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CYCLOBUTENE DERIVATIVES FROM ADDITION OF α-HALOGENO ELECTROPHILIC OLEFINS TO YNAMINES[a]

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Abstract—Reaction of α-chloro- and α-bromoacrylonitrile, α-chloro- and α-bromoacrylic esters with diethylaminomethylacethylene and diethylaminophenylacetylene leads to cyclobutene derivatives of type **3** in high yields. Reaction of *E*- and *Z*-α-bromocrotononitrile takes place in a stereospecific way. A mechanistic scheme for a reaction sequence of cycloaddition and subsequent allylic isomerization is formulated on the basis of stereochemical and kinetic data. The halogen substituents of the cyclobutene derivatives are stereospecifically displaced by the OH or the OEt groups in solvolytic reactions, with retention of configuration. Methylenecyclobutene derivatives are obtained from the 3-methylcyclobutenes by elimination of hydrogen halide with potassium t-butoxide. Hydrolysis of the enamine function of the cyclobutenes leads to the corresponding cyclobutanones. The configurations of four pairs of *cis-trans* isomeric cyclobutenes have been established by ^{1}H- and ^{13}C-NMR spectroscopy.

INTRODUCTION

The addition of electrophilic olefins to the electron-rich triple bond of ynamines constitutes a route to cyclobutene derivatives. The addition has been studied with α,β-unsaturated ketones, aldehydes and esters.[1] With this type of olefins, however, the 1,4-addition mode leading to γ-pyran derivatives is strongly favoured. Only when 1,4-addition is not possible, as in the case of cyclopentenone, cyclobutene derivatives are formed in good yields. Recently it has been shown that cyclobutenes may be obtained in fair yields from addition of α,β-unsaturated nitriles to an ynamine in the presence of an electrophilic catalyst.[2] Ynamine chemistry has been reviewed by Viehe.[3]

In continuation of our work on the reaction of α-halogeno electrophilic olefins with enamines,[4] we have now studied this reaction with ynamines.‡ This reaction leads stereospecifically to cyclobutene derivatives in high yields (Section A). The chemistry of the polyfunctional cyclobutenes produced has been investigated with respect to displacement of the halogen substituents in solvolytic reactions (Section B) methylenecyclobutene forming elimination of hydrogen halide (Section C) and hydrolysis of the enamine function to produce cyclobutanones (Section D). Solution of stereochemical problems by NMR is separately discussed in Section E.

RESULTS AND DISCUSSION

Section A

Additions. The addition of equimolar amounts of the olefins **1a–1e** (Scheme 1) to diethylaminomethylacetylene in ether solution gave rise to smooth exothermic reactions. NMR and IR examination of the crude products obtained after removal of the solvent *in vacuo* revealed that very clean reactions had taken place, producing the cyclobutenes **3a–3e**. The cyclobutene structures **3** follow from elemental analyses and spectral data. The absence of olefinic protons in the NMR immediately rules out open-chain diene structures. Besides signals due to the diethylamino group or ester group each compound shows a singlet (3H) near 1·9δ and an AB-quartet (2H) centered near 2·8δ (J = 10 Hz). This is consistent with cyclobutene structures **2** or **3**. The UV spectra show strong maxima in the range 280–300 nm. In the IR **3a** and **3b** show *very* strong nitrile bands at 2180–70 cm^{-1} and very strong C–C double bond bands at 1640 cm^{-1}. Compounds **3c–3e** show CO bands at 1690–80 cm^{-1} and C–C double bond bands at 1625–15 cm^{-1} (unlike what is usually found the C–C double bond bands are stronger than

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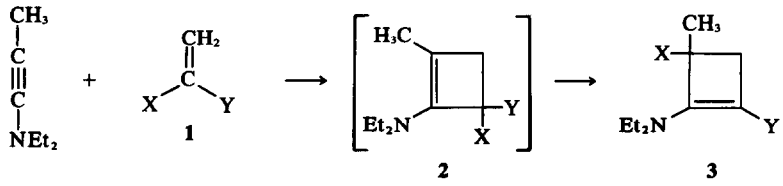
‡After the present work had been achieved there appeared a paper,[5] with the object of synthesising cyclobutadienes, in which this reaction was reported, including the description of compounds **3a** and **3b**.

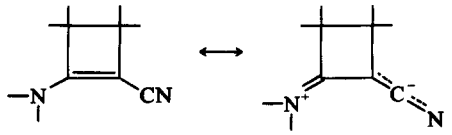


	X	Y	% yield
a:	Cl	CN	88
b:	Br	CN	81
c:	Cl	CO_2Me	89
d:	Cl	CO_2Et	85
e:	Br	CO_2Me	80

SCHEME 1

the CO bands). These data indicate the structure element N–C=C–CN(CO_2R), present in the structures 3.

The cyclobutenes 3 presumably are the results of cycloaddition reactions followed by allylic isomerizations. The primary products from cycloaddition, cyclobutenes **2a–2e**, could not be detected. In all cases we have examined the crude products, obtained after removal of the solvent at low temperature, by IR and NMR. Further, IR examination of an incompletely reacted mixture of the ynamine and olefin **1d**, kept at ice-bath temperature in ether solution, showed the presence of only one product, cyclobutene **3d**. Thus, the allylic isomerizations of 2 to 3 take place readily. Obviously, the driving force is the generation of the conjugated systems of cyclobutenes 3. Conjugation of this type, as in **A**, involving electron donor and electron acceptor groups (push-pull system), was predicted by Roberts[6] to stabilize unsaturated systems. The correctness of this prediction has been unmistakably demonstrated by the synthesis of stable (room temperature), crystalline, push-pull stabilized *o*-quinodimethanes[7] and cyclobutadienes.[8] In the latter case two pairs of push-pull substituents appear to be a condition for stability of this order.[9] The cyclobutenes 3 are stabilized not only relative to the cyclobutenes 2 but also relative to the corresponding open-chain butadienes. In this connection it must be noticed that the general cyclobutene-butadiene equilibrium usually favours the butadiene.[10] None of the cyclobutenes described in this work showed any detectable content of the corresponding butadiene (NMR, CCl_4, ~35°). The stability of the push-pull stabilized olefinic system may be ascribed to an appreciable contribution of a dipolar resonance form, like **B**.



A **B**

Characteristic spectroscopic properties support this description. Certain IR and UV data have already been mentioned. In the NMR (CCl_4, ~35°) the methylene groups of the diethylamino group are non-equivalent, appearing as two sharp quartets in a number of cases. Undoubtedly this is caused by restricted rotation around the carbon-nitrogen bond due to partial double bond character of that bond. The non-equivalency is shown by all systems involving an ester group, but not by all of the nitriles, probably reflecting the larger conjugative interaction in the former systems (steric effects must also be taken in consideration). The phenomenon has been much studied with both open-chain and cyclic compounds.[11] In the carbon-13 NMR (Section E) a very large difference (~86 ppm) between the chemical shifts of C-1 and C-2 of the cyclobutenes **3f** and **3g** also indicates a considerable polarization of the double bond, consistent with an appreciable contribution of resonance structure **B**.

In order to confirm the presumed reaction sequence of cycloaddition and subsequent allylic isomerization, and to obtain more information about it, it was decided to investigate the reaction with a pair of geometrically isomeric olefins. On the basis of the stereochemical and kinetic results of the addition reactions and of solvolytic reactions of the products it became possible to formulate a consistent mechanistic ground for the reaction course anticipated, as outlined in the following. Initially *E* and *Z* methyl α-bromocrotonate were selected for study. However, the addition of the *Z* isomer to diethylaminomethylacetylene was sluggish and unclean; γ-pyran formation from 1,4-addition is a possibility. The *E* isomer was not tried. Instead *E*- and *Z*-α-bromocrotononitrile were chosen, in the following designated *cis* and *trans*, respectively. These olefins are known,[12] but have not been assigned to their geometrical configurations. On the basis of NMR data (Section E) we have made these assignments. This pair of olefins proved suitable to our purpose, although it was difficult to obtain the pure isomers in sufficient quantities.

As expected, for steric reasons, the α-bromo-

crotononitriles reacted much slower than α-bromoacrylonitrile and the other olefins unsubstituted at the β-carbon. The addition of these olefins turned out to be highly stereospecific, Table 1 (structures of products are shown in Scheme 2).

Table 1 shows that the stereospecificity of the addition of the *cis* isomer is less in the more polar solvent acetonitrile. Incomplete stereospecificity is probably not due to isomerizations in the reaction mixtures of the olefins or the products. Thus, heating of the olefins in acetonitrile solution at reflux temperature for 2 hs. did not effect measurable isomerization.* Likewise, no change in isomer ratio of the product mixtures was observed after 1 h heating in acetonitrile solution at reflux temperature. (This treatment, however, led to some decomposition, whereby an ether insoluble material was formed, undoubtedly as a result of elimination of hydrogen bromide followed by resinification, see Section C).

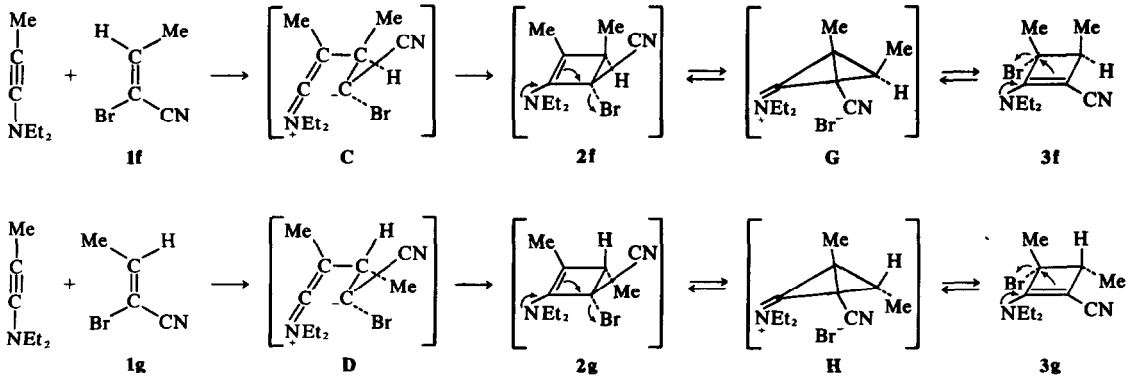
Anticipating a completely stereospecific allylic isomerization reaction (see below) the loss of stereospecificity must take place in the primary addition step. Some knowledge of the nature of this step is gained by considering the dependence of reaction rates on solvent polarity. The addition of *trans*-α-bromocrotononitrile was determined to be 57 times faster in acetonitrile solution than in ether solution, at 20°, Fig 1. Such a large solvent effect on reaction rates points to a polar mechanism. Consequently, the zwitter-ions **C** and **D** (representing two different conformations of the same species) are suggested to be intermediates in the addition reactions. It appears likely that in a polar solvent the lifetime of these zwitter-ions is sufficiently increased to permit rotation about the original olefinic double bond, explaining the incomplete stereospecificity of the addition of the *cis* olefin in acetonitrile solution. In the related field of cycloaddition reactions of electrophilic olefins and electron-rich olefins (vinyl ethers and thioethers) analogous zwitter-ionic intermediates have been formulated. In a number of cases cyclobutane formation was found to take place with complete stereospecificity over a wide range of solvent polarity, but in other cases, involving more stable zwitter-ion intermediates, stereospecificity was not maintained.[13]

*It has note been excluded that the olefins are isomerized by the ynamine, acting as a tertiary amine, in a nucleophilic isomerization process (cf., Ref 15 p. 565).

Table 1. Addition of *cis*- and *trans*-α-bromocrotonitrile to diethylaminomethylacetylene

Solvent	Temp	Isomer (geometrical purity %, GLC)	Product distribution % (NMR) 3f	3g
Ether	Reflux (~40°)	*cis* (95–96)	98	2[a]
		trans (99–100)	5	95
Acetonitrile	50°	*cis* (99–100)	87	13
		trans (99–100)	5	95

[a] This unproportional small amount is explained by combination of two facts, 1. the *cis* olefin reacts about twice as fast as the *trans* isomer, 2. olefin is in excess at the end of the reaction when equimolar amounts of reactants are used.



SCHEME 2

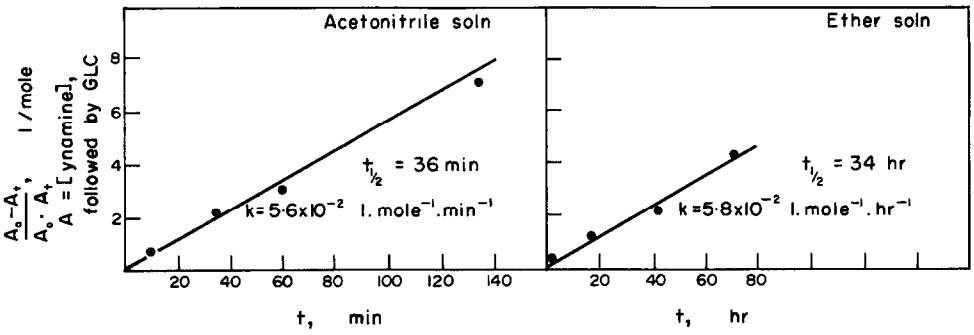
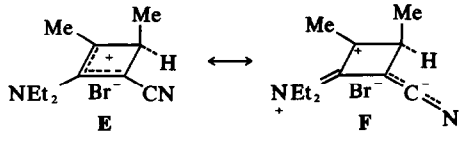


Fig 1. Second-order plots for the addition of *trans*-α-bromocrotonitrile to diethylaminomethylacetylene. 0·5 mole/l initial concentration of both reactants.

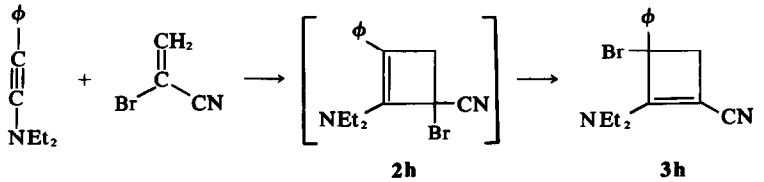
The stereochemistry of the overall reaction requires the allylic isomerization of the primary formed cyclobutenes **2f** and **2g** to take place stereospecifically with retention of the position of the halogen atom relative to the cyclobutene ring. This does not in itself present an unusual situation. For example, the allylic isomerizations (racemizations) of optically active *cis*- and *trans*-5-methyl-2-cyclohexenyl chloride occur without *cis-trans* isomerizations.[14] The Winstein interpretation of this is based on ion-pair intermediates involving cyclohexenyl cations. (For a discussion of allylic reactions see Ref 15). Analogous with this one could then suggest the isomerization of **2f** to pass through the ion-pair **E**, involving a cyclobutenyl cation, although this cation must be destabilized by the unfavourable charge-distribution caused by the "push-pull" effect, as shown in resonance structure **F**.



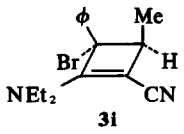
However, if it is assumed that allylic isomerization and solvolysis reactions involve a common intermediate the cyclobutenyl cation must be rejected. Ethanolysis and hydrolysis of the cyclobutenyl bromides **3f** and **3g** proceed stereospecifically with *retention* of configuration (Section B), which cannot be accounted for by an intermediate cyclobutenyl cation. (In contrast, ethanolysis of both of the above mentioned cyclohexenyl chlorides led stereoselectively to the corresponding *trans* ethyl ether, as expected from a cyclohexenyl cation intermediate). Instead we suggest the bicyclobutylideneammonium bromides **G** and **H** (Scheme 2) to be intermediates in isomerization and solvolysis of **3f** and **3g**, respectively. The formation of these immonium ions represents intramolecular enamine alkylations and may conceivably proceed stereospecifically as depicted in Scheme 2. Nucleophilic attack at C-1 or C-3 of the intermediates must take place from the *endo* side, securing retention of configuration in isomerization and solvolysis. Further, these intermediates are shown to fit kinetic data from solvolysis and elimination reactions (Sections B, C). Bicyclobutane chemistry has been reviewed by Wiberg.[16]

In an attempt to isolate a primary addition product of type **2** we carried out the addition of α-bromoacrylonitrile to diethylaminophenylacetylene (Scheme 3). In the primary addition product, **2h**, the olefinic double bond is conjugated with the phenyl group which must result in greater stability of this isomer. Yet, the isomerized cyclobutenyl bromide **3h** was the sole product, isolated as a crystalline compound in 85% yield.

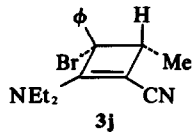
Similarly, addition of *cis*- and *trans*-α-bromocrotononitrile to the same ynamine led directly, and stereospecifically, to **3i** and **3j**, respectively.



SCHEME 3



3i

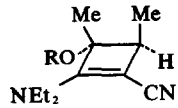


3j

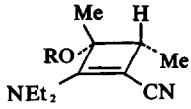
Section B

Solvolysis reactions. The cyclobutenyl halides, **3**, are easily transformed to the corresponding ethoxy and hydroxy compounds by treatment with absolute ethanol and 90% aqueous acetone, respectively, in nearly quantitative yields. The reactions were run at reflux temperature, with two equivalents triethylamine added to trap the liberated hydrogen halide. (Use of stronger base resulted in pronounced elimination, see below). Under these conditions hydrolysis of enamine function (Section B) did not take place.

The solvolytic displacement reactions proceed stereospecifically, with retention of configuration, as seen from Table 2.



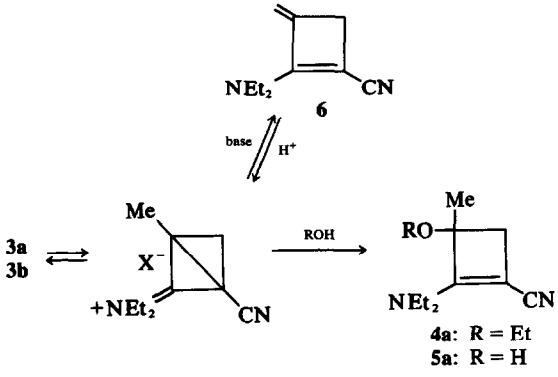
R = Et: **4f**
R = H: **5f**



4g
5g

As already discussed in the preceding section the stereo-chemical course is governed by intermediate bicyclobutylideneammonium ions, **G** and **H** (Scheme 2). Incomplete stereospecificity, barely significant in relation to the NMR-method of isomer ration determination, can be referred to a competing, non-stereospecific, elimination-addition pathway for substitution. As described in the next section the isomeric bromides **3f** and **3g** upon treatment with a strong, non-nucleophilic, base (t-butoxide) eliminate hydrogen bromide, most likely also *via* the intermediates **G** and **H**, to give the methylenecyclobutene **7**. This elimination product was not detected in the solvolysis reactions, but a few procent of the methylenecyclobutene **6** was shown to accumulate in the early stages of ethanolysis of both chloride **3a** and bromide **3b** (Scheme 4). In a control experiment, under the conditions of the ethanolysis reaction (one equivalent of triethylammonium bromide added), **6** was shown to add ethanol slowly,* leading to the ether **4a**. Ethanolysis of **3a** and **3b** with two equivalents of sodium ethoxide added produced considerable amounts of the methylenecyclobutene **6**. Clearly, under such strongly basic conditions elimination is much more favoured, and practically irreversible.

A preliminary kinetic analysis indicates the solvolysis reactions to involve a rapid, reversible formation of the intermediate bicyclobutylideneammonium ions followed by a slower attack by the solvent. Under the standard conditions, 0·33 M solutions of substrate in absolute ethanol or 90% aqueous acetone at reflux temperature with two equivalents triethylamine added, the first-order logarithmic plots were linear from 0 to more than 90% conversion, (Fig 2). Reaction half-time values are given in Table 3. On the other hand, addition of two equivalents sodium ethoxide instead of triethylamine led to a considerable increase in reaction rate of ethanolysis of the chloride **3a**, a factor of at least 3 on initial rate, from which it is inferred that the kinetics observed under the standard conditions is of the pseudo-first-order type.



4a: R = Et
5a: R = H

SCHEME 4

*$t_{1/2}$ ~1 h.

Table 2. Solvolytic reactions of the *cis-trans* isomeric bromides **3f** and **3g**. Experimental conditions, see text.

Reaction	Isomer (geometrical purity %)	Product distribution % (NMR) 4f	4g	5f	5g
Ethanolysis	*cis* (≥98)	~100	~0		
	trans (95)	8	92		
Hydrolysis	*cis* (85)			82	18
	trans (87)			20	80

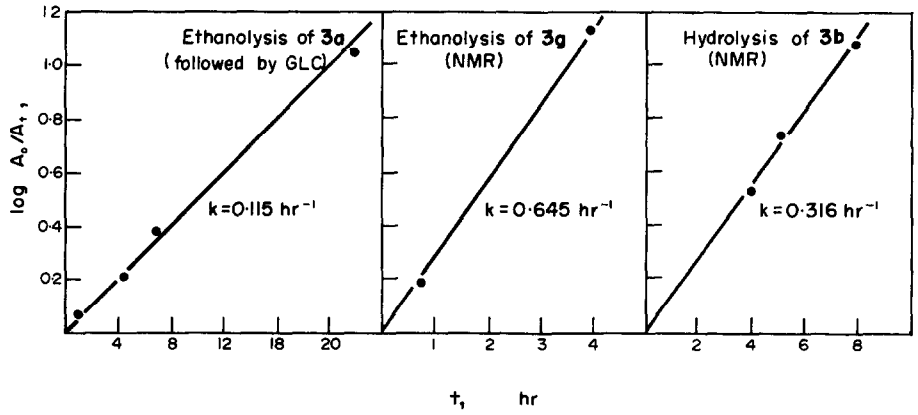


Fig 2. First-order logarithmic plots for solvolytic reactions of cyclobutenyl halides 3.

Table 3. Half-times of ethanolysis and hydrolysis of cyclobutenyl halides 3. Experimental conditions, see text.

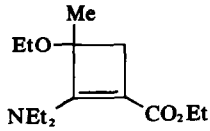
	Ethanolysis $t_{\frac{1}{2}}$, min	Hydrolysis $t_{\frac{1}{2}}$, hr
3a	360	~37[d]
3b	~16[a]	2.2
3d	≤25[b]	
3f	≤5[c]	
3g	64	

[a] 93% conversion in 1 hr. (GLC).
[b] Reaction complete within 150 min.
[c] Reaction complete within 30 min.
[d] 75% conversion in 74 hr. (NMR, GLC).

It is interesting to compare the rates of ethanolysis of the bromides **3b**, **3f**, and **3g** in relation to the mechanistic assumptions involving bicyclobutylideneammonium ion intermediates reacting by nucleophilic attack at C-3 from the *endo* side. Since the *endo* side of the intermediate **H** (Scheme 2) from the *trans* bromide **3g** is sterically shielded by the *endo* 4-Me group it is expected that the *trans* isomer **3g** reacts slower than the *cis* isomer **3f**, whose intermediate **G** has the 4-Me group in *exo* position, and also slower than **3b**, which is unsubstituted at C-4, whereas it is more difficult to predict that the *cis* isomer **3f** reacts faster than **3b**. It appears very plausible, however, that this is due to steric acceleration arising from a relief of steric strain between the two *cis* Me groups of **3f** on passing to the intermediate **G**.

Table 3. shows that the carbethoxy group increases the ractivity relative to the cyano group. Thus, ethanolysis of the chloride **3d**, leading to **4d**, is at least 14 times faster than ethanolysis of the corresponding nitrile **3a**.

Possibly this is caused by greater ractivity of the intermediate, in which the stronger electron-



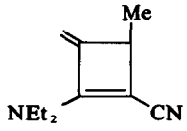
4d

withdrawing carbethoxy group weakens the C-1 – C-3 cross-ring bond more than the cyano group does, making it more susceptible to nucleophilic attack at C-3. But the same argument means a smaller concentration of the intermediate in the equilibrium with substrate, wherefore the effect seems unpredictable.

Section C

Eliminations. Treatment of the bromide **3b** in ether solution at room temperature with excess potassium t-butoxide led to the methylenecyclobutene **6** in quantitative yield. The same product was obtained from the chloride **3a**, but at a much slower rate. The *cis-trans* isomeric bromides **3f** and **3g** produced the common elimination product **7**, likewise in quantitative yield. Because of heterogeneous reaction conditions, 0·33 M solutions of substrate in dry ether at 20° with two equivalents solid potassium t-butoxide added, the elimination reactions were not expected to show a definite kinetic order, but initial reaction half-times of about 5, 8 and 17 hr of the bromides **3b**, **3f**, and **3g**, respectively, were estimated from the non-linear first-order logarithmic plots. The *cis* isomer **3f**, then, reacts faster than the *trans* isomer **3g** (easily demonstrated by following the elimination reaction with a mixture of the isomers). Considering an ordinary E2 mechanism the opposite would be predicted for steric reasons, whereas the fact may be explained, but not safely predicted, by assuming the eliminations to involve the intermediates **G** and **H** (Scheme 2) also. As discussed in the preceding section the formation of **G** very likely

is subject to steric acceleration, but steric retardation in the abstraction of the proton from the intermediate must also be considered. Apparently the steric assistance is the decisive factor for the relative reaction rates of **3f** and **3g**. Apart from the kinetic argument for this two-step mechanism it should also be noticed that elimination was observed in solvolytic reactions where only weak bases were present.



7

The dienes **6** and **7** are rather thermally labile. Samples thoroughly purified by molecular distillation can be kept in the refrigerator (−20°) for only a few weeks. Heating to about 100° results in very rapid polymerization. Treatment of the dienes with dilute hydrochloric acid causes immediate resinification, whereas they are unaffected by aqueous base. In these respects the dienes strongly resemble the parent compound, methylenecyclobutene.[17]

The 3-phenyl bromide **3h** did not eliminate hydrogen bromide (producing a cyclobutadiene) on treatment with potassium t-butoxide. The substrate was quantitatively recovered.

Section D

Hydrolysis of the enamine function. The cyclobutenes **3**, being enamines, are readily hydrolyzed to the corresponding cyclobutanones by treatment with dilute hydrochloric acid at room temperature. The products, **8** (Scheme 5), were obtained in small yields, however, because this type of cyclobutanones, substituted by electron-acceptor groups at the α-position, rapidly undergoes ring-opening in both acidic and basic aqueous medium leading to the open-chain carboxylic acids,[18] **9**. In a number of experiments the best isolated yield of **8a** was 36%. The yield was not improved by using a weaker acid, ammonium chloride, or by carrying out the hydrolysis in a two phase solvent system of water and ether. The NMR indicated **8a** to comprise *cis-trans* isomers in the ratio 2:3. The cyclobutanone **8c** was not isolated, and **8d** was obtained in less than 10% yield.

Section E

Assignments of geometrical configurations by ^{1}H- *and* ^{13}C-NMR *chemical shifts.* It is often possible to assign *cis-trans* isomeric compounds to their geometrical configurations by NMR spectroscopy when both isomers are at hand. Further confirmation may be obtained by comparison with reference substances.

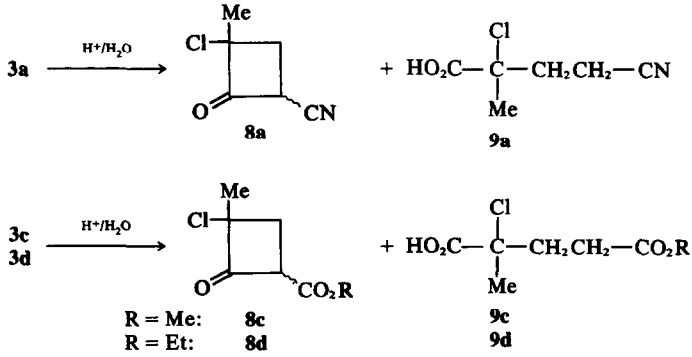
The first problem we had to settle was to assign the isomeric α-bromocrotononitriles to their geometrical configurations. From the parent crotononitriles it is known that the cyano group deshields both β-*cis* hydrogens and β-*cis* Me groups relative to their *trans* counterparts,[19] Table 4 (data from own measurements). As expected this effect gave rise to similar chemical shift differences in the α-bromocrotononitriles, and assignment of configurations has been made in accordance with this, as shown in Table 4.

The configurations of the *cis-trans* isomeric 3,4-dimethylcyclobutenes follow from comparison of the chemical shifts of the 3-Me groups with the shifts of the 3-Me groups of the corresponding 3-methylcyclobutenes, unsubstituted at C-4. As shown in Table 5 we consider three sets of

Table 4. Chemical shifts[a] of β-hydrogen and β-methyl of crotononitriles

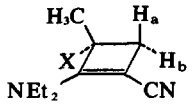
	β-H		β-CH_3	
	cis	*trans*	*cis*	*trans*
Crotononitrile	6·56	6·66	2·03	1·93
α-Bromocrotononitrile	6·81	6·96	2·02	1·95

[a] δ units relative to tetramethylsilane, CCl_4 soln.

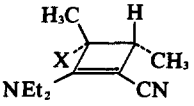


SCHEME 5

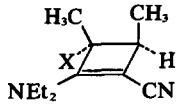
Table 5. Chemical shift data[a] of 3-methyl- and 3,4-dimethylcyclobutenes



"monomethyl"



trans-3,4-dimethyl



cis-3,4-dimethyl

	"monomethyl"	*trans*-3,4-dimethyl	*cis*-3,4-dimethyl
X = Br:	**3b**	**3g**	**3f**
X = EtO:	**4a**	**4g**	**4f**
X = HO:	**5a**	**5g**	**5f**

	3-CH_3			4-CH_3		4-H			
								"monomethyl"	
X	"monomethyl"	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	H_a	H_b
Br	1·96	1·97	1·82	1·28	1·15	2·64	3·28	2·72	3·00
EtO	1·48	1·48	1·31	1·15	1·08	2·58	2·90	2·20	2·68
HO	1·45	1·42	1·27	1·08	1·07	2·58	2·68	2·45	

[a] δ units relative to tetramethylsilane, CCl_4 soln.

cyclobutenes, i.e. three bromides, three ethoxy compounds, and three hydroxy compounds. In each set one of the 3,4-dimethyl isomers shows the 3-Me signal at the same position as the 3-methylcyclobutene. In that isomer the 3-Me group must be situated like the 3-Me group of the monomethylcyclobutene, i.e. *cis* to a H atom, and that isomer must be the *trans*. In the *cis* isomer the 3-Me signal is shifted 0·15–0·17 ppm upfield, reflecting the shielding effect of the *cis* 4-Me group. This shielding effect is known from other cyclobutenes.[20,21] For example, the 3- and 4-Me groups of 1,2,3,4-tetramethylcyclobutene resonate 0·13 ppm at higher field in the *cis* isomer than in the *trans*.[21]

Table 5 also includes the chemical shifts of the 4-Me groups and the 4-hydrogens. It is seen that the 4-hydrogens of the 3,4-dimethylcyclobutenes resonate at highest field when *cis* to the 3-Me group. This relationship makes it possible to identify the components of the AB-quartets arising from the 4-methylene groups of the 3-methylcyclobutenes, as has been done in the last entry of Table 5. The AB-quartets of all of the 3-methylcyclobutenes in this work (8 compounds), except for the hydroxy derivative **5a** which shows a degenerate AB pattern, are asymmetric. The H_b-part shows reduced peak heights and sign of additional splitting from long-range coupling to the 3-Me group.

The configurations of the 3-phenylcyclobutenes **3i** and **3j** also follow from chemical shifts. The 4-Me groups of **3i** and **3j** are observed at 0·63δ and 0·93δ, respectively. The strong shielding of the former Me group must be due to the adjacent *cis*-phenyl group.

Finally, we felt it of interest to test the stereochemical deductions (the correctness of which we did not doubt) with C-13 NMR spectroscopy, and at the same time obtain information about the enaminonitrile "push-pull" system.* The *cis-trans* isomeric bromides **3f** and **3g** were selected for study. Table 6 gives chemical shift data. Peak assignments were made with the aid of off-resonance decoupling, except for C-1, C-2 and the nitrile carbon, the assignments of which follow from the characteristic charge-distribution of the "push-pull" system (*cf* resonance structure **B**, Section A, and data of a reference compound given below), and literature data on nitrile carbon shifts.[22]

As to the stereochemistry if suffice to consider the chemical shift of the 3-Me group, which appear 4·5 ppm at higher field in the *cis* isomer than in the *trans*, in agreement with the steric shift effect.

Table 6. ^{13}C-NMR chemical shift data[a] of *cis-trans* isomeric 3,4-dimethylcyclobutenes

	3f	**3g**
C-1	71·4	70·7
C-2	157·3	157·3
C-3	61·2	65·9
C-4	49·6	46·1
3-CH_3	25·3	29·8
4-CH_3	14·9	19·3
N–$\underline{CH_2}$–	42·8	42·6
N–CH_2–$\underline{CH_3}$	14·0	13·6
–$\underline{C}\equiv N$	116·2	116·6

[a] δ units relative to tetramethylsilane; $(CD_3)_2CO$, CS_2(2.5:1) soln.

*To our knowledge enamines have not been subject to a systematic C-13 NMR study. Work in this field is now in progress (Ref 23).

Carbon atoms that are sterically pertubed appear at higher field than similar carbons that are not sterically crowded.[22] The same holds for the 4-Me group, but here we are faced with the problem of judging the effect of a bromine substituent relative to hydrogen. The data in Table 6 indicate that bromine behaves like hydrogen with respect to the steric shift effect. It is interesting to notice that this also applies to ^{1}H-shielding effects, as seen in Table 5, second entry, and Table 4. The ring-carbons C-3 and C-4 are also quite sensitive to the geometry at these carbons, but rationalizations are not clear to us.

The large difference, ~86 ppm, between C-1 and C-2 indicates a considerable polarization of the double bond, consistent with the "push-pull" interaction of the substituents. The difference is larger than expected for both an α,β-unsaturated nitrile and a simple enamine. We measured the shifts of the acrylonitrile carbons, $C_\alpha = 108{\cdot}0$, $C_\beta = 137{\cdot}4$ and —CN = 117·1. The enamine 1-N-pyrrolidinocyclohexene[23] showed C-1 = 142·4 and C-2 = 93·2. (The nitrile carbon is remarkably insensitive to substitution (see also Ref 22, p. 129)). The conjugated enamine ethyl β-dimethylamino-crotonate[23] also exhibited a large shift difference, ~77 ppm, between the double bond carbons, $C_\alpha = 84{\cdot}5$, $C_\beta = 161{\cdot}1$.

EXPERIMENTAL

All m.ps are corrected; b.ps are uncorrected.

IR spectra were obtained with the Beckman IR 18A.

UV spectra were taken with a Bausch & Lomb spectronic 505.

^{1}H-NMR spectra were measured with a Varian A-60 instrument, 20% v/v solutions in CCl_4 with signals reported relative to internal TMS, δ 0·00 ppm; coupling constants given in Hz.

The ^{13}C-NMR spectra were determined on the Varian XL-100-15.

The mass spectrum (**3h**) was recorded on a AEI MS-902 spectrometer using the direct inlet at an electron energy of 70 eV and an ion source temperature of 120°.

GLC analyses were carried out on an F & M Model 810 equipped with a flame ionization detector, using a 6 ft × 0·125 in of 10% SE-30 on Chromosorb W Column, unless otherwise stated.

We are indebted to Løvens Kemiske Fabrik, Copenhagen, and Novo A/S, Copenhagen, for the microanalyses.

Starting materials and reference compounds. 1-diethylamino-propyne is commercially available (Fluka) and was used without further purification.

Diethylaminophenylacetylene[24] was prepared from chlorophenylacetylene and lithium diethylamide similar to the procedure developed by Viehe[25] for other ynamines.

α-Chloroacrylonitrile (**1a**) was generously supplied by Münzing and Co., Heilbronn, Germany, and was used without further purification.

Compounds **1b**,[26] **1c**,[27] **1d**,[28] **1e**,[27] and *trans* (*Z*) methyl α-bromocrotonate[29] were obtained by halogen addition-dehydrohalogenation procedures according to known methods.

cis (*Z*)- and *trans* (*E*)-Crotonitrile were easily obtained in more than 99% geometrical purity (GLC, carbowax 20 M) by distillation of a nearly equal mixture of the isomers (Fluka) on a spinning band column. The *cis* isomer had b.p. 101°/~760 mm Hg. NMR: 2·03 (dd, 3H, J = 6·9, 1·6), 5·32 (dq, 1H, J = 10·9, 1·6), 6·56 (dq, 1H, J = 10·9, 6·9). The *trans* isomer had b.p. 117°/~760 mm Hg. NMR: 1·93 (dd, 3H, J = 6·8, 1·8), 5·31 (dq, 1H, J = 16·1, 1·8), 6·66 (dq, 1H, J = 16·1, 6·8).

cis (*E*)- and *trans* (*Z*)-α-Bromocrotonitrile[12] were obtained as a nearly equal mixture of the isomers in an overall yield of 56% from crotonitrile (mixture of isomers) by the bromine addition-dehydrobromination procedure, using piperidine in the elimination step, b.p. 40–44°/13 mm Hg. The pure isomers (>99%; GLC, FFAP) were isolated by distillation on a spinning band column. The *cis* isomer had b.p. 79°/83 mm Hg, the *trans* isomer b.p. 86°/83 mm Hg. NMR chemical shifts are given in Table 4; the vicinal coupling constants are 7·2 and 6·8 in the *cis* and *trans* isomer, respectively.

General procedure for the preparation of cyclobutenes **3a-3e**. 1-Diethylaminopropyne (11·1 g; 0·1 mole) were dissolved in dry ether at room temp. The olefin, **1a–1e**, (0·1 mole) was added all at once (dropwise addition did not improve yields or purity of the products). The exothermic reaction ceased in about 10 min, and the solvent was stripped off *in vacuo*. Distillation *in vacuo* of the residual liquids afforded analytical pure products in the yields given in Scheme 1.

3 - *Chloro* - 2 - *diethylamino* - 3 - *methyl* - 1 - *cyclobutenecarbonitrile*, **3a**. B.p. 98–100°/0·3 mm Hg; IR: ν_{max}^{liq} 2180, 1640 cm^{-1}; UV: λ_{max}^{EtOH} 285 nm; NMR: 1·24 (t, 6H, J = 7), 1·84 (s, 3H), 2·68 (d, 1H, J = 10), 2·85 (d, 1H, J = 10), 3·37 (q, 4H, J = 7). Found: C, 60·70; H, 7·98; N, 14·31; Cl, 17·67. $C_{10}H_{15}N_2Cl$ requires: C, 60·44; H, 7·62; N, 14·10; Cl, 17·84%.

3 - *Bromo* - 2 - *diethylamino* - 3 - *methyl* - 1 - *cyclobutenecarbonitrile*, **3b**. B.p. 100–120°/0·2–0·4 mm Hg, with some decomposition, not affecting the purity of the distillate; IR: ν_{max}^{liq} 2170, 1640 cm^{-1}; UV: λ_{max}^{EtOH} 296 nm; NMR: Table 5 and 1·23 (t, 6H, J = 7), 3·37 (q, 4H, J = 7), J_{AB} = 10. Found: C, 49·31; H, 6·21; N, 11·53; Br, 33·13. $C_{10}H_{15}N_2Br$ requires: C, 49·40; H, 6·22; N, 11·52; Br, 32·86%.

Methyl 3 - *chloro* - 2 - *diethylamino* - 3 - *methyl* - 1 - *cyclobutenecarboxylate*, **3c**. B.p. 84–88°/0·3 mm Hg; IR: ν_{max}^{liq} 1690, 1825 cm^{-1}; UV: λ_{max}^{EtOH} 303 nm; NMR: 1·18 (t, 6H, J = 7), 1·81 (s, 3H), 2·55 (d, 1H, J = 10), 2·75 (d, 1H, J = 10), 3·54 (s, 3H), 3·57 (q, 2H, J = 7), 3·62 (q, 2H, J = 7). Found: C, 56·61; H, 7·87; N, 6·10; Cl, 15·80. $C_{11}H_{18}NClO_2$ requires: C, 57·02; H, 7·83; N, 6·05; Cl, 15·30%.

Ethyl 3 - *chloro* - 2 - *diethylamino* - 3 - *methyl* - 1 - *cyclobutenecarboxylate*, **3d**. B.p. 80–82°/0·1 mm Hg; IR: ν_{max}^{liq} 1680, 1615 cm^{-1}; UV: λ_{max}^{EtOH} 303 nm; NMR: 1·18 (t, 6H, J = 7), 1·21 (t, 3H, J = 7), 1·82 (s, 3H), 2·55 (d, 1H, J = 10), 2·75 (d, 1H, J = 10), 3·56 (q, 2H, J = 7), 3·62 (q, 2H, J = 7), 4·01 (q, 2H, J = 7). Found: C, 58·39; H, 8·11; N, 5·74; Cl, 14·78. $C_{12}H_{20}NClO_2$ requires: C, 58·65; H, 8·20; N, 5·70; Cl, 14·43%.

Methyl 3 - *bromo* - 2 - *diethylamino* - 3 - *methyl* - 1 - *cyclobutenecarboxylate*, **3e**. Distillation of this compound in oil-pump *vacuum* (~0·1 mm Hg) resulted in considerable decomposition, whereas molecular distillation (~10^{-4} mm Hg/oil-bath temp 60°) was carried through without loss; IR: ν_{max}^{liq} 1690, 1625 cm^{-1}; UV: λ_{max}^{EtOH} 302 nm; NMR: 1·18 (t, 6H, J = 7), 1·95 (s, 3H), 2·60 (d, 1H J = 10), 2·93 (d, 1H, J = 10), 3·55 (q, 2H, J = 7), 3·56 (s

3H), 3·65 (q, 2H, J = 7). Found: C, 48·07; H, 6·57; N, 5·09; Br, 28·43. $C_{11}H_{18}NBrO_2$ requires: C, 47·84; H, 6·57; N, 5·07; Br. 28·93%.

cis - 3 - *Bromo* - 2 - *diethylamino* - 3,4 - *dimethyl* - 1 - *cyclobutenecarbonitrile*, **3f**. 1-Diethylaminopropyne (1·11 g, 0·01 mole) were dissolved in 10 ml dry ether, and *cis*-α-bromocrotononitrile (1·46 g, 0·01 mole) were added. The mixture was refluxed for 60 hr. After removal of ~0·1 g of an ether insoluble material evaporation of the solvent gave 2·50 g of red-brown, oily product, in which only small amounts of impurities, including a slight excess of olefin, could be detected by NMR. GLC analysis also showed high purity, but, due to thermal lability of the product, was accompanied by decomposition (~10%) producing the methylenecyclobutene **7**. Careful molecular distillation (~10^{-4} mm Hg/oil-bath temp. 60–68°) gave 1·50 g (58%), of >98% geometrical purity, of a pale-yellow oil, which rapidly became red-brown on contact with the air. In other experiments, including reactions performed in acetonitrile soln, the yield of distilled product could be raised to 84%. NMR analysis did not disclose impurities in the distilled product; IR: ν_{max}^{liq} 2180, 1650 cm^{-1}; UV: λ_{max}^{EtOH} 297 nm; NMR: data given in Table 5, and 1·23 (t, 6H, J = 7), 3·35 (q, 2H, J = 7), 3·40 (q, 2H, J = 7), $J_{4\text{-}CH_3,4\text{-}H}$ = 6·5. Found: C, 52·21; H, 6·81; N, 10·92; Br, 29·37. $C_{11}H_{17}N_2Br$ requires: C, 51·37; H, 6·66; N, 10·89; Br, 31·07%.

trans - 3 - *Bromo* - 2 - *diethylamino* - 3,4 - *dimethyl* - 1 - *cyclobutenecarbonitrile*, **3g**, was obtained from *trans*-α-bromocrotononitrile in the same way as the *cis* isomer **3f**. The best yield of distilled product was 74%, of 95% geometrical purity, from a reaction performed in acetonitrile soln on a 0·01 mole scale; IR: ν_{max}^{liq} 2170, 1650 cm^{-1}; NMR: data given in Table 5, and 1·22 (t, 6H, J = 7), 3·35 (q, 4H, J = 7), $J_{4\text{-}CH_3,4\text{-}H}$ = 6·5. Found: C, 52·37; H, 6·82; N, 10·97; Br, 29·21. $C_{11}H_{17}N_2Br$ requires: C, 51·37; H, 6·66; N, 10·89; Br, 31·07%.

3 - *Bromo* - 2 - *diethylamino* - 3 - *phenyl* - 1 - *cyclobutenecarbonitrile*, **3h**. Diethylaminophenylacetylene (1·73 g, 0·01 mole) were dissolved in 20 ml dry ether, and α-bromoacrylonitrile (1·32 g, 0·01 mole) were added. The mixture was allowed to stand at room temp for 24 hr. Evaporation of the solvent gave 3·08 g of a red-brown, crystalline product. Crystallization from 10 ml of ligroin (60–80°) gave, after drying *in vacuo*, 2·6 g (85%) of the title compound. In order to remove coloured impurities the product was recrystallized from 10 ml dibutyl ether, giving 2·24 g (73%) of analytical pure product, m.p. 77–78°, IR: $\nu_{max}^{CCl_4}$ 2185, 1645 cm^{-1}; UV: λ_{max}^{EtOH} 301 nm: NMR: 1·18 (t, 6H, J = 7), 2·83 (d, 1H, J = 9), 3·26 (d, 1H, J = 9), 3·30 (q, 4H, J = 7), 7·1–7·6 (m, 5H). MS: *m/e* (% R.A.) 306–304 (12)(M^+), 225 (19) (M^+-Br), 185 (100). m*, 166·5 ($M^+ \rightarrow 225$). Found: C, 59·07; H, 5·73; N, 9·09; Br, 26·14. $C_{15}H_{17}N_2Br$ requires: C, 59·03; H, 5·62; N, 9·18; Br, 26·18%.

cis - 3 - *Bromo* - 2 - *diethylamino* - 4 - *methyl* - 3 - *phenyl* - 1 - *cyclobutenecarbonitrile*, **3i**. Diethylaminophenylacetylene (0·87 g, 0·005 mole) were dissolved in 10 ml dry acetonitrile, and *cis*-α-bromocrotononitrile (0·73 g, 0·005 mole) of 95% geometrical purity were added. The mixture was heated to 40° for 17 hr. Removal of the solvent gave 1·54 g of partly crystalline, dark product. NMR analysis showed a content of the *trans* isomer **3j** not exceeding 30% relative to the *cis* isomer (the analysis is inaccurate because of overlapping signals). The crude product was rather impure. Crystallization from 10 ml dibutyl ether gave, after washing with light petroleum and drying *in vacuo*, 0·59 g (37%) of crystalline material (blades). NMR analysis showed a content of **3j** of 5–10%. Recrystallization from dibutyl ether gave 0·35 g (22%) of analytical pure material, m.p. 100–101°; IR: ν_{max}^{KBr} 2170, 1655 cm^{-1}; UV: λ_{max}^{EtOH} 301 nm; NMR: 0·63 (d, 3H, J = 6·5), 1·0–1·5 (unresolv. signal, 6H), 2·9–3·7 (unresolv. signal, 4H), 3·47 (q, 1H, J = 6·5), 7·0–7·6 (m, 5H). (The broad, unresolved character of the signals due to the methyl and methylene groups of the diethylamino group indicate severe restrictions to free rotations in the molecule). Found: C, 60·64; H, 6·10; N, 8·71; Br, 25·16. $C_{16}H_{19}N_2Br$ requires: C, 60·20; H, 6·00; N, 8·77; Br, 25·03%.

trans - 3 - *Bromo* - 2 - *diethylamino* - 4 - *methyl* - 3 - *phenyl* - 1 - *cyclobutenecarbonitrile*, **3j**, was obtained from *trans*-α-bromocrotononitrile, of 93% geometrical purity, in the same way as the *cis* isomer **3i**. NMR analysis of the rather impure crude product showed a content of the *cis* isomer **3i** not exceeding 10%. Unfortunately, we did not succeed in obtaining the title compound in an analytical pure state, the material remaining an untractable dark oil. NMR: 0·93 (d, 3H, J = 6·2), 0·8–1·5 (badly resolv. triplets, 6H), 3·0–3·7 (unresolv. signal, ~5H), 6·9–7·9 (m, 5H). The 4-H is hidden.

General procedures for the solvolytic reactions

Ethanolyses. 0·005 mole of substrate were dissolved in 15 ml abs EtOH and 0·010 mole of triethylamine were added. The mixture was refluxed for 6–7 times the time of half-change in order to secure 98–99% conversion. The solvent and excess amine were removed *in vacuo* at ~20°. To the residue 20 ml dry ether was added, and the triethylammonium halide was filtered off, in almost quantitatively yield. Evaporation of the ether *in vacuo* gave the liquid products in nearly quantitatively yields. GLC, NMR and elemental analyses showed high purity. *Hydrolyses* were performed in the same way with 90% aqueous acetone as solvent. Work-up involved removal of most of the solvent *in vacuo*, addition of a few ml of water to the residue followed by extraction with two 10 ml portions of ether. The crude products contained ~5% of impurities.

2 - *Diethylamino* - 3 - *ethoxy* - 3 - *methyl* - 1 - *cyclobutenecarbonitrile*, **4a**. Product from bromide **3b**; IR: ν_{max}^{liq} 2180, 1640 cm^{-1}, UV: λ_{max}^{EtOH} 279 nm; NMR: data given in Table 5, and 1·15 (t, 3H, J = 7), 1·20 (t, 6H, J = 7), 3·28 (q, 2H, J = 7), 3·31 (q, 2H, J = 7), 3·34 (q, 2H, J = 7). $J_{4\text{-}H_a,4\text{-}H_b}$ = 9. Found: C, 68·39; H, 9·69; N, 13·32. $C_{12}H_{20}N_2O$ requires: C, 69·19; H, 9·68; N, 13·45%.

cis - 2 - *Diethylamino* - 3 - *ethoxy* - 3,4 - *dimethyl* - 1 - *cyclobutenecarbonitrile*, **4f**. Product from bromide **3f** (see also Table 2); IR: ν_{max}^{liq} 2180, 1650 cm^{-1}; UV: λ_{max}^{EtOH} 280 nm; NMR: data given in Table 5, and 1·14 (t, 3H, J = 7), 1·18 (t, 6H, J = 7), 3·27 (q, 2H, J = 7), 3·32 (q, 2H, J = 7), 3·35 (q, 2H, J = 7), $J_{4\text{-}CH_3,4\text{-}H}$ = 6·5. Found: C, 69·06; H, 9·74; N, 12·45. $C_{13}H_{22}N_2O$ requires: C, 70·23; H, 9·97; N, 12·60%.

trans - 2 - *Diethylamino* - 3 - *ethoxy* - 3 - *methyl* - 1 - *cyclobutenecarbonitrile*, **4g**. Product obtained from bromide **3g** (of 87% geometrical purity), b.p. 99°/0·2 mm Hg, 83% geometrical purity; IR: ν_{max}^{liq} 2170, 1650 cm^{-1}; UV: λ_{max}^{EtOH} 281 nm; NMR: data given in Table 5, and 1·15 (t, 3H, J = 7), 1·18 (t, 6H, J = 7), 3·27 (q, 2H, J = 7), 3·38 (two partly resolved quarters, 4H, J = 7), $J_{4\text{-}CH_3,4\text{-}H}$ = 6·5. Found: C, 70·11; H, 9·92; N, 12·61. $C_{13}H_{22}N_2O$ requires: C, 70·23; H, 9·97; N, 12·60%.

Ethyl 2 - *diethylamino* - 3 - *ethoxy* - 3 - *methyl* - 1 - *cyclobutenecarboxylate*, **4d**, b.p. 98°/0·2 mm Hg; IR: ν_{max}^{liq}

1680, 1615 cm^{-1}; UV: λ_{max}^{EtOH} 302 nm; NMR: ~1·14 (three partly resolved triplets, 9H, J = 7), 1·21 (t, 3H, J = 7), 1·45 (s, 3H), 2·08 (d, 1H, J = 10), 2·58 (d, 1H, J = 10), 3·1–3·85 (three partly resolved quartets, 6H, J = 7), 3·98 (q, 2H, J = 7). Found: C, 65·90; H, 9·79; N, 5·39. $C_{14}H_{25}NO_3$ requires: C, 65·85; H, 9·87; N, 5·49%.

2 - *Diethylamino* - 3 - *hydroxy* - 3 - *methyl* - 1 - *cyclobutenecarbonitrile*, **5a**. From bromide **3b** (4·86 g, 0·02 mole) 3·42 g of ~95% pure product (90% yield) was obtained. Distillation *in vacuo* gave a main fraction, b.p. 114°/0·15 mm Hg, 2·48 g (69%); IR ν_{max}^{liq} 3400 (broad), 2170, 1640 cm^{-1}; UV: λ_{max}^{EtOH} 280 nm; NMR: data given in Table 5, and 1·18 (t, 6H, J = 7), 3·30 (q, 4H, J = 7), 4·25 (broad singlet, 1H). Found: C, 65·69; H, 8·82; N, 15·17. $C_{10}H_{16}N_2O$ requires: C, 66·64; H, 8·95; N, 15·54%.

cis - 2 - *Diethylamino* - 3 - *hydroxy* - 3,4 - *dimethyl* - 1 - *cyclobutenecarbonitrile*, **5f**. From bromide **3f** (0·30 g, 0·0012 mole) 0·16 g (71%) of oily crude product was obtained (see also Table 2), NMR: data given in Table 5, and 1·17 (t, 6H, J = 7), 3·28 (quartet of broad lines, 4H, J = 7), 3·8 (broad singlet, 1H), $J_{4\text{-}CH_3,4\text{-}H} = 6·5$.

trans - 2 - *Diethylamino* - 3 - *hydroxy* - 3,4 - *dimethyl* - 1 - *cyclobutenecarbonitrile*, **5g**. From bromide **3g** (0·28 g, 0·0011 mole) 0·16 (76%) of crystalline crude product was obtained (see also Table 2). Recrystallization from 0·8 ml carbontetrachloride gave, after drying *in vacuo*, 0·13 g (62%) of analytical pure product, m.p. 92–95°; IR: ν_{max}^{KBr} 3400 (broad), 2170, 1640 cm^{-1}; UV: λ_{max}^{EtOH} 281 nm; NMR: data given in Table 5, and 1·17 (t, 6H, J = 7), 3·29 (quartet of broad lines, 4H, J = 7), 3·5 (broad singlet, 1H), $J_{4\text{-}CH_3,4\text{-}H} = 6·5$. Found: C, 67·81; H, 9·33; N, 14·31. $C_{11}H_{18}N_2O$ requires: C, 68·01; H, 9·34; N, 14·42%.

2 - *Diethylamino* - 3 - *methylene* - 1 - *cyclobutenecarbonitrile*, **6**. Bromide **3b** (2·43 g, 0·01 mol) were dissolved in 30 ml dry ether, and t-BuOK (1·40 g, 0·0125 mole) were added. The heterogeneous mixture was stirred magnetically in a closed vessel at room temp for 24 h. 5 ml of water was then added and stirring continued for a few min. The ether phase was separated, dried over $CaCl_2$ and evaporated, giving 1·61 g of a yellow–brown oil. NMR analysis shoved the product to contain 14% of the starting material, whereas no by-products could be detected, calculated yield: 85%. Molecular distillation (10^{-4}–10^{-3} mm Hg/room temp) gave a colourless product, which rapidly turned yellow on contact with the air; IR: $\nu_{max}^{CHCl_3}$ 2170, 1760, 1640 cm^{-1}; UV: $\lambda_{max}^{cyclohexane}$ 322 nm (log $\epsilon = 3·95$); the NMR spectrum is rather complex involving a strongly coupled 4-spin system, which has not been analyzed: 1·23 (t, 6H, J = 7), 2·82 (partly resolv. "triplet", 2H, J = ~1·1), 3·34 (q, 4H, J = 7), 4·81 (dt, 1H, J = 1·3, 0·9), 5·11 (q, 1H, J = ~1·4). Found: C, 72·75; H, 8·68; N, 16·98. $C_{10}H_{14}N_2$ requires: C, 74·03; H, 8·70; N, 17·27%.

2 - *Diethylamino* - 4 - *methyl* - 3 - *methylene* - 1 - *cyclobutenecarbonitrile*, **7**. A 6:4 mixture of the bromides **3f** and **3g** (1·29 g, 0·05 mole) was treated with t-BuOK (1·12 g, 0·01 mole) in 15 ml dry ether at room temp for 72 h. Work-up as for **6** gave 0·88 g of crude product. NMR showed 82% conversion (no by-products). Repeated treatment with excess t-BuOK in boiling ether for 24 h led to complete conversion. Molecular distillation (10^{-4}–10^{-3} mm Hg/~35°) afforded a colourless product, sensitive to air and heat; UV: λ_{max}^{EtOH} 328 (log $\epsilon = 3·95$); NMR: 1·15 (d, 3H, J = 6·5), 1·22 (t, 6H, J = 7), 3·13 (partly hidden quartet, 1H, J = 6·5), 3·32 (q, 4H, J = 7), 4·78 (dd, 1H, J = 1·4, 0·9), 5·02 (t, 1H, J = ~1·4). Found: C, 74·58; H, 9·12; N, 15·65. $C_{11}H_{16}N_2$ requires: C, 74·96; H, 9·15; N, 15·89%.

Hydrolysis of **3a**. 6·54 g (0·033 mole) of **3a** were stirred with 25 ml of dil HCl at 20° for 1½ h. In 1 h the heterogeneous mixture became homogeneous. Extraction with three 50 ml portions of ether gave, after drying over Na_2SO_4, 4·70 g of an oil (a fourth extraction with 50 ml of ether gave only 0·07 g). IR analysis showed the crude product to be a mixture of **8a** and **9a**. A small amount of the substrate could also be detected. Distillation *in vacuo* gave 1·72 g (36%) of 2 - *chloro* - 2 - *methyl* - 4 - *cyano-cyclobutanone*, **8a**, b.p. 112–116°/12 mm Hg; IR: ν_{max}^{liq} 2240, 1810 cm^{-1}; NMR showed **8a** to comprise two isomers (*cis-trans*) in the ratio 6:4. 1·77 and 1·81 (two singlets, 3H), 2·4 – 3·1 (m, 2H), 4·1–4·8 (m, 1H). Found: C, 50·18; H, 4·31; N, 9·86; Cl, 24·65. C_6H_6NClO requires: C, 50·20; H, 4·21; N, 9·76; Cl, 24·69%.

The distillation residue from above (**9a**) was refluxed with 50 ml MeOH and two drops of conc H_2SO_4 for 24 h. Most of the MeOH was distilled off and the residue dissolved in 50 ml ether. The ether soln was washed with water, dried over Na_2SO_4 and evaporated. Distillation *in vacuo* gave *methyl* 2 - *chloro* - 2 - *methyl* - 4 - *cyanobutyrate*, b.p. 120–123°/10 mm Hg; IR: 2250, 1740 cm^{-1}; NMR: 1·77 (s, 3H), 2·3–2·7 (m, 4H), 3·76 (s, 3H). Found: C, 47·88; H, 5·92; N, 5·68; Cl, 18·74. $C_7H_{10}NClO_2$ requires: C, 47·87; H, 5·74; N, 7·98; Cl, 20·19%.

Hydrolysis of **3c**. 4·63 g (0·02 mole) of **3c** were stirred with 50 ml dil HCl for 1 h at room temp. The mixture remained heterogeneous. Work-up as for hydrolysis of **3a** gave 3·97 g of an oil. IR analysis showed this crude product to contain a carboxylic acid (**9c**), but not a cyclobutanone. Esterification with methanol as for **9a** gave 2·94 g (75%) of 2 - *chloro* - 2 - *methylglutaric acid dimethyl ester*, b.p. 120–126°/12 mm Hg; NMR: 1·72 (s, 3H), 2·0–2·7 (m, 4H), 3·62 (s, 3H), 3·76 (s, 3H). Found: C, 46·33; H, 6·51; Cl, 16·63. $C_8H_{13}ClO_4$ requires: C, 46·06; H, 6·28; Cl, 16·99%.

Hydrolysis of **3d**. 6·15 g (0·025 mole) of **3d** were dissolved in 50 ml ether, and 50 ml dil HCl were added. The mixture was stirred for 2½ h at room temp. The ether phase was separated, and the water phase was extracted with two 50 ml portions of ether. The combined ether solns were dried over Na_2SO_4 and evaporated, giving 4·32 g of an oil. Distillation *in vacuo* gave 0·4 g (8·4%) of 2 - *chloro* - 4 - *carbethoxy* - 2 - *methylcyclobutanone*, **8d**, b.p. 100–120°/10 mm Hg. NMR showed **8d** to comprise two isomers in the ratio 95:5; IR: ν_{max}^{liq} 1800, 1730 cm^{-1}; NMR: 1·25 and 1·30 (two triplets (5:95), 3H, J = 7), 1·65 and 1·73 (two singlets (5:95), 3H), 2·3–3·0 (m, 2H), 4·0–4·6 (m, 1H), 4·19 (q, 2H, J = 7).

Continued distillation of the crude product above gave a sample of 2 - *chloro* - 2 - *methylglutaric acid monoethyl ester*, **9d**, b.p. 120–130°/0·1 mm Hg. In another experiment **9d** was obtained in 41% yield; IR: ν_{max}^{liq} 3200 (broad), 1730 cm^{-1}; NMR: 1·25 (t, 3H, J = 7), 1·77 (s, 3H), 2·1–2·8 (m, 4H), 4·10 (q, 2H, J = 7), 11·40 (s, 1H). Found: C, 46·92; H, 6·63; Cl, 16·00. $C_8H_{13}ClO_4$ requires: C, 46·06; H, 6·28; Cl, 16·99%.

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