On cis-β-Naphthylacrylic Acids

KAI ARNE JENSEN, ANDERS KJÆR and S. CHRISTIANSEN LINHOLT

Chemical Laboratory of the University of Copenhagen, Copenhagen, Denmark

In connection with investigations on 1-naphthylacetalddehyde (Jensen and Christensen ¹) experiments were undertaken to prepare cis-β-(1-naphthyl)-acrylic acid (V) and related compounds.

In analogy with allo-cinnamic acid, cis-β-(1-naphthyl)-acrylic acid could be obtained through the following series of reactions:

\[ \begin{align*}
1 \cdot \text{C}_{10}\text{H}_7 \cdot \text{CH} = \text{CH} \cdot \text{COOH} & \rightarrow 1 \cdot \text{C}_{10}\text{H}_7 \cdot \text{CH} = \text{CH} \cdot \text{COOEt} \\
\text{I (trans)} & \rightarrow \text{II (cis)} \\
1 \cdot \text{C}_{10}\text{H}_7 \cdot \text{CHBr} \cdot \text{CHBr} \cdot \text{COOEt} & \rightarrow 1 \cdot \text{C}_{10}\text{H}_7 \cdot \text{C} = \text{C} \cdot \text{COOH} \\
\text{III} & \rightarrow \text{IV (reduction)} \\
1 \cdot \text{C}_{10}\text{H}_7 \cdot \text{CH} = \text{CH} \cdot \text{COOH} & \rightarrow \text{V (cis)}
\end{align*} \]

1-Naphthaldehyde on treatment with maleic acid in pyridine afforded the trans-acid (I), melting at 210-212° in agreement with previous statements²,³. Bromination of (I), as described by Wojack et al.⁴, did not proceed very satisfactorily in our hands, nor did the subsequent alkali-induced dehydrobromination. Therefore attention was turned to the procedure used by West⁵ according to which the ester (III) was treated with potassium hydroxide but with no better success. After some trials it became obvious that the employment of rigorously purified ester (III) and high alkali concentration were factors of prime import, increasing the yield of the propiolic acid (IV) to 80-90 %. When submitted to hydrogenation with a palladium catalyst precipitated on barium sulfate, the propiolic acid readily took up one mole of hydrogen and the desired β-(1-naphthyl)-acrylic acid (V) was isolated as colourless plates,
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Fig. 1. Ultraviolet absorption spectra of: cis-β-(1-naphthyl)-acrylic acid prepared by hydrogenation of the corresponding propiolic acid I; cis-β-(1-naphthyl)-acrylic acid prepared by rearrangement of the trans-acid II; trans-β-(1-naphthyl)-acrylic acid.

Fig. 2. Ultraviolet absorption spectra of: cis-β-(2-naphthyl)-acrylic acid; trans-β-(2-naphthyl)-acrylic acid.

melting at 156°. This acid is considered as a cis-form on account of the mode of formation, melting point, solubility and UV-spectrum (Fig. 1).

At a late stage of the present investigation Havinga and Nivard reported on the preparation of cis-β-(1-naphthyl)-acrylic acid, m.p. 141-143°, by ultraviolet irradiation of the trans-acid, and presented UV-data for the two geometrically isomeric acids, which although quite similar to our spectroscopical findings differed significantly from these in having the peak for the cis-acid displaced about 10 mμ towards the long wave region.

Shortly afterwards the communication by Lock and Gergely appeared in which the cis-configuration of a photorearranged trans-acid (m.p. 143-145°) seemed to be convincingly established.

These independent findings with their mutual accord in melting points, impelled us to re-examine our cis-acid as to homogeneity and identity. Several attempts to repeat the photoinduced rearrangement as described by Lock and Gergely (l.c.) invariably yielded an acid (m.p. 156°) which by means of mixed melting point, ultraviolet (Fig. 1) and infrared (Fig. 5) spectra proved to be identical with the specimen prepared via the propiolic acid.
In view of the experimental evidence it appears safe to conclude that our acid (m. p. 156°) possesses cis-configuration and that the reported lower-melting acids merit this designation as well. The question remains whether the lower melting preparation represents a dimorphous form. The occurrence of polymorphism in this series would not be surprising, recalling the existence of no less than four different forms of allo-cinnamic acid. The discrepancy in melting points and UV-spectra between Havinga and Nivard's (l. c.) and our cis-acid may, however, be accounted for by the presence of a slight amount of trans-acid in their preparation.

An identical sequence of reactions starting with 2-naphthaldehyde yielded cis-\(\beta\)-(2-naphthyl)-acrylic acid (VI), for which ultraviolet data are presented in Fig. 2.

\[
\begin{align*}
2 \cdot C_{10}H_7 \cdot CH &= CH \cdot COOH \\
2 \cdot C_{10}H_7 \cdot CHBr &\cdot CHBr \cdot COOEt \\
VI &\quad VII \\
2 \cdot C_{10}H_7 \cdot CH &= CBr \cdot COOH \\
VIII
\end{align*}
\]
In contradistinction to what was found in the first series, bromination of the free trans-β-(2-naphthyl)-acrylic acid proceeded smoothly in high yield. Upon short heating of ethyl α,β-dibromo-β-(2-naphthyl)-propionate (VII) with ethanolic potassium hydroxide two isomeric monobromonaphthylacrylic acids were obtained (m.p. 200-202° and 185-186°), which are tentatively designated as trans- and cis-α-bromo-β-(2-naphthyl)-acrylic acids (VIII) respectively, the allocation of structure being made merely on basis of melting points, solubilities and UV-spectra (Fig. 3) of the two isomeric pairs. Again, in the phenyl series the analogous transformation of β-phenyl-α,β-dibromopropionic acid into two isomeric α-bromo-cinnamic acids is well known from in the literature.7,8
On further hydrogenation the cis-β-naphthylacrylic acids were transformed into β-(1-naphthyl)- and β-(2-naphthyl)-propionic acids respectively, having melting points identical with those of the corresponding acrylic acids, although a depression of about 20° was noted in admixture with these. A preliminary suspicion that the reason for the accord in melting points should be sought in nearly identical crystal lattices for the acrylic- and propionic acids were not borne out by the Debye-diagrams which appeared to be quite different.

In Fig. 4 the UV-spectra of the two isomeric β-naphthylpropionic acids are presented.

**EXPERIMENTAL**

1- and 2-Naphthaldehyde. It was found that these aldehydes could very conveniently be prepared by oxidation of 1- and 2-methylnaphthalene with selenium dioxide (cf. ref. 9).

In a three-necked flask provided with a stirrer, thermometer and an air-cooled condenser set for distillation, 2-methylnaphthalene (175 g) was melted and freshly sublimed selenium dioxide (85 g) added with stirring. The well agitated mixture was heated cautiously to 200°, whereupon a vigorous reaction started with water, methylnaphthalene and some aldehyde distilling over. When the reaction subsided, heating was continued for about 10 minutes. The distillate (60 ml) diluted with 150 ml of benzene was added to the cooled reaction mixture and the selenium filtered off. After removal of benzene at atmospheric pressure the residue was fractionated in vacuo. The excess of 2-methylnaphthalene distilled at 110°/10 mm followed by the aldehyde at 150°/12 mm. After recrystallization from ethanol the aldehyde melted at 57°. Yield 55 g or 70 % (calculated on SeO₂). A second recrystallization from ethanol raised the melting point to 59° in accordance with the values in the literature (cf. ref. 10).

The same procedure was employed to prepare 1-naphthaldehyde in 50 % yield. The yields reported here may perhaps be increased by further modification of the procedure.

**1-Naphthyl-derivatives**

*trans-β-(1-Naphthyl)-acrylic acid* (I). Prepared by condensation of 1-naphthaldehyde with malonic acid in pyridine according to Fulton and Robinson. Yield 60 %. M.p. 210—212°, in accordance with the value given by most authors. Willstaedt and Scheiber report the melting point 129-130°, probably attributable to a misprint.

\[
\text{C}_{12}\text{H}_{10}\text{O}_{2} \quad (198.2) \quad \text{Calc.} \quad \text{C} \quad \text{H} \\
\text{Found} \quad \text{78.76} \quad \text{5.08} \\
\text{Micro-hydrogenation:} \quad 9.935 \text{ mg} \sim 1.130 \text{ ml H}_{2} \quad (0°, 760 \text{ mm}) \quad \text{Calc.} \quad 1.124 \text{ ml}
\]

*Ethyl trans-β-(1-naphthyl)-acrylate* (II). Prepared by esterification of the acid, according to known procedures. B.p. 250° at 13 mm. Yield 90 %.

\[
\text{C}_{15}\text{H}_{14}\text{O}_{2} \quad (226.3) \quad \text{Calc.} \quad \text{C} \quad \text{H} \\
\text{Found} \quad \text{79.43} \quad \text{6.24}
\]
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Ethyl β-(1-naphthyl)-α,β-dibromopropionate (III). By bromination of the ester (II) according to West 3. Yield 92%. M.p. 77-78°.

\[ \text{C}_{12}\text{H}_{14}\text{O}_{2}\text{Br}_{2} \]  
Calc. Br 41.45  
Found 41.31

β-(1-Naphthyl)propionic acid (IV). This acid has been described by Wojack et al.4, and by West 3 who obtained it from the dibromopropionic acid and the ethyl dibromopropionate respectively. The ester method seemed to be preferable as the yield by bromination of the free acid is much lower than for the corresponding ester, and since the elimination of hydrogen bromide from the dibromo acid gave only a 40% yield of the propiolic acid. Following the directions of West 3, however, we obtained no propiolic acid at all. After some experiments it became clear that it is essential to use a pure dibromo ester (West used the crude ester) and a very high concentration of potassium hydroxide. In the following way a very satisfactory yield was obtained:

A solution of 0.01 mole (3.86 g) of ethyl β-(1-naphthyl)-α,β-dibromopropionate (III) and 0.12 mole (6.7 g) of potassium hydroxide in 75 ml of 95% ethanol was refluxed for 4 hours. The solution was cooled, filtered and the ethanol removed \textit{in vacuo}. After addition of 25 ml of water the solution was extracted twice with ether. The aqueous solution was heated to expel dissolved ether, cooled in ice and the acid precipitated by addition of dilute sulfuric acid. The crude product was recrystallized from carbon tetrachloride. M.p. 138°. Yield 1.60 g raised by an additional crop from the mother liquor to 1.80 g (92%).

\[ \text{C}_{15}\text{H}_{8}\text{O}_{2} \]  
Microhydrogenation:
\[ \text{Found 4.074 mg} \sim 0.922 \text{ ml H}_2 \ (0^\circ, \text{760 mm}) \]
Calc. 0.930

\textit{cis-β-(1-Naphthyl)-acrylic acid.} The propiolic acid (2.25 g) was dissolved in 50 ml of ethanol; 1.5 g of Pd/BaSO₄ (5%) was added and the mixture hydrogenated at room temperature and atmospheric pressure. After \textit{ca.} two hours, 95% of the theoretical amount of hydrogen (260 ml) had been absorbed. The catalyst was filtered off, the filtrate concentrated to 25 ml and after cooling in the ice-box, 1.5 g of crystals with m.p. 140° were isolated. Three recrystallizations from benzene followed by one from a mixture of carbon tetrachloride and chloroform (1 : 1) raised the melting point to 154-156° (yield 1.06 g).

\[ \text{C}_{15}\text{H}_{10}\text{O}_{2} \]  
Microhydrogenation:
\[ \text{Found 10.00 mg} \sim 1.138 \text{ ml H}_2 \ (0^\circ, \text{760 mm}) \]
Calc. 1.132

The acid crystallizes from ethanol, benzene, carbon tetrachloride or mixtures of carbon tetrachloride and chloroform in nacreous plates, easily soluble in methanol and acetone. The sodium salt is soluble in methanol but insoluble in acetone. The acid sublimates at 140°/0.1 mm without decomposition and with unchanged melting point.

The \textit{cis}-acid was also prepared by ultraviolet irradiation of the \textit{trans}-acid, mainly following the directions of Lock and Gergely 6. The purification of the crude product was
performed in the following way. After evaporation of the ether, the residue was suspended in methanol and unchanged trans-acid filtered off, methanol was removed in vacuo and the residue recrystallized several times from benzene. Starting with 2 g of trans-acid, we obtained 200 mg (m.p. 154-156°), 100 mg (m.p. 151-153°) and 270 mg (m.p. 146-148°), i.e. a total yield of 27 % (Lock and Gergely: 29 %). No depression was observed on admixture with the acid prepared via the propiolic acid. Analysis of the product melting at 154-156° gave the following values:

\[
\begin{align*}
C_{13}H_{10}O_2 \quad & \text{Calc. C 78.76 H 5.08} \\
& \text{Found } 78.94 \quad 5.15
\end{align*}
\]

2-Naphthyl-derivatives

The 2-naphthyl compounds were in most cases prepared according to the directions given for the 1-naphthyl derivatives:


\[
\begin{align*}
C_{13}H_{10}O_2 \quad & \text{Calc. C 78.76 H 5.08} \\
& \text{Found } 78.47 \quad 5.06
\end{align*}
\]

Microhydrogenation: 15.308 mg ~ 1.720 ml H₂ (0°, 760 mm)
Calc. 1.731

Ethyl *trans*-β-(2-naphthyl)-acrylate. Yield 94 %. M.p. 68-69° (recrystallized from ethanol).

\[
\begin{align*}
C_{15}H_{14}O_2 \quad & \text{Calc. C 79.43 H 6.24} \\
& \text{Found } 79.66 \quad 6.17
\end{align*}
\]

Ethyl β-(2-naphthyl)-α,β-dibromopropionate. Yield 92 %. M.p. 82-83° (recrystallized from abs. ethanol).

\[
\begin{align*}
C_{15}H_{14}O_2Br_2 \quad & \text{Calc. C 46.63 H 3.63 Br 41.45} \\
& \text{Found } 46.54 \quad 3.79 \quad 41.68
\end{align*}
\]

β-(2-Naphthyl)-propiolic acid. In contrast to the corresponding 1-naphthyl compound this acid forms a slightly soluble potassium salt and the directions were altered accordingly.

A solution of 0.04 mole (15.4 g) of the dibromo ester (VII) and 0.48 mole (26.8 g) of potassium hydroxide in ethanol (300 ml) was refluxed on a steam bath for 4 hours. After standing in the ice-box overnight, the precipitate was filtered off, washed with a little cold ethanol and dissolved in 400 ml of water at 50—60°. After filtering the solution was cooled to 30°, and the acid precipitated by slow addition of 30 ml of 4-N sulfuric acid. After drying, the crude product was crystallized from carbon tetrachloride. Yield 5.00 g, increased by 0.60 g from the mother liquor. Total yield 71 %. M.p. 145-147°. The acid
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separates from carbon tetrachloride in long colourless needles, easily soluble in the common solvents.

\[
\begin{align*}
\text{C}_{13}\text{H}_{5}\text{O}_{2} (196.2) & \quad \text{Calc.} & \quad \text{C} & \quad 79.56 & \quad \text{H} & \quad 4.11 \\
& \quad \text{Found} & \quad 79.41 & \quad 4.27 \\
\text{Microhydrogenation:} & \quad 9.614 \text{ mg} \sim 2.197 \text{ ml H}_2 (0^\circ, 760 \text{ mm}) \\
& \quad \text{Calc.} & \quad 2.190 & \quad 2.190
\end{align*}
\]

cis-β- (2-Naphthyl)-acrylic acid. Prepared in the same way as the 1-naphthyl compound. The ethanolic solution was concentrated to 15 ml and the crystals deposited (1.35 g, m.p. 130°) recrystallized from carbon tetrachloride; yield 1.20 g, m.p. 134°.

\[
\begin{align*}
\text{C}_{13}\text{H}_{10}\text{O}_{2} (198.2) & \quad \text{Calc.} & \quad \text{C} & \quad 78.76 & \quad \text{H} & \quad 5.08 & \quad \text{Eq. w.} & \quad 198.2 \\
& \quad \text{Found} & \quad 78.84 & \quad 5.11 & \quad \ast & \quad 198.5 \\
\text{Microhydrogenation:} & \quad \text{Found} & \quad 12.738 \text{ mg} \sim 1.432 \text{ ml H}_2 (0^\circ, 760 \text{ mm}) \\
& \quad \text{Calc.} & \quad 1.441 & \quad \ast & \quad \ast
\end{align*}
\]

The acid resembles very much the isomeride, but differs in being more soluble in ethanol and benzene.

β- (2-Naphthyl)-a,β-dibromopropionic acid. trans-β(2-Naphthyl)-acrylic acid (1 g) was suspended in carbon disulfide (20 ml) and a solution of bromine (0.8 g) in carbon tetrachloride added with stirring. During the addition the reaction mixture was exposed to sun light. After removal of excess of bromine by shaking with sulfuric acid, carbon disulfide was removed and the residue recrystallized from ethanol. Yield practically quantitative (1.75 g). M.p. 177-180°.

\[
\begin{align*}
\text{C}_{13}\text{H}_{10}\text{O}_{2}\text{Br}_{2} (358.0) & \quad \text{Calc.} & \quad \text{Br} & \quad 44.70 \\
& \quad \text{Found} & \quad 44.65
\end{align*}
\]

cis- and trans-β- (2-Naphthyl)-a-bromo-acrylic acid. A solution of ethyl β-(2-naphthyl)-a,β-dibromopropionate (3.86 g) and potassium hydroxide (6.7 g) in ethanol (50 ml) was heated to a short boil. After standing overnight a precipitate had formed which contained the slightly soluble potassium salt of the trans-acid and potassium bromide. It was filtered off and dissolved in hot water (175 ml). After filtering, 10 ml of 1-N hydrochloric acid was added to the hot solution. A precipitate of the acid separated and was recrystallized from 50% (v/v) ethanol. Yield 0.75 g (27%). M.p. 200-202°.

\[
\begin{align*}
\text{C}_{13}\text{H}_{3}\text{O}_{2}\text{Br} (277.1) & \quad \text{Calc.} & \quad \text{C} & \quad 56.35 & \quad \text{H} & \quad 3.27 & \quad \text{Br} & \quad 28.83 & \quad \text{Eq. w.} & \quad 277.1 \\
& \quad \text{Found} & \quad 56.53 & \quad 3.26 & \quad 28.98 & \quad \ast & \quad 276.0
\end{align*}
\]

The filtrate from the potassium salt of the trans-acid was evaporated to dryness in vacuo, the residue dissolved in 20 ml of water and the cis-acid precipitated by addition of 30 ml of 1-N hydrochloric acid. Recrystallized from dilute ethanol it melted at 185-187°. Yield 0.85 g (31%).

\[
\begin{align*}
\text{C}_{13}\text{H}_{3}\text{O}_{2}\text{Br} (277.1) & \quad \text{Calc.} & \quad \text{C} & \quad 56.35 & \quad \text{H} & \quad 3.27 & \quad \text{Br} & \quad 28.83 & \quad \text{Eq. w.} & \quad 277.1 \\
& \quad \text{Found} & \quad 56.60 & \quad 3.25 & \quad 28.98 & \quad \ast & \quad 276.1
\end{align*}
\]
The two acids form pale yellow crystals, slightly soluble in water and carbon tetrachloride, easily soluble in ether. In ethanol the trans-acid is moderately, the cis-acid easily soluble.

Microanalyses were performed in this laboratory by Mr. A. Grossmann. Microhydrogenations were run in the apparatus described by Clauson-Kaas and Limborg\textsuperscript{13}. The ultraviolet absorption spectra were determined in methanol using the Beckman model DU spectrophotometer. The infrared data were obtained in Nujol mulls on the recording Beckman IR-2 equipment.

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SUMMARY

The following new substances are described: $\beta$-(2-naphthyl)-propionic acid, cis-$\beta$-(2-naphthyl)-acrylic acid, $\beta$-(2-naphthyl)-$\alpha,\beta$-dibromopropionic acid and its ethyl ester and trans-$\beta$-(2-naphthyl)-$\alpha$-bromoacrylic acid.

Improved procedures for preparing 2-naphthaldehyde, $\beta$-(1-naphthyl)-propionic acid and cis-$\beta$-(1-naphthyl)-acrylic acid are given.

Discrepancies in the physical data of cis-$\beta$-(1-naphthyl)-acrylic acid are discussed.

REFERENCES

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