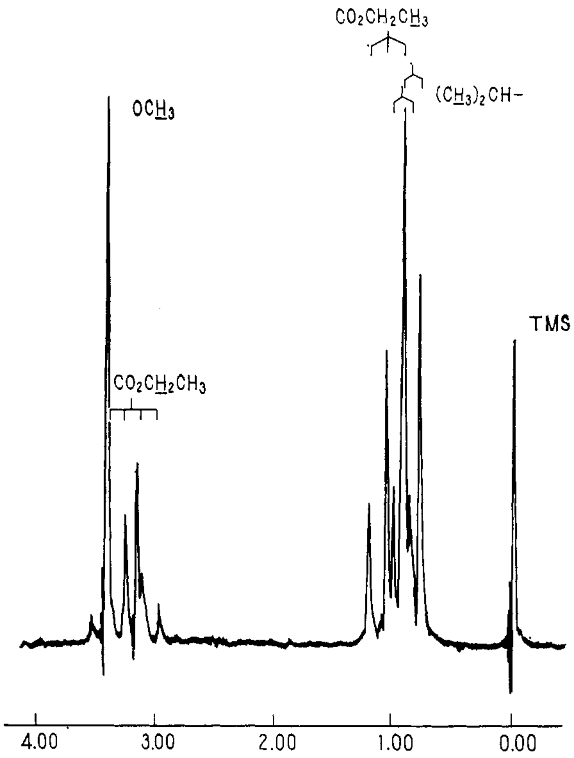

Figure 2.—N.m.r. spectrum of ethyl α-cyano-β-methoxy-β-isopropylacrylate in deuteriochloroform solution.

Jackman and Wiley demonstrated that, in α,β-unsaturated esters, the deshielding of the protons of a *cis*-β-methyl group is fairly constant, being of the order of 0.25 p.p.m.[5a]; we observed that in β-methylcrotonitrile the deshielding of the *cis*-β-methyl protons is 0.10 p.p.m. Consequently, it is expected that substitution of a cyano group in the α-position of the α,β-unsaturated ester would result in a decrease of the differential shielding of the β-methyl protons, and that the deshielding of the *cis*-β-methyl protons would be of the order of 0.15 p.p.m. (Here the effects of distant groups on the local diamagnetic shielding is assumed to be equal for both isomers.[9]) In fact, the separation of the resonance lines between Ia and Ib (0.17 p.p.m.) is in good agreement with the expected value. On the basis of this arguments, Ia is tentatively assigned the *cis* configuration and Ib, the *trans* one.

The higher melting isomer Ia,[10] m.p. 96–98°, is regarded as the stable form, because the lower melting one, Ib,[10] m.p. 75.5–76.5°, was readily isomerized into Ia by heating to 130° or by prolonged standing at room temperature, whereas Ia remained unchanged after heating to 130°. Their ultraviolet absorption spectra showed the maximum peak at the same wave length (284 mμ), although the intensity of Ia (log ϵ 4.17) was slightly stronger than that of Ib (log ϵ 4.07). The values obtained for the dipole moment, μ, of Ia and Ib in benzene are, respectively, 4.57 and 4.73 D. These difference in physical values are too small for diagnostic purposes. Significant difference in the C=O stretching frequency between Ia and Ib was observed in benzene solution (Table II), but not in KBr pellet (1721 cm.$^{-1}$ for both the isomers). Jones, *et al.*,[7b] and leNoble[11] observed that, in the β-halocrotonic esters, the C=O stretching bands of the *cis* esters always appear

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[9] P. T. Narasimhan and M. T. Rogers, *J. Phys. Chem.*, **63**, 1388 (1959).

[10] In the present paper, the stable isomer of a pair is denoted as a and the labile isomer, as b.

[11] W. J. leNoble, *J. Am. Chem. Soc.*, **83**, 3897 (1961).

TABLE I

CHEMICAL SHIFTS[a] IN α-CYANO-β-ALKOXY-β-ALKYLACRYLIC ESTERS

$R_1(R_2O)C{=}C(CN)CO_2R_3$

Compd.	R_1	R_2	R_3	β-Me	Δ	γ-Me	Δ	β-OMe	CO_2Me	CO_2Et Me	CO_2Et CH_2	Ratio, %[b]
Ia	Me	Me	Me	2.62	0.17			4.01	3.78			
Ib	Me	Me	Me	2.45				4.04	3.75			
IIb	Me	Me	Et	2.64				4.03		1.34	4.22	
IIIa	Me	Et	Me	2.62					3.74			
IVa	Me	MeCO	Et	2.57	0.17			2.32[c]		1.35	4.30	53
IVb	Me	MeCO	Et	2.40				2.29[c]		1.31	4.24	47
Va	Et	Me	Me	3.04[d]	0.29	1.21	0.11	4.06	3.77			
Vb	Et	Me	Me	2.75[d]		1.32		4.06	3.74			
VIa	*i*-Pr	Me	Me			1.09	0.10	4.33	3.78			85
VIb	*i*-Pr	Me	Me			1.19		4.33	3.78			15
VIIa	*i*-Pr	Me	Et			1.09	0.10	4.33				85
VIIb	*i*-Pr	Me	Et			1.19		4.33				15
VIIIa	*t*-Bu	Me	Me			1.37	0.13	3.97	3.80			92
VIIIb	*t*-Bu	Me	Me			1.24		3.97	3.80			8

[a] Parts per million from tetramethylsilane. [b] All *cis–trans* ratios were determined by integration. [c] The value of the acetoxy methyl protons. [d] The value of the methylene protons.

TABLE II

INFRARED SPECTRA OF α-CYANO-β-METHOXY-β-METHYLACRYLATE[a]

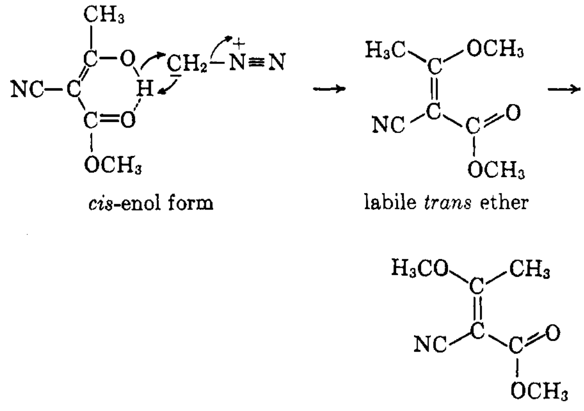
ν, cm.$^{-1}$ Ia	ν, cm.$^{-1}$ Ib	Assignment
2947 w	2943 w	CH stretching
2226 w	2226 w	CN stretching
1722 vs	1736 vs	C=O stretching
	1704 m	
1584 vs	1583 vs	
	1463 w	CH deformation
1438 w	1435 m	
1377 m	1378 m	
	1353 w	
	1334 m	
1312 s		
1290 vs	1237 vs	
	1201 w	
	1158 w	
1131 vs		
1098 m	1068 s	
1023 w		
970 w	958 s	
	881 w	
793 w	793 w	
792 w	795 m	

[a] In benzene solution; w = weak, m = medium, s = strong, vs = very strong.

at lower frequency than those of the *trans* esters, and explained it as being due to a consequence of weak hydrogen bond between the C=O and methyl groups. Thus, infrared spectral data seems to support this assignment, but is not conclusive.

It is confirmed by n.m.r. spectroscopy that α-acetylcyanoacetic ester exists practically all in the *cis*-enol form.[12-15] Therefore, methylation of this ester with diazomethane in dry ether, presumably according to the reaction mechanism proposed by Eistert, *et al.*,[16] might be expected to lead to the formation of the labile *trans* ether, which could thermally isomerize into the stable *cis* ether, as shown in eq. 1. Actually, we obtained an equimolecular mixture of both the isomers.

Ethyl α-cyano-β-acetoxy-β-methylacrylate (IV) was prepared by reaction of ethyl acetylcyanoacetate with ketene.[17] Its stereoisomeric composition consisted of



cis-enol form

labile *trans* ether

stable *cis* ether

(1)

cis and *trans* forms in the ratio of 34:66. However, prolonged standing of its chloroform solution at room temperature resulted in a gradual increase of the *cis* isomer; 5 weeks later, the *cis–trans* composition ratio reached the value of 54:47. Base-catalyzed isomerization led to an equilibrium ratio of 64:36 of *cis–trans*. It is noted that the chemical shift difference in the β-methyl protons between IVa and IVb has the same magnitude as that observed in the case of Ia and Ib.

Methyl α-cyano-β-methoxy-β-ethylacrylate (V) was isolated in two isomeric forms, Va, m.p. 78–79°, and Vb, m.p. 65–66°. The resonance signal of the β-methylene protons occurred at lower magnetic field in Va (3.04 p.p.m.) than in Vb (2.75 p.p.m.). On the basis of the assumption described, Va is assigned the *cis* configuration and Vb, the *trans* one. It is noticed that the peak separation of the β-methylene protons (0.29 p.p.m.) is larger than that of the β-methyl protons (0.17 p.p.m.). This suggests that the conformation Va is

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(12) In this case, by a *cis*-enol form is meant the form in which hydroxyl group and carbonyl group are on the same side of the C=C double bond, according to the notation of Arndt and Eistert.

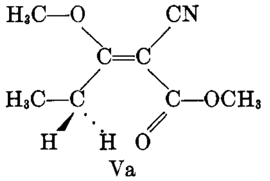
(13) It is expected that, if the *trans*-enol form existed, a signal of the acetyl methyl protons of the form would appear at higher magnetic field by *ca.* 0.17 p.p.m. than that of the *cis*-enol form, but it was not detected.

(14) I. Hori, *Sci. Papers Inst. Phys. Chem. Res.* (Tokyo), **38**, 562 (1962).

(15) J. L. Burdett and M. T. Rogers, *J. Am. Chem. Soc.*, **86**, 2105 (1964).

(16) B. Eistert, F. Arndt, L. Loewe, and E. Ayca, *Chem. Ber.*, **84**, 156 (1951).

(17) This sample was kindly supplied by Professor Osamu Yoda of Ibaraki University.



Va

heavily populated as pointed out by Jackman and Wiley in the case of methyl β-methylglutaconate.[5b]

It is particularly significant that, contrary to the case of the β-methyl protons, the resonance lines of the γ-methyl protons appears at higher magnetic field in the *cis* form than in the *trans* one. Such reversal of the sign of the shielding effect is always true of the γ-methyl protons, as will be reported in the following paper, although the reason is not thoroughly understood. This finding was also used for the configurational assignments of some esters.

Reactions performed at room temperature led to the formation of the stable *cis* isomer, whereas reactions at lower temperatures gave predominantly the labile *trans* isomer. This result can be also interpreted by the similar reaction mechanism shown in eq. 1.

Methyl and ethyl α-cyano-β-methoxy-β-iso-propylacrylates (VI and VII) were both obtained as a stereoisomeric mixture. Since the resonance signals of the β-methine proton were too complex, the signals of the γ-methyl protons were used for the assignments. On the basis of the finding described, the doublet at 1.09 p.p.m. is assigned to the γ-methyl group of the *cis* isomer and the one at 1.19 p.p.m., to that of the *trans* isomer. Both the mixtures consisted of *cis* and *trans* isomers in the ratio of 85:15. Only the *cis* form of methyl ester VIa was isolated pure.

Methyl α-cyano-β-methoxy-β-*t*-butylacrylate (VIII) was obtained as an equilibrium mixture of *cis–trans* isomers. By similar arguments, the resonance peak of the much stronger intensity at 1.37 p.p.m. is assigned to the γ-methyl group of the *trans* isomer and the peak of weaker intensity at 1.37 p.p.m., to that of the *trans* one. The intensity ratio of this mixture was approximately 8:92, and in agreement with the ratio determined by gas chromatography (5:95).[18] This ester, therefore, is exceptionally stable in the *trans* form. Examination of molecular models suggested that the *trans* form is much favored over the *cis* one, because of the large steric requirement of the *t*-butyl group. Accordingly, this assignment seems to be reasonable.

The methods used above are successful, provided both isomers of a pair are available. Ethyl α-cyano-β-methoxy-β-methylacrylate (IIa) and methyl α-cyano-β-ethoxy-β-methylacrylate (IIIa) have, however, been obtained only in one form. Their configurations cannot, therefore, be determined by the method described, but they are probably both in *cis* form, because the chemical shifts of their β-methyl protons appear at the same position as that of the β-methyl protons of Ia.

Consequently, the esters studied, except for methyl α-cyano-β-methoxy-β-*t*-butylacrylate, are stable in the *cis* configurations. It seems to be of interest that compounds, XCMe=CHCOOEt (X = Cl, SEt, SPH, and OEt), of known configurations are also stable in the *cis* configurations.[16,19]

Experimental

Special Measurements.—The n.m.r. spectra were obtained using J.N.M. H-40 high resolution n.m.r. spectrometer operating at a frequency of 40 Mc. The magnet was equipped with a superstabilizer system and associated slow sweep unit to improve stability and resolution. The scale of the spectra was established directly on the recorder trace by the side-band technique. All measurements were made in deuterated chloroform solution containing 10% by weight of solute, using tetramethylsilane as internal standard. All solutions were stored in an icebox until immediately before use, when they were allowed to stand to reach room temperature (22°) just before the spectra were recorded.

Data recorded in Table I were obtained by averaging measurements taken on at least four separate forward and reverse sweeps; the reproducibility in the calibrations of the shifts is within ±0.02 p.p.m. A differential shift between isomers is reproducible to within ±0.005 p.p.m.

The infrared spectra were recorded with a Nippon Bunko DS-201, fitted with a sodium chloride prism, in benzene solution and in KBr pellets.

The ultraviolet absorption spectra were measured with a Cary Model 14 recording spectrophotometer with 1.00-cm. quartz cell. Absolute ethanol was used as solvent.

Material.—α-Cyano-β-alkoxy-β-alkylacrylic esters were synthesized by a modification of the method described by Arndt, Scholz, and Frobel[3] from acylcyanoacetic esters, which were prepared according to the method of Hori and Midorikawa.[20]

Methyl α-Cyano-β-methoxy-β-methylacrylate (Ia, Ib).—These esters were prepared from methyl acetylcyanoacetate according to the method of Arndt, Scholz, and Frobel[3]: Ia, m.p. 97–98°, $\lambda_{\max}^{\text{EtOH}}$ 284 mμ (log ε 4.17); Ib, m.p. 75–76°, $\lambda_{\max}^{\text{EtOH}}$ 284 mμ (log ε 4.07). The yield ratio of Ia to Ib was approximately 1:1. The lower melting isomer, Ib, was readily isomerized into the higher melting one, Ia, by heating to 130°, whereas Ia remained unchanged after heating to 130°.

Ethyl α-Cyano-β-methoxy-β-methylacrylate (IIa).—The ester was similarly prepared in 85.5% yield from ethyl acetylcyanoacetate, m.p. 133–134° (from benzene). An attempt to isolate the labile form of the pair was unsuccessful.

Methyl α-Cyano-β-ethoxy-β-methylacrylate (IIIa).—The potassium salt of methyl acetylcyanoacetate (10 g.) was suspended in 35 ml. of xylene. To the stirred suspension were added 1 g. of potassium carbonate and 9 g. of diethyl sulfate, and the mixture was refluxed in an oil bath for 3 hr. After cooling to room temperature, the mixture was washed twice with water and then evaporated under reduced pressure to remove the xylene. The residue was recrystallized twice from aqueous methanol (1:1); yield, 2.4 g. (25.2%); m.p. 76.5–77.5° (lit.[22] m.p. 76–77°).

Methyl α-Cyano-β-methoxy-β-ethylacrylate (Vb).—An ethereal solution of diazomethane (prepared from 13 g. of *p*-tolylsulfonylmethylnitrosamide) was slowly added at −10° to a solution of 5.1 g. of methyl propionylcyanoacetate [b.p. 134–135° (43 mm.), 116–118° (20 mm.), m.p. 40–41°; lit.[23] b.p. 130° (43 mm.), m.p. 39–40°] in 10 ml. of dry ether. After standing at this temperature for 30 min., the precipitate which formed was collected by filtration, washed with a small amount of cold ether, and then recrystallized from carbon tetrachloride; yield, 2.7 g. (48.6%); m.p. 65–66°.

Anal. Calcd. for $C_8H_{11}NO_3$: C, 56.79; H, 6.55; N, 8.28. Found: C, 57.06; H, 6.66; N, 8.28.

The product Vb was isomerized in ethereal solution into the higher melting isomer (Va, m.p. 78–79°) by prolonged standing.

Methyl α-Cyano-β-methoxy-β-ethylacrylate (Va).—To a solution of 5.1 g. of methyl propionylcyanoacetate in 10 ml. of xylene was slowly added at room temperature an ethereal solution of diazomethane (prepared from 13 g. of *p*-tolylsulfonylmethylnitrosamide). After standing overnight at room temperature, the resulting clear solution was cooled to −50°. The precipitate which formed was collected by filtration, washed with a small amount of cold ether, and recrystallized from carbon tetrachloride; yield, 6.0 g.; m.p. 78–79°.

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[18] Two microliters of the sample was analyzed with a Shimazu gas chromatograph, Model GC-2B, on a silicon 550 column at 194°.

[19] F. Arndt, L. Loewe, and M. Ozansoy, *Chem. Ber.*, **73**, 779 (1962).

[20] I. Hori and H. Midorikawa, *Sci. Papers Inst. Phys. Chem. Res.* (Tokyo) **56**, 216 (1962).

[21] A. Aaller, *Compt. rend.*, **130**, 1224 (1900).

[22] Y. Urushibara, *Bull. Chem. Soc. Japan*, **3**, 263 (1928).

[23] J. Guinchant, *Compt. rend.*, **121**, 72 (1895).

Anal. Calcd. for $C_8H_{11}NO_3$: C, 56.79; H, 6.55; N, 8.28. Found: C, 56.81; H, 6.36; N, 8.35.

Mixture of *cis*- and *trans*-Methyl α-Cyano-β-methoxy-β-Isopropylacrylate (VIa, VIb).—To a solution of 5.9 g. of methyl isobutyrylcyanoacetate [b.p. 137–139° (48 mm.), 119–120° (18 mm.), m.p. 36–37°; lit.[23] b.p. 139° (48 mm.), m.p. 36–37°] in 10 ml. of dry ether was added to −10° an ethereal solution of diazomethane (prepared from 15 g. of *p*-tolylsulfonylmethylnitrosamide) and the mixture was allowed to stand in an icebox overnight. Then, the mixture was subjected to fractional distillation under reduced pressure. The fraction boiling at 136–138° (20 mm.) was collected; it gave a wet mass on cooling; yield, 5.1 g. (80%).

Repeated crystallization of the product from methanol afforded a product as colorless plates melting at 71–72°, which has been the stable isomer VIa of the pair. The labile isomer was not isolated.

Anal. Calcd. for $C_9H_{13}NO_3$: C, 59.00; H, 7.15; N, 7.65. Found: C, 59.06; H, 7.13; N, 7.52.

Mixture of *cis*- and *trans*-Ethyl α-Cyano-β-methoxy-β-isopropylacrylate (VIIa, VIIb).—This mixture was prepared in 63% yield by reaction of diazomethane with ethyl isobutyrylcyanoacetate [b.p. 123–125° (20 mm.), lit.[24] b.p. 135–137° (20 mm.)]. The fraction boiling at 138–140° (20 mm.) was collected and no attempt to isolate the pure isomers was made.

Anal. Calcd. for $C_{10}H_{15}NO_3$: C, 60.89; H, 7.67; N, 7.10. Found: C, 60.73; H, 7.38; N, 7.30.

Mixture of *cis*- and *trans*-α-Cyano-β-methoxy-β-*t*-butylacrylate (VIIIa, VIIIb).—A mixture of 8.0 g. of pivaloylchloride, 6.6 g. of methyl cyanoacetate, and 9.2 g. of anhydrous potassium carbonate in 30 ml. of benzene was refluxed for 3 hr. After cooling, the mixture was dissolved in water, acidified with 15% hydrochloric acid, and then extracted twice with benzene. The combined extracts were dried with sodium sulfate and evaporated to remove benzene. The residue was distilled under reduced pressure giving methyl pivaloylcyanoacetate; yield, 3.0 g. (20.4%); b.p. 119–122° (20 mm.); m.p. 28–30°.

Anal. Calcd. for $C_9H_{13}NO_3$: C, 59.00; H, 7.15; N, 7.65. Found: C, 59.00; H, 7.12; N, 7.54.

To a solution of 10 g. of methyl pivaloylcyanoacetate in 5 ml. of methanol was slowly added at −5° an ethereal solution of diazomethane prepared from 22 g. of *p*-tolylsulfonylmethylnitrosamide, and the mixture was allowed to stand overnight at room temperature. After the solvent was removed, the residue was distilled under reduced pressure to give 8.0 g. of the product, b.p. 129–134° (10 mm.). The product was further purified by shaking with 40 ml. of a solution saturated with cupric acetate to remove unaltered methyl pivaloylcyanoacetate and extracting with benzene. The benzene layer was dried over sodium sulfate. The benzene was distilled *in vacuo*, and the distillation was continued to give 5.0 g. (46.5%) of methyl α-cyano-β-methoxy-β-*t*-butylacrylate, b.p. 134–135° (10 mm.).

Anal. Calcd. for $C_{10}H_{15}NO_3$: C, 60.89; H, 7.67; N, 7.10. Found: C, 60.97; H, 7.50; N, 7.15.

Isomerization of Ethyl α-Cyano-β-acetoxy-β-methylacrylate (IV).—Isomerization of the ester was induced by a trace amount of sodium methoxide. The sample was allowed to stand at room temperature through a week, and then was distilled under vacuum.

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Mechanism of Hydrolysis of Ethyl Benzimidates in Acidic Solutions

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The effects of aryl substituents and temperature on the kinetics of acid hydrolysis of a series of *m*- and *p*-substituted ethyl benzimidates and the deuterium oxide solvent isotope effect on the hydrolysis of one of them were studied. The data obtained and data from the literature suggest that acid hydrolysis of ethyl benzimidates involves rate-determining general base catalyzed dissociation of a tetrahedral hydrated conjugate acid into an ethyl benzoate and ammonium ion.

Hydrolysis of conjugate acids of the simple imidic esters was first studied by Pinner, who found that ammonium ion and a carboxylate ester are the initial reaction products.[1] He observed that hydrolysis of

$$RC(=NH_2)OR'^+ + H_2O \longrightarrow RCO_2R' + NH_4^+$$

low molecular weight aliphatic imidic ester hydrochlorides is rapid, while hydrolysis of benzimidic and higher aliphatic imidic ester hydrochlorides is considerably slower.

The kinetics and mechanisms of imidic ester hydrolyses have received little attention. The only kinetic studies thus far have involved ethyl benzimidates. Stieglitz and co-workers, in the course of their early study of the mechanism of acid catalysis, investigated the hydrolysis of the hydrochlorides of ethyl benzimidate and ethyl *m*-nitrobenzimidate.[2] Stieglitz demonstrated that the catalytic effect of hydrogen ion on benzimidate hydrolysis is due to formation of the conjugate acid of the ester, and that addition of acid to a solution of the ester hydrochloride actually slows the hydrolysis reaction. This was confirmed by Edward and Meacock, who found that the rate of hydrolysis of methyl benzimidate decreases sharply as the hydrochloric acid concentration of the reaction solution increases above 0.1 *N*.[3] More recently, Hand and Jencks found that hydrolysis of ethyl benzimidate is general acid catalyzed in acetate buffers.[4]

In order to gain additional information pertinent to the mechanism of benzimidic ester hydrolysis, we studied the effects of aryl substituents and temperature on the kinetics of acid hydrolysis of a series of *m*- and *p*-substituted ethyl benzimidates, and the deuterium oxide solvent isotope effect on the hydrolysis of one of them.

Experimental

Preparation of Ethyl Benzimidates.—The imidic ester hydrochlorides were prepared from the corresponding nitriles by the

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