Base-Catalyzed Reactions of α,β-Unsaturated Esters and Nitriles. II. Potassium-Catalyzed Di- and Trimerization of 2-Butenenitrile

Joseph Shabtai* and Eva Ney-Igner

Department of Organic Chemistry, The Weizmann Institute of Science, Rehovot, Israel

Herman Pines*

The Ipatieff Catalytic Laboratory, Department of Chemistry, Northwestern University, Evanston, Illinois 60201

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In the presence of a potassium–benzylpotassium catalyst system, at 110° and toluene as a solvent, 2-butenenitrile (1) undergoes oligomerization yielding 20–23% dimer, 2-ethylidene-3-methylglutaronitrile (2), and 67–75% cyclic trimer, identified as 1,3,5-tricyano-2,4,6-trimethylcyclohexane (3). Compound 2 is a mixture of the two possible geometric isomers; the component with a vinylic hydrogen cis to the conjugated cyano group represents 67% dimer. Trimer 3, which contains a dominant stereoisomer (75–80%), yields on acid hydrolysis the monoamide of 2,4,6-trimethyl-1,3,5-cyclohexanetricarboxylic acid (4), rather than the free triacid. Resistance to complete hydrolysis is tentatively ascribed to the presence of a sterically hindered nitrile group in 3. It is proposed that formation of 3 could be initiated either by α-vinylic or by allylic metalation of 1, and that termination of the oligomerization process is caused by fast cyclization of an intermediate trimeric carbanion, followed by protonation.

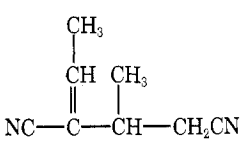
It was reported previously[1] that ethyl crotonate undergoes selective dimerization in the presence of a potassium–benzylpotassium catalyst to give the diethyl ester of 2-ethylidene-3-methylglutaric acid in nearly quantitative yield. This finding indicated that promoted alkali metal catalysts, previously used for dimerization[2,3] and aralkylation[4–7] of styrenes, as well as a variety of other processes,[8] could be conveniently employed for similar reactions of α,β-unsaturated esters. As an extension of these studies the potassium-catalyzed reactions of 2-butenenitrile (crotononitrile, 1) were investigated with the objective of developing suitable procedures for selective oligomerization of α,β-unsaturated nitriles.

While high molecular weight polymerization and copolymerization reactions of 1 have been studied to some extent,[9–13] and a process for preparation of sterically regular polycrotononitrile has been reported,[14] there are only limited data on the oligomerization of this nitrile. An early study[15] indicates that in the presence of ethylmagnesium bromide 1 yields a mixture of oligomers, mainly a trimer, the structure of which could not be elucidated. It was subsequently reported[16] that monomer 1 is readily oligomerized in the presence of sodium ethoxide to give a mixture of dimeric, trimeric, and higher products of unspecified structure.

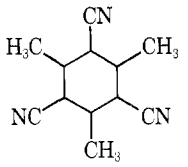
Experiments with 1 in the present study were carried out at 110°, using a large excess of toluene or methylcyclohexane as a solvent (1/solvent molar ratios of 1:6 to 1:10). About 0.2 g-atom of metallic potassium and 0.05 mol of *o*-chlorotoluene per mole of monomer 1 were used in the preparation of the potassium–benzylpotassium catalyst. Under these conditions (see Experimental Section), 1 reacts almost quantitatively to yield a mixture containing 20–23% of a dimer, 67–75% of a trimer, and 5–15% of unidentified high-boiling products. This product distribution is sharply different from that observed in the potassium-catalyzed reaction of ethyl crotonate, which yields almost exclusively a dimer under identical experimental conditions.[1]

In oligomerization experiments with sodium–benzylsodium as a catalyst, under otherwise identical conditions, the conversion of 1 is considerably lower (30–35%), while the dimer/trimer ratio remains similar to that observed with the potassium–benzylpotassium system.

The dimer of 1, bp 82–83° (0.2 mm), was identified as 2-ethylidene-3-methylglutaronitrile (2), whereas the structure of the trimer, bp 152–155° (0.2 mm), was elucidated as that of 1,3,5-tricyano-2,4,6-trimethylcyclohexane (3).



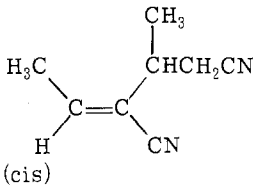
2



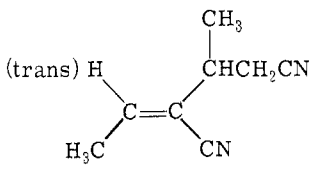
3

Compound 2 was identified by a combination of NMR, ir, and mass spectral analysis (see Experimental Section), and by conversion into derivatives.

Hydrolysis of 2 yielded 2-ethylidene-3-methylglutaric acid, identified by comparison with a reference sample obtained by independent means.[1] The distribution of 2 into the two possible stereoisomers **2a** and **2b** could not be determined by direct NMR analysis, since the differential shielding of cis and trans vinylic protons by a β-cyano group is only ca. 0.05 ppm.[17]



2a



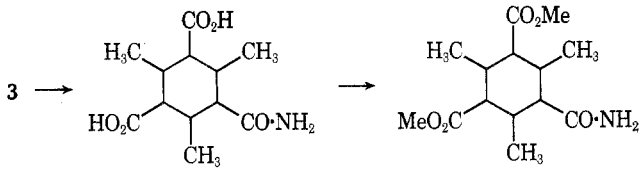
2b

Resolution of 2 into stereoisomers **2a** and **2b** was achieved by gas chromatography on a 300-ft capillary column coated with trifluoropropylmethylpolysiloxane. The molar ratio of **2a:2b** was 67:33. Structure assignment for the two stereoisomers was based on NMR analysis of the corresponding diester isomers, obtained by base hydrolysis of 2 under mild conditions and subsequent esterification with diazomethane. The differential shielding of the cis and trans vinylic protons by the β-carbomethoxy group in the produced dimethyl 2-ethylidene-3-methylglutarate was found to be 1.0 ppm, which allows for facile quantitative determination of the two stereoisomeric components.

Trimer 3 on gentle heating (80–100°) exhibits mercury-like mobility, viz., it does not wet glass, porcelain, and metal surfaces. Gas chromatographic analysis of 3 shows the presence of a dominant stereoisomer (75–80%), accompanied by small amounts of at least two other stereoisomeric components. The NMR, ir, and mass spectra of the tri-

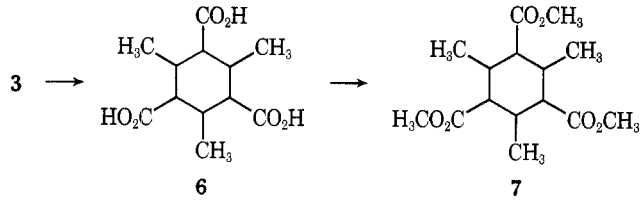
mer fully corroborated structure **3**, while the ^{13}C NMR spectrum indicated the absence of any significant amounts of an unsymmetrically substituted isomer, e.g., 1,2,4-tricyano-3,5,6-trimethylcyclohexane (see Experimental Section).

Hydrolysis of **3** with a 25% solution of sulfuric acid in glacial acetic acid yielded the monoamide of 2,4,6-trimethyl-1,3,5-cyclohexanetricarboxylic acid (**4**), which was subsequently transformed into the corresponding monoamide diester **5** by interaction with a diazomethane solution.



4 **5**

The NMR, ir, and mass spectra of the two derivatives were in agreement with structures **4** and **5** (see Experimental Section). Complete acid-catalyzed hydrolysis of **3** to the tricarboxylic acid **6** is extremely difficult and is practically not observed for reaction times of 20–24 hr. The reaction takes place to a very limited extent (10–15% by weight) at prolonged reaction time (>50 hr), and is accompanied by considerable loss of substrate.

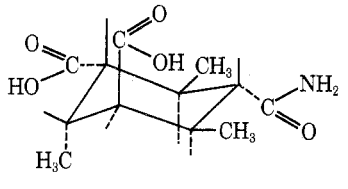


6 **7**

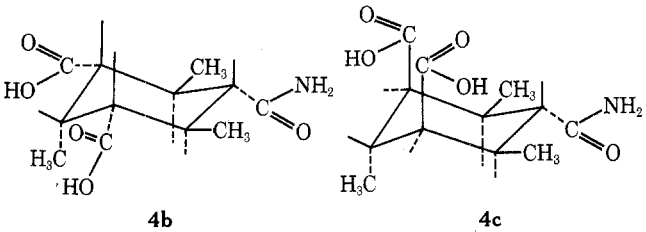
A sample of **6**, obtained by repeated fractional crystallization of the acid hydrolysis product (reaction time, 54 hr), was converted to the corresponding trimethyl ester **7** by reaction with diazomethane.

Separate experiments showed that basic reagents, e.g., potassium hydroxide in benzyl alcohol, are similarly ineffective for complete hydrolysis of **3**.

The observed phenomenon is probably related to the stereochemistry of compound **3**, as one of the three nitrile groups in the dominant stereoisomer could be sterically hindered. Examination of possible conformation models of the hydrolysis product **4** shows indeed that if an equatorial amide group is flanked by two equatorial methyl groups, as for instance in stereoisomers **4a**, **4b**, or **4c**, the approach to the former by the hydrolyzing species is sterically hindered.



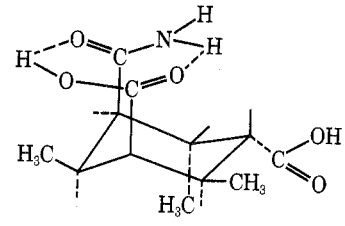
4a



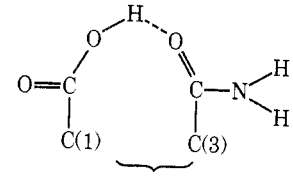
4b **4c**

Isomers **4a**, **4b**, and **4c** are derivable from stereoisomeric forms of the original trinitrile **3**, containing (a) two equatorial and one axial cyano groups; (b) three equatorial cyano groups; and (c) one equatorial and two axial cyano groups, respectively. It should be noted that in the trinitrile precursors of stereoisomers **4a** and **4b** only one of the equatorial cyano groups is flanked by two equatorial methyl groups. Furthermore, models indicate that trinitrile stereoisomers corresponding to **4a** and **4b** have a minimal extent of steric interactions, and, therefore, should be energetically favored. The NMR spectra of esters **5** and **7**, derived from **4**, show two well-resolved signals for the two stereochemically distinct types of methyl groups[18] (in the ratio 2:1) in agreement with structures **4a**, **4b**, or **4c** (see Experimental Section).

An alternative but more remote possibility regarding the resistance of the trimer to complete hydrolysis is that the intermediate **4** contains an axial amido group which is stabilized by intramolecular hydrogen bonding[19] with a coaxial carboxylic group. Formation of a cyclic hydrogen bond complex, as in **4d** would require that the hydroxyl group, as well as the NH_2 group, rotate out of coplanarity with the respective carbonyl groups, which may be energetically feasible at the hydrolysis temperature employed (above 100°). Examination of models shows that single hydrogen bonding with preservation of coplanarity within (and between) the carboxylic and amide groups, as for instance in **4e**, is also possible, requiring only slight distortion of bond angles.

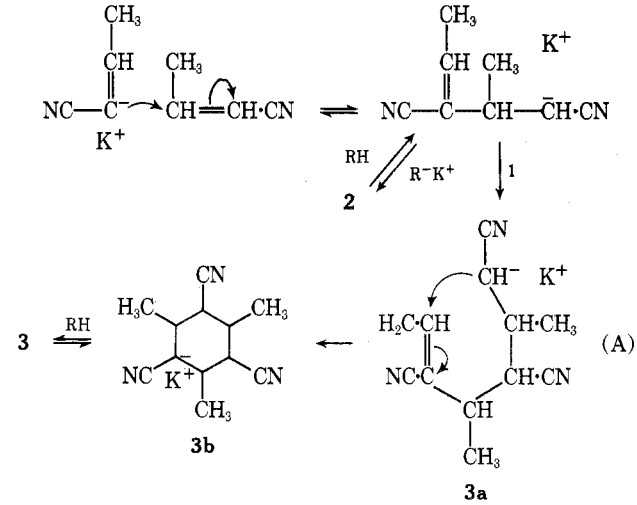


4d



4e

By analogy with the mechanism proposed for the dimerization of ethyl crotonate,[1] the potassium-catalyzed reaction of **1**, leading to **2** and **3**, could be initiated by metalation at the α-vinylic position. Formation of higher oligomers is prevented by cyclization of an intermediate trimeric carbanion (**3a**) to give the resonance-stabilized trimer precursor **3b** (sequence A).

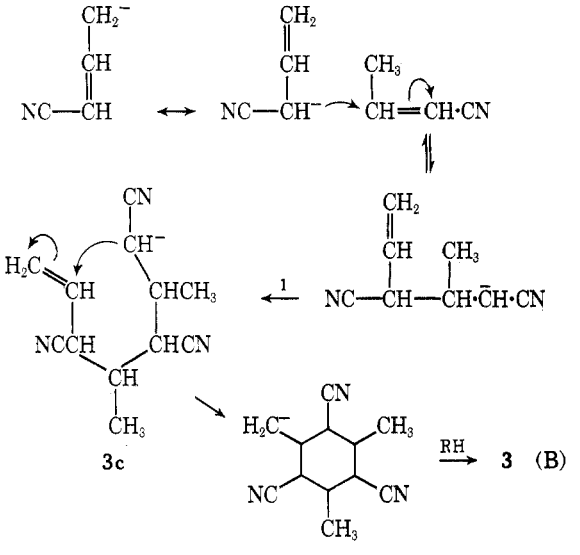


3b **3a** (A)

Cyclization of unsaturated carbanions to resonance-stabilized tertiary carbanions, which are protonated to form five- or six-membered ring systems, has been found previously in the sodium-catalyzed reaction of α-methylstyrene.[3] On the other hand, the absence of any appreciable amount of an open-chain trimer of **1** in the reaction prod-

uct suggests that in the present case the trimerization and cyclization steps could proceed by a concerted mechanism, i.e., through an intermediate which is not a fully developed trimeric carbanion.

Alternatively, oligomerization of 1 could be initiated by allylic metalation. In such case formation of 3 may involve cyclization of a secondary trimeric carbanion (3c) to give an energetically favored primary carbanion (3d) as precursor of 3 (sequence B, K^+ omitted).

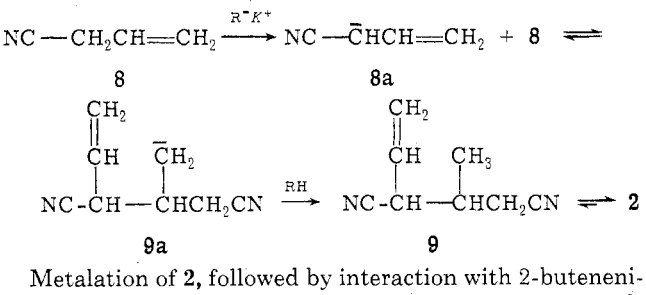


3c 3d

Similar cyclizations of $\Delta^{4,5}$-, $\Delta^{5,6}$-, or $\Delta^{6,7}$-unsaturated carbanions, stabilized by charge delocalization, into localized primary carbanions which undergo fast irreversible protonation have been shown to occur in the potassium-catalyzed reaction of 1-phenyl-1,3-pentadiene, yielding 3-methyl-4-phenylcyclobutene,[2] as well as in the conversion of 6-phenyl-1-hexene and 7-phenyl-1-hexene to 1-phenyl-2-methylcyclopentane and 1-phenyl-2-methylcyclohexane, respectively.[20] Intramolecular cyclizations of ω-(3-pyridyl)-1-alkenes and ω-(4-pyridyl)-1-alkenes provide a further illustration of this type of carbanionic reaction.[21]

For comparison, experiments with 3-butenenitrile (allyl cyanide, 8) as starting monomer were also carried out. It is found that, like 1, compound 8 undergoes smooth reaction in the presence of potassium–benzylpotassium as catalyst (conversion, 80–85% at 110°; see Experimental Section), giving the same type of oligomers as obtained from 1. However, gas chromatographic analysis of the product from 8 shows a dimer/trimer ratio of ca. 60:40 (% by weight), which is higher by a factor of about 8 compared to that found with 1. Further, analysis of the unreacted monomer indicates that isomerization of 8 into the conjugated isomer 1, during the oligomerization process, is incomplete.

The high dimer yield obtained from 8 may be due to fast protonation of a localized primary dimeric carbanion (9a) expected by interaction of the monomeric carbanion 8a with a second molecule of 8.



8 8a

9a 9

Metalation of 2, followed by interaction with 2-butenenitrile (from isomerization of 8), could give trimer 3 according to either sequence A or B. The low yield of 3 may be due to a low metalation rate of 2, or to a relatively low concentration of 2-butenenitrile needed for the trimerization–cyclization step. Interaction of carbanion 9a, or of the carbanion derived from 2, with a third molecule of monomer 8, followed by cyclization, should give cyclohexane derivatives possessing cyanomethyl substituents. No such compounds were detected in the product, indicating that the conjugated monomer 1, rather than 8, is involved in the final, trimerization–cyclization step.

It should be noted that the alkali metal catalyzed cyclotrimerization of 1 is different from base- or acid-induced cyclotrimerizations of aromatic nitriles, which involve participation of the cyano groups in the oligomerization process, and lead to 1,3,5-triazines.[22] The present process is also different from cyclotrimerization reactions involved in the termination of anionic oligomerization and polymerization processes of acrylates, initiated by organolithium or organomagnesium compounds. In such reactions initiation consists in addition of the organometallic initiator across the double bond of the monomer, while the termination step involves intramolecular nucleophilic attack on an ester group in the intermediate trimeric complex, leading to a cyclic β-keto ester.[23,24] In contrast, with promoted alkali metal catalysts there is no addition of the initiating species to the monomer, and oligomerization proceeds selectively with preservation of the ester or nitrile functional group.

Experimental Section

Materials. Crotononitrile (2-butenenitrile), supplied by Fluka A.G., was dried over anhydrous magnesium sulfate, and then distilled at 100 mm through a fractionating column. The purified (99.2%) monomer contained 76% cis and 24% trans isomer.

Allyl cyanide (3-butenenitrile), obtained from Borden Chemical Co., was dried and then redistilled at atmospheric pressure to give a sample of more than 99% purity.

Oligomerization Procedure. The preparation of the potassium–benzylpotassium catalyst, and a typical large-scale oligomerization experiment, were performed as follows.

Toluene (30 g) was introduced in a 500-ml three-neck flask equipped with a constant-rate dropping funnel, a reflux condenser, and a high-speed, 10,000 rpm stirrer provided with a metal dispersing blade. The apparatus was purged with dry nitrogen, 3 g (0.075 mol) of freshly cut potassium was added to the flask, and the mixture was brought to boiling and kept for 10 min without mixing. The molten metal was then stirred under reflux for 1 hr, and subsequently 2.5 g (0.02 mol) of *o*-chlorotoluene, dissolved in 10 g of toluene, was added dropwise to the fine dispersion, which acquired a black color at this stage. The catalyst preparation was completed by slowly adding (1 hr) another portion of toluene (120 g), while keeping the mixture under reflux.

Crotononitrile (25.2 g, 0.375 mol), dissolved in 45 g of toluene, was added at a constant rate to the stirred catalyst dispersion (45 min) and the mixing continued for another hour. A slow stream of nitrogen was kept throughout the experiment. The reaction mixture was quickly cooled to −5° and the catalyst decomposed by slowly adding 15 ml of absolute ethanol; decomposition above 0° causes side reactions. The product was washed with 10% aqueous hydrochloric acid, 10% aqueous sodium bicarbonate, and water, and finally dried over anhydrous magnesium sulfate. The solvent and unreacted monomer were removed at 100 mm and the remaining product (22.3 g, conversion 88.5%) was distilled to give a dimeric fraction, bp 80–85° (0.2 mm), 4.8 g (19.2%), a trimeric fraction, bp 150–155° (0.2 mm), 15.7 g (70.4%), and a high-boiling residue, ca. 1.5 g (ca. 7%).

2-Ethylidene-3-methylglutaronitrile (2). The dimeric product from several experiments was combined and redistilled to give a sample of 2 in more than 99% purity: bp 81–83° (0.2 mm); $n^{25}D$ 1.4730; ir (neat) 852 ($R_1R_2C{=}CHR_3$, =C–H out-of-plane deformation),[25] 963, 1006, 1075, 1123, 1380 ($R_1R_2C{=}CHR_3$, =C–H in-plane deformation),[25] 1420, 1445, 1594–1628 (C=C, splitting due to conjugation with CN group), 2212 (conjugated CN), 2241 cm^{-1} (nonconjugated CN); ir ($CHCl_3$) 849 (=C–H out-of-plane deformation), 963, 1002, 1070, 1119, 1385 (=C–H in-plane deformation), 1423, 1455, 1597–1639 (C=C), 2198 (conjugated CN), 2228

(nonconjugated CN), 2905, 2955 cm^{-1}; NMR (CCl_4) δ 1.25 (d, 3, J = 6.3 Hz, CH_3 at C-3), 1.98 (d, 3, J = 7.0 Hz, $=CHCH_3$), 2.45 (d, 2, J = 5.7 Hz, $CHCH_2CN$), 2.5–3.0 (m, 1, H at C-3), 6.48 (q, 1, J = 7.1 Hz, $=CHCH_3$); m/e 134 (M^+).

Anal. Calcd for $C_8H_{10}N_2$: C, 71.61; H, 7.51; N, 20.88. Found: C, 71.74; H, 7.36; N, 20.60.

Dimethyl 2-Ethylidene-3-methylglutarate (2c). Stereoisomeric Composition of Dimer 2. A 10-ml portion of 20% aqueous sodium hydroxide was added to 1.0 g (7.46 mmol) of **2**, and the mixture was refluxed for 24 hr. The hydrolysate was washed with ether to remove any unreacted **2**, acidified with aqueous hydrochloric acid, and then extracted with ether to give 2-ethylidene-3-methylglutaric acid, 1.04 g (6.05 mmol), 81%, identified by comparison with a reference sample.[1] A 0.40-g (2.32 mmol) portion of the acid, recrystallized from a mixture of carbon tetrachloride and ethyl acetate, was dissolved in ether and treated with an excess ethereal solution of diazomethane. The mixture was left for 4 hr, the solvent was removed, and the produced ester **2c**, 0.43 g (2.15 mmol), 93%, was subjected to quantitative NMR analysis in the 5.0–8.0-ppm region. The intensity of a quartet, centered at 6.8 ppm and due to the isomer with a vinylic hydrogen cis to the carbomethoxy group, relative to the intensity of a second quartet, centered at 5.8 ppm and due to the isomer with a vinylic hydrogen trans to the carbomethoxy group,[1] was 69:31, reflecting the distribution of the corresponding dinitrile stereoisomers **2a** and **2b** in the original dimeric fraction. Direct gas chromatographic analysis of dimer **2** on a capillary column (see Analytical) gave two well-resolved peaks in the ratio 67:33, in good agreement with the NMR determination.

1,3,5-Tricyano-2,4,6-trimethylcyclohexane (3). The redistilled trimer, bp 152–155° (0.2 mm), $n^{25}D$ 1.4950, $n^{30}D$ 1.4926, m/e 201 (M^+), was 99% pure and free of any dimer or higher oligomer.

Anal. Calcd for $C_{12}H_{15}N_3$: C, 71.61; H, 7.51; N, 20.88. Found: C, 71.41; H, 7.49; N, 20.59.

Gas chromatography of **3** (see Analytical) reveals the presence of at least three stereoisomers, including a dominant component (75–80%): ir ($CHCl_3$) 966, 1390 (CH_3, symmetrical C–H deformation),[26] 1460 (CH_3, asymmetrical C–H deformation),[26] 2238 (CN stretching), 2910 (ring C–H stretching), 2960 cm^{-1} (CH_3, C–H stretching); NMR ($CDCl_3$) δ 1.38 (d superimposed on weaker m, 9, J = 6.2 Hz, $CHCH_3$), 1.9–2.3 (m, 3, CH_3CH), 2.5–3.0 (m, 3, NCCH).

The ^{13}C NMR spectrum of **3** shows a single line in the nitrile region, indicating the absence of any significant amounts of an unsymmetrically substituted isomer, containing separated as well as adjacent nitrile groups, e.g., 1,2,4-tricyano-3,5,6-trimethylcyclohexane, which should give rise to more than one signal in this region.

2,4,6-Trimethyl-1,3,5-cyclohexanetricarboxylic Acid Monoamide (4). A 5-g (0.025 mol) portion of trimer **3** was dissolved with gentle warming in 12 ml of glacial acetic acid, and to this was added 25 ml of concentrated sulfuric acid in 30 ml of water. The mixture was refluxed for 24 hr, and then cooled down to room temperature, diluted with 100 ml of saturated aqueous sodium chloride, and filtered, and the filtrate was continuously extracted with ether. The extract was treated with activated charcoal and silica gel, filtered, and dried. Removal of the solvent gave 4.6 g (0.018 mol), 72%, of crystalline monoamide **4**. Recrystallization from glacial acetic acid gave a pure sample of **4**: mp 274–276°; m/e 257 (M^+); ir (KBr) 1375 (CH_3, symmetrical C–H deformation), 1425 (CO_2H, C–O– stretching),[27] 1460 (CH_3, asymmetrical C–H deformation), 1595 (NH_2 deformation), 1690 ($CONH_2$, C=O stretching),[27] 1715 (CO_2H, C=O stretching),[27] 2970, 3180–3300 (bonded N–H stretching),[27] 3490 cm^{-1} (OH stretching).

Anal. Calcd for $C_{12}H_{19}O_5N$: C, 56.02; H, 7.44; N, 5.44. Found: C, 56.10; H, 7.17; N, 5.18.

2,4,6-Trimethyl-3,5-dicarbomethoxy-1-cyclohexanecarboxamide (5). A 100-mg (0.388 mmol) portion of monoamide **4** was dissolved in 20 ml of absolute methanol, and the solution was treated with an excess ethereal solution of diazomethane. The mixture was left for 1 hr at room temperature, and the solvent was removed, leaving 108 mg (0.380 mmol), conversion 98%, of the esterified product **5**: m/e 285 (M^+); ir ($CHCl_3$) 1165 (CO_2Me, C–O– stretching), 1440, 1465, 1600 (NH_2 deformation), 1690 (C=O in $CONH_2$),[27] 1745 (C=O in CO_2Me),[27] 3000, 3500 cm^{-1} ($CONH_2$, nonassociated N–H stretching);[27] NMR ($CDCl_3$) δ 0.90 (d, 6, J = 6.2 Hz, CH_3), 1.05 (d, 3, J = 6.5 Hz, CH_3), 1.80–2.80 (m, 6, ring CH), 3.53 (s, 6, OCH_3), 5.28–5.76 (broad signal, 2, NH_2).

2,4,6-Trimethyl-1,3,5-cyclohexanetricarboxylic Acid (6). A 1.9-g (0.094 mol) portion of trimer **3** was dissolved with gentle heating in 8 ml of glacial acetic acid. To this was added 12.5 ml of concentrated sulfuric acid dissolved in 15 ml of water, and the mixture was refluxed for 24 hr. A fresh portion of 12.5 ml of sulfuric acid in 15 ml of water was added to the mixture and refluxing was continued for another 30 hr. After cooling, 30 ml of water was added, and the hydrolysate was filtered and then continuously extracted with ether for 4 days. The extract was washed with water and dried over anhydrous magnesium sulfate, and the solvent was removed, leaving a partially crystalline residue which after repeated fractional crystallization from glacial acetic acid gave 0.26 g (1.05 mmol, yield 11.2%) of acid **6**: mp 284–286°; m/e 258 (M^+); ir (KBr) 1460 (CH_3), 1720 (C=O), 2970, 3550 cm^{-1} (OH); NMR (pyridine) δ 0.9–1.5 (two closely spaced d, 9, CH_3), 2.3–3.4 (m, 6, ring CH), 11.1 (broad signal, 3, CO_2H).

Anal. Calcd for $C_{12}H_{18}O_6$: C, 55.80; H, 7.03. Found: C, 55.91; H, 7.18.

Trimethyl 2,4,6-Trimethyl-1,3,5-cyclohexanetricarboxylate (7). A 50-mg (0.194 mmol) portion of triacid **6** was dissolved in 10 ml of absolute methanol and treated with excess ethereal solution of diazomethane. The mixture was left for 1 hr at room temperature and the solvent was removed under vacuum, leaving 57 mg (0.190 mmol, yield 98%) of triester **7**: m/e 300 (M^+); NMR ($CDCl_3$) δ 0.87 (d, 6, J = 6.2 Hz, CH_3), 1.02 (d, 3, J = 6.6 Hz, CH_3), 1.9–2.9 (m, 6, ring CH), 3.58 (s, 9, OCH_3).

Anal. Calcd for $C_{15}H_{24}O_6$: C, 59.98; H, 8.05. Found: C, 59.70; H, 8.13.

The chemical shift difference between the two sharp, well-resolved doublets at 0.87 and 1.02 ppm, i.e., 0.15 ppm, is the expected one for equatorial and axial methyl groups in a symmetrically substituted cyclohexane.[18] The two signals provide further evidence for the absence of an unsymmetrical, 1,2,4-trimethyl-substituted component in the trimer, since the chemical shift difference for adjacent and separated methyls in such an isomer should be larger, and adjacent methyl substituents should produce methyl–methyl long-range coupling, i.e., a more complex pattern than observed.

Potassium-Catalyzed Oligomerization of 3-Butenenitrile (8). The preparation of the potassium–benzylpotassium catalyst, and the oligomerization of **8**, were carried out using the same procedure as described above for **1**.

In a typical experiment, 1.5 g (0.038 g-atom) of potassium, 1.25 g (0.01 mol) of *o*-chlorotoluene, and 75 g of toluene were used in the catalyst preparation, while 12.6 g (0.187 mol) of monomer **8** in 30 g of toluene was used in the oligomerization. The product, 9.65 g (conversion 76%), contained 63.0% of dimer **2**, 36.2% of trimer **3**, and ca. 0.8% of higher products, as determined by gas chromatography. The average oligomer distribution from several experiments was (% by weight) **2**, 61.0; **3**, 38.2; and higher components, ca. 0.8.

Analytical. Quantitative gas chromatography of oligomerization products was performed on a 6 ft × 0.125 in. column, packed with 10% UCC-W-982 silicone gum rubber, methyl vinyl type, on 80–100 mesh Diatoport S. Separation of **3** into stereoisomeric components was achieved on the same column, using slow programming in the 150–215° range. The resolution of **2** into stereoisomers **2a** and **2b** was carried out on a 300 ft × 0.01 in. Golay column, coated with QF-1 (trifluoropropylmethyl silicone), at 140° and a nitrogen pressure of 20 psi.

A Bruker 90, 90-MHz, Model HFX-10 high-resolution NMR spectrometer was used for measurement of the NMR spectra, while ir analysis was performed with a Perkin-Elmer Model 457A spectrophotometer.

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Registry No.—*cis*-**1**, 1190-76-7; *trans*-**1**, 627-26-9; **2a**, 22485-85-4; **2b**, 22485-84-3; *cis*-**2c**, 16657-04-8; *trans*-**2c**, 16657-03-7; **3**, 54181-86-1; **4a**, 54119-93-6; **4b**, 54163-74-5; **4c**, 54163-75-6; **5**, 54119-98-1; **6**, 54119-99-2; **7**, 54120-00-2; **8**, 109-75-1.

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Notes

Reductive Decyanation of β,γ-Epoxy Nitriles. A New Synthesis of β-Isopropylidene Alcohols

James A. Marshall,* C. Patrick Hagan, and Gary A. Flynn

Department of Chemistry, Northwestern University, Evanston, Illinois 60201

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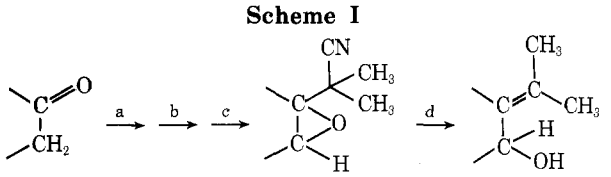
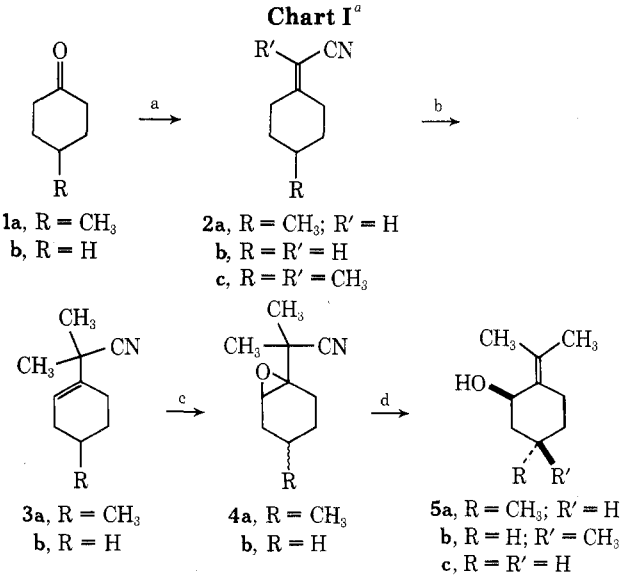
In the course of studies aimed at the synthesis of natural sesquiterpenoids we discovered that β,γ-epoxy nitriles underwent reductive decyanation–elimination to allylic alcohols upon treatment with sodium in liquid ammonia.[1] The epoxy nitriles could be prepared quite easily from ketones by a sequence involving (a) condensation with diethyl sodiocyanomethylphosphate, (b) geminal alkylation with methyl iodide, and (c) epoxidation with *m*-chloroperoxybenzoic acid (Scheme I). Since this initial discovery we have examined a number of additional substrates to ascertain the generality of the sequence and to optimize the reaction conditions. We have also carried out some preliminary studies of the oxidation of the allylic alcohol products. These results are reported herein.

Scheme I



Condensation of 4-methylcyclohexanone (**1a**) with diethyl sodiocyanomethylphosphonate afforded the nitrile **2a.** Alkylation of this nitrile in tetrahydrofuran using excess lithium diisopropylamide as the base and excess methyl iodide gave only the monomethylated conjugated nitrile **2c.** Presumably addition of the amide to the conjugated double bond effectively competes with proton abstraction, as is found for conjugated esters.[2] Schlessinger found that a 1:1 complex of lithium diisopropylamide and hexamethylphosphoric triamide (HMPA) showed a strong preference for proton abstraction in such cases.[2] Following his procedure we obtained an 80:20 mixture of di- and monomethylated product. However, with a 3:1 ratio of HMPA to base, dimethylation proceeded smoothly to give nitrile **3a.** Epoxidation of unsaturated nitrile **3a** afforded the epoxy nitrile **4a** as an apparent mixture of stereoisomers. Reduction–elimination of this mixture with sodium in liquid ammonia gave a roughly 2:1 mixture of alcohols **5a** and **5b,** *trans*- and *cis*-pulegol, in nearly 90% yield (Chart I).

Chart I[a]



[a] a, $NaCH(CN)PO(OEt)_2$; b, $(i\text{-}Pr)_2NLi$, CH_3I, HMPA; c, $m\text{-}ClC_6H_4CO_3H$; d, Na, NH_3.

Application of the above scheme to cyclohexanone (**1b**) afforded 2-isopropylidenecyclohexanol (**5c**) in 46% overall yield. Similarly, cycloheptanone was converted to 2-isopro-