

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES, LOS ANGELES 24, CALIF.]

## Electrophilic Substitution at Saturated Carbon. XII. Stereochemical Capabilities of Alkyl-substituted Acetonitrile Anions<sup>1</sup>

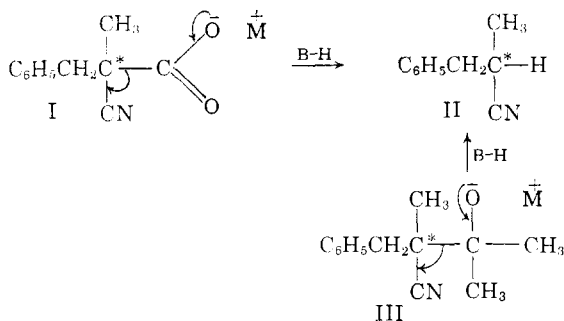
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The steric course of the base-catalyzed decarboxylation of (+)-2-cyano-2-methyl-3-phenylpropanoic acid (I), and the steric course and kinetics of the cleavage of (+)-3-cyano-2,3-dimethyl-4-phenyl-2-butanol (III) to (+)- or (-)-2-cyano-1-phenylpropane (II) has been studied. Both rates and steric course were found to vary with solvent, and in some solvents with the nature of the cation of the base. Reaction conditions were found which gave product with greater than 8% net retention, and greater than 16% net inversion. In ethylene glycol, the steric course was invariably net inversion, and the stereospecificity was effected little if at all by the nature of the cation of the base, but was dependent on the leaving group (carbon dioxide in system I and acetone in system III). In cleavage of III in *n*-butyl alcohol, the steric direction of the reaction depended on the nature of the cation of the base. The rates of cleavage of III correlate with the hydrogen-bonding properties of the solvent, and with changes in the character of the cation of the base.

The steric course and mechanism of electrophilic substitution at saturated carbon has previously been studied in systems in which carbon-carbon bonds cleave heterolytically, and the carbanions produced are captured by proton donors in the medium. The carbanion intermediates were stabilized by only a phenyl group in most of the systems studied,<sup>2</sup> and by both cyano and phenyl groups in one of the systems examined.<sup>3</sup> The less stabilized carbanion appeared to be consumed by fast proton transfer reactions,<sup>2</sup> but the more stabilized and longer lived carbanion had a somewhat different stereochemical fate.<sup>3</sup>

The present study deals with two systems which cleave to give an anion stabilized only by a cyano group. The base-catalyzed decarboxylation<sup>4</sup> of 2-cyano-2-methyl-3-phenylpropanoic acid (I) and cleavage of 3-cyano-2,3-dimethyl-4-phenyl-2-butanol (III) both lead to 2-cyano-1-phenylpropane (II). The steric courses of these electrophilic substitution reactions have been investigated, and the results compose this paper.



### Results

Optically pure (+)-2-cyano-2-methyl-3-phenylpropanoic acid ((+)-I)<sup>5</sup> was converted through its

(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 donors of this fund.

(2) D. J. Cram, A. Langemann, J. Allinger and K. R. Kopecky, *J. Am. Chem. Soc.*, **81**, 5740 (1959); (b) D. J. Cram, F. Hauck, K. R. Kopecky and W. D. Nielson, *ibid.*, **81**, 5767 (1959); (c) D. J. Cram, J. L. Mateos, F. Hauck, A. Langemann, K. R. Kopecky, W. D. Nielson and J. Allinger, *ibid.*, **81**, 5774 (1959); (d) D. J. Cram and B. Rickborn, *ibid.*, **83**, 2178 (1961); (e) D. J. Cram, L. K. Gaston and H. Jäger, *ibid.*, **83**, 2183 (1961).

(3) D. J. Cram and P. Haberfeld, *ibid.*, **83**, 2354 (1961).

(4) See ref. 3 for a summary of previous literature.

(5) J. Kenyon and W. A. Ross, *J. Chem. Soc.*, 3407 (1951).

ester to optically pure (+)-3-cyano-2,3-dimethyl-4-phenyl-2-butanol. Since determination of the stereospecificity of the reactions under study depends on a knowledge of the rotation of both optically pure reactants and products, (+)-2-cyano-1-phenylpropane was prepared with optically pure 2-methyl-3-phenylpropanoic acid<sup>6</sup> as starting material. The substance was converted to its amide which was dehydrated with phosphorus pentoxide to the desired nitrile. Three separate conversions of the same acid to nitrile gave rotations of  $\alpha^{25D} +34.3^\circ$ ,  $+35.6^\circ$  and  $+37.4^\circ$  (*l* 1 dm., neat). Use of phosphorus oxychloride as dehydrating agent gave  $\alpha^{25D} +33.0^\circ$  (*l* 1 dm., neat), a value identical with that obtained by Kipping and Hunter.<sup>6</sup> These authors prepared nitrile from optically pure acid by dehydration of amide with phosphorus oxychloride. When hydrolyzed, the nitrile gave acid which had a 2% higher rotation than the starting acid. However, the authors conclusion that no racemization occurred in any of the stages of this cyclic series of conversions was negated by their crystallization of the amide, which might have led to removal of racemic contaminant. Their results taken together with ours suggest that the value of  $\alpha^{25D} \pm 37.4^\circ$  (*l* 1 dm., neat) is at least close to maximum rotation.

Unfortunately, no completely conclusive means were found by which the configurations of the two starting materials could be related to that of the product. However, the pattern of results of the decarboxylation and cleavage reactions of I and III (see Tables I and II) in ethylene glycol is similar to that observed for other systems whose internal configurational relationships have been unequivocally established. In this solvent or in the closely similar diethylene glycol, cleavage of two ketones,<sup>7</sup> two *sec*-alcohols,<sup>8</sup> seven *t*-alcohols<sup>2,7,8</sup> and one decarboxylation of an acid<sup>3</sup> gave net inversion, irrespective of the nature of the metal or quaternary nitrogen cation employed.<sup>9</sup> In runs

(6) F. S. Kipping, and A. E. Hunter, *ibid.*, 1005 (1903).

(7) D. J. Cram, K. R. Kopecky, F. Hauck and A. Langemann *Am. Chem. Soc.*, **81**, 5754 (1959).

(8) D. J. Cram, A. Langemann and F. Hauck, *ibid.*, **81**, 5750 (1959).

(9) Of the large number of systems examined, only 2-methyl-3-phenyl-2,3-butanediol cleaved in ethylene glycol to give product with net retention. This anomalous result is undoubtedly due to the presence of an internal proton source in the carbanion intermediate (ref. 2e).

TABLE I

Run	Solvent	Base		$T$ , °C.	Time, hr.	% yld.	Product <sup>b</sup> $\alpha^{25}_D$	Net steric course
		Nature	Concn., $M$					
1	HOCH <sub>2</sub> CH <sub>2</sub> OH	NH <sub>3</sub>	0.025	135	110	72	+1.69°	5% inv.
2	HOCH <sub>2</sub> CH <sub>2</sub> OH	K <sub>2</sub> CO <sub>3</sub>	.0125	125	47	69	+1.60	5% inv.
3	C <sub>6</sub> H <sub>5</sub> OH	NH <sub>3</sub> + -	.10	135	288	53	+0.53	1.5% inv.
4	C <sub>6</sub> H <sub>5</sub> OH	(CH <sub>3</sub> ) <sub>4</sub> NOH	.10	125	114	33	-.17	0.5% ret.
5	(CH <sub>3</sub> ) <sub>3</sub> COH	NH <sub>3</sub>	.10	125	47	38	-.20	0.5% ret.

<sup>a</sup> Solutions 0.10  $M$  in optically pure acid were used. <sup>b</sup> Optically pure 2-cyano-1-phenylpropane has a presumed rotation of  $\alpha^{25}_D$  +37.4° ( $l$  1 dm., neat). <sup>c</sup>  $l$  = 1 dm., neat.

TABLE II

RESULTS OF CLEAVAGE REACTIONS OF 0.10  $M$  SOLUTIONS OF (+)-3-CYANO-2,3-DIMETHYL-4-PHENYL-2-BUTANOL (III) IN 0.10  $M$  BASE

Run <sup>a</sup>	Solvent	Base	$T$ , °C.	10 <sup>3</sup> $k_1$ , sec. <sup>-1b</sup>	Time, hr.	% yld.	Product <sup>c</sup>			Net steric course
							$\alpha^{25}_D$	10 <sup>3</sup> $k_1$ , sec. <sup>-1b</sup>	% max. race- miz. <sup>d</sup>	
6	HOCH <sub>2</sub> CH <sub>2</sub> OH	KOH	83		39	35	+5.32°	6	56	14% inv.
7	HOCH <sub>2</sub> CH <sub>2</sub> OH	LiOCH <sub>2</sub> CH <sub>2</sub> OH	83		72	62	+4.70	5	70	13% inv.
8	HOCH <sub>2</sub> CH <sub>2</sub> OH	(CH <sub>3</sub> ) <sub>4</sub> NOH	83	1	48	41	+3.14		64	8% inv.
9	CH <sub>3</sub> OH	KOH	65		163	76	-1.22	1.5	67	3% ret.
10	CH <sub>3</sub> OH	LiOCH <sub>2</sub>	65		159	76	-1.48	1.5	53	4% ret.
11	CH <sub>3</sub> OH	(CH <sub>3</sub> ) <sub>4</sub> NOH	65	0.6	113	72	-2.66		53	7% ret.
12	C <sub>6</sub> H <sub>5</sub> OH	LiOC <sub>2</sub> H <sub>5</sub>	65		19	70	-1.14	10	53	3% ret.
13	<i>n</i> -C <sub>4</sub> H <sub>9</sub> OH	KOC <sub>4</sub> H <sub>9</sub> - <i>n</i>	65	20	3.3	55	-0.41		61	1% ret.
14	<i>n</i> -C <sub>4</sub> H <sub>9</sub> OH	LiOC <sub>4</sub> H <sub>9</sub> - <i>n</i>	65	2	11.2	69	+3.72	7	25	10% inv.
15	<i>n</i> -C <sub>4</sub> H <sub>9</sub> OH	(CH <sub>3</sub> ) <sub>4</sub> NOH	65	50	1.75	75	-2.30	80	40	6% ret.
16	86% (CH <sub>3</sub> ) <sub>2</sub> SO 14% CH <sub>3</sub> OH	KOCH <sub>3</sub>	25	20	1.85	48	+1.86	130	58	5% ret.
17	95% O(CH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> O 5% CH <sub>3</sub> OH									
		KOCH <sub>3</sub>	25	3.5	40.3	76	+0.15	2	28	0.5% inv.

<sup>a</sup> Runs are numbered consecutively throughout this paper. <sup>b</sup> Estimated first-order rate constants for cleavage reaction; probable error for all values less than 50%. <sup>c</sup> Optically pure 2-cyano-1-phenylpropane has presumed rotation of  $\alpha^{25}_D$  ±37.4° ( $l$  1 dm., neat). <sup>d</sup>  $l$  = 1 dm., neat. <sup>e</sup> Calculated from rates of racemization of 2-cyano-1-phenylpropane. In calculation, rate of cleavage of III was assumed to be instantaneous; thus the estimated percentages of racemization of product once formed are maximal. <sup>f</sup> By volume.

1 and 2, (+)-I decarboxylated to (+)-II with 5% stereospecificity in ethylene glycol with ammonia and potassium carbonate catalysts, respectively. In runs 6-8, (+)-III cleaved to (+)-I with 8-14% stereospecificity in ethylene glycol with potassium hydroxide, lithium ethylene glycolate or tetramethylammonium hydroxide as catalysts. Had the product once formed not itself undergone racemization (see below), the data suggest that the stereospecificities in these runs would have been very close to one another. These results taken together with the fact that the *relative* configurations and (+)-I and (+)-III are known strongly support the thesis that runs, 1, 2, 6, 7 and 8 in ethylene glycol went with net inversion, as did similar reactions in systems of known configuration. This conclusion allows the relative configurations of I, II and III to be assigned, and the stereochemical directions of the other runs of Tables I and II to be determined.

Although the conditions of the decarboxylation reactions (Table I) were such as to preserve the optical integrity of the product, alcohol III would not cleave under conditions mild enough so that the product once formed did not partially racemize. Rates of racemization of the product II were determined under the conditions of most of the runs of Table II, and the maximum racemization of the

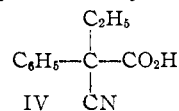
product after its formation calculated (see Table II). Thus the observed stereospecificities for the cleavage reactions of Table II are minimal, and only differences in steric direction and gross differences (factor of 2) in stereospecificities are worthy of discussion.

In runs 8, 11, 13, 14, 15, 16 and 17, the rates of cleavage were estimated from the loss of optical activity of the reaction mixture as the reaction proceeded (see Experimental).

The base-catalyzed nature of the cleavage of III was demonstrated in two representative solvents, ethylene glycol and 1-butanol. No reaction occurred when III was submitted to the conditions of runs 7 and 15 in the absence of base.

#### Discussion

**Decarboxylation Reaction.**—Temperatures 100° higher were required for decarboxylations of acid I as compared to acid IV.<sup>3</sup> Even in the presence of the cyano group, the ability of phenyl to stabilize



the transition state for breaking of the carbon-carbon bond is much in evidence. Although in most runs the temperature differences in the reac-

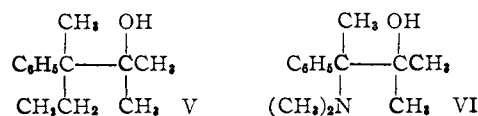
tions of I and IV make comparisons of stereochemical results difficult, the conditions of decarboxylation of the ammonium salts of the two systems in phenol are close enough together to admit comparison. The salt of IV cleaved at 48° and 100° to give product with 13.5% retention (runs 21 and 24 of ref. 3), whereas that of I at 135° gave product with 1.5% inversion. If the role of the phenyl group was solely that of stabilizing the carbanion and therefore extending its life, system IV should have given the less stereospecific result. It seems more probable that two stereospecific mechanisms are competing with one another in reactions of both systems, and that retention, inversion and racemization reaction paths are delicately balanced. Thus the presence of a phenyl group at the seat of substitution might make a small difference in the relative rates of proton capture by an asymmetrically enveloped carbanion from the side of, and the side remote from the leaving group. Certainly the side remote from the leaving group is less hindered in I than in IV. "Back side" solvation of the carbanion intermediate by solvent should be more important in the reaction of I than in that of IV.

**Alcohol Cleavage Reactions.**—The rate of cleavage of alcohol III (see Table II) increases as the hydrogen-bonding ability of the solvent decreases. Thus with tetramethylammonium hydroxide as base, the rate in 1-butanol was about two powers of ten faster than the rate in methanol (runs 11 and 15). Had the rates been determined at the same temperature, the rate of reaction in methanol (run 11) would have been faster than that in ethylene glycol. Similarly, the rate in dioxane-methanol (potassium methoxide as catalyst) was much greater than that in methanol (runs 17 and 9, respectively). The general trend is in accord with observations made previously<sup>10</sup> for the base-catalyzed cleavages of  $\beta$ -hydroxyacids, and supports the hypothesis that the rate-determining step in the cleavage reaction is the formation of an intermediate carbanion. In passage from the alcohol anion to the transition state, charge would be delocalized, and hydrogen bonds would be broken. The stronger the hydrogen bond, the slower would be the reaction. Had comparable temperatures been employed, the rate of cleavage in dimethyl sulfoxide-methanol (run 16) would have been the greatest of all, in spite of the fact that this medium is probably the most polar of any employed. The ability of dimethyl sulfoxide to hydrogen-bond with methanol left the alkoxide anion relatively free of hydrogen bonds, and as a result the reaction was greatly accelerated.

A second trend in rates is worthy of comment. In cleavage of III in 1-butanol solvent, as the cation of the base is changed from lithium to potassium to quaternary ammonium,  $k$  (sec.<sup>-1</sup>) increases from 2 to 20 to 50  $\times 10^{-5}$  (see runs 13, 15 and 14 of Table II). This effect is attributed to differences in stability of the three different intimate ion pairs which are presumed to be the main species in this solvent (not necessarily the main species

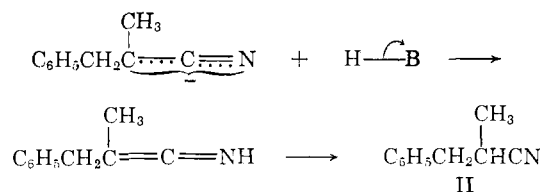
that cleaves). The lithium-oxygen bond is undoubtedly stronger than the potassium-oxygen bond, which in turn is stronger than the purely ionic bond between oxygen and the quaternary ammonium ion.

As expected, the presence of the electron-distributing cyano group at the seat of electrophilic substitution plays an important role in governing the rate of the cleavage reactions of alcohol III. In all of the solvents examined (see Table II), this alcohol underwent reaction at considerably lower temperatures than alcohols V<sup>2b,7</sup> and VI,<sup>2c</sup> which have the same leaving groups but different substituents attached to the seat of substitution. Apparently negative charge is widely dispersed in the transition states for the cleavage reaction,



and the superiority of the cyano over the phenyl group at distributing negative charge correlates with these results.

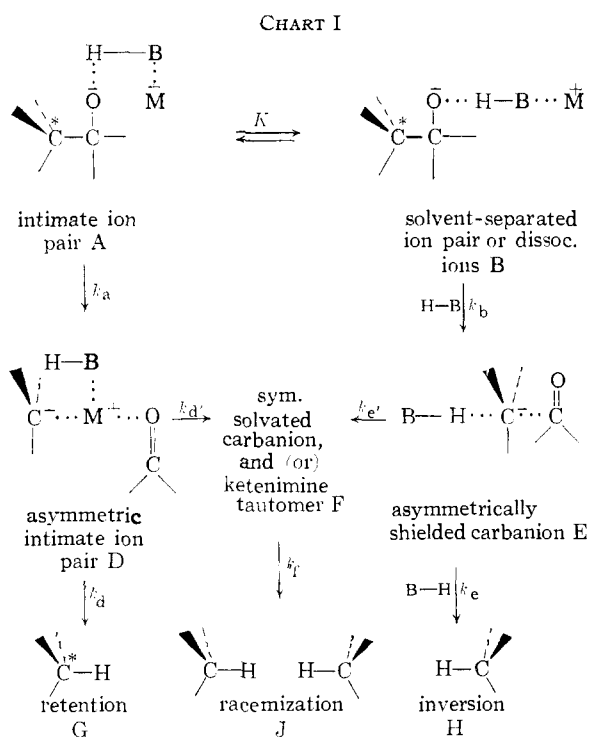
The cleavage reactions of alcohol III tend to be much less stereospecific than those of alcohols such as V and VI. Two effects are apparent in these results. (1) The 2-cyano-3-phenylpropyl anion, which is presumed to be an intermediate in the reaction, is longer lived than carbanions stabilized by a phenyl group, and therefore is more likely to pass into a symmetrical environment before proton transfer occurs. (2) Due to the greater electronegativity of nitrogen as compared with carbon, proton transfer to nitrogen might be the favored reaction path for disposal of the carbanion intermediate.



A number of other differences in the stereochemistry of electrophilic substitution in system III and those studied previously are apparent. For example, in cleavage of aminoalcohol VI in *t*-butyl alcohol, replacement of potassium *t*-butoxide with tetramethylammonium hydroxide reduced the stereospecificity from 96 to 6% net retention (runs 14 and 16 of paper X of this series).<sup>2c</sup> In cleavage of III in *n*-butyl alcohol, replacement of potassium *n*-butoxide with tetramethylammonium hydroxide increased the stereospecificity from 1 to 6% net retention. The lack of correlation is not surprising when one considers the complex of rate and equilibrium constants that govern the stereochemical outcome of the reaction.

In the mechanism of Chart I,<sup>2c</sup> cleavage of intimate ion pairs leads to product of retained configuration (A  $\rightarrow$  D  $\rightarrow$  G) whereas cleavage of solvent-separated ion pairs or dissociated ions leads to product of inverted configuration (B  $\rightarrow$  E  $\rightarrow$  H).

(10) C. S. Rondestvedt and M. E. Rowley, *J. Am. Chem. Soc.*, **78**, 3804 (1956).



The relative contributions of D and E to the product is governed by eq. 1.<sup>2b</sup>

$$D/E = \frac{k_s}{k_bK} \quad (1)$$

In addition to, and competing with, the two stereospecific processes are the non-stereospecific reaction sequences  $A \rightarrow D \rightarrow F \rightarrow J$  and  $B \rightarrow E \rightarrow F \rightarrow J$ . Conceivably, low net inversion could be the observed stereochemical result even though more intimate ion-pairs cleaved than solvent-separated ion pairs or dissociated ions. Such a result could be observed should  $k_a > k_bK$ , but  $k_d' \gg k_d$  and  $k_e \gg k_e'$ . Similarly, low net retention would result if  $k_bK > k_a$  but  $k_e' \gg k_e$  and  $k_d > k_d'$ . Since only low stereospecificities were observed in the cleavages of system III, detailed interpretation of the steric results is impossible.

### Experimental

(+)-2-Cyano-2-methyl-3-phenylpropanoic acid (I) was prepared and resolved as reported previously,<sup>5</sup> m.p. 88–89°,  $[\alpha]^{25}_D +25.7^\circ$  (*c* 2.4,  $\text{CHCl}_3$ ); literature<sup>6</sup> m.p. 87.5–88.5°,  $[\alpha]^{25}_D +25.1^\circ$  (*c* 2.4,  $\text{CHCl}_3$ ).

(+)-3-Cyano-2,3-dimethyl-4-phenyl-2-butanol (III).—To 10.0 g. of optically pure (+)-2-cyano-2-methyl-3-phenylpropanoic acid dissolved in 20 ml. of ether was added a solution of excess diazomethane in 250 ml. of ether. The solution was allowed to stand for 15 minutes at 25°, the excess diazomethane was decomposed with formic acid, and the solution was washed with saturated sodium carbonate solution, with 2*N* hydrochloric acid and finally with water. The solution was dried, evaporated and the residual oil was distilled at 2 mm. (pot temperature 160°) to yield 10.0 g. of (+)-methyl 2-cyano-2-methyl-3-phenylpropanoate,  $n^{25}_D$  1.5055,  $\alpha^{27}_D +26.72^\circ$  (*l* 1 dm., neat).

To 200 ml. of an ethereal solution of a Grignard reagent prepared from 5.0 g. of magnesium and 30 g. of iodomethane was added 10 g. of the above ester. The reaction mixture was stirred at 0° for 30 minutes, a saturated ammonium chloride solution was then added and the ether phase separated. The ether solution was dried and evaporated to yield 0.7 g. of alcohol, m.p. 88.5–91.5°. Four recrystalliza-

tions of this material from ether-pentane gave 5.7 g. of alcohol III, m.p. 108–109°,  $[\alpha]^{25}_D +22.33^\circ$  (*c* 10%,  $\text{CHCl}_3$ ).

Anal. Calcd. for  $\text{C}_{13}\text{H}_{17}\text{ON}$ : C, 76.81; H, 8.43; N, 6.89. Found: C, 77.07; H, 8.39; N, 7.06.

(+)-2-Cyano-1-phenylpropane (II).<sup>11</sup>—Resolution of 2-methyl-3-phenylpropanoic acid was accomplished by a modification of the original resolution.<sup>6</sup> The quinine salt was formed and recrystallized nine times from 50% aqueous ethanol instead of ethyl acetate. From 267 g. of racemic acid was obtained 74 g. of optically pure material,  $\alpha^{25}_D +20.68^\circ$  (*l* 1 dm., neat), literature  $\alpha_D +20.26^\circ$  (*l* dm., neat). A solution of 22 g. of this acid was dissolved in 32 g. of thionyl chloride and the mixture allowed to stand at room temperature for 3 hours. The excess thionyl chloride was evaporated at 20 mm., and the residual acid chloride was poured carefully into concentrated ammonium hydroxide held at 0°. The resulting solid amide was collected, and repeatedly washed with pentane (low solubility) and dried; wt. 18.4 g., m.p. 100–105°. This amide was mixed with 22 g. of  $\text{P}_2\text{O}_5$ , and was placed under a 20 mm. pressure, and the mixture heated. The material that distilled (pot temperature 150–180°) was dissolved in ether, and the ether solution was washed repeatedly with sodium carbonate solution and water. The ether solution was dried, evaporated, and the residue was distilled. The nitrile product, 12.4 g. (64%), had  $\alpha^{25}_D +37.44^\circ$  (*l* 1 dm., neat) [lit.<sup>6</sup>  $\alpha_D +33^\circ$  (*l* 1 dm., neat)] and  $n^{25}_D$  1.5091. Other preparations of the same nitrile by the same procedure from the same acid gave  $\alpha^{25}_D +34.28^\circ$  and  $+35.64^\circ$ . Substitution of  $\text{POCl}_3$  for  $\text{P}_2\text{O}_5$  resulted in slightly more racemized material,  $\alpha^{25}_D +33^\circ$ .

**Representative Decarboxylation Reactions of (+)-2-Cyano-2-methyl-3-phenylpropanoic Acid: Run 2.**—Optically pure (+)-2-cyano-2-methyl-3-phenylpropanoic acid, 0.378 g., and 0.0346 g. of potassium carbonate were dissolved in 20 ml. of ethylene glycol. The rotation of this solution when held at 100° for 6 days decreased from  $\alpha^{25}_D +0.40^\circ$  to  $\alpha^{25}_D +0.37^\circ$  (*l* 1 dm.), so the solution was heated at 125° for 47 hours, after which the rotation had diminished to  $\alpha^{27}_D +0.02^\circ$  (*l* 1 dm.). The solution was added to 100 ml. of water (*pH* of mixture, 8) and extracted with two 20-ml. portions of pentane. The pentane phases were washed with a 100-ml. portion of water and dried. The pentane was evaporated and the residue distilled at 2 mm. (pot temperature 120°) to yield 0.21 g. of 2-cyano-1-phenylpropane,  $n^{25}_D$  1.5091,  $\alpha^{26}_D +1.69^\circ$  (*l* 1 dm.).

**Run 5.**—Optically pure acid, 2.0 g., was dissolved in 30 ml. of ether, and into this solution was passed ammonia gas. The resulting precipitate of ammonium salt amounted to 1.7 g., m.p. 272–273° dec. This salt, 0.412 g., was dissolved in 20 ml. of *t*-butyl alcohol. For 6 days at 100° the rotation of this solution,  $\alpha^{25}_D +0.30^\circ$  (*l* 1 dm.), remained unchanged. After 47 hours at 125°, the rotation had diminished to  $\alpha^{25}_D 0.00^\circ$  (*l* 1 dm.). The solution was poured into 100 ml. of water and extracted with two 200-ml. portions of pentane. The pentane phases were washed with three 100-ml. portions of water and dried. The pentane was evaporated and the residue distilled at 2 mm. (pot temperature 120°) to give 0.11 g. of 2-cyano-1-phenylpropane,  $n^{25}_D$  1.5093,  $\alpha^{27}_D -0.20^\circ$  (*l* 1 dm., neat).

Runs 3 and 4 were carried out and the product isolated by a procedure similar to that employed in decarboxylation of 2-cyano-2-phenylbutanoic acid.<sup>3</sup> Run 1 was similar in procedure to that employed in runs 2 and 5. The infrared spectrum of the 2-cyano-1-phenylpropane produced in runs 1, 4 and 5 was compared with that of authentic material, and all samples were found to be identical in detail with one another.

**Representative Cleavage Reactions of (+)-3-Cyano-2,3-dimethyl-4-phenyl-2-butanol (III): Run 6.**—Optically pure alcohol, 0.203 g., was dissolved in 10 ml. of a solution of 0.10 *M* potassium hydroxide in pure ethylene glycol. After standing at 83° for 39 hours, the solution was diluted with 100 ml. of water, and extracted with two 30-ml. portions of pure pentane. The organic layers were washed with 100 ml. of water and dried. The pentane layer was evaporated and the residue absorbed on a 2 by 30 cm. column of neutral activated alumina. The product was eluted with 150 ml. of 5% ether-pentane, and the solvent was evaporated. The residue was distilled at 2 mm. at a pot temperature of

(11) The authors are indebted to Dr. Bruce Nickborn for this preparation.

120° to give 0.050 g. of 2-cyano-1-phenylpropane,  $n_D^{25}$  1.5087,  $\alpha_D^{25} +5.32^\circ$  ( $l$  1 dm., neat). Further elution of the column with pure ether yielded no additional material. Extraction of the aqueous layer (from the pentane extractions) with 200 ml. of ether and evaporation of the ether gave 0.050 g. of starting alcohol, m.p. 103–106°,  $[\alpha]_D^{25} +17.6^\circ$  ( $c$  4.9,  $\text{CHCl}_3$ ).

**Run 10.**—Optically pure alcohol III, 0.203 g., was refluxed in a solution of 10 ml. of 0.10 *M* lithium methoxide in methanol for 159 hours. The cooled solution was diluted with 50 ml. of water and extracted with two 20-ml. portions of pentane. The pentane layer was washed with two 50-ml. portions of water, dried, evaporated, and the residue was distilled at 2 mm. to give 0.11 g. of 2-cyano-1-phenylpropane,  $n_D^{25}$  1.5089,  $[\alpha]_D^{25} -2.96^\circ$  ( $l$  1 dm., neat).

**Run 15.**—Optically pure alcohol III, 0.203 g., was heated in 10 ml. of 0.10 *M* tetramethylammonium hydroxide at 65° for 105 minutes. The solution was acidified with glacial acetic acid, and most of the solvent evaporated at 100° and 20 mm. The residual oil was chromatographed on a 2 by 20 cm. column of neutral activated alumina with 5% ether-pentane as developer. The first 200 ml. of eluant was evaporated and the residue distilled at 2 mm. (pot temperature 120°) to give 0.11 g. of 2-cyano-1-phenylpropane,  $n_D^{25}$  1.5089,  $\alpha_D^{25} -2.30^\circ$ .

**Other Runs.**—Runs 7 and 8 were carried out by the procedure for run 6; runs 9, 11, 12, 16 and 17 by the procedure for run 10; and runs 13 and 14 by the procedure for run 15. The indices of refraction of the product were in all cases between  $n_D^{25}$  1.5087 to  $n_D^{25}$  1.5093. Infrared spectra of the product of runs 8, 10, 16 and 17 were taken and found to be identical in detail with that of authentic material.

**Stability of (+)-3-Cyano-2,3-dimethyl-4-phenyl-2-butanol (III) in Solvent in the Absence of Base.**—Optically pure III (0.101 g.) was dissolved in 5 ml. of methanol,  $\alpha_D^{25} +0.33^\circ$  ( $l$  1 dm.). The solution was heated at 65° for 23 hours, after which the solution had  $\alpha_D^{25} +0.34^\circ$  ( $l$  1 dm.). The solvent was evaporated and the residue recrystallized from ether-pentane to give 0.097 g. of starting material,

m.p. 108–109°. A solution of 0.203 g. of optically pure III in 10 ml. of ethylene glycol showed no rotational change when held at 100° for 44 hours. The initial and final rotations were  $\alpha_D^{25} +0.44^\circ$  ( $l$  1 dm.).

**Typical Rate Measurements for Cleavage of (+)-3-Cyano-2,3-dimethyl-4-phenyl-2-butanol (III): Run 14.**—A solution of 0.203 g. of optically pure III in 10 ml. of a 0.10 *M* solution of lithium *n*-butoxide in *n*-butyl alcohol was placed in a 65° constant temperature bath; aliquots were taken at intervals, and their rotations measured in a 1-dm. tube. First-order rate constants were calculated and averaged.

Time, hr.	$[\alpha]_D^{25}$	$k_1$ , sec. <sup>-1</sup> × 10 <sup>3</sup>
0.0	+0.29°	..
2.0	+ .26	1.7
4.0	+ .19	2.8
7.5	+ .13	2.8
10.5	+ .08	
		Av. 2.4

The rate constants, which are recorded in Table II, are clearly very approximate.

**Approximate Rates of Racemization of (–)-2-Cyano-1-phenylpropane Under Conditions of Its Formation.**—Approximate rates of racemization were measured for (–)-2-cyano-1-phenylpropane (II), under the exact conditions of its formation in runs 6, 7, 9, 10, 12, 14, 15, 16 and 17, except that an 0.10 *M* solution of II was substituted for the 0.10 *M* solution of III used in the cleavage reaction. Aliquot techniques were employed, five to eight points were taken, and the reaction was carried through several half-lives. Probable errors for all values for the first-order rate constants (Table II) are less than 50%.<sup>12</sup>

(12) An extensive kinetic investigation of racemization rates of II with a variety of bases and solvents has been carried out, the results of which will be reported in a later study.

(CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY, NEW YORK 27, N. Y.)

## Triarylcylopropenium Ions. Synthesis and Stability in the Phenyl *p*-Anisyl Series<sup>1</sup>

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A novel synthesis is reported for triarylcylopropenium ions, involving the reaction of an arylchlorocarbene with a diarylacetylene. Using this reaction, the triphenyl-, diphenyl-*p*-anisyl-, di-*p*-anisylphenyl- and tri-*p*-anisylcylopropenium ions have been prepared, and their spectra and  $pK_R$ 's determined. The  $pK_R$ 's are correlated with the predictions of molecular orbital theory.

Although the synthesis of the triphenylcylopropenium ion was described some time ago,<sup>2,3</sup> the approach was not suited to the preparation of substantial amounts of materials, and more seriously the scheme, involving reaction of phenyldiazoacetonitrile with diphenylacetylene, and subsequent conversion of the resulting triphenylcylopropenyl cyanide to the cation with boron trifluoride, has proved unsuitable for extension to the anisyl series, and thus does not promise to be a general method. We accordingly have investigated an alternative approach, and have found that phenylchlorocarbene, generated from benzal chloride and potassium *t*-butoxide, reacts with diphenylacetylene to form triphenylcylopropenyl chloride.<sup>4</sup>

(1) This work was supported by a grant from the National Science Foundation.

(2) R. Breslow, *J. Am. Chem. Soc.*, **79**, 5318 (1957).

(3) R. Breslow and C. Yuan, *ibid.*, **80**, 5991 (1958). Through a typographical error,  $\Delta D.E.$  for triphenylcylopropenyl cation was reported to be 4.38 instead of 2.38, the correct value.

Under the conditions of the experiment this is of course converted to triphenylcylopropenyl *t*-butyl ether, and interestingly this is hydrolyzed to bis-triphenylcylopropenyl ether during aqueous washing of the reaction product. Neither of these compounds need be isolated, however, for they are converted quantitatively to triphenylcylopropenyl bromide (I)<sup>3</sup> by treatment with hydrogen bromide, and since this salt is insoluble in non-polar solvents it can be isolated easily from the crude extracts. Accordingly, with the proper choice of reaction conditions large amounts of diphenylacetylene can be converted quantitatively to triphenylcylopropenyl bromide in a few hours.

The reaction works also on *p*-anisylphenylacetylene and on di-*p*-anisylacetylene, or with *p*-anisal chloride instead of benzal chloride, and using the appropriate combinations it has been possible to

(4) This method was first reported at the Boston, Mass., Meeting of the American Chemical Society, April, 1960.