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# Influence of steric and polar effects in determining the equilibrium position for *cis–trans*-olefin pairs

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Received January 30, 1970

A series of α,β-unsaturated nitriles and esters substituted by *t*-butyl or isopropyl groups at the β-position along with methoxyl, thioethoxyl dimethylamino, chloro, and hydrogen at the other β-position have been prepared. Evaluation of the isomer stability from *cis–trans* equilibrations achieved catalytically or thermally supports earlier observations that steric and polar factors maintain a strong tendency for a β-methoxyl group to be *trans* to a nitrile or carbomethoxy group even when opposed by a *t*-butyl group. The tendency for a chloro group to prefer to be *trans* to a carbomethoxy group in methyl β-chlorocrotonate is overcome by replacing the β-methyl by isopropyl or *t*-butyl.

Canadian Journal of Chemistry, 48, 2110 (1970)

In the preceding paper (1) the position of thermodynamic equilibrium for the *E* and *Z* forms (highest priority groups *cis* for *Z* and *trans* for *E* (2)) of several 3-substituted methacrylonitriles was measured. It was noted that interactions non-steric in origin were dominant in determining the position of equilibrium. In a similar interplay of effects it is well recognized that the β-halocrotonic acid derivatives are more stable in the *E* form in which the smaller halogen group is *trans* to the carbonyl containing group (3). To further evaluate the contribution of steric and polar factors in determining the position of equilibrium for *cis–trans* pairs of isomers, we have prepared a number of α,β-unsaturated nitriles and esters for study.

Chart 1 lists the compounds which have been studied along with the equilibrium data. New compounds in Chart 1 were prepared by standard methods. Reaction of α-bromo-β-alkylacrylonitriles with sodium methoxide in methanol gave **1** and **12**. The *Z* form of all of the β-methoxy compounds **1**, **6**, **7**, **10**, and **12** were prepared by addition of diazomethane to the appropriate β-keto-nitrile or ester. The *E* isomers could be obtained by irradiation of the *Z* isomers in a silica flask with a mercury lamp. The chloronitrile **5** and the chloroester **9** were separately obtained from the corresponding aldehyde, 3-chloro-4,4-dimethyl-2-pentenal (4), the former by use of the Corey procedure (5), the latter by dehydration of the aldoxime. The chloro compounds **5** and **9** could not be obtained by reaction of phosphorus pentachloride with the corresponding β-keto-nitrile or ester (6). Under these conditions the β-ketonitrile was recovered essentially unchanged and the β-ketoester underwent chlorination α to the carbonyl groups. Compounds **2–4** and **8** were prepared from the corresponding β-chloro derivatives **5** and **9** by nucleophilic substitution. Attempts to prepare corresponding β-enaminoesters from **9** were unsuccessful. The β-chloroesters **11** and **13** were obtained from the known acids by esterification.

## Assignment of Configuration

In some cases it was possible to assign the configuration about the double bond on the basis of chemical evidence. Thus the enol ether **7**, obtained from the reaction of diazomethane with ethyl 4,4-dimethyl-3-ketopentanoate (6) was assigned the *Z* configuration on the following basis. First the β-ketoester, which was shown by nuclear magnetic resonance (n.m.r.) spectroscopy to exist approximately 40% in the enol form, gave a positive ferric chloride test, and secondly, in the absence of methanol only 10% of the β-ketoester reacted with diazomethane. This is in line with earlier studies on the reaction of β-ketoesters with diazomethane which demonstrated that *cis* enols require methanol catalysis and give the *Z* methyl ether (22).

Stereoselective preparation of **1** and **2** from 2-bromo-4,4-dimethyl-2-pentenitrile (*E* or *Z*) is expected to occur by *trans* addition to the acetylene intermediate (7, 8) and thus should lead to product rich in the *Z* isomer. The chloronitrile **5** and the chloroester **9** also may react with nucleophiles via an acetylenic intermediate although this was only definitely confirmed for the reaction of **5** and **9** with sodium methoxide.

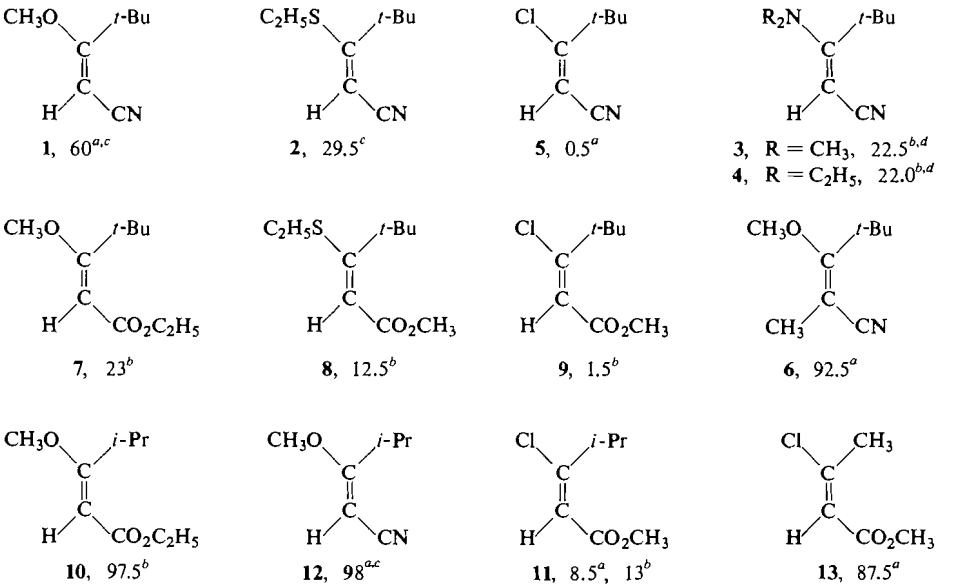


CHART 1

Percent composition at equilibrium for the *E* form of the compounds studied.

Procedures used for equilibrations, as described elsewhere (1), were: (*a*) bromine in sunlight at about 30°; (*b*) thermally in sealed tubes at 210°; (*c*) catalytically with 1 equ of sodium methoxide in methanol at 60°; (*d*) equilibrium approached from one isomer only.

Finally, where appropriate, the corresponding isopropyl compounds have been synthesized and comparisons made between the like physical and spectroscopic properties of the two series.

In the majority of cases, where chemical evidence of structure was not available, assignment of configuration has been based on n.m.r. spectroscopic measurements. The data collected is shown in Tables 1 and 2. Assignments were possible because in every case both stereoisomers were available. There is little doubt that a β-hydrogen *cis* to a nitrile or carbomethoxy group will be to lower field (9). For each pair of isomers studied the chemical shift of the *t*-butyl group was assumed to be at lower field in those isomers in which the *t*-butyl group and nitrile group are *cis* orientated. This effect was larger than for the methyls in an isopropyl group due to the necessity of a *t*-butyl group to have at least one methyl in close proximity of the nitrile. Although this appears contrary to the observations of Hayashi *et al.* (10, 11) on alkylidenecyanoacetic esters it is significant that the magnitude of the chemical shift differences for the *t*-butyl groups is more pronounced for most of the nitriles (0.00–0.21 p.p.m.) than for the esters (0.00–0.12 p.p.m.), a situation which is different from that observed for β-methyls. This change in relative effects will be the result of the difference between the form of the shielding cone of a nitrile and a carbonyl and their different relative geometry. A β-methyl is strongly shielded by a carbonyl but weakly shielded by a nitrile. A β-*t*-butyl group will have the methyls placed favorably over the nitrile for stronger shielding than from a carbonyl.

Further supporting evidence was obtained by comparison of the chemical shift of the olefinic protons. Jones *et al.* (12) and Pizey and Truce (13) have shown for a series of 3-substituted crotonates that the α-olefinic proton is more deshielded when it is *trans* to the electron-donating group at position 3 than when it is *cis*. Apart from the chloroesters and chloronitriles where the difference is small the present results are fully in accord with those of the aforementioned workers.

Pizey and Truce (13) further showed that the chemical shift of the α-olefinic proton in the 3-substituted crotonates moves to higher field as the electron-donating ability (14) of the 3-

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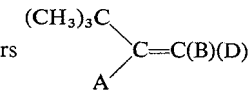
TABLE 1

Chemical shifts and coupling constants for the β-*t*-butylacrylonitriles and esters

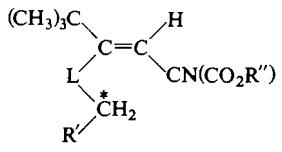


| Compound no. | Configuration | A | B | D | Chemical shift (τ)* —C(CH₃)₃ | A | B | D | J (Hz) |
|---|---|---|---|---|---|---|---|---|---|
| **15** | *E* | H | H | CN | 8.90 | 3.34d | 4.78d | — | 16.5 |
| **15** | *Z* | H | H | CN | 8.75 | 3.69d | 4.82d | — | 12.0 |
| **16** | *E* | H | $CH_3$ | CN | 8.82 | 3.77q | 8.02d | — | 1.5 |
| **16** | *Z* | H | $CH_3$ | CN | 8.79 | 3.94q | 8.06d | — | 1.5 |
| **17** | *E* | H | Br | CN | 8.74 | 3.32 | — | — | — |
| **17** | *Z* | H | Br | CN | 8.74 | 3.12 | — | — | — |
| **1** | *E* | $CH_3O$ | H | CN | 8.70 | 6.40 | 5.66 | — | — |
| **1** | *Z* | $CH_3O$ | H | CN | 8.91 | 5.81 | 5.58 | — | — |
| **6** | *E* | $CH_3O$ | $CH_3$ | CN | 8.70 | 6.32 | 8.11 | — | — |
| **6** | *Z* | $CH_3O$ | $CH_3$ | CN | 8.80 | 6.09 | 8.03 | — | — |
| **2** | *E* | $CH_3CH_2S$ | H | CN | 8.59 | 7.32q, 8.67t | 5.24 | — | 7.5 |
| **2** | *Z* | $CH_3CH_2S$ | H | CN | 8.80 | 6.78q, 8.68t | 4.44 | — | 7.0 |
| **5** | *E* | Cl | H | CN | 8.58 | — | 4.42 | — | — |
| **5** | *Z* | Cl | H | CN | 8.77 | — | 4.48 | — | — |
| **3** | *E* | $(CH_3)_2N$ | H | CN | 8.58 | 7.33 | 5.71 | — | — |
| **3** | *Z* | $(CH_3)_2N$ | H | CN | 8.78 | 6.96 | 5.64 | — | — |
| **4** | *E* | $(CH_3CH_2)_2N$ | H | CN | 8.64 | 7.11q, 8.96t | 5.53 | — | 7.0 |
| **4** | *Z* | $(CH_3CH_2)_2N$ | H | CN | 8.81 | 6.69q, 8.91t | 5.28 | — | 7.0 |
| **7** | *E* | $CH_3O$ | H | $CO_2CH_2CH_3$ | 8.88 | 6.40 | 5.13 | 5.94q, 8.77t | 7.0 |
| **7** | *Z* | $CH_3O$ | H | $CO_2CH_2CH_3$ | 8.88 | 6.10 | 4.97 | 5.94q, 8.77t | 7.0 |
| **8** | *E* | $CH_3CH_2S$ | H | $CO_2CH_3$ | 8.67 | 7.35q, 8.83t | 4.73 | 6.35 | 7.0 |
| **8** | *Z* | $CH_3CH_2S$ | H | $CO_2CH_3$ | 8.79 | 7.18q, 8.83t | 4.01 | 6.39 | 7.0 |
| **9** | *E* | Cl | H | $CO_2CH_3$ | 8.71 | — | 4.02 | 6.35 | — |
| **9** | *Z* | Cl | H | $CO_2CH_3$ | 8.76 | — | 4.04 | 6.35 | — |

*d, Doublet; t, triplet; q, quartet. All resonances are singlets unless otherwise marked.

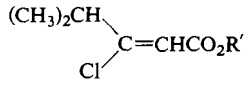
substituent increases. A similar effect has been found particularly in the *E* series for the nitriles **3** > **1** > **2** > **5** and esters **7** > **8** > **9** presently studied, the chemical shift (τ) of the olefinic proton decreasing in the series $(CH_3)_2N$— > $CH_3O$— > $C_2H_5S$— > Cl.

Like the *t*-butyl group, the hydrogens on the carbon C* at the γ position in other β-substituents are also deshielded by the nitrile or ester group to a greater extent than expected. This may suggest an *S-cis* configuration with respect to the double bond for $LC^*H_2R'$ (L = O, S, N; R′ = H, $CH_3$) as in structure **14**.

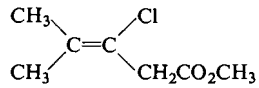


**14**

Our assignment of the *Z* configuration to the more stable chloro isopropyl ester **11** is based on the position of the methine hydrogen at 7.40 τ in that isomer compared to the less stable isomer with the methine hydrogen at 5.75 τ. This large chemical shift difference is in line with the view that the methine hydrogen is oriented for steric reasons towards the carbomethoxy group in the *E* form and experiences a maximum deshielding effect (11, 15). Pizey and Truce (13) prepared the ethyl ester **21** and assigned the *E* configuration to the more stable isomer by analogy with stabilities in the β-chlorocrotonate series. Our preparation of **11** was from 3-chloro-4-methyl-2-pentenoic acid (16) by esterification with methanol and contained both isomers of **11** as well as small amounts of the β,γ-isomer, methyl 3-chloro-4-methyl-3-pentenoate (**22**). Attempts to obtain the *E* isomer of **11** pure by vapor phase chromatography (v.p.c.) were unsuccessful. In every case samples isolated contained large amounts of a new component identified below. On the other hand a sample of **11** (*Z*-) was isolated containing less than 6% of the β,γ-isomer **22** as



**11** R′ = $CH_3$
**21** R′ = $C_2H_5$



**22**

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TABLE 2

Chemical shifts and coupling constants for the β-isopropylacrylonitriles and esters $(CH_3)_2CH$, A, C=C(B)(D)

| Compound no. | Configuration | A | B | D | Chemical shift (τ)* $(CH_3)_2$—C—(d) | —C—H(m) | A | B | D | *J* (Hz) |
|---|---|---|---|---|---|---|---|---|---|---|
| **18** | *E* | H | H | CN | 8.91 | 7.15–7.95 | 3.22q | 4.73q | — | *trans* = 16.5<br>$CH_1CH$ = 6.5<br>$CH_1CH_3$ = 6.5 |
| **18** | *Z* | H | H | CN | 8.89 | 6.70–7.50 | 3.74q | 4.82d | — | *cis* = 11.0<br>$CH_1CH$ = 9.5<br>$CH_1CH_3$ = 6.5 |
| **19** | *E* | H | Br | CN | 8.86 | 6.90–7.40 | 3.50d | — | — | $CH_1CH$ = 9.5<br>$CH_1CH_3$ = 7.0 |
| **19** | *Z* | H | Br | CN | 8.90 | 6.85–7.50 | 3.40d | — | — | $CH_1CH$ = 9.0<br>$CH_1CH_3$ = 6.5 |
| **12** | *E* | $CH_3O$ | H | CN | 8.86 | 6.50–7.20 | 6.36 | 5.79 | — | $CH_1CH_3$ = 7.0 |
| **12** | *Z* | $CH_3O$ | H | CN | 8.96 | 7.40–8.15 | 5.90 | 5.75 | — | $CH_1CH_3$ = 7.0 |
| **20** | *E* | H | H | $CO_2CH_3$ | 8.91 | 7.94 | 3.14q | 4.32q | 6.34 | *trans* = 15.8<br>$CH_1CH$ = 1.4, 6.5<br>$CH_1CH_3$ = 6.7 |
| **20** | *Z* | H | H | $CO_2CH_3$ | 8.99 | 6.35 | 4.03q | 4.43d | 6.36 | *cis* = 11.4<br>$CH_1CH$ = 9.2<br>$CH_1CH_3$ = 6.6 |
| **10** | *E* | $CH_3O$ | H | $CO_2CH_2CH_3$ | 8.94 | 6.10 | 6.39 | 5.19 | 5.96, 8.78 | $CH_2CH_3$ = 7.0 |
| **10** | *Z* | $CH_3O$ | H | $CO_2CH_2CH_3$ | 8.91 | 7.30–8.00 | 6.07 | 5.10 | 5.96, 8.78 | $CH_1CH_3$ = 7.0<br>$CH_2CH_3$ = 7.0 |
| **11** | *E* | Cl | H | $CO_2CH_3$ | 8.87 | 5.40–6.10 | — | 4.07 | 6.31 | $CH_1CH_3$ = 6.5 |
| **11** | *Z* | Cl | H | $CO_2CH_3$ | 8.80 | 7.00–7.80 | — | 4.06 | 6.32 | $CH_1CH_3$ = 6.5 |

*d, Doublet; t, triplet; q, quartet or two doublets; m, multiplet. All resonances are singlets unless marked otherwise.

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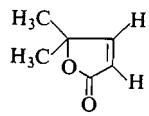
the only impurity. Photolysis of **11** (*Z*-) gave a mixture of isomers in which the n.m.r. spectrum of **11** (*E*-) could clearly be identified.

Equilibration of **11** (*Z*-) at 210° gave, in addition to the three isomers **11** (*Z*- and *E*-) and **22**, substantial quantities of a new component which has been identified as the butenolide **23** by comparison of its n.m.r. spectrum with that recently reported for **23** (17). Formation of **23** from **11** by



**23**

loss of methyl chloride is not without precedent and we are examining this reaction further in our laboratories (18, 19). Preliminary results indicate **23** is formed from **22** and not **11**. The equilibration results at 210° are complicated by the side reaction to form **23**, however the fact that the value of 13% *E* is close to the value 8.5% *E* found by the light initiated bromine catalyzed method suggests it is of the right order of magnitude.

## Equilibration Studies

The effect of an alkyl group alone at the β-position in acrylonitriles and acrylates is shown in Table 3. In all cases, except where the group is *t*-butyl, there is a significant amount of the *cis*-isomer. For vinyl ketones and aldehydes a β-methyl or β-halogen effectively destabilizes the *cis* form so that less than 2% is present at equilibrium (20, 21). The marked sensitivity of the carbonyl compounds to *cis*-substituents at the β-position is undoubtedly due to the requirement that for maximum conjugation the carbonyl must be in the plane of the double bond and in this form is very sensitive to steric effects. The contribution of the zwitterion form to the stability

TABLE 3

The % of *cis* isomer at equilibrium for β-alkylacrylonitriles and acrylates

| β-Substituent | Nitriles | Acrylates |
|---|---|---|
| $CH_3$ | 58 (24) | 18 (25) |
| $CH_3CH_2$ | — | 12.5 (15) |
| $(CH_3)_2CH$ | 28 (26), 33* | 10 (15) |
| $(CH_3)_3C$ | 1.5* | |

*Present work.

TABLE 4

The % of *Z*-isomer at equilibrium for β-substituted methacrylates (compare to methacrylonitriles (1))

| β-Substituent | % *Z* |
|---|---|
| $CH_3$ | 17 (27) |
| Br | <1* |
| $CH_3O$ | <0.2* |

*Y. Y. Wigfield, this laboratory.

of aldehydes and ketones would be greater than for esters and thus aldehydes and ketones would show a greater sensitivity to steric inhibition of conjugation. The importance of the zwitterion form in esters is increased when an electron-donating (by resonance) group is attached at the β-position and here also a *trans* configuration is strongly favored (see particularly methyl β-methoxymethacrylate in Table 4).

For compounds of Chart 1 we have an interplay of all these factors. Of particular note is the large % of the *E* form for the β-methoxy compounds **1**, **6**, and **12**. The methoxyl group by conjugation would be in the plane of the double bond and thus may have an effective bulk greater than a *t*-butyl group. Such an argument cannot also explain the equilibrium position for **7**. We feel that coupled with the steric effect there is a repulsive term between the methoxyl and the nitrile or ester groups which is analogous to the interaction between halogen and ester found in **13**. This is in line with the many reports concerning β-methoxy ketones which have those two groups *trans* in the more stable isomer (21, 22).

The repulsive term between halogen and ester is illustrated by the β-chlorocrotonate **13** which is 87.5% in the form with the chlorine (which sterically is expected to be smaller than the methyl) *trans* to the ester and β-bromomethacrylate (Table 4). This repulsive term is more than offset by the isopropyl group in **11** and completely overcome by the *t*-butyl group in **5**.

The positions of equilibrium for the β-dialkyl amino compounds and β-thioethoxy compounds are more nearly where one might predict with the recognition that the dialkyl amino group is held in the plane of the double bond. The importance of conjugation here is noted from the ease with which these and other vinyl amines undergo *cis–trans* isomerization (23).

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## Experimental

The v.p.c. analysis and preparative separation were carried out on commercial (Varian Aerograph) 10 ft × 1/4 in. stainless steel columns containing the appropriate packing. Boiling points were determined by the micro-capillary method and are uncorrected. The n.m.r. spectra in τ values were recorded on a Varian A60 instrument using 20% by volume samples in carbon tetrachloride. All new compounds gave infrared (i.r.) spectra consistent with their respective structures.

*4-Methyl-2-pentenitrile (**18**)*

Condensation of isobutyraldehyde with cyanoacetic acid in pyridine (28) yielded a crude reaction mixture containing *cis*-4-methyl-2-pentenitrile (18%), *trans*-4-methyl-2-pentenitrile (19%), and 4-methyl-3-pentenitrile (63%). After distillation, separation was effected by preparative v.p.c. on a column of 15% QF1 – 5% carbowax-20M at 145°.

*4,4-Dimethyl-2-pentenitrile (**15**)*

A mixture of *cis*- and *trans*-4,4-dimethyl-2-pentenitrile in the ratio 21:79 was obtained from pivaldehyde in an analogous manner to that described above. The physical properties of the *cis*-isomer, b.p. 147–148°, $n_D^{20}$ 1.4328, do not appear to have been reported previously.

Anal. Calcd. for $C_7H_{11}N$: C, 77.07; H, 10.09. Found: C, 77.30; H, 9.92.

*3-Keto-2,4,4-trimethylpentanitrile*

Condensation of propionitrile with methyl pivalate by means of sodium amide in liquid ammonia (29) yielded the title β-ketonitrile of 93% purity in 75% yield. An analytical sample, b.p. 46°/0.3 mm, $n_D^{17.5}$ 1.4288, was obtained by v.p.c. on S.E. 30 at 155°.

Anal. Calcd. for $C_8H_{13}NO$: C, 69.07; H, 9.35. Found: C, 68.40; H, 9.56.

*3-Hydroxy-2,4,4-trimethylpentanitrile*

Sodium borohydride reduction of the above β-ketonitrile readily yielded an *erythro–threo* mixture of alcohols (83% yield), b.p. 64–65°/0.3 mm.

Anal. Calcd. for $C_8H_{15}NO$: C, 68.10; H, 10.64; N, 9.93. Found: C, 67.89; H, 10.55; N, 9.93.

*2,4,4-Trimethyl-2-pentenitrile (**16**, E- and Z-)*

*(1)* To the above mixture of alcohols (2.82 g) dissolved in pyridine (3.2 ml) was added, dropwise with stirring and cooling, thionyl chloride (3 ml). After the addition was complete the reaction mixture was allowed to attain and maintain room temperature for 3 h, then it was heated at 80° for 2 h. After work-up (30) and distillation, a mixture of 2,4,4-trimethyl-2-pentenitrile (*E*- and *Z*-, 1.40 g, 57%) was obtained containing 80% of the *Z* isomer. The two isomers were separated by v.p.c. on QF1-carbowax at 130°, the following physical properties being recorded.

The *E* isomer, b.p. 165–166°, $n_D^{17.5}$ 1.4440.

Anal. Calcd. for $C_8H_{13}N$: C, 78.05; H, 10.57. Found: C, 77.88; H, 10.49.

The *Z* isomer, b.p. 147–148°, $n_D^{17.5}$ 1.4380.

Anal. Found: C, 78.14; H, 10.77.

*(2)* Dehydration of the cyanohydrin of 4,4-dimethyl-2-pentanone (31) (1.35 g) was effected by means of thionyl chloride (1.46 ml) and pyridine (1.62 ml). The distilled product (0.5 g) contained mainly 85% of a mixture of 2,4,4-trimethyl-2-pentenitrile (*Z*-) and 4,4-dimethyl-2-methylenepentanitrile in the ratio 16:7. Found *M* (mass spectrum) 122. The n.m.r. ($CCl_4$) on mixture (data only given for the methylenenitrile), 8.99 (singlet, 9 protons), 7.87 (doublet, 3 protons, $J$ = 1.5 Hz), 4.38 (quartet, 1 proton, $J$ = 1.5 Hz), 4.11 (doublet, 1 proton, $J$ = 1.5 Hz).

A minor product (3%), which was not identified, had an identical v.p.c. retention time (QF1-carbowax at 150°) with 2,4,4-trimethyl-2-pentenitrile (*E*-).

*2-Bromo-4-methyl-2-pentenitrile (**19**)*

Crude 2,3-dibromo-4-methylpentanitrile, prepared by the addition of bromine to *cis*-4-methyl-2-pentenitrile, was dehydrobrominated with sodium acetate in acetic acid (32). The crude reaction product contains the *E* and *Z* isomers of 2-bromo-4-methyl-2-pentenitrile in the ratio 47:53. After distillation, the two isomers were separated by v.p.c. on QF1-carbowax at 160°. A correct elemental analysis could not be obtained for either isomer although both isomers appeared to be homogeneous from v.p.c. and n.m.r. analysis. The following physical properties were, however, obtained.

2-Bromo-4-methyl-2-pentenitrile (*E*-), b.p. 160–161°, $n_D^{20}$ 1.4766, *M* (mass spectrum) 173.

2-Bromo-4-methyl-2-pentenitrile (*Z*-), b.p. 168–169°, $n_D^{20}$ 1.4780, *M* (mass spectrum) 173.

The equilibrium mixture, determined from each isomer by irradiation of a sample in carbon tetrachloride containing 1% bromine, contained 42% of the *E* form.

*2-Bromo-4,4-dimethyl-2-pentenitrile (**17**, E- and Z-)*

Treatment of a *cis–trans* mixture of 4,4-dimethyl-2-pentenitrile (containing 88% *trans* isomer) with bromine, followed by dehydrobromination with sodium acetate in acetic acid, yielded the required bromo-nitriles (*E*:*Z* ratio = 2:1). The following physical properties were determined.

2-Bromo-4,4-dimethyl-2-pentenitrile (*E*-), b.p. 179–180°, $n_D^{20}$ 1.4829.

Anal. Calcd. for $C_7H_{10}BrN$: C, 44.68; H, 5.32. Found: C, 44.75; H, 5.32.

2-Bromo-4,4-dimethyl-2-pentenitrile (*Z*-), b.p. 190–191°, $n_D^{20}$ 1.4821.

Anal. Found: C, 44.74; H, 5.22.

In a further experiment, starting from 4,4-dimethyl-2-pentenitrile (79% *trans*), a mixture of 2-bromo-4,4-dimethyl-2-pentenitrile (*E*- and *Z*-) was obtained containing over 85% of the *E* isomer. An attempt to increase the amount of *Z* isomer in this mixture photochemically was unsuccessful. Irradiation of an ether solution of the mixture at 2537 Å through Pyrex caused virtually no isomerization, whilst irradiation through silica for 6 h yielded *trans*-4,4-dimethyl-2-pentenitrile as the major product.

The equilibrium position determined as above contained 81% of the *E* form.

*3-Methoxy-4-methyl-2-pentenitrile (Z-) (**12**)*

*(1)* Treatment of 2-bromo-4-methyl-2-pentenitrile (either isomer) with sodium methoxide (1.1 equ) in methanol at room temperature for 1.5 h yielded an *E–Z*

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mixture of 3-methoxy-4-methyl-2-pentenitrile containing over 90% of the thermodynamically less stable *Z* isomer. After distillation and purification by v.p.c. on QF1-carbowax at 160° a sample of pure *Z* isomer was obtained, the n.m.r. and i.r. spectra of which were identical with those of a sample prepared as below.

*(2)* 3-Keto-4-methylpentanitrile was prepared in 80% yield by the sodium amide catalyzed condensation of acetonitrile and methyl isobutyrate (29). The ketonitrile, b.p. 60°/0.1 mm, $n_D^{19}$ 1.4752, is a colorless liquid which decomposes on heating or standing. It is completely stable, however, when stored in the solid form at −78°.

Anal. Calcd. for $C_6H_9NO$: C, 64.86; H, 8.11; N, 12.61. Found: C, 64.96; H, 8.22; N, 12.75.

The n.m.r. 8.87 (doublet), 7.20 (septet), 6.36 (singlet, $J$ = 7.0 Hz).

Yamashita (33) has previously obtained this compound as a light yellow oil, b.p. 102–104°/12 mm, using sodium ethoxide as condensing agent. The yield, however, was only 45% and the procedure more tedious than that described here.

Treatment of 3-keto-4-methylpentanitrile (4 g) with an ethereal solution of diazomethane (from 12 g of *N*-nitroso-*N*-methylurea) resulted in an instantaneous evolution of nitrogen. After 16 h at room temperature the ether was removed and the residue distilled at 73–85°/15 mm. The resulting white liquid (3.65 g, 81%) contained the *E* and *Z* isomers of 3-methoxy-4-methyl-2-pentenitrile in the ratio 3:97. A sample of pure *Z* isomer, b.p. 184.5–185.5°, $n_D^{17.5}$ 1.4602, was obtained by v.p.c. on QF1-carbowax at 160°.

Anal. Calcd. for $C_7H_{11}NO$: C, 67.20; H, 8.80. Found: C, 67.02; H, 8.92.

*3-Methoxy-4-methyl-2-pentenitrile (E-) (12)*

Irradiation of an ether solution of the above *Z* isomer through silica at 2537 Å for 3 h yielded a mixture containing 95% of the *E* isomer. Separation was effected by v.p.c. on QF1-carbowax at 160° to give 3-methoxy-4-methyl-2-pentenitrile (*E*-), b.p. 196.5–197.5°, $n_D^{15}$ 1.4553.

Anal. Found: C, 67.44; H, 9.05.

*4,4-Dimethyl-3-methoxy-2-pentenitrile (Z-) (1)*

This was prepared by analogous methods to those used for the corresponding isopropyl compound, either by treatment of 2-bromo-4,4-dimethyl-2-pentenitrile with sodium methoxide in methanol or, more conveniently, by the reaction of β-cyanopinacolone (34) with diazomethane (35). After purification by distillation and v.p.c. on QF1-carbowax at 160°, 4,4-dimethyl-3-methoxy-2-pentenitrile (*Z*-), b.p. 191–192°, $n_D^{20}$ 1.4572 (lit. (35) b.p. 87–88° at 19 mm, $n_D^{30}$ 1.4482), was obtained.

Anal. Calcd. for $C_8H_{13}ON$: C, 69.07; H, 9.35. Found: C, 69.27; H, 9.45.

*4,4-Dimethyl-3-methoxy-2-pentenitrile (E-) (1)*

Irradiation of an ether solution of the above *Z* isomer through silica at 2537 Å for 5 h yielded a mixture containing 42% of the *E* isomer. After separation by v.p.c. on QF1-carbowax at 160° pure *E* isomer, b.p. 215–216°, $n_D^{20}$ 1.4630, was obtained.

Anal. Found: C, 68.96; H, 9.51.

*3-Methoxy-2,4,4-trimethyl-2-pentenitrile (E-) (6)*

3-Keto-2,4,4-trimethylpentanitrile (4 g) was treated with diazomethane (from 10.3 g of *N*-nitroso-*N*-methylurea) in ether (100 ml). As evolution of nitrogen did not occur, methanol (20 ml) was added to the reaction mixture. After 16 h the solvent was evaporated and the distilled residue (3.7 g) examined by v.p.c. Since the distillate contained (v.p.c.) 33% unchanged starting material, it was treated with a further portion of diazomethane (as above). Work-up yielded a colorless liquid (3.34 g) containing 82% of the *E* and 4% of the *Z* isomer of 3-methoxy-2,4,4-trimethyl-2-pentenitrile. An analytical sample of the *E* isomer, b.p. 203–204°, $n_D^{17.5}$ 1.4588, was obtained by v.p.c. on S.E. 30 at 165°.

Anal. Calcd. for $C_9H_{15}NO$: C, 70.58; H, 9.80. Found: C, 68.93; H, 9.90.

*3-Methoxy-2,4,4-trimethyl-2-pentenitrile (Z-) (6)*

Irradiation of a 2.5% ethereal solution of the distillate from the previous experiment through silica at 2537 Å for 2.5 h increased the amount of *Z* isomer to 15%.

*3-Chloro-4,4-dimethyl-2-pentenal (with B. D. Page)*

Vilsmeier formylation of pinacolone with phosphorous oxychloride and dimethylformamide was carried out as described by Bodendorf and Mayer (4). A 61% yield of the chloroaldehyde was obtained which was shown (36) by n.m.r. spectroscopy to contain only the *Z* isomer.

*Oxime of 3-Chloro-4,4-dimethyl-2-pentenal (Z-)*

3-Chloro-4,4-dimethyl-2-pentenal (*Z*, 6.37 g) and hydroxylamine hydrochloride (3.63 g, 1.2 equ) were dissolved in pyridine (25 ml). An exothermic reaction occurred and after 5 min, a second liquid layer (approximately 5 ml) separated at the bottom of the flask. After 17.5 h, water was added and the mixture was extracted twice with ether. The combined ether extracts were washed with three portions of 3 *N* hydrochloric acid then dried over magnesium sulfate. Removal of the ether under reduced pressure yielded the required oxime (95% crude yield) as a viscous oil which was used immediately in the next experiment.

Once, when the liquid oxime was allowed to stand at room temperature for 24 h, it partially solidified with evolution of heat. Dehydration of this semi-solid oxime in an analogous manner to that described below gave, besides the required nitrile, a 30% yield of 5-*t*-butylisoxazole.

*3-Chloro-4,4-dimethyl-2-pentenitrile (Z-) (5)*

The crude liquid oxime (5.54 g) was dissolved in dry benzene (10 ml) and added to a syrup of ethanol and phosphorus pentoxide (prepared from 2.8 g of ethanol and 6.3 g of phosphorus pentoxide by the method of Mukaiyama and Hata (37)). The reaction mixture was stirred and boiled under reflux for 35 min, then cooled and the benzene layer decanted. The residual syrup was dissolved in water, extracted with ether and the organic layer dried over magnesium sulfate. After removal of the solvent from the combined ether and benzene extracts, the resulting liquid was distilled. The v.p.c. analysis indicated the distillate (4.25 g, 82% based on the chloroaldehyde) to be >98% pure. An analytical sample of

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3-chloro-4,4-dimethyl-2-pentenitrile (*Z*-), b.p. 198–199°, $n_D^{17.5}$ 1.4679, was obtained by v.p.c. purification on Apiezon J at 168°.

Anal. Calcd. for $C_7H_{10}ClN$: C, 58.55; H, 6.97. Found: C, 58.45; H, 7.14.

*3-Chloro-4,4-dimethyl-2-pentenitrile (E-) (5)*

Irradiation of an ether solution of the above *Z* isomer through silica at 2537 Å for 2.5 h yielded only 4% of the *E* isomer. An enriched sample, containing 15% of the *E* isomer was obtained by v.p.c.

*4,4-Dimethyl-3-dimethylamino-2-pentenitrile (3)*

To 3-chloro-4,4-dimethyl-2-pentenitrile (*Z*-, 1.5 g) dissolved in ether (2 ml) was added dimethylamine (10 ml) and the reaction mixture was kept in a tightly-stoppered tube for 13 days. More ether was then added and the dimethylamine hydrochloride was removed by filtration. Evaporation of the solvent yielded an oil which was distilled at 120–130°/20 mm to give 4,4-dimethyl-3-dimethylamino-2-pentenitrile (1.5 g, 94%). An analytical sample containing 17% *E* and 83% *Z* isomers was obtained by v.p.c. on Apiezon J at 210°.

Anal. Calcd. for $C_9H_{16}N_2$: C, 71.06; H, 10.53. Found: C, 70.80; H, 10.80.

*4,4-Dimethyl-3-diethylamino-2-pentenitrile (13)*

Reaction of 3-chloro-4,4-dimethyl-2-pentenitrile with a large excess of boiling diethylamine for 24 h yielded a small amount of unchanged starting material and an *E–Z* mixture of the required enaminonitrile containing >90% of the *Z* isomer.

Anal. Calcd. for $C_{11}H_{20}N_2$: C, 73.33; H, 11.11. Found: C, 73.11; H, 11.21.

The above *E–Z* mixture of enaminonitriles was also prepared, though less conveniently, by reaction of 2-bromo-4,4-dimethyl-2-pentenitrile (*Z*-) with boiling diethylamine. The *E* form of the bromonitrile reacted only very slowly with both diethyl- and dimethylamine.

*4,4-Dimethyl-3-thioethoxy-2-pentenitrile (Z-) (2)*

To 3-chloro-4,4-dimethyl-2-pentenitrile (*Z*-, 1 g) cooled in ice was added, with stirring, a solution of sodium thioethoxide (2 equ) in methanol. After 1.5 h the reaction mixture was neutralized with acetic acid and diluted with ether. After filtration, the solvent was removed and the residue was distilled under reduced pressure. The v.p.c. analysis of the distillate (0.64 g) showed the presence of both isomers of 4,4-dimethyl-3-thioethoxy-2-pentenitrile (*E*:*Z* ratio = 3:97). Further purification on FFAP at 168° yielded pure *Z* isomer, b.p. 227–228°, $n_D^{20}$ 1.5032.

Anal. Calcd. for $C_9H_5NS$: C, 63.90; H, 8.88. Found: C, 63.94; H, 9.18.

The above *Z* isomer was also prepared by treating 2-bromo-4,4-dimethyl-2-pentenitrile (*E*- or *Z*-) with 2 equ of sodium thioethoxide in methanol.

*4,4-Dimethyl-3-thioethoxy-2-pentenitrile (E-) (2)*

The title compound was most conveniently prepared by heating of the *Z* isomer at 210° for 28 h, the resulting equilibrium mixture containing 30% of the *E* isomer. After purification on FFAP at 168° pure *E* isomer, b.p. 231–232°, $n_D^{18.5}$ 1.5228, was obtained.

Anal. Found: C, 64.20; H, 8.67; N, 8.38.

*Ethyl-4,4-dimethyl-3-methoxy-2-pentenoate (Z-) (7)*

Ethyl 4,4-dimethyl-3-ketopentanoate was prepared by the action of sodium amide in liquid ammonia on a mixture of pinacolone and diethyl carbonate (6). To the ketoester (1.5 g) in methanol (10 ml) was added diazomethane (from 5.2 g of *N*-nitroso-*N*-methylurea) in ether (50 ml). After 6 days the solvent was removed and the residue was distilled under reduced pressure. The resulting distillate (1.5 g) was purified further by v.p.c. on QF1-carbowax at 175° to give ethyl 4,4-dimethyl-3-methoxy-2-pentenoate (*Z*-), b.p. 205–206°, $n_D^{20}$ 1.4490.

Anal. Calcd. for $C_{10}H_{18}O_3$: C, 64.52; H, 9.68. Found: C, 64.27; H, 9.53.

*Ethyl-4,4-dimethyl-3-methoxy-2-pentenoate (E-) (7)*

Irradiation of a 2.5% ether solution of the above *Z* isomer through silica at 2537 Å for 2 h yielded an *E–Z* mixture containing 46% of the *E* isomer (from n.m.r. spectral analysis). The two isomers were only partially separable by v.p.c.

*Ethyl-3-methoxy-4-methyl-2-pentenoate (Z-) (10)*

The title compound was prepared from ethyl isobutyrylacetate and diazomethane in an identical fashion to that described above. Attempts to purify the crude *Z* isomer by v.p.c. on QF1-carbowax at 175° resulted in *cis–trans* isomerization, the collected sample containing both *E* and *Z* isomers in the ratio 7:9.

Anal. Calcd. for $C_9H_{16}O_3$: C, 62.79; H, 9.30. Found: C, 62.41; H, 9.37.

*Ethyl-3-methoxy-4-methyl-2-pentenoate (E-) (10)*

Heating of the above *E–Z* mixture at 210° for 17.6 h yielded a mixture containing approximately 90% of the *E* isomer, 2% of the *Z* isomer, and 8% of the β,γ-isomer ethyl 3-methoxy-4-methyl-3-pentenoate. No attempt was made to purify the *E* isomer.

*Ethyl-2-chloro-4,4-dimethyl-3-ketopentanoate*

To a suspension of phosphorus pentachloride (8.3 g) in benzene (10 ml) was added dropwise over 1.5 h, with stirring, ethyl 4,4-dimethyl-3-ketopentanoate (3.44 g). After 6 days water (10 ml) was added, with cooling, and the reaction mixture was stirred for a further 24 h. Extraction of the aqueous layer with ether yielded a product identical with that obtained from the benzene layer (total yield 2.7 g after distillation under reduced pressure). An analytical sample, b.p. 230–231°, was obtained by v.p.c. on DC 550 at 200°.

Anal. Calcd. for $C_9H_{15}ClO_3$: C, 52.29; H, 7.26. Found: C, 52.20; H, 7.59.

The n.m.r. ($CCl_4$): 8.72 (singlet, 9 protons), 8.69 (triplet, $J$ = 7.0 Hz), 3 protons), 5.73 (quartet, $J$ = 7.0 Hz, two protons), 4.90 (singlet, one proton).

*Methyl 3-Chloro-4,4-dimethyl-2-pentenoate (Z-) (9)*

Active manganese dioxide (38) (20 g) was added to a stirred solution of 3-chloro-4,4-dimethyl-2-pentenal (2 g), sodium cyanide (3.6 g), and acetic acid (2 ml) in methanol (110 ml). After 16.5 h, the manganese dioxide was removed by filtration and the methanol evaporated under reduced pressure. Water and ether were added to the residue and the aqueous layer was then extracted with two further portions of ether. The combined organic

TABLE 5

Pyrolysis of methyl 3-chloro-4-methyl-2-pentenoate (*Z*-) (**11**)

| Time (h) | Chloro ester (*E*-) (**11**) | Chloro-ester (*Z*-) (**11**) | *E*:*Z* ratio | β,γ-Chloro-ester (**22**) | Butenolide **23** |
|---|---|---|---|---|---|
| 0 | 0.0 | 95.0 | 0:95 | 5.0 | 0.0 |
| 92 | 9.5 | 55.6 | 1:5.9 | 22.9 | 12.0 |
| 116 | 8.8 | 50.2 | 1:5.7 | 27.6 | 13.4 |
| 169 | 6.0 | 40.7 | 1:6.8 | 30.4 | 22.9 |
| 265 | 2.6 | 18.65 | 1:7.2 | 25.9 | 52.85 |

extracts were dried over magnesium sulfate and the solvent was then removed. Distillation of the residue under reduced pressure yielded methyl 3-chloro-4,4-dimethyl-2-pentenoate (*Z*-) as a clear liquid (1.9 g, 79%) which was shown by v.p.c. to be 98% pure. An analytical sample, b.p. 203–204°, $n_D^{17}$ 1.4655, was obtained by v.p.c. on QF1-carbowax at 165°.

Anal. Calcd. for $C_8H_{13}ClO_2$: C, 54.41; H, 7.36. Found: C, 54.70; H, 7.54.

*Methyl 3-Chloro-4,4-dimethyl-2-pentenoate (E-) (**9**)*

Irradiation of a 2% ethereal solution of the above *Z* isomer through silica at 2537 Å for 3.5 h gave an *E*–*Z* mixture containing 20% of the *E* isomer. The two isomers were separated by v.p.c. on QF1-carbowax at 165° to give methyl 3-chloro-4,4-dimethyl-2-pentenoate (*E*-), b.p. 178–179°, $n_D^{15}$ 1.4585.

Anal. Found: C, 54.59; H, 7.48.

*Methyl 3-Chloro-4-methyl-2-pentenoate (Z-) (**11**)*

Crude 3-chloro-4-methyl-2-pentenoic acid (13) was converted to the methyl ester by the method of Scheibler and Voss (16). The crude ester was initially purified by distillation under reduced pressure. The distillate was further separated into its components by v.p.c. on Apiezon J at 150°. The first product isolated was a mixture of methyl 3-chloro-4-methyl-2-pentenoate (*E*-) and an unidentified component (see below). The latter appeared to be a decomposition product formed during the v.p.c. separation as it was not present in the original distillate. The second product isolated was a mixture, b.p. 181–182°, of methyl 3-chloro-4-methyl-2-pentenoate (*Z*-) and methyl 3-chloro-4-methyl-3-pentenoate in the ratio 94:6.

Anal. Calcd. for $C_7H_{11}ClO_2$: C, 51.69; H, 6.77. Found: C, 51.76; H, 7.00.

*Pyrolysis of Methyl 3-Chloro-4-methyl-2-pentenoate (Z-)*

*(1)* Pyrolysis of the chloroester (40 ml) at 235° for 88 h gave a dark-brown liquid. Analysis of this liquid by v.p.c. on Apiezon J at 153° indicated the presence of only one non-volatile product. Isolation of this product by v.p.c. yielded a small amount of a clear liquid, the n.m.r. spectrum of which was identical with that recently reported (17) for 5,5-dimethyl-3-butenolide (**23**).

*(2)* The chloroester (4 × 10 μl) was pyrolyzed in sealed Pyrex tubes at 195°, samples being removed at fixed intervals for v.p.c. analysis (Apiezon J, 153°). The results after different time intervals are shown in Table 5.

*Reaction of Methyl 3-Chloro-4,4-dimethyl-2-pentenoate (Z-) with Dimethylamine*

To the title chloroester (1.4 g) in ether (3 ml) was added dimethylamine (10 ml) and the reaction mixture was kept in a screw-cap jar at room temperature for 11 days. The v.p.c. analysis (S.E. 30, 205°) of the crude product indicated starting material (6%) together with two minor products (18%) and one major product (76%). Purification of the major product was effected by distillation under reduced pressure, followed by v.p.c. on SE 30 at 205° to give a white solid, m.p. 45–46° after recrystallization from petroleum ether (b.p. 30–60°). Elemental analysis, n.m.r. and mass spectroscopy indicated the solid to be the dimethylamide of 3-chloro-4,4-dimethyl-2-pentenoic acid (*Z*-).

Anal. Calcd. for $C_9H_{16}ClNO$: C, 56.99; H, 8.44; N, 7.39; Cl, 18.74. Found: C, 57.05; H, 8.57; N, 7.12; Cl, 18.51.

The n.m.r. ($CCl_4$): 8.78 (singlet, 9 protons), 7.09, 7.03 (2 singlets, 3 protons each), 4.07 (singlet, 1 proton).

Methyl 3-chloro-4,4-dimethyl-2-pentenoate (*Z*-) was recovered essentially unchanged after 65 h in boiling diethylamine and 16 h in boiling dimethylformamide (39).

*Methyl 4,4-Dimethyl-3-thioethoxy-2-pentenoate (**8**)*

Treatment of methyl 3-chloro-4,4-dimethyl-2-pentenoate (*Z*-) with sodium thioethoxide (2 equ) in methanol at 0° for 1.5 h gave, after distillation under reduced pressure, a mixture of methyl 4,4-dimethyl-3-thioethoxy-2-pentenoate (*E*- and *Z*-) in the ratio 7:93.

Anal. Calcd. for $C_{18}H_{18}O_2S$: C, 59.40; H, 8.91. Found: C, 59.24; H, 8.89.

A sample of pure *Z* isomer, $n_D^{20}$ 1.4931, was obtained by v.p.c. on FFAP at 165°.

Irradiation of a 2% solution of the above mixture of isomers through silica at 2537 Å for 7 h only increased the amount of *E* isomer to 11%. A mixture containing 20–25% of the *E* isomer was, however, obtained by treating methyl 3-chloro-4,4-dimethyl-2-pentenoate (*E*-) with 1.1 equ of sodium thioethoxide in methanol.

*Methyl 3-Chlorocrotonate (**13**)*

Methylation of 3-chlorocrotonic acid (*E*-) with an ethereal solution of diazomethane yielded methyl 3-chlorocrotonate (*E*-) in 90% yield. The corresponding *Z* isomer was prepared by irradiation of an ethereal solution of the *E* isomer.

A fellowship to D.V.G. and financial support from NRCC are gratefully acknowledged.

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