

for 6 hours. Customary processing gave 1.23 g. of a product showing only a single VLPC peak. The efflux time and infrared spectrum of the collected sample corresponded to those noted for 2-phenylethanol, indicating that nuclear

debromination without C1-C2 cleavage was the predominant reaction occurring in this experiment.

STANFORD, CALIF.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

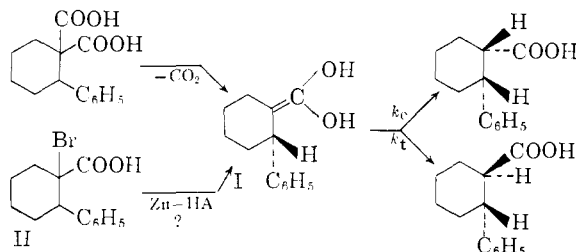
## The Stereochemistry of Ketonization. X.<sup>1</sup> Enols from $\alpha$ -Haloacids<sup>2</sup>

By HOWARD E. ZIMMERMAN AND THEODORE W. CUTSHALL

RECEIVED DECEMBER 27, 1958

Both stereoisomers of 1-bromo-2-phenylcyclohexanecarboxylic acid have been prepared and subjected to reduction with zinc and a proton donor. Evidence is presented that the reaction does proceed *via* the enol of the debrominated acid. Also, for the first time it has proved possible to determine the temperature dependence of the stereoselectivity of ketonization with sufficient precision to decide whether this selectivity stems from an entropy or an enthalpy effect.

In paper VI<sup>3</sup> of this series<sup>1,3-10</sup> dealing with our investigations of the stereochemistry of ketonization of enols, the behavior of the enol I of 2-phenylcyclohexanecarboxylic acid was described. For this study enol I was generated as an unstable intermediate by the decarboxylation of 2-phenylcyclohexane-1,1-dicarboxylic acid. There were several reasons why a second study seemed of interest, one in which an attempt would be made to generate enol I by debromination of the corresponding  $\alpha$ -bromoacid II.



Most important, in our decarboxylation study an attempt had been made to study the temperature dependence of stereoselectivity so that it might be ascertained whether the observed selectivity stemmed from an energy or instead from an entropy effect. Unfortunately, the experimental scatter obscured any temperature dependence which might have been present.<sup>11</sup> However, in

analogy to the facile debromination of  $\alpha$ -bromo ketones with zinc and a proton donor<sup>1,4,6,10</sup> the zinc debromination of 1-bromo-2-phenylcyclohexanecarboxylic acid promised to provide a means of generating enol I relatively free of by-products, allowing improved precision.

Of course the possibility had to be entertained that the debromination of II might not afford enol I as an intermediate. Moreover, there was reason for such concern. While pointing out the general tendency for  $\alpha$ -halocarbonyl compounds to be reduced by way of the enol,<sup>12</sup> Brewster had made the interesting observation<sup>13</sup> that zinc-acetic acid reduction<sup>14</sup> of  $\alpha$ -chloro- $\alpha$ -phenylpropionic acid proceeds with inversion of configuration.<sup>15</sup> Also, subsequent to the initiation of the present research, the opinion was offered that the zinc debromination of ethyl 1-bromo-2-phenylcyclohexanecarboxylate proceeds with retention of configuration.<sup>16</sup>

Our investigation began with the bromination of *cis*-2-phenylcyclohexanecarboxylic acid in thionyl chloride followed by hydrolysis of the bromoacid chloride mixture in aqueous acetone. The mixture of bromoacids thus obtained was chromatographed on silica gel affording the desired 1-bromo-2-phenylcyclohexanecarboxylic acid stereoisomers, melting at 116 and 153°, as well as recovered starting material and non-crystalline bromine-containing by-products.

Due to the good fortune of isolating both *cis* and *trans* isomers of 1-bromo-2-phenylcyclohexanecarboxylic acid, a test of the reality of enol I as a debromination intermediate was possible; while inversion and retention mechanisms would produce one stereoisomer of 2-phenylcyclohexanecarboxylic acid from the 116° bromoacid and the other from the 153° bromoacid, the intervention of a common intermediate, enol I, in the debromination would require the same product distribution from the two bromoacids.

(1) For paper IX of this series see H. E. Zimmerman and A. Mais, *THIS JOURNAL*, **81**, 3644 (1959).

(2) Abstracted from the M.S. thesis of T. W. Cutshall presented to Northwestern University.

(3) For paper I of this series and an introduction to the problem, see H. E. Zimmerman, *J. Org. Chem.*, **20**, 549 (1955).

(4) H. E. Zimmerman, *THIS JOURNAL*, **78**, 1168 (1956).

(5) H. E. Zimmerman and H. J. Giallombardo, *ibid.*, **78**, 6259 (1956).

(6) H. E. Zimmerman, *ibid.*, **79**, 6554 (1957).

(7) H. E. Zimmerman and T. E. Nevins, *ibid.*, **79**, 6559 (1957).

(8) H. E. Zimmerman and T. W. Cutshall, *ibid.*, **80**, 2893 (1958).

(9) H. E. Zimmerman and B. S. Thyagarajan, *ibid.*, **80**, 3060 (1958).

(10) H. E. Zimmerman and W.-H. Chang, *ibid.*, **81**, in press (1959).

(11) The problem is experimentally more difficult than the usual one of obtaining the enthalpy of activation for a single process from the absolute rate equation,  $\ln(k/T) = -(\Delta H^\ddagger/RT) + \Delta S^\ddagger/R + \ln(k'/h)$ , by plotting the rate constant *k* over *T* versus  $(1/T)$  and taking the slope as equal to  $-(\Delta H^\ddagger/R)$ . In the ketonization problem, stereoselectivity is controlled by the ratio of the two rate constants, *k<sub>c</sub>* and *k<sub>t</sub>*, and the rate equation becomes  $\ln(k_c/k_t) = -(\Delta\Delta H^\ddagger/RT) + (\Delta\Delta S^\ddagger/R)$ , where  $\Delta\Delta H^\ddagger = \Delta H^\ddagger_c - \Delta H^\ddagger_t$  and  $\Delta\Delta S^\ddagger = \Delta S^\ddagger_c - \Delta S^\ddagger_t$ . The quantity  $\Delta\Delta H^\ddagger$  is a small difference between two large numbers; hence the stereoselectivity will have a relatively small temperature dependence.

(12) J. H. Brewster, *THIS JOURNAL*, **76**, 6361 (1954).

(13) J. H. Brewster, *ibid.*, **78**, 4061 (1956).

(14) E. Ott and K. Krämer, *Ber.*, **68**, 1655 (1935).

(15) The intriguing possibility was considered (ref. 13) that reduction of the haloacid molecule, adsorbed with the halogen atom oriented toward the metal surface, yields a carbanion which is protonated from the solution side faster than desorption can occur. Another possible mechanism is the protonation of a free enolic intermediate by the optically active  $\alpha$ -haloacid reactant, which is the strongest acid present. Such a process could give an excess of one enantiomeric ketonization product (*i.e.*, asymmetric induction).

(16) J. Klein and G. Levin, *THIS JOURNAL*, **80**, 1707 (1958).

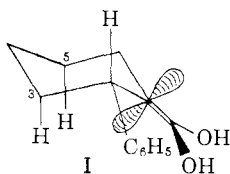
The stereoisomeric 1-bromo-2-phenylcyclohexanecarboxylic acids were debrominated with zinc in acetic acid as well as with zinc and collidinium chloride in collidine, and the resultant mixtures of the stereoisomeric 2-phenylcyclohexanecarboxylic acids were analyzed by the infrared technique described earlier.<sup>4,8-10</sup> The results of analyses of known mixtures are given in Table III of the Experimental section; these suggest a probable accuracy of  $\pm 0.6\%$  *cis*-acid. The results of the debromination runs are given in Table I.

TABLE I  
DEBROMINATION OF THE 1-BROMO-2-PHENYLCYCLOHEXANE  
CARBOXYLIC ACIDS

Ex-periment	Bromo-acid reactant	Debrominating agent	T, °C.	Time	<i>cis</i> -Prod-uct, %	<i>cis</i> -Prod-uct, <sup>a</sup> %
1	153°	Zn-HOAc	20	1 hr.	82.1	85.3
2	116°	Zn-HOAc	35	1 hr.	81.6 <sup>b</sup>	84.8 <sup>b</sup>
3	153°	Zn-HOAc	35	1 hr.	82.9	86.2
4	153°	Zn-HOAc	50	20 min.	80.5	83.7
5	153°	Zn-HOAc	60	20 min.	75.6	78.6
6	153°	Zn-HOAc	75	15 min.	76.2	79.2
7	153°	Zn-HOAc	90	15 min.	74.3	77.2
8	153°	Zn-HOAc	115	15 min.	72.6	75.5
9	116°	Zn-collidinium chloride in collidine	35	25 hr.	63.1	68.4
10	153°	collidine	35	25 hr.	62.8	68.1
11	116°	Zn-HCl in HOAc	35	1 hr.	83.4	86.0
12	153°	HOAc	35	1 hr.	80.9	83.4

<sup>a</sup> Corrected for isomerization of *cis*-product under reaction conditions. <sup>b</sup> Average of two runs.

Inspection of these results reveals that the debromination reaction is non-stereospecific,<sup>17</sup> the same product distribution resulting from the two stereoisomeric acid reactants under any given set of conditions. Thus in the zinc-acetic acid debromination runs at 35° (experiments 2 and 3) 84.8% *cis*-2-phenylcyclohexane-carboxylic acid resulted starting with the 116° bromoacid while 86.2% *cis*-product was obtained from the 153° bromoacid. The zinc-acetic acid-HCl runs (experiments 7 and 8) afforded an average of  $84.7 \pm 1.3\%$  *cis*-product from the bromoacid reactants. With zinc-collidinium chloride-collidine (experiments 11 and 12)  $68.2 \pm 0.2\%$  *cis*-product was observed from the two bromoacids. Therefore, it may be concluded that enol I is indeed a debromination intermediate.



(17) We have recently suggested [H. E. Zimmerman, L. Singer and B. S. Thyagarajan, *THIS JOURNAL*, **81**, 103 (1959); H. E. Zimmerman and L. Ahramjian, *ibid.*, **81**, 2086 (1959)] that a distinction be made between the terms "stereospecific" and "stereoselective." A stereospecific process is one in which there is a definite configurational relationship between reactant and product which holds at least for both stereoisomers of the reactant. A stereoselective process is one in which such a relationship is lacking, both stereoisomers leading to the same product, but in which there is a definite driving force for formation of one stereoisomer.

The preferential formation of *cis*-2-phenylcyclohexanecarboxylic acid is again observed as in the case of ketonization of enol I generated by the decarboxylation of 2-phenylcyclohexane-1,1-dicarboxylic acid.<sup>8</sup> This has been rationalized as due to the decreased accessibility for protonation of the lower lobe of the  $\alpha$ -carbon p-orbital due to blocking by axial hydrogen atoms at carbons 3 and 5.

It having been convincingly demonstrated that enol I occurs in the debromination reaction as an unstable intermediate, consideration of the temperature dependence of the observed stereoselectivity of ketonization is in order. The data of experiments 1 through 8 of Table I were utilized to plot  $\log(k_c/k_t)$  versus  $1/T$  as in Fig. 1; the numerical details are given in Table IV in the Experimental section. The line drawn was obtained by the method of least squares.<sup>18</sup> By equating the slope of the plot to  $-\Delta\Delta H^\ddagger_{c-t}/(2.303R)$ , where  $\Delta\Delta H^\ddagger_{c-t} = \Delta H^\ddagger_c - \Delta H^\ddagger_t$ ,  $\Delta\Delta H^\ddagger_{c-t}$  was found to be  $-1.8$  kcal./mole with a probable error<sup>18</sup> of  $\pm 0.3$  kcal./mole. Interestingly, if enthalpy alone controlled the two rates of ketonization,  $k_c$  to yield *cis*-2-phenylcyclohexanecarboxylic acid and  $k_t$  to afford *trans* product, then the reaction would be almost completely stereoselective since  $-1.8$  kcal./mole corresponds to formation of 96% *cis* product. The observed lower stereoselectivity is due to a counteracting entropy effect.

TABLE II  
DIFFERENTIAL QUANTITIES OF ACTIVATION CONTROLLING  
THE STEREOSELECTIVITY OF KETONIZATION

$$\Delta\Delta F^\ddagger_{c-t} = \Delta F^\ddagger_c - \Delta F^\ddagger_t = -1.0 \pm 0.1 \text{ kcal./mole}$$

$$\Delta\Delta H^\ddagger_{c-t} = \Delta H^\ddagger_c - \Delta H^\ddagger_t = -1.8 \pm 0.3 \text{ kcal./mole}$$

$$\Delta\Delta S^\ddagger_{c-t} = \Delta S^\ddagger_c - \Delta S^\ddagger_t = -2.7 \pm 1.0 \text{ cal./mole-deg.}$$

The hindrance to prototopic attack on the lower lobe of the  $\alpha$ -carbon p-orbital of I is thus seen to manifest itself as a rise in energy of the ketonization transition state. Actually, two effects may be operative. In addition to a rise in the less favored transition state energy due to van der Waals repulsions between the proton donor and the enol substrate, an added effect may ensue from a greater desolvation of the proton donor being required in order to provide a small species capable of delivering the proton from the more hindered approach. That such desolvation is indeed required is suggested by the more positive entropy of activation observed for the more hindered approach.

### Experimental<sup>19</sup>

*cis*- and *trans*-2-Phenylcyclohexanecarboxylic Acids.—These acids were most conveniently obtained on a preparative scale by the Diels-Alder condensation of acrylic acid and 1-phenylbutadiene as described by Meek, Lorenzi and Cristol,<sup>20</sup> hydrogenation of the mixture of stereoisomers in ethyl acetate with platinum oxide and chromatography of the mixed *cis*- and *trans*-2-phenylcyclohexanecarboxylic acids on silica gel as described by us earlier.<sup>8</sup> *cis*-2-Phenylcyclohexanecarboxylic acid thus obtained melted at 75.0–75.5° (reported<sup>21</sup> 76–77°), while *trans*-2-phenylcyclohexane-

(18) H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., p. 500.

(19) All melting points were taken on a Fisher-Johns block checked with compounds of known melting point.

(20) J. Meek, F. Lorenzi and S. Cristol, *THIS JOURNAL*, **71**, 1830 (1949).

(21) C. D. Gutsche, *ibid.*, **70**, 4150 (1948).

carboxylic acid exhibited a melting point of 107.0–108.0° (reported<sup>21</sup> 107–108°).

**The Stereoisomeric 1-Bromo-2-phenylcyclohexanecarboxylic Acids.**—To 10.0 g. (0.049 mole) of *cis*-2-phenylcyclohexanecarboxylic acid was slowly added 100 g. (0.84 mole) of thionyl chloride with stirring and cooling below 10°. When the solid had dissolved 2.82 ml. (8.8 g., 0.055 mole) of bromine was added, and the mixture was then refluxed gently until at the end of 30 min. the bromine had been completely decolorized. The excess thionyl chloride was removed *in vacuo*. The crude bromoacid chloride residue was dissolved in 100 ml. of acetone and 50 ml. of water, and the solution was refluxed for one hour. Acetone was removed by concentration *in vacuo*, whereupon the acidic product separated from the aqueous phase as an oil. The mixture was ether extracted, and the ether extracts were washed with water, dried over sodium sulfate and concentrated under vacuum, leaving 15.1 g. of an oily product. This was chromatographed on a 41 × 700 mm. silica gel column (40–200 mesh, Davidson), slurry packed with 5% ether in hexane. Twenty-seven fractions were collected: fraction 1, 500 ml. of 5% ether in hexane, containing 10 mg.; fraction 2, 800 ml. of 5%, 10 mg.; 3, 400 ml. of 10%, 8 mg.; 4, 200 ml. of 10%, 245 mg.; 5, 200 ml. of 10%, 846 mg.; 6, 200 ml. of 10%, 331 mg.; 7, 200 ml. of 10%, 86 mg.; 8 and 9, 200 ml. of 10%, 56 mg.; 10, 100 ml. of 15%, 27 mg.; 11, 100 ml. of 15%, 37 mg.; 12, 100 ml. of 15%, 45 mg.; 13, 100 ml. of 15%, 75 mg.; 14, 100 ml. of 15%, 88 mg.; 15, 100 ml. of 15%, 190 mg.; 16, 100 ml. of 15%, 305 mg.; 17, 100 ml. of 15%, 704 mg.; 18, 100 ml. of 15%, 1,233 g.; 19, 100 ml. of 15%, 993 mg.; 20, 100 ml. of 15%, 993 mg.; 21, 125 ml. of 15%, 980 mg.; 22, 100 ml. of 15%, 614 mg.; 23, 100 ml. of 20%, 503 mg.; 24, 125 ml. of 20%, 2,582 g.; 25, 100 ml. of 20%, 3,590 g.; 26, 100 ml. of 20%, 30 mg.; 27, 500 ml. of ether, 28 mg.

The infrared spectra of fractions 17 through 22 were similar and melted in the range 106–108°. These were combined and recrystallized from hexane to a constant melting point of 115.0–116.0°, representing pure lower melting isomer of 1-bromo-2-phenylcyclohexane carboxylic acid.

*Anal.* Calcd. for C<sub>13</sub>H<sub>16</sub>O<sub>2</sub>Br: C, 55.14; H, 5.34. Found: C, 54.95; H, 5.28.

Likewise, fractions 24 and 25 contained similar material melting in the range 132–136°. Recrystallization from hexane brought the melting point to 152.0–153.0°. This represented pure higher melting isomer of 1-bromo-2-phenylcyclohexanecarboxylic acid.

*Anal.* Calcd. for C<sub>13</sub>H<sub>16</sub>O<sub>2</sub>Br: C, 55.14; H, 5.34. Found: C, 54.99; H, 5.34.

Infrared analysis of fractions preceding 11 indicated the presence of unreacted starting material. Fractions 11 through 14 contained material whose infrared spectra indicated *p*-brominated phenyl groups to be present.

By bromination of 5.0 g. of *trans*-2-phenylcyclohexanecarboxylic acid in 50 g. of thionyl chloride with 1.41 ml. of bromine and hydrolysis of the acid chloride mixture as before, there was obtained 7.26 g. of an oil whose infrared spectrum was only slightly different from that of the material obtained from bromination of *cis*-2-phenylcyclohexanecarboxylic acid.

**Zinc-Acetic Acid Debromination of the 1-Bromo-2-phenylcyclohexanecarboxylic Acids.**—A 75-mg. (0.265 mmole) sample of the 1-bromo-2-phenylcyclohexanecarboxylic acid stereoisomer to be used was mixed with 346 mg. (5.3 mmoles) of zinc dust. This was added to 10 ml. of glacial acetic acid stirred and kept at the temperature of the run. For runs at 60° or higher an additional 346 mg. of zinc dust was first added to the hot acetic acid, this preventing formation of the acetoxy acid. The stirring was continued for the desired time and the mixture was then cooled, diluted with ether and filtered free of zinc. Ether and acetic acid were removed *in vacuo* and the residue taken up in ether again. The ether solution was washed once, dried over sodium sulfate and concentrated under vacuum. The composition of the residual mixture of *cis*- and *trans*-2-phenylcyclohexanecarboxylic acids was determined by quantitative infrared analysis.

The infrared spectra of the mixtures analyzed indicated complete debromination. This was verified by debrominating 250 mg. (0.883 mmole) of the 116° isomer of 1-bromo-2-phenylcyclohexanecarboxylic acid at 35° and chromato-

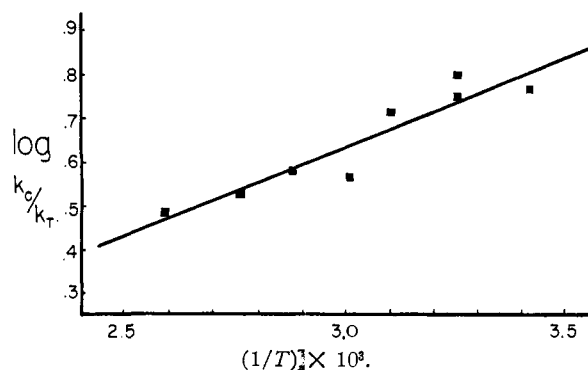


Fig. 1.—Log ratio of *cis*- to *trans*-2-phenylcyclohexanecarboxylic acid plotted versus  $1/T$ .

graphing the product on silica gel, eluting with 15% ether in hexane. There was obtained 86 mg. of *cis*-2-phenylcyclohexanecarboxylic acid, 10 mg. of *trans*-2-phenylcyclohexanecarboxylic acid and 25 mg. of a mixture of the two stereoisomers.

The results of these debromination runs are listed in Table I.

**Debromination of the Stereoisomeric 1-Bromo-2-phenylcyclohexanecarboxylic Acids with Zinc and Hydrochloric Acid in Acetic Acid.**—A 75-mg. (2.65 mmoles) sample of the given 1-bromo-2-phenylcyclohexanecarboxylic acid stereoisomer was mixed with 173 mg. (2.65 mmoles) of zinc dust and this was added to 5.0 ml. of acetic acid, stirred and maintained at 35°. A total of 0.20 ml. of concd. hydrochloric acid was added to the stirred mixture over 30 min. Stirring was continued for an additional 30 min. and the mixture was worked up as in the runs made without hydrochloric acid (*vide supra*). The mixtures of the stereoisomeric 2-phenylcyclohexanecarboxylic acids were analyzed by quantitative infrared; the results are to be found in Table I.

TABLE III

INFRARED ANALYSES OF KNOWN MIXTURES							
Actual % <i>cis</i> - acid	D'	D''	Q	Actual R	Calcd. P	Calcd. R	Actual % <i>cis</i> - acid
0.0	0.431	0.136	...	...	..	...	..
25.0	.337	0.251	0.314	0.333	1.06	0.327	24.6
50.0	.296	.408	0.979	1.00	1.02	1.02	50.4
75.0	.244	.569	2.86	3.00	1.05	2.98	74.8
100.0	.180	.720	...	...	..	...	..

TABLE IV

DATA USED TO PLOT FIG. 1			
Expt.	T, °K.	1/T	log (kc/kt)
1	293	0.00314	0.764
2	308	.00325	.747
3	308	.00325	.796
4	323	.00310	.711
5	333	.00300	.565
6	348	.00287	.581
7	363	.00276	.530
8	388	.00258	.489

**Debromination of the Stereoisomeric 1-Bromo-2-phenylcyclohexanecarboxylic Acids with Zinc and Collidinium Chloride in Collidine.**—A mixture of 75 mg. (0.265 mmole) of the given 1-bromo-2-phenylcyclohexanecarboxylic acid stereoisomer, 346 mg. (5.3 mmoles) of zinc dust and 419 mg. (2.65 mmoles) of collidinium chloride was added with stirring to 5.0 ml. of collidine kept at 35°. The reaction mixture was then stirred for 25 hr. At the end of this time the mixture was diluted with 100 ml. of ether and filtered. The ether solution was extracted with two 40-ml. portions of 10% sodium hydroxide solution and the aqueous layer was acidi-

fied with 20% hydrochloric acid to a congo red end-point and extracted twice with 75-ml. portions of ether. The ether extract was washed with water and dried over sodium sulfate. Concentration *in vacuo* left a residue of the stereoisomeric 2-phenylcyclohexanecarboxylic acids which was analyzed by quantitative infrared.

**Stability of *cis*-2-Phenylcyclohexanecarboxylic Acid under Debromination Conditions.**—A 75-mg. sample (0.368 mmole) of *cis*-2-phenylcyclohexanecarboxylic acid was treated in the same manner as the bromoacid in the corresponding debromination run described above. The percentage conversion to *trans*-2-phenylcyclohexanecarboxylic acid was determined by infrared analysis of the resulting material. These results were used in correcting the ketonization product distribution for isomerization of *cis*-2-phenylcyclohexanecarboxylic acid under reaction conditions. The corrected values are given in Table I.

**Quantitative Infrared Analysis.**—The analytical method employed in our earlier study<sup>8</sup> was utilized here. The ratio of *cis*- to *trans*-2-phenylcyclohexanecarboxylic acid in a mixture is given by  $R = QF$  where  $Q = D''_m D'_t - D'_m D''_t / D'_m D''_c - D''_m D'_c$  and  $F$  is determined empirically. The subscripts *m*, *c* and *t* refer to a given mixture, pure *cis* isomer

and pure *trans* isomer, respectively; the superscripts refer to absorption at 7.71 and 7.98  $\mu$ .

All analyses were run at a concentration of 40 mg./0.50 ml. of CS<sub>2</sub> in 0.1-mm. cells. The results of analyses of known mixtures given in Table III indicate a probable accuracy of  $\pm 0.6\%$  *cis* isomer. In calculating the results in the last two columns of Table III an average value of  $F = 1.04$  was used.

**Calculation of Differential Free Energy, Enthalpy and Entropy of Activation.**—The difference in free energy of activation for the two processes forming *cis*- and *trans*-2-phenylcyclohexanecarboxylic acid was obtained for 20° by using the product distribution obtained in experiment 1 of Table I and the relation  $\Delta\Delta F^\ddagger = -RT \ln (k_c/k_t)$ ; here it is assumed that both processes have the same kinetic order so that the ratio of products gives the ratio of rates.

The differential enthalpy of activation was obtained by taking the slope of the plot in Fig. 1 equal to  $-(\Delta\Delta H^\ddagger / 2.303R)$ . The differential entropy of activation resulted from a solution of the relation  $\Delta\Delta F^\ddagger_{c-t} = \Delta\Delta H^\ddagger_{c-t} - T\Delta\Delta S^\ddagger_{c-t}$ .

EVANSTON, ILL.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF J. T. BAKER CHEMICAL CO.]

## Polymerization of Thiolmethacrylate Esters

BY GENE SUMRELL,<sup>1</sup> JOSEPH BRISKIN, GEORGE E. HAM AND CHARLES H. SCHRAMM

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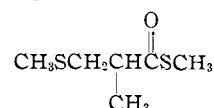
Data from the polymerization of seven thiolmethacrylates are presented. The polymers had higher softening points than those from the analogous methacrylate esters. The primary and secondary alkyl thiolmethacrylates had a tendency to give cross-linked homopolymers and copolymers, a striking difference from the behavior of similar esters in the thiolacrylate series.

The increasing interest in thiolacrylic-type esters prompts us to report some of our findings from polymerization studies of monomers of this type prepared in our laboratories.<sup>2-4</sup> Marvel and co-workers<sup>3a</sup> have extensively investigated the alkyl thiolacrylate series. Our work has been primarily in the thiolmethacrylate series. We note some similarities and some differences in comparing these two series.

A striking difference was the tendency of the primary and secondary alkyl thiolmethacrylates to give insoluble and presumably cross-linked homopolymers and copolymers, whereas such behavior apparently did not occur in the thiolacrylate series. Marvel reports soluble homopolymers of a variety of primary and secondary alkyl thiolacrylates in conversions of 50-70%. Much copolymerization data are given with a variety of comonomers including styrene, with no mention of cross-linking. In our work, we obtained soluble homopolymers of methyl, ethyl and isopropyl thiolmethacrylate in conversions of 20-25%, but at higher conversions the polymers exhibited swelling in a variety of organic

solvents, but did not dissolve. A slight tendency to give insoluble copolymers with styrene was also noted. This tendency was much greater with methyl methacrylate and some of the data are given in the Experimental section. Since we did not obtain insoluble homopolymers or copolymers with tert-butyl thiolmethacrylate, or with the aryl thiolmethacrylates, we are inclined to associate the cross-linking with the presence of a hydrogen attached to the carbon next to the sulfur atom in the thiol ester grouping. If chain transfer occurs readily at this point, the results would be equivalent to having a bifunctional monomer which would be expected to give cross-linked polymers.

The fact that we were able to produce insoluble poly-(methyl methacrylate) polymers (see Experimental) in the presence of as little as 1% by weight of methyl 2-methyl-3-thiomethoxythiolpropionate



is further evidence of active chain transfer at the site mentioned above. It is known<sup>5</sup> that aliphatic sulfides may be incorporated into poly-(methyl methacrylate), but we are not aware of any evidence that crosslinked polymers are ever obtained using simple alkyl sulfides. Since cross-linking requires that the agent become attached to polymer chains in at least two places, it is of interest to consider the points at which the above pictured

(1) To whom inquiries for reprints should be sent. Southwest Research Institute, 8500 Culebra Rd., San Antonio 6, Tex.

(2) For the preparation of these monomers see G. Sumrell, G. E. Ham and E. D. Hornbaker, *THIS JOURNAL*, **80**, 2509 (1958).

(3) We are aware of the following literature bearing on this subject: (a) C. S. Marvel, S. L. Jacobs, W. K. Taft and B. G. Labbe, *J. Polymer Sci.*, **19**, 59 (1956); (b) S. L. Jacobs, Ph.D. Thesis, University of Illinois; *C. A.*, **49**, 10804 (1955); (c) M. M. Koton, T. M. Kiselyeva and K. S. Podgorskaya, *Zhur. Obshchei Khim.*, **26**, 475 (1956); *C. A.*, **50**, 13815 (1956); (d) G. Braude, *J. Org. Chem.*, **22**, 1675 (1957); (e) W. Reppe, *Ann.*, **582**, 13 (1953).

(4) L. A. Mikeska, U. S. Patent 2,475,246, July 5, 1949, assigned to Standard Oil Development Co.

(5) B. M. Marks, U. S. Patent 2,565,141, August 21, 1951, assigned to E. I. du Pont de Nemours and Co.