Synthesis of 2,3,6,7-Tetramethylnaphthalene from 2,3-Dimethylsuccinic Anhydride and *o*-Xylene

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2,3,6,7-Tetramethylnaphthalene (**7b**) was prepared from 2,3-dimethylsuccinic anhydride (**1**) and *o*-xylene in five steps, and the configurations of their intermediates were studied. The higher-melting isomer (*threo* form) of **1** gave higher-melting products in each step, while the lower-melting isomer (*erythro* form) of **1** gave lower-melting ones. The configurations of the intermediates were confirmed by the MNR spectral data of tetramethyltetralines (**6b**). Similar reactions were carried out with 3-benzoyl-2,3-dimethylpropionic acid (**2a**) in order to learn the configurations of the intermediates. 3-Aroyl-2,3-dimethylpropionic acids (**2**) gave 2,3-dimethyl-4-aryl-3-buten-4-oildes (**3**) upon heating with hydrochloric acid.

In the course of the investigation of thermally stable polyimide polymers derived from naphthalenetertacarboxylic acid anhydrides and aromatic diamines, we realized the necessity of a convenient method of synthesizing 2,3,6,7-naphthalenetetracarboxylic acid. The anhydride of this acid has been prepared by the dehydrogenation of 1,2,3,4,5,6,7,8-octahydronaphthalene-2,3,6,7-tetracarboxylic acid dianhydride[1-3] with bromine.[4,5] 2,3,6,7-Tetramethylnaphthalene, which is oxidizable to the tetracarboxylic acid, has been synthesized by Mosby[6] and Rieke *et al.*[7] but these procedures are inadequate for obtaining the acid in quantity. 4-Arylbutyric acids, which give rise to naphthalene derivatives by cyclization, have been prepared by the Clemmensen reduction of 3-aroylpropionic acids[8] or by catalytic hydrogenation over palladium in acetic acid.[9-11] A partial hydrogenation of 3-benzoylpropionic acid over palladium in alcoholic ammonia gives 4-phenylbutyrolactone.[12]

The present paper will deal with the synthesis of 2,3,6,7-tetramethylnaphthalene (**7b**) from 2,3-dimethylsuccinic anhydride (**1**) and *o*-xylene in five steps, as is shown in Scheme 1, where the *threo* isomer has been designated as an example. A mixture of the diastereoisomer of the starting material could be used for the synthesis of **7b**. When optically inactive *threo* **1** was used, the products of each step in Scheme 1 were of the *threo* form, with a retention of the configuration. Similarly, *erythro* **1** gave *erythro* products. Similar reactions with **2a** were carried out as an adjunct for the investigation of the configuration. The intermediates reported here are new compounds.

Results and Discussion

3-Aroyl-2,3-dimethylpropionic Acids (*2*). In the Friedel-Crafts reaction of **1** with benzene alone or with *o*-xylene in tetrachloroethane, the higher-melting isomer (*threo* form) of **1** gave predominantly the higher-melting isomer of **2a** or **b**. On the other hand, the lower-melting isomer (*erythro* form) of **1** gave the lower-melting isomer of **2a** or **b**. These results suggest that the configuration is retained in the reaction.[13] The NMR and IR spectral data of **2** are summarized in Table 1.

The *threo* **2a** was insoluble in carbon tetrachloride, whereas the *erythro* isomer was soluble. On the other hand, *threo* and *ertyhro* **2b** could not be separated into two diastereoisomers by solvent extraction; rather, they were characterized on the basis of the NMR spectra. The *threo* or *erythro* **2a** was converted to a mixture of nearly equal amounts of them in a strong alkaline solution, while in a weak alkaline solution only a small portion of *threo* **2a** was epimerized, as is shown in Table 2.

2,3-Dimethyl-4-aryl-3-buten-4-olides (*3*). On the Clemmensen reduction of *threo* **2a**, compounds **3a** (racemate) and **4a** (*threo* and *erythro* mixture) were obtained in a molar ratio of 37 : 63, while a mixture of *threo* and *erythro* **2b** (about 1 : 1) gave **3b** (racemate) and **4b** (*threo* and *erythro* mixture) in a 62 : 38 ratio. Refluxing a mixture of **2** and hydrochloric acid gave racemic **3**[14] (Table 3). The IR and NMR spectral data of **3** are shown in Table 4.

TABLE 1. NMR AND IR DATA OF 2

Compound		NMR (δ, ppm)								IR (in Nujol, cm^{-1})	
		2-CH_3	3-CH_3	Ar-CH_3	2-CH	3-CH	Ar-H	CO_2H	$CHCl_3$	ν_{CO}	δ_{Ar-H}
2a	*threo*[a]	1.16, 3H d, J=7 Hz	1.23, 3H d, J=7 Hz	—	2.84—3.14 1H, quint	3.61—3.91 1H, quint	7.35—7.95 5H, m	—	7.24 1H, s	1705 s 1680 s	699 s
	erythro[a]	1.18, 3H d, J=7 Hz	1.26, 3H d, J=7 Hz	—	2.84—3.14 1H, oct	3.61—3.91 1H, oct	7.36—7.99 5H, m	—	7.25 1H, s	1700 s 1674 s	699 s
2b	*threo*[b]	1.12, 3H d, J=7 Hz	1.19, 3H d, J=7 Hz	2.31 6H, s	2.79—3.10 1H, quint	3.62—3.90 1H, quint	7.09—7.65 3H, m	10.65 1H, s	—	1705 s 1676 s	882w 836w
	erythro[b]	1.16, 3H d, J=7 Hz	1.22, 3H d, J=7 Hz	2.31 6H, s	2.75—3.05 1H, oct	3.52—3.82 1H, oct	7.13—7.70 3H, quart	10.76 1H, s	—	1698 s 1673 s	885w 840w

a) NMR: in 2% $CDCl_3$. b) NMR: in 10% CCl_4.

Table 2. Epimerization of **2a** in aqueous alkaline solution

Reactant		Product, %		
Compound	Base	Yield	*threo*	*erythro*
threo	KOH	91	53	47
threo	Na_2CO_3	94	>91	<9
erythro	KOH	92	42	58

Table 3. Lactonization of **2** to **3** with hydrochloric acid

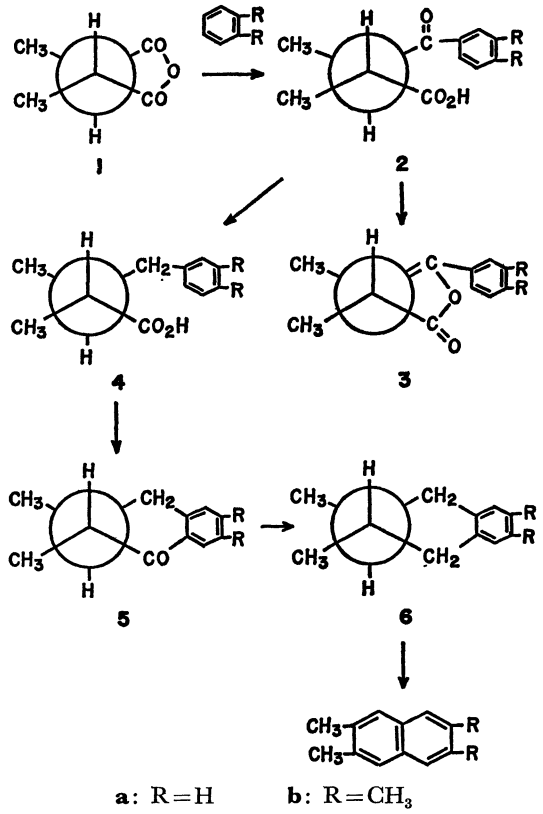
Reactant **2**	Recovered **2**, %	Product **3**, %
a *threo*	6	83
erythro	4	82
b *threo*	4	88

The aliphatic methyl hydrogen signal which appeared upfield in the NMR spectra of racemic **3a** and **b** has triplet bands, while that downfield has a sextet. The downfield signal was changed to a triplet by decoupling with the methine proton. The splitting into a triplet can not be explained at present.

An attempt to esterify the racemic **3b** with methanol in the presence of sulfuric acid failed, and the lactone was recovered. The Clemmensen reduction of racemic **3b** for 10 hr gave a mixture of *threo* and *erythro* **4b** in a 13.5% yield, and 76% of the racemic **3b** was recovered. The hydrolysis of racemic **3b** with potassium hydroxide in aqueous ethanol gave a mixture of the diastereoisomers of **2b**. A reddish color was observed at the initial stage of the hydrolysis, in analogy with angelicalactone.[15]

4-Aryl-2,3-dimethylbutyric Acids (*4*). On the catalytic hydrogenation with palladium on carbon in glacial acetic acid, the higher-melting isomers (*threo* form) of **2a** and **b** gave higher-melting ones of **4a** and **b** respectively, and the lower-melting isomers (*erythro* form) of **2a** and **b** were converted to the lower-melting ones of **4a** and **b**, as is shown in Table 5. The NMR and IR data are summarized in Table 6. It is interesting to note that the carbonyl band of *threo* **4** in the IR spectra appeared at a lower frequency than that of *erythro* ones.

Tetralones (*5*). The cyclization of the acid chloride of *threo* **4a** with anhydrous aluminum chloride in tetrachloroethane gave predominantly the higher-melting isomer of **5a**, while *erythro* **4a** and **b** gave



Scheme 1. *threo*-Isomer.

lower-melting ones of **5a** and **b** respectively, as is shown in Table 7. The cyclization of *threo* or *erythro* **4a** and **b** with polyphosphoric acid (PPA), on the other hand, gave a mixture of the diastereoisomers of **5a** and **b** respectively. The ratio of *threo* and *erythro* **5a** and **b** could be determined by fractional crystallization from petroleum ether or methanol. After heating the *erythro* **5b** with PPA at 115 °C for 1 hr, the recovered tetralone (mp 65—95 °C) was composed of a mixture of nearly equal amounts of the diastereoisomers of **5b**. These results suggest that the configuration is retained during the cyclization by the Friedel-Crafts reaction. It is assumed that the configuration is retained at the cyclization step with PPA, but the tetralone obtained is rapidly epimerized through the enolization catalyzed by the proton.

The NMR data of **5** are summarized in Table 8. The aliphatic methyl proton signals of *threo* and *erythro* **5** overlapped, but they could be distinguished from each other. The methylene and 3-methyl proton

Table 4. NMR and IR data of **3**

Compound	NMR (δ, ppm, in 10% CCl_4)					IR (cm^{-1})			
						ν_{CO}		$\nu_{C=C}$	
	3-CH_3	2-CH_3	2-CH	Ar-CH_3	Ar-H	In 5% CCl_4	Liquid	In 5% CC_4	Liquid
a	1.72, 3H, t	1.77, 3H, sextet	5.51, 1H, b	—	7.06—7.36, 5H, m	1762 s	1759 s	1689m	1691m, 1680m
b	1.76, 3H, t	1.83, 3H, sextet	5.39, 1H, b	2.24, 6H, s	6.80—7.08, 3H, quart	1760 s	1741 s [a]	1685m	1681m[a], 1673m[a]

a) In Nujol.

Table 5. Catalytic hydrogenation of **2** to **4**

Material, **2**	Product, **4** Yield, %	Mp or bp/mmHg	Material, **2**	Product, **4** Yield, %	Mp or bp/mmHg
a *threo*	92	mp 76.5—77.5 °C	**b** *threo*	99	mp 72.5—73.5 °C
erythro	81	bp 151 °C/4.5	*erythro*	85	mp 56—58 °C

Table 6. NMR and IR data of **4**

Compound	NMR (δ, ppm, in 10% CCl_4) 3-CH_3	2-CH_3	Ar-CH_3	CH and CH_2	Ar-H	CO_2H	IR (cm^{-1}, in Nujol or liquid film) ν_{CO}	δ_{Ar-H}
a *threo*	0.87, 3H d, J=6.5 Hz	1.16, 3H d, J=7 Hz	—	2.12—2.88, 4H, m	7.04—7.44 5H, m	11.84 1H, s	1694 s	727m, 694 s
erythro	0.90, 3H d, J=6.5 Hz	1.19, 3H d, J=7 Hz	—	2.08—2.52, 3H, m (3-C**H**, 4-CH_2) 2.76—2.95, 1H, quart (2-C**H**)	7.04—7.36 5H, m	11.70 1H, s	1705 s 1687 s	738m, 700 s
b *threo*	0.84, 3H d, J=6.5 Hz	1.12, 3H d, J=7 Hz	2.20 6H, s	2.2—2.7, 4H, m	6.82—7.04 3H, quart	11.93 1H, s	1696 sh 1687 s	887w, 820m
erythro	0.89, 3H d, J=6.5 Hz	1.19, 3H d, J=7 Hz	2.17 6H, s	2.13—2.56, 2H, m (4-CH_2) 2.68—2.84, 2H, quart (2-C**H**, 3-C**H**)	6.73—7.00 3H, quart	12.16 1H, s	1701 s	892w, 827w

Table 7. Cyclization of **4** to **5**

Material	Recovered **4**, %	Product (**5**) Yield, %	*threo* : *erythro*	
With $AlCl_3$ and acid chloride				
a *threo*	8	58	~100	
erythro[a]	4	93	b)	b)
b *erythro*	4	94	27	73
With PPA				
a *threo*	0	86	b)	b)
erythro[a]	0	80	b)	b)
b *threo*	0	96	49	51
erythro	0	96	48	52

a) Contaminated with 9% of *threo* isomer. b) Could not be isolated.

signals in **5** and **6** exhibited similar chemical shifts, whereas the 2-methyl proton signal of **5** was shifted to a lower field as compared with that of **6** (see Table 10) as a result of the deshielding by the carbonyl group. The lower-field shift of the signal of 8-H as compared with that of 5-H in **5b** may also be attributed to deshielding by the carbonyl group.

Tetralines (**6**). The catalytic hydrogenation of *threo* **5a** and **b** over palladium on carbon in glacial acetic acid at 70—80 °C gave predominantly higher-melting isomers of **6**, as is shown in Table 9. The ratios of the *threo* and *erythro* isomers were determined by means of the aliphatic methyl proton signals in the NMR spectra. The NMR spectral data of **6** summarized in Table 10 support the theory that the two methine protons in the higher-melting isomer are axial and hence the aliphatic methyl groups are equatorial, and that the methine protons in the lower-melting isomer are one axial and one equatorial.[16] Therefore, it may be concluded that the higher-melting isomers in each step have the *threo* (*trans*) configuration, while the lower-melting isomers have the *erythro* (*cis*) one.

2,3,6,7-Tetramethylnaphthalene (**7**) *and -Naphthalenetetracarboxylic Acid.* The diastereoisomer of **6a** and **b** was dehydrogenated with palladium on carbon at 300 °C to 2,3-dimethylnaphthalene and 2,3,6,7-tetramethylnaphthalene respectively. The tetra-

Table 8. NMR data of **5** (δ, ppm in 10% CCl_4)

Compound	3-CH_3	2-CH_3	CH	CH_2	Ar-CH_3	Ar-H
a *threo*	1.14, 3H d, J=7 Hz	1.20, 3H d, J=7 Hz	1.80—2.80 2H, m	2.56—3.05 2H, m	—	7.03—7.88, 4H, m
erythro[a]	0.95 d, J=7 Hz	1.12 d, J=7 Hz	1.75—3.10, m		—	7.02—7.86, m
b *threo*	1.15, 3H d, J=6.5 Hz	1.21, 3H d, J=6.5 Hz	1.76—2.20 2H, m	2.44—2.96 2H, m	2.27 6H, s	6.89, 1H s (5-H) 7.66, 1H s (8-H)
erythro[a]	0.95 d, J=7 Hz	1.14 d, J=7 Hz	1.96—3.08, m		2.28, s	6.97, s 7.76, s

a) Contaminated with *threo* isomer.

Table 9. Isomer ratio of reduction product (6)

Material (5)	Product (6) Yield, %	*threo* : *erythro*	
a *threo*	34	94	6
b *threo*	92	95	5

Table 10. NMR data of 6 (δ, ppm in 10% CCl_4)

Compound	Aliph-CH_3	Ar-CH_3	CH	CH_2	Ar-H
a *threo*	1.01, 6H d, J=6 Hz	—	1.24—1.65 2H, m	2.25—2.87 4H, m	6.90 4H, s
erythro[a)]	0.91 d, J=6.5 Hz	—	1.88—2.07 m	2.28—2.96 m	7.02 s
b *threo*	1.02, 6H d, J=6 Hz	2.12, 6H, s	1.14—1.57 2H, m	2.16—2.76 4H, oct	6.64 2H, s
erythro	0.88, 6H d, J=7 Hz	2.12, 6H, s	1.66—2.13 2H, quart	2.26—2.94 4H, oct	6.68 2H, s

a) A mixture of *erythro* and *threo* isomers (57 : 43).

methylnaphthalene was then oxidized to the corresponding naphthalenetetracarboxylic acid with aqueous sodium bichromate at 275 °C for 20 hr under an autogeneous pressure in the presence of pyridine to avoid the sublimation of hydrocarbon.

Experimental

All the melting points are uncorrected. The compounds described here are optically inactive. The IR spectra were recorded with a JASCO IR-G Spectrophotometer. The NMR spectra were measured with a JEOL JIM PS 100 apparatus (with TMS as the internal standard).

2,3-Dimethylsuccinic Anhydride (1). Diethyl 2-cyano-2,3-dimethylsuccinate[18,19)] was hydrolyzed with hydrochloric acid to give a mixture of *threo* and *erythro* 2,3-dimethylsuccinic acids. *erytho* (*cis*, *meso*) Acid was obtained by recrystallization from diluted hydrochloric acid[20)]; mp 205 °C (decompn.) (lit, mp 209 °C[20,21)]). The *threo* (*trans*, *racemic*) isomer was isolated from the original mother liquors by extraction with ether; mp 119 °C (lit, mp 127 °C,[20)] 129 °C,[21)] and 128—130 °C[22)]). These acids were then converted to the corresponding acid anhydrides (**1**) by treating them with acetyl chloride.[23)] *threo* **1**: bp 115—120 °C/8—10 mmHg, mp 81—82 °C (lit, mp 89 °C[21)]), NMR (δ, ppm) **CH** 2.68, m in 5% CCl_4, 2.78, m in 2% $CDCl_3$ (lit, 2.76 in $CDCl_3$[21)]) and CH_3 1.41, d, J=7 Hz in 5% CCl_4 1.46, d in 2% $CDCl_3$ (lit, 1.40 in $CDCl_3$[21)]). *erythro* **1**: bp 102—104 °C/7 mmHg, mp 36—37 °C (lit, mp 39—40 °C[20)]), NMR (δ) **CH** 3.18, m in 10% CCl_4, 3.24, m in 2% $CDCl_3$ (lit, 3.23 in $CDCl_3$[21)]) and CH_3 1.26, d, J=7.5 Hz in 10% CCl_4, 1.30, d in 2% $CDCl_3$ (lit, 1.30 in $CDCl_3$[21)]). These acid anhydrides (**1**) exhibited slightly lower melting points than the literature values, but they were NMR spectroscopically pure substances. Therefore, **1** was used in the subsequent reactions without further purification.

3-Aroyl-2,3-dimethylpropionic Acids (2). A mixture of *threo* **1** (24.0 g, 0.188 mol) and anhydrous aluminum chloride (50.5 g, 0.376 mol) in 200 ml of benzene was stirred for 0.5 hr in an ice-water bath, heated for 1 hr at 50 °C, and then poured into 200 ml of ice water containing 30 ml of concd. hydrochloric acid. The precipitate was filtered and washed with benzene. The solid was dissolved in sodium carbonate (8.0 g) in 200 ml of hot water, treated with active carbon, and then acidfied with hydrochloric acid to give 26.7 g of *threo* **2a**; mp 147—148 °C. The benzene solution was extracted with 7.0 g of sodium carbonate in 150 ml of water. The aqueous solution was acidified with hydrochloric acid, and the solid was recrystallized from 40 ml of carbon tetrachloride (treated with active carbon) to give 1.9 g of *threo* **2a**; mp 145—147 °C. The removal of the solvent gave 2.3 g of *erythro* **2a**; mp 69—80 °C. The total yield of **2a** was 28.6 g (79.6%), and the ratio of the *threo* and *erythro* isomers was 92.6 : 7.4. Pure *threo* **2a** was obtained by recrystallization from methanol; mp 148.5—149.5 °C. Found: C, 69.94; H, 6.98%. Calcd for $C_{12}H_{14}O_3$: C, 69.89; H, 6.84%.

A mixture of *erythro* **1** (26.0 g, 0.203 mol) and anhydrous aluminum chloride (54.5 g, 0.408 mol) in 200 ml of benzene was treated as above. The benzene solution was then extracted with 14.0 g of sodium carbonate in 200 ml of water. After the acidification of the aqueous solution, the separated oily material was extracted with ether. The subsequent removal of the solvent gave 37.8 g (90.4%) of *erythro* **2a**; mp 75—78 °C. Found: C, 69.67; H, 6.89%.

o-Xylene (16.6 g, 0.156 mol) was added to a solution of *threo* **1** (20.0 g, 0.156 mol) and anhydrous aluminum chloride (42.0 g, 0.315 mol) in 150 ml of tetrachloroethane chilled with an ice-water bath, after which the reaction mixture was treated as above. *threo* **2b** was obtained from the aqueous alkaline extract; 27.1 g (59.4%); mp 110—113 °C. Recrystallization from aqueous ethanol (1 : 1 vol) gave a pure sample; mp 116.5—117.5 °C. Found: C, 71.51; H, 7.56%. Calcd for $C_{14}H_{18}O_3$: C, 71.75; H, 7.74%.

From the reaction product of *o*-xylene and *erythro* **1**, pasty *erythro* **2b** was obtained in a 92.1% yield.

Epimerization of 2a. A mixture of 10.3 g of *threo* or *erythro* **2a**, 4.5 g of potassium hydroxide (or 3.8 g of sodium carbonate), and 100 ml of water was heated at 85 °C for 3 hr. The solution was then acidified with hydrochloric acid, filtered, and dried over soda lime under a vacuum. The solid was heated with 100 ml of carbon tetrachloride to separate the undissolved *threo* isomer. The *erythro* isomer was obtained from the mother liquors (Table 2).

Clemmensen Reduction of 2. After the Clemmensen reduction of *threo* **2a** (40 g) for 10.5 hr, the product was extracted with benzene. The removal of benzene gave a pasty product; bp 157—160 °C/5 mmHg; 29.9 g. The distillate was added to aqueous sodium carbonate and extracted with benzene. Racemic **3a** was obtained from the benzene solution; bp 149 °C/4 mmHg; 8.3 g (29%). A mixture of *threo* and

erythro **4a** was obtained by the acidification of the aqueous solution; bp 143—144 °C/2.5 mmHg; 17.0 g (49%). The molar ratio of **3a** : **4a** was 33 : 67. Similarly, a mixture of *threo* and *erythro* **2b** was reduced for 12 hr to give **3b** (racemate) and **4b** (*threo* and *erythro* mixture) in a molar ratio of 62 : 38.

The racemic **3b** was recrystallized from methanol to give a pure sample; mp 66.5—67.5 °C. Found: C, 77.50; H, 7.51%. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46%.

Lactonization of **2** *to* **3**. A mixture of *threo* (or *erythro*) **2a** (16.0 g) 80 ml of concd. hydrochloric acid, and 20 ml of water was heated at 150 °C for 1 hr. The product was then treated as above to separate lactone (**3**) and ketonic acid (**2**)) Table 3).

Catalytic Hydrogenation of **2** *to* **4**. Compound (**2**) was hydrogenated to **4** with 5% Pd/C in glacial acetic acid at 60—80 °C for 1 hr under an initial pressure of hydrogen of 60—80 kg/cm² in an autoclave. The product, which was contaminated with 2–5% of ring-hydrogenated compound, was filtered and washed with methanol. After the removal of the solvent, the residue was recrystallized from petr. ether or distilled under a vacuum to give **4** (Table 5). *threo* **4a**: Found: C, 74.61; H, 8.51%. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39%. An analysis of NMR spectra of *erythro* **4a** showed it to contain 18% of the *threo* isomer. *threo* **4b**: Found: C, 76.07; H, 9.38%. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15%. *erythro* **4b**: Found: C, 75.96; H, 9.42%.

The catalytic hydrogenation of racemic **3** required a higher temperature (*ca.* 115 °C) than that of **2**, and the product was comtaminated with 20—40% of a ring-hydrogenated compound.

Cyclization of **4** *to* **5**. *A)*: A mixture of 15.0 g (0.078 mol) of *threo* or *erythro* **4**, 15 g of thionyl chloride, and 30 ml of benzene was heated in an oil bath at 90 °C for 2 hr. The excess thionyl chloride and solvent were then removed under reduced pressure. The resulting acid chloride, dissolved in 30 ml of tetrachloroethane, was added to 10.4 g of anhydrous aluminum chloride in 60 ml of tetrachloroethane chilled with an ice-water bath. Stirring was continued for 0.5 hr at this temperature and then for 1 hr at 60—70 °C. The product was subsequently treated in the usual manner. Fractional crystallization from methanol or petr. ether gave pure *threo* and *erythro* **5b** (Table 7). *threo* **5a** (mp 33.5—34.5 °C): Found: C, 82.49; H, 8.05%. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10%. *threo* **5b** (mp 112.5—113.0 °C): Found: C, 83.41; H, 9.11%. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97%. *erythro* **5b** (mp 51.5—52.5 °C): Found: C, 83.34; H. 9.12%.

B): *threo* or *erythro* **4** (10.0 g) was added to PPA (prepared from 50 ml of 85% phosphoric acid and 60 g of phosphorous pentoxide) at 120 °C. The mixture was stirred for 50 min at this temperature and then poured into 200 ml of ice water. The product was extracted with 100 ml of benzene, and the organic layer was washed with aqueous sodium hydroxide. After the removal of the solvent under reduced pressure, the residue was treated as above to give **5** (Table 7).

Catalytic Hydrogenation of **5** *to* **6**. *threo* **5b** (15.0 g, 0.075 mol) was hydrogenated to give 12.9 g of **6b** in glacial acetic acid (150 ml) in the presence of 5% Pd/C (0.7 g) at 70—80 °C for 1—2 hr under an initial pressure of 60 kg/cm². Subsequent recrystallization from methanol gave a pure sample (mp 104—105 °C); IR (Nujol), 856 cm^{-1} (aromatic one free hydrogen). Found: C, 89.55; H,11.03%. Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71%.

erythro **5b** was hydrogenated to give *erythro* **6b**, contaminated with the *threo* isomer, in a 93—98% yield. Fractional crystallization from petr. ether gave a pure sample; mp 51.5—52.5 °C.

threo **5a** (2.9 g) gave *threo* **6a**; mp 34—35 °C.

Dehydrogenation of **6** *to* **7**. *threo* **6b** (40.0 g) was dehydrogenated to **7b** in the presence of 3.3 g of 5% Pd/C and 10 ml of α-methylnaphthalene at 290—300 °C for 6 hr. The product was extracted with 500 ml of hot benzene and then filtered. The subsequent removal of the solvent gave 35.0 g (89%) of **7b**; mp 192—193.0 °C (from benzene) (lit, mp 191.2—191.8 °C[6] and 188—190 °C[7]). IR (Nujol): 894 cm^{-1} (aromatic one free hydrogen). NMR (δ. ppm in 2% CCl_4): 2.41 (12H, s, Ar-C**H**$_3$) (lit, τ=7.66[7] and 7.64[24]) and 7.44 (4H, s, C**H**) (lit, τ=2.63[7]).

Similarly, *erythro* **6b** gave **7b** in an 82.5% yield. *threo* **6a** gave **7a** in an 83% yield; mp 103.5—104.5 °C (from methanol).

Oxidation of **7b** *to 2,3,6,7-Naphthalenetetracarboxylic Acid.* A mixture of 9.2 g (0.05 mol) of **7b**, 75 g (0.25 mol) of dihydrate of sodium bichromate, 10 ml of pyridine, and 150 ml of water was stirred in an autoclave (300 ml) at 275 °C for 20 hr under autogeneous pressure (40—50 kg/cm²). The product was filtered while hot, and the filtrate was acidified with hydrochloric acid to give 10.1—11.2 g (67—74%) of 2,3,6,7-naphthalenetetracarboxylic acid. The tetramethyl ester had a mp of 184.0—185.0 °C (from 3 : 1 vol methanol/benzene) (lit, mp 181—183 °C[5]). IR (Nujol): ν_{CO} 1734 cm^{-1} (lit[5], 1740 cm^{-1})

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16) Two methylene proton signals of **6b** had octet of two AB type couplings. The observed J_{vic} of CH–CH$_2$ in *threo* **6b** is 10 Hz (δ=2.16—2.24 ppm) and 5 Hz (δ=2.56—2.76),

and that of *erythro* isomer is 7 Hz (δ=2.25—2.51) and 6 Hz (δ=2.65—2.87). The observed $|J_{gem}|$ of *threo* and *erythro* isomers are both 16 Hz. From the Karplus's equation,[17] the dihedral angles of two sets of vicinal protons in *threo* **6b** are calculated to be 180° and 38°, and those of *erythro* **6b** are 22° and 31°, respectively. The NMR spectra of **6a** had more complicated feature which could not be solved by decoupling technique.

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