

1485, 1390, 1320, 1280, 1250, 1210, 1160, 1150, 1125, 850, 825, 795, 770, 700  $\text{cm}^{-1}$ .

*2,4-Dichloro-6-p-(phenyldimethylsilyl)-s-triazine.* Under an atmosphere of argon, *p*-phenyldimethylsilylphenylmagnesium bromide reacted with cyanuric chloride to form the above product in 22% yield, m.p. 120–122°.

*Anal.* Calcd. for  $\text{C}_{17}\text{H}_{15}\text{Cl}_2\text{N}_3\text{Si}$ : C, 56.57, H, 4.20. Found: C, 56.12; H, 4.55.

Infrared absorption was observed at 1535, 1490, 1395, 1320, 1285, 1255, 1123, 850, 780, 710  $\text{cm}^{-1}$ .

*Reaction of 2,4-dichloro-6-p-(trimethylsilylphenyl)-s-triazine with anhydrous ammonia.* In a 50 cc. Erlenmeyer flask was placed 0.5 g. (0.0017 mole) of cyanuric chloride in 20 cc. of dry ether. Dry acetone proved to be of equal value. Anhydrous ammonia was bubbled through for 15 min. A white precipitate formed almost immediately and became heavier as the reaction continued. The precipitate was filtered off. In the case of the reaction run in ether, the solvent was evaporated off and the residue recrystallized from hexane-acetone. In the case of the run carried out in acetone, after filtration, hexane was added to the filtrate at the boiling point until crystals appeared. The product appeared as colorless platelets, yields 0.43 g. (from the ether reaction), 0.40 g. (acetone). Fractional crystallization yielded two fractions, as shown below.

Fraction I: 2-amino-4-chloro-6-p-(trimethylsilylphenyl)-s-triazine, m.p. 162–163°.

*Anal.* Calcd. for  $\text{C}_{15}\text{H}_{13}\text{ClN}_3\text{Si}$ : C, 52.4; H, 5.45; N, 20.1, mol. wt. 278. Found: C, 53.20; H, 5.71; N, 19.12; mol. wt., 256.

Fraction II: 2,4-diamino-6-p-(trimethylsilylphenyl)-s-triazine, m.p. 166–167°.

*Anal.* Calcd. for  $\text{C}_{15}\text{H}_{17}\text{N}_5\text{Si}$ : C, 55.56; H, 6.61; N, 27.1; mol. wt., 259. Found: C, 55.41; H, 6.71; N, 26.96; mol. wt., 243.

Infrared absorption on both compounds showed bands at 3300, 3140, 2950, 1660, 1570, 1540, 1500, 1400, 1320, 1280, 1226, 1100, 1010, 840, 810, 730, 710  $\text{cm}^{-1}$ .

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## Two Acids Containing the Active 2-Heptyl Group

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Received November 27, 1961

Previous work has shown that both stereoisomers of 3-methylnonanoic acid<sup>2</sup> and 3-methylhendecanoic acid<sup>3</sup> can be obtained optically pure by decarboxylation of the active, crystalline 2-octylmalonic and 2-decylmalonic acids, respectively. Cason and Coad<sup>4</sup> discovered that this procedure failed to

(1) This work was abstracted from the Master of Science thesis of John E. Spikner submitted to the faculty at DePaul University (1952).

(2) F. S. Prout, R. J. Klimkowski, and D. E. Dickson, *J. Org. Chem.*, **24**, 826 (1959).

(3) F. S. Prout, J. Cason, and A. W. Ingersoll, *J. Am. Chem. Soc.*, **70**, 298 (1948).

(4) J. Cason and R. A. Coad, *J. Am. Chem. Soc.*, **72**, 4695 (1950).

produce pure, active 2-pentylmalonic acid needed to furnish active 3-methylhexanoic acid.

Upon repeating the malonic acid scheme<sup>2,3</sup> with (–)-2-bromoheptane [ $\alpha^{23}\text{D} -37^\circ$  (homogeneous)] the pure (–)-2-heptylmalonic acid [m.p. 131–132°, [ $\alpha$ ]<sup>25</sup><sub>D</sub> –9.68° (95% ethanol)] proved to be separable from the *dl*-form (m.p. 101.5–102°) by crystallization. Decarboxylation of this acid furnished (–)-3-methyloctanoic acid, [ $\alpha$ ]<sup>26</sup><sub>D</sub> –4.95 (homogeneous). Levene and Marker<sup>5</sup> reported [ $\alpha$ ]<sup>23</sup><sub>D</sub> –5.14° for this acid when resolved with quinine. The stereochemistry of these reactions has recently been reviewed by Le Goff, Ulrich, and Denney.<sup>6</sup>

The alkylation of ethyl methylmalonate with (–)-2-bromoheptane ( $\alpha^{24}\text{D} -37^\circ$ ) produced the butyl (–)-2-heptylmethylmalonate with a surprisingly high rotation [ $\alpha$ ]<sup>25</sup><sub>D</sub> –12.01° (homogeneous)]. Hydrolysis of this ester led to the (–)-2-heptylmethylmalonic acid [m.p. 100–102°, [ $\alpha$ ]<sup>25</sup><sub>D</sub> –23.35° (95% ethanol)] which was easily obtained pure in 50% yield by crystallization from pentane. (The *dl* acid was exceedingly hard to crystallize.)

Decarboxylation of the (–)-2-heptylmethylmalonic acid gave an active 2,3-dimethyloctanoic acid, [ $\alpha$ ]<sup>25</sup><sub>D</sub> –14.1° (homogeneous). This acid is probably antipodally pure at C-3 but is certainly partially racemic at C-2, the active site created in the decarboxylation. The rotation of the amide, [ $\alpha$ ]<sup>25</sup><sub>D</sub> –29.1° (95% ethanol), suggests that the maximum rotatory value of 2,3-dimethyloctanoic acid is much higher than the 14° observed.

## EXPERIMENTAL

All melting and boiling points were uncorrected. Densities are reported in absolute units (g./cc.). The hexane and pentane were Skellysolves B and F (b.p. 65° and 35°, respectively) sold by Skelly Oil Co., Kansas City, Mo. Elemental analyses were by Micro-Tech Laboratories, Skokie, Ill., and Drs. Weiler and Strauss, Oxford, England. Fractionations were effected through a 60-cm., heated Vigreux column having no head. Optical rotations were observed in a Rudolf Universal High Precision polarimeter through a 1 dm. tube except where noted.

(+)-2-Heptanol. *dl*-2-Heptanol was prepared in 84% yield by action of *n*-amylmagnesium bromide with acetaldehyde: b.p. 156.5–157.3°;  $n^{24}\text{D}$  1.4189;  $d^{25}$  0.835. 2-Heptanol was converted in 82.5% yield to crude 2-heptyl hydrogen phthalate.<sup>7</sup> Crystallization of a small sample from hexane gave pure half acid; m.p. 66.5–67.5°; sapon. equiv., 135, 137 (calcd. 132.1). Pickard and Kenyon<sup>8</sup> reported m.p. 57–58°. The brucine salt was made from 353 g. of 2-heptyl hydrogen phthalate and 421 g. of brucine in 4 l. of acetone. Eventually systematic crystallization produced 246 g. (30%) of the desired salt; m.p. 137–138.5°; [ $\alpha$ ]<sup>24</sup><sub>D</sub> –4.50° (95% ethanol). Pickard and Kenyon<sup>8</sup> reported m.p. 137–138°, [ $\alpha$ ]<sub>D</sub> –4.42° (ethanol). The pure brucine salt (262 g.)

(5) P. A. Levene and R. E. Marker, *J. Biol. Chem.*, **91**, 95 (1931); **95**, 19 (1932).

(6) E. Le Goff, E. S. Ulrich, and D. B. Denney, *J. Am. Chem. Soc.*, **80**, 623 (1958).

(7) Cf. J. Kenyon, *Org. Syntheses*, Coll. Vol. I, 418 (1941).

was decomposed with hydrochloric acid. The crude ester (102 g., 96.5%) obtained after extraction with ether was used for subsequent steps. Pure half-ester was crystallized from hexane; m.p. 75–76.5°;  $[\alpha]^{25}_D + 51.2^\circ$  (95% ethanol, *c* 5, 2 d.). Kenyon and Walch<sup>9</sup> reported m.p. 74.5–75° and  $[\alpha]^{20}_D + 48.5^\circ$  (absolute alcohol). Boiling of 57.6 g. of half-ester for 30 min. in a mixture of 55 g. of potassium hydroxide, 200 ml. of 95% ethanol, and 100 ml. of water gave ultimately 13.5 g. (77.2%) of pure (+)-2-heptanol; b.p. 157–159.5°;  $n^{25}_D$  1.4178;  $d^{25}$  0.835;  $\alpha^{25}_D + 10.11$  (homogeneous),  $[\alpha]^{25}_D + 12.10^\circ$ .

Repetition of the reaction with crystallized half-ester gave the same results. Pickard and Kenyon<sup>8</sup> recorded  $[\alpha]^{20}_D + 10.32^\circ$  (ethanol), b.p. 73.5° (20 mm.), and  $d^{20}$  0.8185.

**2-Bromoheptane.** The *dl*-2-bromoheptane was prepared with phosphorus tribromide<sup>10</sup> in 71% yield; b.p. 64–66° (20–22 mm.);  $n^{25}_D$  1.4452;  $d^{25}$  1.143. The (–)-2-bromoheptane was prepared from 19.3 g. of (+)-2-heptanol ( $\alpha^{25}_D + 10.11^\circ$ ) and 150 g. of phosphorus tribromide. The yield was 21.0 g. (70.7%); b.p. 81.5–82.5° (40 mm.);  $d^{25}$  1.142;  $n^{25}_D$  1.4450;  $\alpha^{25}_D - 36.95^\circ$  (homogeneous),  $[\alpha]^{25}_D - 32.3^\circ$ .

This bromide was considerably racemized (*cf.* (+)- or (–)-2-bromooctane where the reported specific maxima are  $\pm 39^\circ$ ).<sup>11</sup> Furthermore, starting with 2-heptanol with an observed rotation of +7.45°, the value of the product was also  $\alpha^{25}_D - 37^\circ$ .

**Butyl *dl*-2-heptylmalonate.** This ester was prepared<sup>3</sup> by using 10 g. of sodium, 200 ml. of butanol, 60 g. of ethyl malonate and 37.5 g. of *dl*-2-bromoheptane. Work-up and fractionation gave 46 g. (70%) of butyl *dl*-2-heptylmalonate: b.p. 163–185° (12–13 mm.),  $n^{25}_D$  1.4359. The fraction boiling at 184–186° (12–13 mm.) was used for analysis.

*Anal.* Calcd. for  $C_{18}H_{34}O_4$ : Sapon. equiv., 157.1. Found: Sapon. equiv., 162.5, 160.5.

The yield was equally good when only 1 hr. of reflux was employed, but the product contained more ethyl ester. The yield was 45% when potassium and 1-butanol were used.

**Butyl (+)-2-heptylmalonate.** The procedure described for the *dl* ester was followed using 4.1 g. of sodium, 70 ml. of 1-butanol, 28.2 g. of ethyl malonate and 21.0 g. of (–)-2-bromoheptane ( $\alpha^{25}_D - 37^\circ$ ). Fractionation furnished 18.3 g. (49.7%) of purified ester; b.p. 165–168° (3–5 mm.);  $n^{25}_D$  1.4359;  $\alpha^{25}_D + 0.14^\circ$  (homogeneous); sapon. equiv. 159.8 (calcd., 157.1). [An additional 10.5 g. (28%) of ester, b.p. 130–165° (3–5 mm.),  $n^{25}_D$  1.4325–1.4338, was also obtained and was probably contaminated with ether ester.]

***DL*-2-Heptylmalonic acid.** The butyl ester [21.4 g., b.p. 179–185° (13 mm.)] was heated under reflux for 3 hr. with a solution of 12.0 g. of potassium hydroxide in 200 ml. of 80% ethanol. The mixture was diluted, acidified with sulfuric acid, and extracted with ether. The ether was removed and the product was recrystallized from hexane (cooled in acetone–Dry Ice) to give the *dl*-2-heptylmalonic acid; m.p. 101.5–102°; 4.5 g. (35%).

*Anal.* Calcd. for  $C_{10}H_{18}O_4$ : Neut. equiv., 101.7. Found: Neut. equiv., 101.1. The amide had m.p. 216–217°.

**(–)-2-Heptylmalonic acid.** The butyl ester [10.5 g.,  $\alpha^{25}_D + 0.14^\circ$ , b.p. 130–165° (4 mm.)] was saponified with 10 g. of sodium hydroxide in 100 ml. of 80% ethanol. The acid was extracted with ether after diluting and acidifying the reaction mixture. Removal of the ether gave 9.83 g. (145%) yield of solid, m.p. 121–125°. The crude acid was dissolved in 200 ml. of hexane and 10 ml. of alcohol, filtered, and concentrated to 150 ml. After crystallization the product collected [3.2 g. (47%)] had a melting point of 127–128.5°. Systematic crystallization of the acid gave 4.17 g.

(8) R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, 99, 45 (1911).

(9) J. Kenyon and A. M. Walch, *J. Chem. Soc.*, 2721 (1949).

(10) The method of C. H. Hseuh and C. S. Marvel, *J. Am. Chem. Soc.*, 50, 857 (1928).

(11) W. Gerrard, *J. Chem. Soc.*, 848 (1945).

(72%) of acid melting above 126–127°. The purest acid, 1.7 g., m.p. 131–132°,  $[\alpha]^{25}_D - 9.68^\circ$  (95% ethanol, *c* 4, 2 d.) was used for analysis.

*Anal.* Calcd. for  $C_{10}H_{18}O_4$ : C, 59.38; H, 8.96; neut. equiv., 101.7. Found: C, 59.41; H, 9.15; neut. equiv., 101.7.

The amide had m.p. 212–214°,  $[\alpha]^{25}_D - 4.73^\circ$  (95% ethanol).

*Anal.* Calcd. for  $C_{10}H_{20}O_2N_2$ : N, 13.99. Found: N, 13.18.

***dl*-3-Methyloctanoic acid.** The crude acid obtained by saponifying 36.3 g. of butyl 2-heptylmalonate and 4.5 g. of crystallized *d*′ acid were combined and heated to 170–190° for 1 hr. After decarboxylation the mixture was distilled; b.p. 224–228°; 18 g.;  $n^{25}_D$  1.4271. Since the neutralization equivalents were high (237.2, 234.6; calcd., 158.2) 16.4 g. of this crude acid was heated under reflux for 1 hr. in a solution of 20 g. of potassium hydroxide in 100 ml. of 80% ethanol. This reaction mixture was diluted with 400 ml. of water and extracted with three portions of ether. The aqueous phases were acidified with sulfuric acid and extracted with three portions of ether. The ether extracts were washed with four portions of water and filtered through magnesium sulfate. The acid was distilled to give 9.0 g. (54%) of acid; b.p. 234–236°;  $n^{25}_D$  1.4286.

*Anal.* Calcd. for  $C_9H_{18}O_2$ : Neut. equiv., 158.23. Found: Neut. equiv., 162.0. The amide had a m.p. of 82–84.5°.

**(–)-3-Methyloctanoic acid.** (–)-2-Heptylmalonic acid [7.4 g., m.p. 130–131°,  $[\alpha]^{25}_D$  9.15° (95% ethanol)] was heated 1.5 hr. at 165–200°. The acid was then distilled; b.p. 117.5° (3 mm.); 5.3 g. (91%);  $n_D$  1.4288;  $d^{25}_D$  0.902;  $\alpha^{25}_D - 4.47^\circ$  (homogeneous),  $[\alpha]^{25}_D - 4.95^\circ$ .

*Anal.* Calcd. for  $C_9H_{18}O_2$ : Neut. equiv., 158.1. Found: Neut. equiv., 161.0. The amide had a melting point of 85.6–86°;  $[\alpha]^{25}_D - 5.03^\circ$  (95% ethanol). Levene and Marker<sup>5</sup> reported  $[\alpha]^{25}_D - 6.68^\circ$  (75% ethanol).

*Anal.* Calcd. for  $C_9H_{19}ON$ : N, 8.91. Found: N, 9.30.

**Butyl *dl*-2-heptylmethylmalonate.** The alkylation as previously described was performed using 135 ml. of 1-butanol, 17.3 g. of sodium, 132 g. of ethyl methylmalonate,<sup>12</sup> and 90 g. of *dl*-2-bromoheptane. After stirring for 6 hr. at 100° under nitrogen and working up, 98.0 g. (59%, calcd. as butyl ester) of product was obtained, b.p. 139–172.5° (6–4 mm.). The wide boiling point range probably resulted from incomplete transesterification. Part of the ester probably represented the dibutyl ester; b.p. 168–172.5° (4 mm.) 34.1 g.,  $n^{25}_D$  1.4390–1.4395. Sapon. equiv. values were high.

**Butyl (–)-2-heptylmethylmalonate.** The procedure described for the *dl* ester was followed using 50 ml. of 1-butanol, 4.1 g. of sodium, 30.6 g. of ethyl methylmalonate, and 21.0 g. of (–)-2-bromoheptane ( $\alpha^{25}_D - 37^\circ$ ). Fractionation furnished 15.1 g. (39.2%) of reasonably pure ester: b.p. 140–167° (4 mm.),  $n^{25}_D$  1.4391,  $\alpha^{25}_D - 12.01^\circ$  (homogeneous).

***dl*-2-Heptylmethylmalonic acid.** Twenty-four grams of butyl *dl*-2-heptylmethylmalonate was heated under reflux for 1.25 hr. in a solution of 56 g. of potassium hydroxide in 100 ml. of 80% ethanol. The mixture was diluted with water and was extracted with ether. The aqueous phases were acidified and the acid was extracted with hexane. After washing the hexane extract, the solvent was removed to give 22.2 g. of crude acid. The acid was then dissolved in 300 ml. of 7.5% sodium bicarbonate and extracted with ether to remove neutral material (as 1-butanol). The acid recovered from the aqueous layer after acidifying and extracting with ether was 18.5 g. (117%) of crude oil. The crude acid was dissolved in 35 ml. of pentane (b.p. 30–60°) and cooled at 5° for 2 days to give a small amount of hard, nearly amorphous crystals, m.p. 90–91°. Recrystallization from pentane gave m.p. 91–92°.

*Anal.* Calcd. for  $C_{11}H_{20}O_4$ : Neut. equiv., 108.1. Found: Neut. equiv., 109.5. The amide had m.p. 136–137°.

(12) Prepared by the reliable method of R. F. B. Cox and S. M. McElvain, *Org. Syntheses, Coll. Vol. II*, 272, 279 (1943).

(-)-2-Heptylmethylmalonic acid. The hydrolysis procedure used with the *dl* ester was followed using 15.1 g. of butyl (-)-2-heptylmethylmalonate, 26.5 g. potassium hydroxide, and 100 ml. of 80% ethanol. The crude acid weighed 10.7 g. (108%). One crystallization from pentane furnished 4.45 g. (50%) of the active acid, 99–101°. A second crystallization gave pure acid; m.p. 100–102°;  $[\alpha]^{25}_D -23.35^\circ$  (95% ethanol, *c* 4, 2 d.).

*Anal.* Calcd. for  $C_{11}H_{20}O_4$ : C, 61.09; H, 9.32; neut. equiv., 108.14. Found: C, 61.04; H, 9.43; neut. equiv., 108.2.

The amide had m.p. 135–136°,  $[\alpha]^{25}_D -18.5^\circ$  (95% ethanol).

*Anal.* Calcd.  $C_{11}H_{22}N_2O_2$ : N, 13.07. Found: N, 13.34.

*dl*-2,3-Dimethyloctanoic acid. Twenty-seven grams of crude 2-heptylmethylmalonic acid from the saponification of 36 g. of butyl *dl*-2-heptylmethylmalonate was heated at 165–180° to decarboxylate. Distillation furnished 24.2 g. of product; b.p. 126–150° (19 mm.);  $n^{25}_D 1.4330$ , neut. equiv. 295 (calcd., 172.6). Since the acid was contaminated with butyl ester, this crude acid (23.3 g.) was heated under reflux for 4 hr. with 75 ml. of absolute ethanol and 2.5 ml. of concd. hydrochloric acid. The reaction mixture was diluted, was extracted with ether and 22.3 g. of ester was eventually distilled; b.p. 94–104° (2 mm.);  $n^{25}_D 1.4230$ ; sapon. equiv., 207.8 (calcd., 200.3).

The ethyl 2,3-dimethyloctanoate (17.9 g.) was saponified by boiling for 3 hr. in 100 ml. of 20% alcoholic potassium hydroxide. The reaction mixture was diluted and extracted with hexane. Acidification of the aqueous phases followed by extraction with ether gave a solution of the acid which was distilled to give two fractions: (1) 4.0 g., b.p. 125° (5 mm.); and (2) 6.8 g. (28%, based on butyl ester), b.p. 131.5° (5 mm.),  $n^{25}_D 1.4338$ .

*Anal.* Calcd. for  $C_{10}H_{20}O_2$ : Neut. equiv., 172.6. Found: Neut. equiv. 169.5. The amide had a m.p. 85–86°.

(-)-2,3-Dimethyloctanoic acid. Three grams of pure (-)-2-heptylmethylmalonic acid was heated at 180–220° for 2 hr. and distilled; b.p. 115° (1 mm.); 1.92 g. (80%);  $n^{25}_D 1.4341$ ;  $d^{25} 0.9079$ ;  $\alpha^{25}_D -12.73^\circ$  (homogeneous);  $[\alpha]^{25}_D -14.1^\circ$ .

*Anal.* Calcd. for  $C_{10}H_{20}O_2$ : C, 69.72; H, 11.70; neut. equiv., 172.6. Found: C, 69.82; H, 11.90; neut. equiv. 172.5.

The amide melted at 76–78°;  $[\alpha]^{25}_D -29.1^\circ$  (95% ethanol).

*Anal.* Calcd. for  $C_{10}H_{21}ON$ : N, 8.28. Found: N, 7.86.

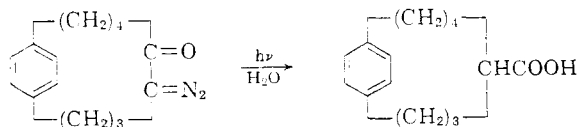
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## Communications TO THE EDITOR

### The Synthesis of Highly Strained Medium Rings.<sup>1</sup> [8]Paracyclophane-4-carboxylic Acid

Sir:

The photolysis of an  $\alpha$ -diazoketone is a type of Wolff rearrangement which has recently been shown to yield ring contraction of small rings, even when the product being formed is highly strained.<sup>2</sup> We have applied the reaction to the synthesis of a strained medium ring system, the [8]-paracyclophane. This compound is of theoretical interest because of the fact that models indicate



that the benzene ring is deformed from planarity, and such a deformation should have an effect on the ultraviolet spectrum.<sup>3</sup> This compound long

defined synthesis,<sup>4</sup> but was recently reported<sup>5</sup> as obtained by an ingenious reaction sequence, which lacks generality, however. The synthesis reported herein was developed as what is believed will be a general method applicable in particular to strained medium and large rings.<sup>6</sup>

The known 4,5-diketo-[9]paracyclophane monohydrazone<sup>7</sup> was treated with excess activated manganese dioxide and a trace of potassium hydroxide in ether-dioxane at 25° for two hours.<sup>8</sup> Filtration of the solution and evaporation of the ether left the diazoketone in dioxane, infrared absorption at 2030  $cm^{-1}$  and 1640  $cm^{-1}$ . A little water was added and the solution was irradiated with a 250-watt Sylvania sun lamp at 100° for 3 hours. The product, [8]paracyclophane-4-carboxylic acid, was isolated and twice recrystallized

(4) D. J. Cram, N. L. Allinger, and H. Steinberg, *ibid.*, **76**, 6132 (1954).

(5) D. J. Cram, and G. R. Knox, *J. Am. Chem. Soc.*, **83**, 2204 (1961).

(6) Subsequent to completion of this work A. T. Blomquist and F. W. Schlaefer, *J. Am. Chem. Soc.*, **83**, 4547 (1961), reported the application of this method to the preparation of other medium rings, and mentioned that [8]-paracyclophane-4-carboxylic acid was also obtained by this method.

(7) D. J. Cram and M. F. Antar, *J. Am. Chem. Soc.*, **80**, 3103 (1958).

(8) H. Morrison, S. Danishefsky, and P. Yates, *J. Org. Chem.*, **26**, 2617 (1961).

(1) This work was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

(2) J. Meinwald and P. G. Gassman, *J. Am. Chem. Soc.*, **82**, 2857 (1960), and references therein.

(3) D. J. Cram and H. Steinberg, *ibid.*, **73**, 5691 (1951).