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THE REACTION OF ENAMINES WITH α -CHLOROACRYLONITRILE[†]

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Abstract—Addition of α -chloroacrylonitrile to aldehyde enamines has been shown to give cyclobutanes, whereas addition to enamines derived from cyclic ketones produces quaternary salts. It is proposed that these salts result from an intramolecular reaction of initially formed alkylation products. Ethyl β -methyl-aminocrotonate gives a pyrroline derivative, in which case the initial alkylation product undergoes an intramolecular condensation with subsequent hydrogen chloride elimination. The dienamine, 1-N-morpholino-1,3-butadiene, adds to α -chloroacrylonitrile by a Diels-Alder reaction.

ADDITION of electrophilic olefins to enamines has been found, in general, to produce an alkylated enamine, \mathbf{a} , and/or a cyclobutane, \mathbf{b} .



Both reactions may take place simultaneously, but because of the reversibility of the cyclobutane formation, the Stork alkylation product,^{1, 2} being the more stable, may be the only product, depending on the conditions as discussed below. Acidcatalyzed hydrolysis of the alkylated enamine produces the alkylated carbonyl compound. Since the cyclobutane **b** can also lead to the alkylated carbonyl compound upon hydrolysis,^{3, 4} it is not possible to determine the nature of the initial addition product in this way. However, some characteristic features of the reaction of enamines with electrophilic olefins are known: The reaction rate is enhanced in polar solvents which fact supports the formulation of the zwitterion intermediate c^3 .

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Further, the solvent polarity has been observed to influence the product distribution very markedly:⁵ A polar solvent stabilizes the zwitterion, favouring proton-transfer, whereas a non-polar solvent may lead to immediate collapse of the zwitterion, when formed, and thus favouring cyclobutane formation. The temperature is also of importance to the course of the reaction. Higher temperature and prolonged reaction times favour the irreversible alkylation reaction, reflecting the reversibility of the cyclobutane formation.^{3,4} Finally, structural effects have been observed: Cyclobutanes seem to be the "normal" products from aldehyde enamines, whereas enamines of ketones produce cyclobutanes of low thermal stability.^{3,4} This is expected to be so because in the case of ketone enamines the proton-transfer, necessary to the conversion of the zwitterion to the alkylation product, may take place through an energetically favourable 6-membered transition state, but in the case of aldehyde enamines a less favourable 4-membered transition state is required for proton-transfer.^{1,6}



The present work deals with the addition of α -chloroacrylonitrile to a number of structurally different enamines, and also to a dienamine. The results are well understood on the basis of the foregoing discussion. The morpholine enamines of iso-



butyraldehyde, butyraldehyde, and acrolein dimer were reacted with α -chloroacrylonitrile in boiling acetonitrile. The well-crystallizing cyclobutanes I, II and III were obtained in 82%, 83% and 50% yield, respectively. I and III are indefinitely stable in the solid state, whereas II slowly decomposes by standing at room temperature.

The cyclobutane structure of the adducts is indicated by the IR spectra (CCl₄ soln). I and II show no absorption between 2000 and 1500 cm⁻¹, III shows a sharp band of medium intensity at 1630 cm⁻¹, characteristic for the vinyl ether double bond of dihydropyran. It is interesting to note that the cyano group absorption (≈ 2220 cm⁻¹) is extremely weak in these compounds, virtually absent in I. On the basis of the polar addition mechanism the constitution of these cyclobutanes is expected to be as indicated.

Reaction of α -chloroacrylonitrile with the morpholine enamine of cyclohexanone, in warm acetonitrile, gave two products: the high-melting quaternary ammonium salt IV, 23% yield, and the cyclobutane V, 39% yield.



FIG. 1.



As indicated in the reaction scheme, the chloride salt, IV, is presumed to arise by intramolecular cyclization of the alkylated enamine, whereas the cyclobutane, V, is formed by collapse of the initial zwitterion. IV is a completely stable, water-soluble, neutral substance, easily purified by recrystallization from acetonitrile. It has been further characterized as the perchlorate salt. The quaternary ammonium chlorides, VI, VII, and VIII (see below) have also been converted to the perchlorates, which yield very satisfactory elemental analyses. This was not the case for the chlorides, VII and VIII (Experimental). The structure of IV, the position of the double bond being a question of special interest, is strongly confirmed by its NMR spectrum (D₂O soln) (Fig. 1). A doublet of doublets (coupling constants 6.8 c/s and 2.6 c/s, as measured directly from the spectrum) centered at 5.93 ppm, integrating for one proton, is associated with the X proton of the ABX system consisting of the hydrogen alpha to the cyano group and the positive nitrogen and the methylene hydrogens at the next carbon. The A and B resonances are hidden in multiplet signals at 3.25-4.50 ppm (10 H), associated with the morpholine hydrogens. Two unresolved signals centered at 2.42 ppm and 1.88 ppm, each integrating for four protons, may clearly be assigned to the eight hydrogens attached to the cyclohexene ring. The IR spectrum (KBr) of IV shows a weak band at 1630 cm⁻¹ as the only absorption between 2000 and 1500 cm^{-1} .

Compound V is a basic, water-insoluble, solid compound which appears to comprise a single isomer. It is easily obtained in a pure crystalline condition by recrystallization from ligroin, but on prolonged standing at room temperature, it decomposes and becomes oily. The IR spectrum (CCl_4 soln) shows no absorption between 2000 and 1500 cm⁻¹. The "saturated" character of V is also indicated by the NMR spectrum (CCl_4 soln), in which no resonance appear below 40 ppm.

The more reactive piperidine enamine of cyclohexanone produces the quaternary ammonium salt, VI, in 80% yield as the sole product, by reaction with α -chloro-acrylonitrile in acetonitrile solution. VII is obtained in 63% yield from the piperidine enamine of 4-methylcyclohexanone. As indicated the constitution of VI and VII differs from that of IV in the position of the double bond. The vinyl hydrogen in VI shows a multiplet centred at 6.51 ppm in the NMR spectrum (D₂O soln) (Fig. 2);



the hydrogen alpha to the cyano group shows a doublet (coupling constant 6.5 c/s) of multiplets centered at 5.52 ppm. As expected, the NMR spectrum (D_2O soln) of VII is very similar.



The pyrrolidine enamine of cyclohexanone gives a strong exothermic reaction with α -chloroacrylonitrile in acetonitrile solution. When the olefin is added to a solution of the enamine at such a rate that the temperature does not exceed 40°, two products are obtained: the quaternary salt, VIII, crystallizes directly from the cooled reaction mixture in 38% yield, and a viscous red-yellow oil, IX, is left when the solvent is removed.



In the NMR spectrum (CDCl₃ soln) of VIII, the resonances associated with the vinyl hydrogen and the hydrogen alpha to the cyano group are overlapping, showing a multiplet at 64-69 ppm integrating for two protons. Unlike the salt, VI, which can be recovered completely unaltered after one hour's boiling in acetonitrile solution, VIII is highly unstable in solution. For this reason VIII could not be purified very effectively by recrystallization from acetonitrile (this solvent proved to be unique among a large number of solvents for the recrystallization of the quaternary salts described in this report). A great proportion of VIII is converted to the oily product, IX, when the salt is dissolved in warm acetonitrile. However, the difficulty in obtaining satisfactory elemental analysis for VIII is overcome by preparing the perchlorate salt, as mentioned earlier. Likewise, the oily substance, IX, is the sole product when the temperature is not controlled in the reaction of α -chloroacrylonitrile with the pyrrolidine enamine of cyclohexanone. The structure of IX has not been established, but treatment with aqueous silver nitrate shows that IX is not a chloride salt. Its formation from VIII appears to be irreversible. When IX is subjected to distillation in vacuo, hydrogen cyanide is eliminated and the tetrahydroindole derivative, X, distills over (31%) yield). X is a colourless liquid, which rapidly turns dark-red on contact with the atmosphere (a black solid actually precipitates on prolonged standing). The NMR spectrum (CCl₄ soln) (Fig. 3), is very informative



FIG. 3.





about the structure of X. Two doublets (coupling constant 2.7 c/s) at 6.28 ppm (1 H) and 5.69 ppm (1 H) are clealy associated with the hydrogens at C-2 and C-3, respectively. The methylene hydrogens alpha to the chlorine and the nitrogen give rise to multiplet signals centered at 3.69 ppm (2 H) and 3.40 ppm (2 H). The remaining methylene hydrogens are divided into two groups : the four allylic hydrogens produce

an unresolved signal centered at 2.45 ppm and another unresolved signal centered at 1.75 ppm integrates for eight protons. The mass spectrum of X (Fig. 4) exhibits peaks at m/e 133 and m/e 121 corresponding to ionized tetrahydroquinoline and tetrahydroindole, respectively. These ions may be formed by fragmentations similar to those proposed for N-butylpyrrole.⁷ Loss of four hydrogens from these ions produce the fully aromatic ions at m/e 129 and m/e 117.

Addition of electrophilic olefins to enamines derived from β -dicarbonyl compounds has not been as extensively studied as addition to simple enamines. However, the great utility of this kind of enamines in the synthesis of pyridine derivatives has been known for a long time^{8,9} and the electrophilic olefins used have been a variety of α,β -unsaturated carbonyl compounds. Recently α,β -unsaturated acids¹⁰ were shown to conform to this general reaction which most probably may be described as an ordinary enamine alkylation followed by cyclizising condensation. We were therefore not surprised to find that reaction of α -chloroacrylonitrile with ethyl β -methylaminocrotonate lead to the formation of the pyrroline derivative, XI. The reaction was performed in boiling acetonitrile with triethylamine added. A nearly quantitative amount of the amine hydrochloride could be isolated and XI was



obtained in 60% yield. The alkylated enamine **d** may reasonably be postulated as an intermediate in this reaction.

The NMR spectrum (CCl₄ soln) is consistent with structure XI: The hydrogen at C-5 shows a triplet centered at 4.21 ppm (coupling constant 9.1 c/s). The methylene hydrogens at C-4 appear as a doublet at 2.93 ppm, thus being equivalent; the coupling constant is about 9 c/s, the value cannot be accurately measured because the high field part of the doublet is overlapped by the N-Me singlet at 2.82 ppm, and further because the doublet signals are multiplets. This is due to homoallylic coupling to the Me group at C-2; accordingly this Me group shows a triplet (coupling constant 1.5 c/s) at 2.18 ppm.

When XI is pyrolyzed *in vacuo*, hydrogen cyanide is eliminated, and the pyrrole derivative, XII¹¹, is produced.

The 60 Mc/s NMR spectrum (CCl₄ soln) of XII is remarkably simple: the hydrogens at C-4 and C-5 appear to be equivalent, showing a quite sharp singlet at 6.31 ppm. However, in a 100 Mc/s spectrum (CDCl₃ soln) these protons give rise to an AB-pattern centered at 6.41 ppm (coupling constant 3.2 c/s).

Numerous attempts to obtain pyrrole derivatives from ethyl β -aminocrotonate and from ethyl 2-phenylaminocrotonate were all unsuccessful.

 α -Chloroacrylonitrile has also been reacted with 1-N-morpholino-1,3-butadiene in ether solution. When the mild exothermic reaction is finished, the solvent is removed *in vacuo*, leaving a dark coloured liquid. On attempted distillation *in vacuo* elimination of hydrogen cyanide occurred. The residue was easily identified as N-phenylmorpholine hydrochloride. The initial product then must be the Diels-Alder adduct, XIII, and the pyrolysis not only involves elimination of hydrogen cyanide but also expulsion of hydrogen chloride.



The orientation in Diels-Alder additions of this type has been shown to follow from electronic effects.¹² The zwitterion intermediate e will lead to the formation of XIII.

EXPERIMENTAL

The IR spectra were recorded on a Perkin-Elmer model 21 IR spectrophotometer, the UV spectra on a Perkin-Elmer model 137 UV spectrophotometer, and the NMR spectra on a Varian A-60 spectrometer, using TMS as an internal standard.

Microanalyses were carried out by Dr. Alfred Bernhardt, Mülheim (Ruhr), Germany.

M.ps and b.ps are uncorrected.

The morpholine enamine of acrolein dimer. In a round-bottomed flask fitted with a water separator and a reflux condenser were placed 112 g (1 mole) acrolein dimer, 130 g (1.5 mole) morpholine, and 200 ml benzene. The mixture was refluxed for 1.5 hr, when 18 ml water had been collected. Excess morpholine was distilled off and the main fraction obtained at b.p. $73-74^{\circ}/0.15 \text{ mm Hg}$, $n_b^{20} = 1.5328$, yield 170 g (94%). (Found: C, 66.33; H, 8.41; N, 7.89. C₁₀H₁₅O₂N requires: C, 66.27; H, 8.34; N, 7.73%).

1-Chloro-2-N-morpholino-3,3-dimethyl cyclobutane carbonitrile (I). α -Chloroacrylonitrile^{*} (17.5 g; 0.2 mole) were added dropwise to a stirred soln of 28.2 g (0.2 mole) 1-N-morpholino-isobutene in 200 ml acetonitrile at room temp. No spontaneous warming was observed, and the mixture was heated to gentle reflux for 2 hr. The solvent was removed under reduced press, leaving a dark coloured crystal mass (37 g, 82%) which was recrystallized from abs. alcohol 3 times, yielding 26.5 g (58%) of I as colourless crystals, m. p. 98°. No absorption was visible in the IR spectrum in the 2000–1500 cm⁻¹ region. (Found: C, 57.88; H, 7.34; N, 12.12; Cl, 15.44. C₁₁H₁₇N₂OCl requires: C, 57.76; H, 7.49; N, 12.24; Cl, 15.50%).

1-Chloro-2-N-morpholino-3-ethyl cyclobutane carbonitrile (II). Reaction of the morpholine enamine of n-butyraldehyde with α -chloroacrylonitrile was carried out as described. In this case, a weak exothermic

* Generously supplied by Münzing and Comp., Heilbronn, Germany.

reaction was observed, when the olefin was added to the soln of the enamine, and the mixture was refluxed for 1 hr only. Evaporation of the solvent gave an oil which crystallized when it was cooled to 0°. Recrystallization from petrol gave to crystalline forms, m.p. 69° (83.0% yield) and m.p. 55° (~3%); v_{mx}^{CCL} 2220 cm⁻¹. No absorption was visible in the IR spectrum in the 2000–1500 cm⁻¹ region. (Found: C, 57.98; H, 7.57; N, 12.34; Cl, 15.42. C₁₁H₁₂N₂OCl requires: C, 57.76; H, 7.49; N, 12.24; Cl, 15.50%).

7-N-morpholino-8-chloro-8-cyano-spiro[5.3]-1-oxa-nonene-2 (III). The reaction of the morpholino enamine of acrolein dimer with α -chloroacrylonitrile was carried out as described for 1. The reaction mixture was refluxed for 1 hr. The adduct crystallized when most of the solvent had been evaporated. Recrystallization from abs. alcohol gave a pure sample (50% yield). Repeated recrystallizations produced colourless crystals, m.p. 155–160° (dec); $v_{max}^{CCL_4}$ 2220, 1630 cm⁻¹. (Found: C, 58-15; H, 6-57; N, 10-29; Cl, 13-19. C₁₃H₁₇N₂O₂Cl requires: C, 58-09; H, 6-38: N, 10-43; Cl, 13-20%).

Compound IV. α -Chloroacrylonitrile (17.5 g; 0.2 mole) were added dropwise to a stirred soln of 33.4 g (0.2 mole) 1-N-morpholinocyclohexene in 175 ml acetonitrile at room temp. Some spontaneous warming was observed for the first 15 min. The mixture was heated to 50–60° for 15 min, and a white ppt was formed. After cooling, the mixture was kept in the refrigerator (-15°) overnight. Filtration of the cold mixture gave 11.6 g (23%) of IV as a white solid, m.p. 175–185°. Recrystallization from acetonitrile gave a pure sample, m.p. 200°, v_{max}^{BBT} 1630 cm⁻¹. The NMR spectrum (D₂O) (Fig. 1) displayed a doublet of doublets (1 H, J = 6.8, 2.6 c/s) at 5.93 ppm, broad multiplets (10 H) at 3.25–4.50 ppm, a multiplet (4 H) at 2.42 ppm, and a multiplet (4 H) at 1.88 ppm. (Found : C, 60.88; H, 7.79; N, 10.82; Cl, 13.84. C_{1.3}H_{1.9}N₂OCl requires : C, 61.29; H, 7.52; N, 11.01; Cl, 13.92%).

Compound IV was converted to the perchlorate salt by mixing dilute solns of the chloride salt and sodium perchlorate in water at room temp; the perchlorate crystallized after standing for some time, m.p. 146–148°. (Found: C, 48.94; H, 6.01; N, 8.62; Cl, 11.06. $C_{13}H_{19}N_2O_5Cl$ requires: C, 49.00; H, 6.03; N, 8.79; Cl, 11.12%).

1-N-morpholino-8-chlorobicyclo[4.2.0] octane-8-carbonitrile (V). The filtrate from above was concentrated under vacuum to $\frac{1}{2}$ of the original volume and cooled to -15° ; filtration gave 20.0 g (39%) of V, m.p. 87-90°. Recrystallization from petrol (b.p. 60-80°) gave a pure sample, m.p. 90°. No absorption was visible in the IR spectrum in the 2000-1500 cm⁻¹ region. (Found: C, 61-45; H, 7-61; N, 11-01; Cl, 13.77. C₁₃H₁₉N₂OCl requires: C, 61-29; H, 7-52; N, 11-01; Cl, 13-92%).

Compound VI. α -Chloroacrylonitrile (17.5 g; 0.2 mole) were added dropwise to a stirred soln of 33.0 g (0.2 mole) 1-N-piperidinocyclohexene in 300 ml acetonitrile at room temp. A mild exothermic reaction took place, and the temp of the reaction mixture rose to 45°. A white ppt was formed. The mixture was refluxed for 15 min and after cooling to -15° , 40.2 g (80%) of the product was removed by filtration, m.p. 195°. Recrystallization from acetonitrile gave a pure sample, m.p. 200°. The NMR spectrum (D₂O), (Fig. 2) displayed a multiplet (1 H) at 6.51 ppm; a doublet of multiplets (1 H, J = 6.5 c/s) at 5.52 ppm, and unresolved signals (19 H) at 1.0-4.2 ppm. (Found: C, 66.47; H, 8.60; N, 10.83; Cl, 14.13. C₁₄H₂₁H₂Cl requires: C, 66.52; H, 8.37; N, 11.08; Cl, 14.03%).

The perchlorate had m.p. 200°. (Found: C, 52.96; N, 8.58; Cl, 11.14. $C_{14}H_{21}N_2O_4Cl$ requires: C, 53.08; H, 6.68; N, 8.84; Cl, 11.20%).

Compound VII. Reaction of the piperidine enamine of 4-methylcyclohexanone with α -chloroacrylonitrile was carried out as described for the case of cyclohexanone. The product was obtained in 63% yield as a hygroscopic solid, m.p. 140–150°, raised to 150–155° after recrystallization from acetonitrile. (Found : C, 66·35; H, 8·78; N, 10·92; Cl, 13·86. C₁₅H₂₃N₂Cl requires: C, 67·52; H, 8·69; N, 10·50; Cl, 13·29%).

The perchlorate had m.p. 125°. (Found : C, 54·36; H, 6·95; N, 8·50; Cl, 10·76. C₁₅H₂₃N₂O₄Cl requires : C, 54·46; H, 7·01; N, 8·47; Cl, 10·72%).

Compound VIII. α -Chloroacrylonitrile (17.5 g; 0.2 mole) were added dropwise to a stirred soln of 30.2 g (0.2 mole) 1-N-pyrrolidinocyclohexene in 220 ml acetonitrile, initially at room temp. The temp of the strong exothermic reaction was kept below 40° by slow $(1\frac{1}{2} hr)$ addition of the olefin. A white solid started to precipitate when $\frac{2}{3}$ of the olefin had been added. Filtration of the cooled (-15°) reaction mixture gave 18.0 g (38%) of the product, m.p. 115–125°. Recrystallization from acetonitrile raised the m.p. to 131–133°. The NMR spectrum (CDCl₃) displayed a multiplet (2 H) at 6.4–6.9 ppm, and unresolved signals (17 H) at 1.0–4.7 ppm. (Found : C, 60.42; H, 8.48; N, 10.78; Cl, 13.60. C_{1.3}H_{1.9}N₂Cl requires : C, 65.39; H, 8.02; N, 11.73; Cl, 14.85%).

The perchlorate had m.p. 112-113°. (Found: C, 51·61; H, 6·52; N, 9·44; Cl, 11·65. C₁₃H₁₉N₂O₄Cl requires: C, 51·57; H, 6·33; N, 9·25; Cl, 11·71%).

Compound X. The filtrate from above was evaporated in vacuo, leaving a viscous oil. Distillation in

vacuo gave 13.0 g (31%) of X between 140–150° at 1 mm Hg, elimination of HCN accompanied the distillation of X. A purer sample was obtained by repeated distillation, b.p. 124–126°/0.35 mm Hg, $n_{\rm b}^{25} = 1.5308$. The NMR spectrum (CCl₄) (Fig. 3) displayed a doublet (1 H, J = 2.7 c/s) at 6.28 ppm, a doublet (1 H, J = 2.7 c/s) at 5.69 ppm, a multiplet (2 H) at 3.69 ppm, a multiplet (2 H) at 3.40 ppm, a multiplet (4 H) at 2.45 ppm, and a multiplet (8 H) at 1.75 ppm. The mass spectrum is shown in Fig. 4. Transitions supported by the presence of an appropriate metastable ion are indicated by an asterisk. (Found: C, 67.65; H, 8.82; N, 7.19; Cl, 16.53. C₁₂H₁₈NCl requires: C, 68.07; H, 8.57; N, 6.62; Cl, 16.75%).

1,2-Dimethyl-3-ethoxycarbonyl-5-cyano- Δ^2 -pyrroline (XI). α -Chloroacrylonitrile (17.5 g; 0.2 mole) and 20.2 g (0.2 mole) Et₃N were added to a stirred soln of 21.5 g (0.15 mole) ethyl β -methylaminocrotonate in 100 ml acetonitrile. The mixture was refluxed for 4 hr. After $\frac{1}{2}$ hr crystalline Et₃N·HCl had been formed. The reaction mixture was kept in the refrigerator (-15°) overnight. Filtration of the cold mixture gave 19.0 g (0.14 mole) Et₃N·HCl. The solvent was removed completely; recrystallization of the dark residue from petrol gave 17.5 g (60%) of the product, m.p. 50-55°, raised to 58° after repeated recrystallization; ν_{max}^{lig} 1680 cm⁻¹ (conjugated CO), 1605 cm⁻¹ (conjugated double bond), and 2220 cm⁻¹ (CN); λ_{max}^{EiOH} 302 mµ (log ε = 4.10); the NMR spectrum (CCl₄) displayed a triplet (1 H, J = 9.1 c/s) at 4.21 ppm, a quartet (2 H, J = 6.9 c/s) at 4.05 ppm, a doublet of multiplets (2 H, J = 9 c/s) at 2.93 ppm, a singlet (3 H) at 2.82 ppm, a triplet (3 H, J = 1.5 c/s) at 2.18 ppm, and a triplet (3 H, J = 6.9 c/s) at 1.21 ppm. (Found : C, 61.68; H, 7.50; N, 14.25. C₁₀H₁₄N₂O₂ requires: C, 61.83; H, 7.27; N, 14.42%).

1,2-Dimethyl-3-ethoxycarbonyl-pyrrole (XII). When crude XI was subjected to distillation in vacuo, HCN was eliminated and XII distilled over in a moderate yield; b.p. $80-82^{\circ}/0.15-0.20 \text{ mm Hg}$, $n_D^{24} = 1.5089$. (Lit.¹¹ : b.p. $136^{\circ}/9 \text{ mm Hg}$); ν_{max}^{liq} 1690 cm⁻¹ (CO), 1550 and 1500 cm⁻¹ (pyrrole nucleus); λ_{max}^{EOH} 256 mµ (log $\varepsilon = 3.85$); the 60 Mc/s NMR spectrum (CCl₄) displayed a singlet (2 H) at 6.31 ppm, a quartet (2 H, J = 7.0 c/s) at 4.16 ppm, a singlet (3 H) at 3.42 ppm, a singlet (3 H) at 2.40 ppm, and a triplet (3 H, J = 7.0 c/s) at 1.29 ppm; the 100 Mc/s NMR spectrum (CDCl₃) displayed a doublet (1 H, J = 3.2 c/s) at 6.46 ppm, a doublet (1 H, J = 3.2 c/s) at 6.38 ppm, a quartet (2 H, J = 7.0 c/s) at 4.21 ppm, a singlet (3 H) at 3.43 ppm, a singlet (3 H) at 2.43 ppm, and a triplet (3 H, J = 7.0 c/s) at 1.31 ppm. (Found : C, 64.69; H, 7.88; N, 8.72. Calc. for C₉H₁₃NO₂: C, 64.65; H, 7.84; N, 8.38%).

Compound XIV. α -Chloroacrylonitrile (17.5 g; 0.2 mole) dissolved in 75 ml dry ether was added dropwise to a stirred soln of 27.8 g (0.2 mole) 1-N-morpholino-1,3-butadiene in 125 ml dry ether. The reaction mixture was cooled by an ice-bath during the addition of the olefin (20 min). When the ice-bath was removed, the temp rose to 30° for $\frac{1}{2}$ hr. The mixture was stirred for another 4 hr at room temp. The solvent (and other low boiling materials) was removed *in vacuo*, leaving 27.5 g of a dark oil. 15.0 g of this oil were pyrolyzed *in vacuo* between 130–160° (oil-bath temp) at 0.15 mm Hg for 1 hr, producing 10.0 g of a dark, partly crystalline, solid material. Sublimation 110°/0.12 mm Hg, of 2.0 g of this material gave 1.7 g (39%, based on starting materials) of pure XIV, m.p. 170°. (Lit.¹³: m.p. 169–170°).

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