

reacted. Dione **3**, 143.7 g (1.01 mol) in 250 ml of  $\text{CHCl}_3$ , is added to the mixture at such a rate as to maintain a gentle reflux. After allowing the mixture to cool to room temperature, the  $\text{CHCl}_3$  is washed with saturated  $\text{K}_2\text{CO}_3$  and  $\text{H}_2\text{O}$ , dried  $\text{CaCl}_2$ , filtered, and evaporated. The crude white solid residue is recrystallized from ether-petroleum ether giving 120.1 g (76.5% yield) of **4**: mp 37.5°; ir ( $\text{CCl}_4$ ) 1796, 1750, 1375, 1360  $\text{cm}^{-1}$ ; nmr ( $\text{CCl}_4$ )  $\delta$  1.29 (s, 6), 1.50 (s, 6); mass spectra (70 eV, rel intensity)  $m/e$  156 ( $m^+$ , 4), 141 (2), 128 (20), 113 (20), 71 (10), 70 (100), 43 (23), 42 (62), 41 (25), 39 (51), metastable peak 25.4. *Anal.* Calcd for  $\text{C}_8\text{H}_{12}\text{O}_2$ : C, 61.52; H, 7.74. Found: C, 61.79; H, 7.89.

Registry No.—**3**, 933-52-8; **4**, 4387-74-0.

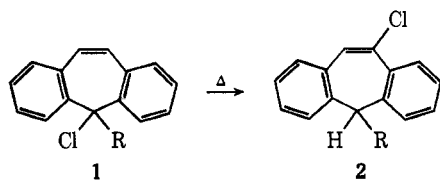
### Sigmatropic Chlorine Migration in 5-Chloro-5H-dibenzo[a,d]cycloheptenes

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The scope of the thermal chlorine migration exemplified by the isomerization<sup>1</sup> of 5,5-dichloro-5H-dibenzo[a,d]cycloheptene (**1a**) to the 5,10 isomer **2a** has been examined. The intent was to uncover the driving force for the migration, since it was not clear why it should occur. When there is one hydrogen and one chlorine atom at position 5, no rearranged product is formed; only decomposition occurs upon heating. When one substituent is chlorine and the other is phenyl (**1c**) or 1-naphthyl (**1d**), the chlorine atom migrates to position 10 affording **2c** and **2d**, respectively. Thus, two large groups on carbon 5 appear necessary for migration to occur. This suggests that relief of crowding between the equatorial substituent on carbon 5 and the peri hydrogen atoms may be the reason for migration, since the rearranged product now has the smaller hydrogen atom in the sterically unfavorable equatorial position. Molecular models of these compounds confirm the presence of the suggested steric interactions.

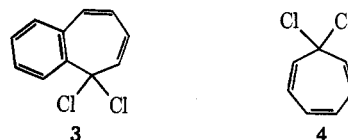


- a, R = Cl  
b, R = H  
c, R = phenyl  
d, R = 1-naphthyl

A comparison of the nmr spectra of the unrearranged (**1**) and rearranged (**2**) chlorides supports the hypothesis that crowding is relieved by migration. All chlorides with two large groups at carbon 5 (**1a**, **1c**, **1d**) have a two-proton multiplet downfield ( $\tau$  1.3–1.8) from the other aromatic protons. This absorption can be assigned to the protons on carbon 4 and carbon 6, which are very close to the equatorial substituent at position 5. This downfield shift of the aromatic pro-

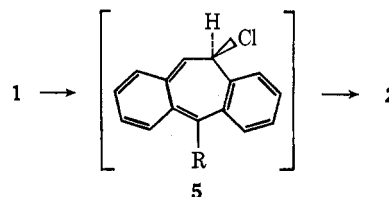
tons is analogous to that observed for the peri hydrogen atom in 1-substituted naphthalenes.<sup>2</sup> When migration occurs, leaving a hydrogen atom to occupy the equatorial position (**2a**, **2c**, **2d**), this absorption disappears. The lowest resonance in these compounds is a one-proton multiplet at  $\tau$  2.0–2.2, which is assigned to the aromatic hydrogen peri to the vinyl chlorine atom.

Two gem-dichlorides void of the suggested steric interaction were pyrolyzed to see if migration would occur. Neither 5,5-dichloro-5H-benzocycloheptene (**3**) nor chlorotropylium chloride (**4**) gave thermally rearranged chlorides. Decomposition occurred in a



manner very similar to the behavior of 5-chloro-5H-dibenzo[a,d]cycloheptene (**1b**), and led to unidentifiable material.

The original reaction path suggested<sup>1</sup> for this chlorine migration involved ionic intermediates. A better proposal appears to be a concerted 1,5-sigmatropic chlorine migration (**1**  $\rightarrow$  **5**), followed by a 1,5-hydrogen shift (**5**  $\rightarrow$  **2**). Both processes can occur in the allowed suprafacial manner in this ring system.



#### Experimental Section<sup>3</sup>

**5-Chloro-5-phenyl-5H-dibenzo[a,d]cycloheptene (1c).**—A solution of 8.2 g (0.029 mol) of 5-hydroxy-5-phenyl-5H-dibenzo[a,d]cycloheptene<sup>4</sup> in 25 ml of thionyl chloride was heated at reflux for 1 hr. The solvent was removed leaving a white solid, mp 191–193°. An analytical sample was prepared by repeated recrystallization from ligroin (bp 63–75°): mp 201–203° dec (depends upon rate of heating); nmr  $\tau$  3.40 (s, 2, vinyl), 2.5–3.4 (m, 8, aromatic), 1.5–1.7 (m, 2, aromatic at C-4 and C-6).

*Anal.* Calcd for  $\text{C}_{21}\text{H}_{18}\text{Cl}$ : C, 83.3; H, 5.0; Cl, 11.7. Found: C, 83.3; H, 5.3; Cl, 11.4.

**10-Chloro-5-phenyl-5H-dibenzo[a,d]cycloheptene (2c).**—The crude chloride **1c** (from 10 g of the alcohol) was heated at 205° for 1 hr and recrystallized from ligroin (bp 63–75°): 6.5 g (74%); mp 114–116°; nmr  $\tau$  4.70 (s, 1, benzylic), 2.5–3.5 (m, 12, aromatic), 2.0–2.2 (m, 1, aromatic peri to Cl).

*Anal.* Calcd for  $\text{C}_{21}\text{H}_{18}\text{Cl}$ : C, 83.3; H, 5.0; Cl, 11.7. Found: C, 83.0; H, 4.8; Cl, 11.4.

**5-Chloro-5-(1-naphthyl)-5H-dibenzo[a,d]cycloheptene (1d).**—A solution of 10 g (0.030 mol) of 5-hydroxy-5-(1-naphthyl)-5H-dibenzo[a,d]cycloheptene<sup>5</sup> in 50 ml of thionyl chloride was heated at reflux for 1 hr and concentrated, and the solid was recrystallized from methylcyclohexane: 2.75 g (25%); mp 171–172°; nmr  $\tau$  2.2–3.6 (m, 15, aromatic and vinyl), 1.3–1.6 (m, 2, aromatic at C-4 and C-6).

**10-Chloro-5-(1-naphthyl)-5H-dibenzo[a,d]cycloheptene (2d).**—A solution of 1.0 g (0.0028 mol) of **1d** in 20 ml of *o*-dichlorobenzene was heated at reflux for 45 min, concentrated, and chromatographed on Florisil. The benzene-ligroin (1:1) fraction gave a white solid, which was recrystallized from ligroin: 0.57 g

(2) V. Balasubramanian, *Chem. Rev.*, **66**, 567 (1966).

(3) Melting points and boiling points are uncorrected. The nmr spectra were measured on a Varian Associates A-60 instrument in deuteriochloroform, with TMS as an internal standard.

(4) W. Treibs and H. Klinkhammer, *Chem. Ber.*, **84**, 671 (1951).

(5) J. J. Looker, *J. Org. Chem.*, **36**, 1045 (1971).

(1) J. J. Looker, *J. Org. Chem.*, **31**, 3599 (1966).

(57%); mp 141–142°; nmr  $\tau$  4.00 (s, 1, benzylic), 2.2–3.3 (m, 15, aromatic and vinyl), 2.0–2.2 (m, 1, aromatic peri to Cl).

*Anal.* Calcd for  $C_{25}H_{17}Cl$ : C, 85.0; H, 4.9; Cl, 10.1. Found: C, 84.7; H, 4.9; Cl, 10.4.

**5,5-Dichloro-5H-benzocycloheptene (3).**—A solution of 4.5 g (0.029 mol) of 5H-benzocyclohepten-5-one<sup>6</sup> in 25 ml of dry methylene chloride was cooled in an ice bath while phosgene was passed in until 10 g (excess) had dissolved. The solution was left at room temperature under nitrogen overnight and the product was distilled: 5.6 g (92%); bp 105° (0.10 mm); nmr  $\tau$  4.9–5.0 (m, 1, vinyl), 3.9–4.1 (m, 2, vinyl), 3.1–3.2 (m, 1, vinyl), 2.4–2.8 (m, 3, aromatic), 2.0–2.2 (m, 1, aromatic). The dichloride should be kept in a freezer or under nitrogen because it decomposes when left at room temperature in air.

*Anal.* Calcd for  $C_{11}H_9Cl_2$ : C, 62.6; H, 3.8; Cl, 33.6. Found: C, 62.5; H, 3.6; Cl, 33.3.

The dichloride (1.0 g) was dissolved in 10 ml of 10% water in tetrahydrofuran, heated at reflux for 30 min, concentrated, and distilled (0.70 g, 95%). The nmr spectrum of the product was identical with that of 5H-benzocyclohepten-5-one.

**Thermal Decomposition of Chlorides 1b,<sup>7</sup> 3, and 4.<sup>8</sup>**—When each of these chlorides was heated at 180–200° for 10–30 min, black tars resulted. Chloroform extracts afforded poor nmr spectra with no benzylic proton absorption. Column chromatography of the extracts gave no identifiable materials. Similar results were obtained when the chlorides were heated at reflux in *o*-dichlorobenzene until decomposition occurred.

**Registry No.**—1c, 33482-70-1; 1d, 33482-71-2; 2c, 33482-72-3; 2d, 33482-73-4; 3, 33482-74-5.

(6) G. L. Buchanan and D. R. Lockhart, *J. Chem. Soc.*, 3586 (1969).

(7) G. Berti, *J. Org. Chem.*, **22**, 230 (1957).

(8) B. Föhlisch, P. Brügge, and D. Krockenberger, *Chem. Ber.*, **101**, 2717 (1968).

### Enantiomeric Purity of

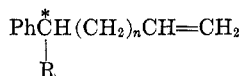
### 3-Phenyl-4,4-dimethyl-1-pentene. A Chemical Interrelation between the Maximum Rotations of $\alpha$ -*tert*-Butylphenylacetic Acid and $\beta$ -*tert*-Butyl- $\beta$ -phenylpropionic Acid

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In the course of CD investigations of  $\alpha$  olefins I,<sup>1</sup> we found it necessary to obtain optically active 3-phenyl-4,4-dimethyl-1-pentene (5) for which the relationship between optical purity and  $[\alpha]_D$  could be determined with a reasonable reliability by starting from optically active compounds used in the same synthesis. The



I, R = Me, Et, *i*-Pr, *tert*-Bu;  $n = 0, 1, 2$

absolute configuration of  $\alpha$ -*tert*-butylphenylacetic acid (7) and  $\beta$ -*tert*-butyl- $\beta$ -phenylpropionic acid (1) has been recently determined<sup>2–4</sup> and the maximum rotations of

(1) L. Lardicci, R. Menicagli, and P. Salvadori, *Gazz. Chim. Ital.*, **98**, 738 (1968).

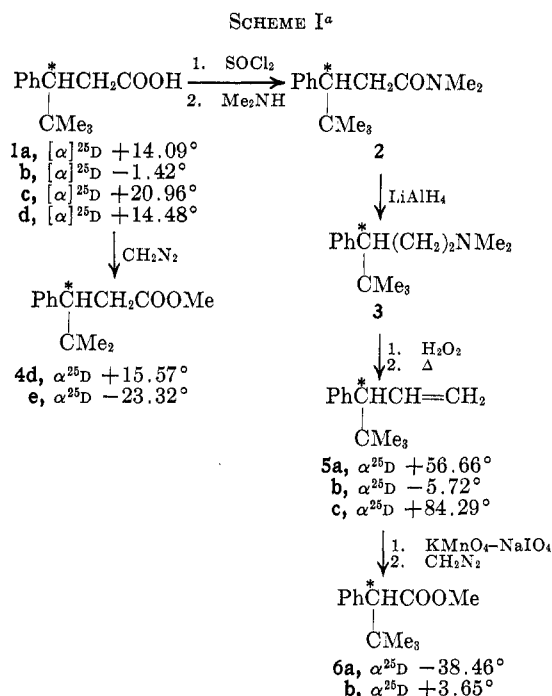
(2) D. R. Clark and H. S. Mosher, *J. Org. Chem.*, **35**, 1114 (1970).

(3) J. Almy, R. T. Uyeda, and D. J. Cram, *J. Amer. Chem. Soc.*, **89**, 6768 (1967).

(4) The configuration assigned to (+)- $\beta$ -*tert*-butyl- $\beta$ -phenylpropionic acid by Cram, *et al.*,<sup>3</sup> was confirmed and correctly designated *R* by Clark and Mosher.<sup>2</sup> In a subsequent paper by Almy and Cram [*ibid.*, **91**, 4460 (1969)] the correct configurational formulas were used but the wrong configurational rotation was assigned to this acid and several derivatives.

1 and 7 have been established from optical resolution criteria.<sup>5,6</sup>

In the present paper we report the synthesis of optically active 5 (Scheme I), the relationship between



<sup>a</sup> All specific rotations are in  $\text{CHCl}_3$  and all observed rotations are  $l = 1$  dm, neat.

its optical purity and optical rotation (Scheme I), and some evidences of the reliability of the maximum rotations of 1 and 7 previously reported<sup>5,6</sup> and now interrelated by a chemical method (Schemes I and II).

(*S*)- and (*R*)-*N,N*-dimethyl-3-phenyl-4,4-dimethylpentylamine (3) were prepared<sup>1</sup> (80–90% yield), *via* 2, from the corresponding optically active  $\beta$ -phenyl- $\beta$ -*tert*-butylpropionic acid (1) (Scheme I), in its turn obtained by resolution of the racemic acid<sup>7</sup> with brucine and cinchonidine.<sup>5</sup>

By pyrolysis of the amine 3 oxide at 120° (1.5 mm),<sup>1,8</sup> isomer-free (*S*)- and (*R*)-5 were recovered in high yield (86–88%) and high chemical purity (99%) (Scheme I). The olefin 5,  $\alpha^{25}_D + 56.66^\circ$ , was oxidized by permanganate-periodate reagent in 60% aqueous *tert*-butyl alcohol<sup>9</sup> to yield optically active  $\alpha$ -*tert*-butylphenylacetic acid (7), converted by diazomethane into the methyl ester 6a,  $\alpha^{25}_D - 38.46^\circ$ .<sup>10</sup>

According to our experimental data the optical purity of 6a is 65.5% [based on  $[\alpha]^{25}_D$  max 62.9° ( $\text{CHCl}_3$ ) for the optically pure acid 7]<sup>6</sup> and that of 1a, used in the synthesis of 5 (Scheme I), is 63.4% [based on  $[\alpha]^{25}_D$  max 22.2° ( $\text{CHCl}_3$ ) for optically pure acid 1].<sup>5</sup>

By assuming that the oxidative degradation of 5

(5) J. Almy and D. J. Cram, *ibid.*, **91**, 4467 (1969).

(6) C. Aaron, D. Dull, J. L. Schmiegel, D. Jaeger, Y. Ohashi, and H. S. Mosher, *J. Org. Chem.*, **32**, 2801 (1967).

(7) C. F. Koelsch, *J. Amer. Chem. Soc.*, **65**, 1640 (1943).

(8) L. Lardicci, R. Menicagli, and P. Salvadori, *Chim. Ind. (Milan)*, **52**, 83 (1970).

(9) E. Gil-Av and J. Shabtai, *J. Org. Chem.*, **29**, 261 (1964).

(10) Since the recovered crude acid 7 could be further resolved during the purification, we preferred to check its minimum optical purity by converting it into the methyl ester 6a, for which the relationship between optical purity and  $\alpha_D$  has been established in the present investigation.