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Isomerization of acetylenic acids with sodium salt of 1,2-diaminoethane: a one step synthesis of megatomoic acid¹

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A number of isomeric tetradecynoic acids were isomerized with the sodium salt of 1,2-diaminoethane. Isomers having the triple bond near the carboxyl group rearranged to E,Z-3,5- and E,E-3,5-tetradecadienoic acids (1 and 2), the former compound being the sex pheromone of the black carpet beetle. Isomers having the triple bond closer to the terminus of the chain afforded some 13-tetradecynoic acid along with 1 and 2. Delocalized anions 12 and 13 are thought to contribute to the formation of 1 and 2.

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On a isomérisé un certain nombre d'acides tétradécynoïques isomères avec le sel de sodium du diamino-1,2 éthane. Les isomères ayant une triple liaison près du groupe carbonyle se transposent en acides tétradécadiènoiques-E,Z-3,5 et E,E-3,5 (1 et 2). Le premier de ces composés est la phéromone sexuelle de l'abeille de tapis noir. Les isomères ayant une triple liaison tout près de l'extrémité de la chaîne fournissent l'acide tétradécyne-13 oïque ainsi que les acides 1 et 2. On pense que les anions délocalisés 12 et 13 contribuent à la formation des composés 1 et 2.

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Introduction

Very strong bases isomerize internal triple bonds of hydrocarbons and alkyn-1-ols to the terminal position in high yield. The first successful isomerization reagent, the potassium salt of 1,3-diaminopropane, was discovered by Brown and Yamashita (1, 2). We have developed alternative reagents, the sodium salts of 1,3-diaminopropane (3, 4) or 1,2diaminoethane,² which effect the same transformation and which can be prepared simply, reproducibly, and with greater safety.

In the course of developing a general route for the synthesis of naturally occurring terminally hydroxylated fatty acid derivatives, we sought to extend the use of these reagents to the isomerization of acetylenic acids, anticipating that an internal triple bond would be isomerized to give the terminal acetylenic acid. That is, it was thought that the base would abstract one proton from the carboxylic acid group and another from a carbon next to the triple bond. Protonation would give either the starting acetylenic acid or an allenic isomer. Abstraction by the base of an allenic proton would, after reprotonation, give the allenic acid, the original acetylenic acid, or a positional isomer. In the alkyn-1-ol case, such reversible random rearrangements are rapid with our reagents; the reaction sequence is completed when the terminal triple bond is formed and the relatively acidic acetylenic proton abstracted to give the disodium alkoxide acetylide salt.

Although alkali metal alkyl amides had not previously been employed as isomerization reagents, rearrangements of acetylenic acids with other bases have been carried out. Vigorous treatment with molten alkali results in cleavage of the carbon skeleton (the Varrentrapp reaction) (5). Reaction of 4-hexynoic and 4-pentynoic acids at $120-160^{\circ}$ C with 9 N potassium hydroxide affords the conjugated 2,4-dienoic acids in good yield (6). Under milder conditions the usual acetylene-allene interconversions are observed; a series of 2-alkynoic acids rearranged by sodium amide in ammonia gives mixtures of 3-alkynoic and 2,3alkadienoic acids (7). Both potassium carbonate (8) and aqueous sodium hydroxide (9) lead to interconversion of short chain 3-alkynoic, 2,3alkadienoic, and 2-alkynoic acids.

From the foregoing, base mediated rearrangements of alkynoic acids would be expected to follow a course parallel to that of the acetylenic alcohols. We thus anticipated that isomerization of acetylenic acids with our reagents would proceed rapidly to produce as sole products carboxylic acids containing a terminal triple bond. However, the rearrangement did not take the expected course, but rather followed a novel pathway. We now report a study of alkali metal alkyl amide mediated rearrangements of some isomeric tetradecynoic acids including a one step synthesis of the sex pheromone of the black carpet beetle (Attagenus megatomia), E,Z-3,5-tetradecadienoic acid (1) (10).

Results and discussion

The fourteen carbon tetradecynoic acid series was chosen to study triple bond isomerizations because the twelve possible isomers are all easily handled, known compounds (11-13). Interconver-

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FIG. 1. Products of rearrangement of 2-, 3-, 5-tetradecynoic acid with sodium salt of 1,2-diaminoethane.

sions could be conveniently followed by gas chromatographic analysis of the methyl esters. Isomerizations were carried out by employing a five-fold excess of the sodium salt of 1,2-diaminoethane (DAE) in DAE at 60°C. The reagent was prepared just before use by reaction of sodium hydride with DAE at 60°C for 0.5-1.0 hour.

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Isomerization of 5-tetradecynoic acid (3) for 2.5 hours gave none of the anticipated 13-tetradecynoic acid (4), but rather rearranged smoothly to a 1:1 mixture of two other isomeric compounds (Fig. 1). No intermediate reaction products could be detected by glc. Separation of the crude product by silver resin chromatography gave E,Z- and E,E-3,5-tetradecadienoic acids (1 and 2) in 67% yield. Structure and stereochemistry were established by comparison with published infrared spectra (14), mass spectral and nmr data (15).

To gain further insight into this unusual rearrangement, 2-tetradecynoic acid (5) was subjected to the same isomerization conditions. Quenching after 5 minutes, followed by esterification and chromatography, afforded methyl 3-tetradecynoate (6a) in 33% yield. The $\Delta 3$ isomer, 3-tetradecynoic acid (6), prepared independently, was also isomerized for 5 minutes to give a mixture of three components: starting material (50%), and the same two products 1 and 2 (50%, 1:1) isolated from the 5-tetradecynoic acid rearrangement reaction (1 and 2). The $\Delta 2$ to $\Delta 3$ isomerization appears to be irreversible; no 2-tetradecynoic acid was observed in the product of isomerization of 3-tetradecynoic acid. As well, allenic intermediates were not seen, and thus, if formed, must rearrange quickly under the reaction conditions.

To study how far along the carbon skeleton the effect of the carboxyl group extends, tetradecynoic acids with the triple bond closer to the methyl terminus were isomerized (Table 1). 7-Tetradecynoic acid was rearranged cleanly to the same mixture of 1 and 2 observed with the 5-tetradecynoic acid isomerization. Gas-liquid chromatography did not allow distinction between the Δ 7- and Δ 5-methyl esters. Although 5-tetradecynoic acid

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Triple bond position of starting acetylenic acid	Reaction time (min)	Product distribution (%)				
		1	2	4	6	Other isomeric tetradecynoic acids
2^a	5	0	0	0	88	12
2	120	42	42	0	0	16
3	5	25	25	0	50	0
50	150	43	49	0	0	8
7 ^c	5	41	38	0	0	21
9	50	29	31	21	0	19
11	60	24	18	27	0	21
13	60	0	0	100	0	0

TABLE 1. Product distributions of rearrangements of isomeric tetradecynoic acids with sodium salt of 1,2-diaminoethane determined by glc analysis of methyl esters

^a33% isolated methyl 3-tetradecynoate.
^b67% isolated 1 and 2.
^c65% isolated 1 and 2.

was not isolated, it seems reasonable to postulate that the normal acetylene-allene interconversions occur and that 7-tetradecynoic acid is isomerized to 5-tetradecynoic acid which, in turn, is rearranged to 1 and 2. Isomerization of 9-tetradecynoic acid, in which the triple bond at the $\Delta 9$ position is equidistant from C-5 and C-13, gave 1, 2 (60%), and 13-tetradecynoic acid (4) (20%). The carboxyl group still affects the course of the rearrangement even when the triple bond starts eight positions away. Isomerization of 11-tetradecynoic acid gave similar results: conversion to 13-tetradecynoic acid was 27% and the 3,5-dienoic acids comprised 42% of the crude reaction mixture. Subjection of 13tetradecynoic acid to the isomerization conditions left the terminal triple bond unchanged.

Fractions of dienoic acids rich in each isomer were subjected to the isomerization reaction conditions. In each case 70% of the material was recovered. Little change in the ratio of isomers was observed. Thus it appears that the isomers do not interconvert and are stable to the reaction conditions.

Based upon these results it seems likely that the triple bond of the fourteen carbon acid is isomerized along the carbon chain in a random fashion through acetylenic and allenic isomers. There appear to be two thermodynamic minima in the system. One, that was anticipated at the beginning of the study, is the terminal acetylenic acid 4. Its stability is derived from the presence of acidic protons at each end of the molecule. The second thermodynamic well is the 3,5-dienoic acid system.

The formation of the 3,5-tetradecadienoic acids 1 and 2 may be accounted for by consideration of the relative acidities of the various protons in the postulated intermediate species. It is known that some alkali metal alkyl amides, notably lithium diisopropylamide, abstract two protons from carboxylic acids: one from the COOH and one from the carbon α to the carboxyl group (16). The sodium salt of DAE also appears to abstract the α proton. Reaction of 2,2-dideuterohexadecanoic acid with the sodium salt of DAE, followed by quenching with water, results in complete loss of deuterium. The loss of both deuterium atoms may be due to protonation of the dianion with the solvent 1,2-diaminoethane. Dianions may be contributing species in acetylenic acid rearrangements. Thus, $\Delta 5$ isomer 3 may give 7 which could be reprotonated by solvent (Fig. 2). Other possible intermediates may be 8 to 11. Proton shifts from C-3 to C-5 in 10 and from C-6 to C-4 in 11 would result in extended delocalized pi (π) systems 12 and 13 which should have added stability. Protonation of 12 and 13 at C-2 would give the observed products 1 and 2. Quenching of dianions 12 and 13 with methyl iodide would be anticipated to introduce a methyl group at C-2 giving 14 and 15 (17).

To test this hypothesis, isomerization of 7-tetradecynoic acid was carried out and the reaction quenched with methyl iodide. Two major products (total 90%, 1:1), each closely followed by minor products (10%, 1:1) were observed in the glc of the esterified reaction mixture. The mass spectra of the two major products were identical with those of 1 and 2. The fragmentation patterns of 1 and 2 are superimposable: 238 (M⁺), 179 (M⁺ – COOCH₃, α -cleavage) and 164 (M⁺ – CH₃COOCH₃, McLafferty rearrangement). The mass spectra of the two minor components were also superimposable, and consistent with 14 and 15 which are alkylated at C-2: 252 (M⁺), 193 (M⁺ – COOCH₃, α -cleavage), and 164 (M⁺ - H₂CCH₃COOCH₃, McLafferty

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FIG. 2. Postulated intermediates in isomerization of tetradecynoic to 3,5-tetradecadienoic acids.

rearrangement). The peak at m/z 164 found in the spectra of the minor compounds and 1 and 2 establishes that alkylation occurs at C-2.

Ionic species having extensive delocalization of the negative charge such as 12 and 13 can only be formed if the starting alkynoic acid has an abstractable proton at C-2. As a further test for the intermediacy of 12 and 13 a 2,2-disubstituted alkynoic acid was prepared and subjected to the isomerization reaction conditions (Fig. 3). Thus, isobutyric acid was treated with two equivalents of lithium diisopropylamide to form the dianion, followed by addition of 1-bromohexadec-7-yne affording 2,2-dimethyloctadec-9-ynoic acid (16) according to the method of Cregar (17). Rearrangement of **16** with the sodium salt of 1,2-diaminoethane produced a single isomer, that containing the terminal triple bond, 2,2-dimethyloctadec-17-ynoic acid (**17**).

It appears from the methyl iodide trapping experiment and from the rearrangement of the 2,2-disubstituted alkynoic acid to the terminally substituted isomer that the formation of a delocalized dianion system may be the driving force for the rearrangement of acetylenic to 3,5-dienoic acids. The stereochemistry observed in 1 and 2 is consistent with protonation of 12 and 13. The barrier for interconversion of 1 and 2 or 12 and 13 must be

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FIG. 3. Synthesis and isomerization of 2,2-dimethyloctadec-9-ynoic acid.

quite high as 1 and 2 did not equilibrate under the reaction conditions.

The rearrangement of a triple bond in the fourteen carbon acetylenic acids affords an improved synthesis of E,Z-3,5-tetradecadienoic acid (1), megatomoic acid, a component of the sex pheromone of the black carpet beetle (Attagenus megatoma). This insect is a serious pest in stored grain and flour and also attacks fabrics in clothing, rugs, and padding of furniture. The published synthesis of megatomoic acid gives 1 and 2 in 14% yield over 6 steps (15). Rearrangement of either 5- or 7-tetradecynoic acids gives mixtures of 1 and 2 cleanly and in good isolated yield (67% and 65%, respectively).

Experimental

Infrared spectra were obtained with a Perkin Elmer 237B instrument employing chloroform solutions or neat films. Proton nmr spectra were recorded on an HA-100 spectrometer using deuterochloroform with internal tetramethylsilane as reference. Gas chromatographic separations were carried out on a Varian 3700 instrument with an SP 2100 capillary column (J and W Scientific, 30 m) with a flame ionization detector, and were run isothermally at 160° or 140°C. Acids were converted to methyl esters with diazomethane prior to glc analysis. Mass spectra were recorded on a Finnigan 4000E gc/ms instrument with an Incos 2300 data system and using an SP 2100 column. Mass spectra are reported in mass to charge units (m/z) with the relative intensities as percentages of the base peak. Accurate mass measurements were provided by the mass spectrometry laboratory, Psychiatric Research Unit, University of Saskatchewan, with an MS902S instrument with VG console update.

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Accurate masses were obtained at 1500 resolution and 3 s/ decade using accurate mass – low resolution software with PFTBA internal standard. Elemental analyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, Michigan, U.S.A.

The 7 tetradecynoic acids employed in this study are all known compounds. Each was prepared from the corresponding alcohol by Jones oxidation. The 2-, 5-, 7-, 9-, and 11-tetradecyn-1-ols were obtained by alkylation of the appropriate ω -tetra-hydropyranyloxy alkyne using lithium amide in dimethoxy-ethane and alkyl halides as described previously (3). 2- Tetradecyn-1-ol was isomerized with the lithium salt of 1,3-diaminopropane at -11°C for 10 min to give 3-tetradecyn-1-ol (5) (81% conversion); product purified by chromatography over silica gel. Treatment of 2-tetradecyn-1-ol with the sodium salt of 1,3-diaminopropane at 60°C gave 13-tetradecyn-1-ol as previously reported (3).

All rearrangement reactions were carried out using the same experimental conditions, varying only the substrate and reaction time. An isomerization reaction of 7-tetradecynoic acid is described in full.

Isomerization of 7-tetradecynoic acid

To a 100 mL flask (flame dried under vacuum), fitted with a magnetic stirring bar and rubber septum through which a slight positive pressure of dry nitrogen was introduced, was added NaH (680 mg, 57% in mineral oil, 17 mmol). The mineral oil was removed with 3 hexane washes and 1,2-diaminoethane (DAE, previously distilled from BaO and stored over molecular sieves, 8 mL) was added. The mixture was stirred and heated at 60°C for 1h by which time H₂ evolution had ceased and a purple solution resulted. A solution of 7-tetradecynoic acid (900 mg, 4 mmol) in DAE (8 mL) was added to the reagent at 60°C. After 5 min the reaction was quenched by addition of ice/water. The mixture was acidified with HCl and was extracted 3 times with ether. The combined extracts were washed with H2O and NaCl solution, dried over Na₂SO₄, filtered, and the solvent evaporated to give 620 mg of product. Gas-liquid chromatographic analysis (160°C) indicated 3 major components in the mixture: methyl tetradecynoates, 12%; 1a, 41%; 2a, 38%. The crude acidic product was chromatographed over an ion exchange column (Lewatit SP 1080 GR, Merck, Na⁺ ions replaced by Ag⁺) eluting with methanol. First to elute was E, E-3, 5-tetradecadienoic acid (2), 180 mg, mp 55.5-57.0°C (plates from petroleum ether), followed by a mixed fraction of 80 mg 1 and 2, and then by E, Z-3, 5-tetradecadienoic acid (1), 120 mg as an oil. The acids were characterized as the methyl esters: methyl E, Z-3, 5-tetradecadienoate (1a); ir v_{max} (neat film): 1740 (s), 1050 (w), 960 (m), and 940 (m) cm⁻¹; ¹H nmr δ : 5.2 to 6.7 (m, olefinic H, 4H), 3.68 (s, OCH₃, 3H), 3.14 (d, J = 8 Hz, OCCH₂, 2H), 2.0 to 2.2 (m, CH₂C=, 2H), 1.2 to 1.4 (m, CH₂, 12H), and 0.90 (t, J = 6 Hz, CH₃, 3H); mass spectrum: 238 (M^+ , 5.3%), 179 (M^+ COOCH₃, 1.6%), 178 (M⁺ - HCOOCH₃, 1.5%), 164 (M⁺ -H₃CCOOCH₃, 5.6%), 79 (81%), 41 (100%). Methyl E,E-3,5tetradecadienoate (2a); ir v_{max} (neat film): 1740(s), 980(s) cm⁻¹; ¹H nmr δ: 5.4 to 6.2 (m, olefinic H, 4H), 3.63 (s, OCH₃, 3H), 3.05 $(d, J = 8 Hz, OCCH_2, 2H), 1.9 to 2.3 (m, CH_2C=C, 2H), 1.1 to$ 1.6 (m, CH₂, 12H), 0.88 (t, J = 6 Hz, CH₃, 3H); mass spectrum: 238 (M⁺, 4.3%), 179 (M⁺ - COOCH₃, 1.8%), 178 (M⁺ -HCOOCH₁, 1.2%), 164 (M⁺ – H₃CCOOCH₃, 5.3%), 79 (89%), 41 (100%).

Attempted isomerizations of E,E-3,5-tetradecadienoic acid (2) and of E,Z-3,5-tetradecadienoic acid (1)

A sample of 3,5-tetradecadienoic acids rich in the *E*,*E*-isomer (86:14), 200 mg, was subjected to the isomerization reaction conditions. After 2 h 140 mg product was recovered, glc analysis gave 78% 2*a* and 13% 1*a*.

Similarly a sample rich in E,Z-3,5-tetradecadienoic acid

(79:17), 105 mg, was submitted to the reaction conditions for 2 h; 70 mg was recovered. Gas-liquid chromatographic analysis indicated 73% 1a and 17% 2a.

Reaction of 2,2-dideuterohexadecanoic acid with the sodium salt of DAE

To the sodium salt of DAE (7.2 mmol in 4.0 mL DAE) at 60°C was added a solution of 2,2-dideuteropalmitic acid in DAE (300 mg, 1.2 mmol in 3.2 mL DAE). The reaction was quenched after 15 min and worked up to give 300 mg white solid. A small sample was esterified with diazomethane and 'H nmr integration of OCH₃ to CH₂CO was 3:2 indicating complete exchange of protons for deuterons.

Isomerization of 7-tetradecynoic acid quenched with methyl iodide

The isomerization reaction of 7-tetradecynoic acid was repeated using 250 mg Δ 7. After 5 min the reaction was cooled in an ice/salt bath and methyl iodide (0.6 mL, 9 equiv.) was added dropwise. After the usual work-up 260 mg product was obtained; glc of the methyl esters at 160°C showed two new products each with slightly longer retention times than 1a and 2a: methyl tetradecynoates, 11%; 1a, 38%; 14a, 3.4%; 2a, 35%; 15a, 3.5%. Mass spectrum of 14a: 252 (M⁺, 5.5%), 193 (M⁺ - COOCH₃, 2.7%), 164 (M⁺ - CH₃COOCH₃, 3.1%), 81 (94%), 41 (100%); mass spectrum of 15a: 252 (M⁺, 6.0%), 193 (M⁺ - COOCH₃, 7.4%), 192 (M⁺ - HCOOCH₃, 2.4%), 164 (M⁺ - CH₃COOCH₃), 81 (100%). Quenching with a larger excess of methyl iodide led to the same ratios of products.

2,2-Dimethyloctadec-9-ynoic acid (16)

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To a cooled solution of diisopropylamine (1.6 mL, 12 mmol) in dry tetrahydrofuran (THF, distilled from benzophenone ketyl, 50 mL) was added a solution of *n*-butyllithium in hexane (7.0 mL, 14 mmol) maintaining internal temperature less than 0°C. The pale yellow solution was kept at 0°C for 0.5h, then a solution of isobutyric acid (0.56 mL, 6.0 mmol, distilled from P₂O₅) in THF (5 mL) was added. Still at 0°C, after 0.5 h, to the gold solution was added 1-bromohexadec-7-yne (1.6 g, 10 mmol) in THF (10 mL). After warming to ambient temperature and stirring overnight the reaction mixture was poured into ice/ dilute HCl and the product extracted 3× with ether. The combined organic phases were washed with NaCl solution, dried over Na₂SO₄, filtered, and the solvent evaporated to give 2.8g product. Filtration over silica gel, eluting first with hexane, gave 550 mg recovered bromide and then with ether gave 16 (1.15 g,3.7 mmol, 62%) having bp 200°C at 0.1 Torr; ir v_{max} (neat film): 3100 (br s), 1700 (s) cm⁻¹; ¹H δ : 2.12 (m, $w_{1/2} = 5$ Hz, H₂CC==C, 4H), 1.2–1.6 (m, $w_{1/2} = 15$ Hz, CH₂, 22H), 1.15 (s, CH₃, 6H), 0.86 (t, J = 6 Hz, CH₃, 3H). Anal. calcd. for C₂₀H₃₆O₂: C 77.86, H 11.76; found: C 77.46, H 11.79. The methyl ester gave glc retention time 16.7 min at 210°C; mass spectrum m/z: 322 (M⁺, 1%), 102 ((H₃COCOHC(CH₃)₂)⁺, McLafferty rearrangement, 100%); molecular ion Exact Mass calcd.: 322.2872; found: 322.2892.

ABRAMS

2,2-Dimethyloctadec-17-ynoic acid (17)

To the sodium salt of DAE (5.0 mmol in 2.0 mL DAE) at 60°C was added a solution of 16 (250 mg, 0.8 mmol) in DAE (3.0 mL). After 3 h, the reaction was quenched and worked up to give 340 mg crude product. The glc of methyl esters at 210°C gave 2 peaks: retention time 16.7 min (7%) and 17.5 min (92%). The product was distilled at 240°C (0.1 Torr) to give pure 17, 120 mg (48%); ir v_{max} (CHCl₃): 3610 (m), 3300 (s), 3100 (br s), 2100 (w), 1700 (s) cm⁻¹; ¹H nmr 8: 2.16 (m, $w_{1/2} = 12$ Hz, H₂CC \equiv C, 2H), 1.88 (t, J = 1.5 Hz, C \equiv CH, 1H), 1.2–1.6 (m, $w_{1/2} = 4$ Hz, 26H), 1.20 (s, CH₃, 6H). *Anal*. calcd. for C₂₀H₃₆O₂: C 77.86, H 11.76; found: C 78.27, H 12.14. The methyl ester gave glc retention time 17.5 min at 210°C; mass spectrum m/z: 322 (M⁺, 1%), 102 ((H₃COCOHC(CH₃)₂)⁺, McLafferty rearrangement, 100%); molecular ion *Exact Mass* calcd.: 322.2872; found: 322.2869.

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