photometer using either 0.5 mm. or 0.1 mm. sodium chloride cells. The spectra were recorded at slow speed using a 2X setting of the slit width. The infrared analyses were also made on a Perkin Elmer model 21 spectrophotometer, using sodium chloride optics. Analytical conditions for the runs using a 0.1 mm. sodium chloride cell: slits at 387 μ, gain 5.5, supression 0, response 1:1, scattered light filter in. The alkyl bromide samples were quantitatively prepared by diluting accurately weighed samples to 1 ml. in volumetric flasks with carbon disulfide (Mallinckrodt, analytical reagent). The absorbance of the analytical bands were determined by using the base line technique. In most cases the spectral region being studied was recorded three times and an average absorbance calculated.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

Three Membered Rings. II. The Stereochemistry of Formation of Some 1,1,2,2-Tetrasubstituted Cyclopropanes

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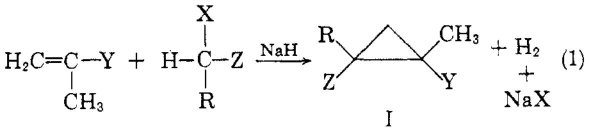
A number of 1,1,2,2-tetrasubstituted cyclopropanes have been formed by the reaction of α-halo esters, nitriles, or ketones with methyl methacrylate or methacrylonitrile in the presence of sodium hydride. In all cases, the predominant or exclusive product isomer is that in which the activating groups, ester, nitrile, or carbonyl, are *cis* to each other. The effect of several variables on the yields and *cis-trans* isomer ratios has been determined.

The formation of 1,2-cyclopropanedicarboxylic acid esters by reaction of α-haloesters with α,β-unsaturated esters in the presence of a base has been described.[1] Some extensions and additional examples of this reaction have been reported.[2–7]

The present report gives a more detailed examination of certain aspects of the general problem. This study has been limited to the relatively simple cases in which the cyclopropane product is substituted at only two ring carbons. As a result, only one pair of *cis-trans* isomers is possible in each case. Further, the examples have been picked so that no hydrogens are present *alpha* to the activating groups. Consequently, base catalyzed equilibration of the isomers is not possible, and whatever *cis-trans* isomer ratio is formed in the ring closure reaction is frozen.[8]

Specifically, this study involved three interrelated purposes. The first was to determine how yields of cyclopropane products varied as some of the reaction variables were changed. The second was to observe how the isomer ratios varied with these same changes. Finally, it was of interest to determine if substituents other than methyl, and activating groups other than esters, the groups used in the initial investigation,[1] could be incorporated into the reaction. The systems actually used may be summarized in the general reaction:



(1)

I

R is $-CH_3$, $-C_6H_5$, $-Cl$

Y, Z are $-COOCH_3$, $-C{\equiv}N$, $-\overset{O}{\overset{\|}{C}}C_6H_5$

X is $-Cl$, $-Br$, $-I$

Not all combinations were examined; the results of those that were observed are given in Table I.

Variables affecting yields. A change in the reaction temperature from about 25° to 115° had essentially no effect on the yield (Runs 1 and 2, 5 and 6). A pronounced affect on the yield was observed, however, when the halogen, X of reaction 1, was changed from chlorine to bromine to iodine (Runs 2–4, 6–7). Similar variations have been noted previously,[1,2,5] but not all were quite so marked. In comparable cases the chloro compound gives the best results and is strongly preferred. Some systems may give acceptable yields with the bromo derivatives.[4] The iodo compounds

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(1) L. L. McCoy, *J. Am. Chem. Soc.*, **80**, 6568 (1958).

(2) R. Fraisse and R. Jacquier, *Bull. soc. chim. France*, 986 (1957).

(3) M. Mousseron and R. Fraisse, *Compt. rend.*, **248**, 887 (1959).

(4) M. Mousseron, R. Fraisse, R. Jacquier, and G. Bonavent, *Compt. rend.*, **248**, 1465 (1959).

(5) M. Mousseron, R. Fraisse, R. Jacquier, and G. Bonavent, *Compt. rend.*, **248**, 2840 (1959).

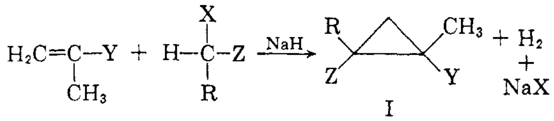
(6) D. T. Warner, *J. Org. Chem.*, **24**, 1536 (1959).

(7) S. Wawzonek and C. E. Morreal, *J. Am. Chem. Soc.*, **82**, 439 (1960); O. Widman, *Ber.*, **51**, 533, 907 (1918).

(8) The *cis-trans* isomer ratio has been reported to vary with the base used (ref. 3,5). Unfortunately, all but one of the examples have a hydrogen *alpha* to an ester group. No evidence was presented that the isomers are stable under the reaction conditions, and in two cases (ref. 3) it was shown that warming the reaction product with strong base could cause a complete inversion of the isomer ratio, 95% *cis* to 95% *trans*. The one example with no α-hydrogens was run with only one base. Consequently, although these variations in isomer ratio with base used are valid for the reactions studied, it is not clear that they represent the isomer ratios produced during the ring closure reaction; the observed ratios may arise by base catalyzed partial isomerization subsequent to ring closure.

TABLE I

PRODUCTS OF THE REACTION



									Acids[c]	
Run	Y	Z	R	X	Procedure[a]	Yield I, %	% *cis* I[b]	% *trans* I[b]	% *cis*	% *trans*
1	$COOCH_3$	$COOCH_3$	CH_3	Cl	A	71	93	7	72[d]	<3[d]
2	$COOCH_3$	$COOCH_3$	CH_3	Cl	B	69	85	15		
3	$COOCH_3$	$COOCH_3$	CH_3	Br	B	32	68	32		
4	$COOCH_3$	$COOCH_3$	CH_3	I	B	21[e]	50	50		
5	$C{\equiv}N$	$COOCH_3$	CH_3	Cl	A	59	75	25		
6	$C{\equiv}N$	$COOCH_3$	CH_3	Cl	B	61	73	27	32	15
7	$C{\equiv}N$	$COOCH_3$	CH_3	Br	B	33	53	47		
8	$COOCH_3$	$C{\equiv}N$	CH_3	Cl	B	0				
9	$C{\equiv}N$	$C{\equiv}N$	CH_3	Cl	B	2				
10	$COOCH_3$	$COOCH_3$	Cl	Cl	C	74	100	0	90	0
11	$C{\equiv}N$	$COOCH_3$	Cl	Cl	C	64	80	20	48	4
12	$COOCH_3$	$C{\equiv}N$	Cl	Cl	C	0				
13	$C{\equiv}N$	$C{\equiv}N$	Cl	Cl	C	0				
14	$COOCH_3$	$COOCH_3$	C_6H_5	Cl	C				38	0
15	$COOCH_3$	COC_6H_5	CH_3	Cl	C				35	0

[a] See experimental section. [b] *Cis* and *trans* refers to the relationship between the groups Y and Z; see experimental. [c] These acids are obtained by hydrolysis of the various isomeric product mixtures, I; see experimental. [d] These are values previously reported for a different, but very similar, run (ref. 1). [e] This is based on total distillation fraction obtained, but by gas chromotography about one-third of this was unchanged iodo ester.

probably should be ignored. When an unsaturated nitrile is used in place of the corresponding methyl ester, the yields are slightly less (Runs 1 and 5, 2 and 6, 10 and 11), but not invariably so (Runs 3 and 7). A nitrile used in place of a methyl ester in the halogen component, however, consistently gives unsatisfactory results (Runs 8, 9, 12, 13). These reactions invariably produced black tars; apparently the olefinic component was polymerizing more rapidly than cyclopropane formation was taking place. As the yields in some other systems have been found to be influenced markedly by the base used,[4,5] it is possible that these nitriles would work satisfactorily with some other base.[9]

Variables affecting the cis-trans isomer ratio. Although various trends may be discerned in Table I, one fact is glaringly obvious: The *cis* isomer is the predominant or exclusive product in all cases. This confirms the previous statement of the fact,[1] and is in general agreement with the results obtained by Mousseron, *et al.*[3,5] It had been hoped that in this study conditions would be found under which the *trans* isomer would predominate. With systems containing α-hydrogen atoms formation of *cis* isomers offers no problem, because the *cis* isomers may be equilibrated by strong base to mixtures rich in the more stable isomer, usually *trans*.[3] In the present series such equilibration is not possible. The *trans* isomers are obtained as minor products in some cases, but no conditions have been found in which the *trans* isomer predominates. The slight trends observed in Table I are not very encouraging.

An increase in reaction temperature reduces the *cis/trans* ratio slightly (Runs 1 and 2, 5 and 6). A somewhat larger reduction in the ratio may be observed in going from chloro to bromo to iodo compounds (Runs 2–4, 6–7). Unfortunately, this is also the direction of decreasing yields. A more consistent reduction in the ratio is obtained by substituting a nitrile for the methyl ester in the olefinic component (Runs 1 and 5, 2 and 6, 3 and 7, 10 and 11).

Thus, a high stereoselectivity in forming the *cis* isomers results from low temperatures for the reaction, and the use of chloro compounds. The *trans* isomers usually may be obtained in poor to fair yield as minor products in most systems by using high reaction temperatures (reflux), bromo compounds, and substitution of nitriles for the corresponding olefinic esters.

Introduction of various substituents. The results presented here were essentially completed when the report by Mousseron, *et al.*[4] became available to the present author. With the additional reports of Warner,[6] and Wawzonek and Morreal,[7] a fairly wide variety of substituents and activating groups have been investigated. Consequently, the use of other activating groups (Y, Z in equation 1) was not examined further in this work.[10] In summary of

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[9] Run 12 was repeated using a procedure involving sodium methoxide (ref. 1) with equally unsatisfactory results. However, a different base or set of conditions might be found that would give reasonable results.

[10] Further work along these lines, however, is planned. The use of α,β-unsaturated nitro compounds, sulfones, and similar types of materials will be explored.

these various reports, for reaction 1, Y and Z may be esters, nitriles, or carbonyl compounds, and R may be hydrogen, alkyl, aryl, chloro, or ester. A few other combinations not covered by reaction 1 are included in the reports mentioned, and it seems reasonable that various other examples will be found. However, not all of the possible combinations so far reported have proved satisfactory. With several variables, temperature, base, solvent, *etc.*, to manipulate, conditions may be found in which many of the presently unsatisfactory combinations will become usable.

This method is a satisfactory general method for the preparation of polyfunctional cyclopropanes. For some compounds, the product of run 11, Table I, for instance, this reaction may be the only reasonable method of preparation.

The reaction is stereoselective in forming the *cis* isomer, at least for those cyclopropanes substituted on only two ring carbons. This work is being continued and it is hoped that conditions may be found under which the *trans* isomer will be formed stereoselectively. The stereochemistry of the more difficult cases in which all three ring carbons are substituted is also being investigated. So far, no completely satisfactory explanation of the stereochemical results has been found, but some possible explanations are being evaluated at this time.

EXPERIMENTAL[11]

The previously described method of preparing 1,2-cyclopropanedicarboxylic acids using sodium hydride dispersed in oil[1] was applied throughout this study. An occasional run presented an induction period, a phenomenon not observed in the previous work.[1] These induction periods were eliminated by adding several drops of methanol to the ester or nitrile mixtures.

Three different temperature control procedures were used. A. The reaction flask was immersed in a cooling bath. This was maintained at the minimum temperature which allowed a slow but steady rate of hydrogen evolution; the bath temperature was usually about 20–30°. Each of these reactions took several hours for completion; most were allowed to run overnight for a total reaction time of about 20 hr. B. The reaction mixtures was maintained at gentle reflux, estimated at about 115°, and the reaction was controlled solely by the rate of addition of the ester or nitrile mixture. These reactions were quite fast and usually complete in about an hour. Shorter times would be possible except for the vigor of the reaction. C. The reaction was allowed to warm without external heating, but occasional cooling was required to control the reaction. No temperatures were observed in these cases, but it is estimated that the temperature range was about 30–60°. In general, the reactions run at lower temperatures were somewhat lighter in color. This lighter color is of some importance in the workup, as the colored materials distribute between the organic and aqueous phases and when present in appreciable quantity make the boundary between phases difficult to distinguish.

For those runs in which the esters or nitriles were isolated, the separation of products from solvent and any unchanged starting materials was very clean cut. With the exception of the runs using methyl α-bromo- and α-iodo-propionates, gas phase chromatograms of the products showed only one or two peaks corresponding to the *cis* and/or *trans* isomers of the products. The product from the methyl α-bromopropionate run showed one additional very small peak corresponding to less than one percent of total material; it apparently was unchanged bromo ester. Similarly, the methyl α-iodopropionate run gave an additional peak corresponding to unchanged iodo ester, but here the peak represented about one-third of the material. The results of the vapor phase chromatography analyses are summarized as part of Table I; they are given as the percent of each isomer present in the mixture of isomers.

The reaction mixtures of runs 15 and 16 and the ester or nitrile mixtures of several other runs were hydrolyzed to the acids and the isomers separated by methods previously described.[1] No attempt was made to find conditions which would give maximum recovery of each isomer. These results also are summarized in Table I.

In the following descriptions of specific experiments, it should be understood that the reaction solvents, toluene or benzene, were dried over sodium hydride. The amounts in grams of sodium hydride used refer to the weights of the sodium hydride dispersions; throughout, the dispersions were 51.1% sodium hydride dispersed in oil. The run numbers correspond to those in Table I.

Dimethyl 1,2-dimethyl-1,2-cyclopropanedicarboxylate. 1. Methyl methacrylate (10.0 g., 0.10 mole), methyl α-chloropropionate (12.3 g., 0.10 mole), sodium hydride (4.7 g., 0.10 mole), and toluene (10 ml.) were allowed to react at about 20–30°. The diester, 13.3 g., 71% yield, boiled at 110–114°/22 mm., n_D^{26} 1.4465. 2. The reaction was repeated under gentle reflux. The diester, 12.9 g., 69% yield, boiled at 109–112°/22 mm., n_D^{26} 1.4461. 3. Methyl α-bromopropionate (16.7 g., 0.10 mole) was used in place of the chloro compound and the reaction was run under gentle reflux. The diester, 6.0 g., 32% yield, boiled at 106–110°/22 mm., n_D^{26} 1.4450. 4. Methyl α-iodopropionate[12] (21.4 g., 0.10 mole) was used in place of the chloro compound and the reaction was run under gentle reflux. The product, 4.0 g., boiled at 70–107°/20 mm. By gas chromatography, about one-third of this distillate was unchanged iodo ester.

Methyl 1,2-dimethyl-2-cyanocyclopropanecarboxylate. 5. Methacrylonitrile (6.7 g., 0.10 mole), methyl α-chloropropionate (12.3 g., 0.10 mole), sodium hydride (4.7 g., 0.10 mole), and toluene (10 ml.) were allowed to react at about 20–30°. The ester-nitrile, 9.0 g., 59% yield, boiled at 88–120°/22 mm., n_D^{31} 1.4489. 6. The reaction was repeated under gentle reflux and the product, 9.4 g., 61% yield, boiled at 100–124°/20 mm., n_D^{31} 1.4487. This material was roughly fractionated to give a low boiling fraction, b.p. 90–105°/12 mm., n_D^{26} 1.4480, and a high boiling fraction b.p. 105–110°/12 mm., n_D^{26} 1.4533. Hydrolysis of the two fractions gave 15% of the *trans* diacid and 32% of the *cis* diacid, and showed that the low boiling fraction was almost all *trans* and the higher boiling fraction almost all *cis* isomer. The *cis* and *trans* acids were identified by their infrared spectra.[1] 7. Methyl α-bromopropionate (16.7 g., 0.10 mole)

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[11] Melting points and boiling points are uncorrected. Analyses were performed by Micro-Tech Laboratories. Infrared spectra were obtained with a Perkin-Elmer Infracord. Gas chromatographic analyses were carried out on a Wilkens Instrument and Research, Inc., Aerograph, Model A-90-C with a Craig polyester column.

[12] α-Iodopropionic acid [E. Abderhalden and M. Guggenheim, *Ber.*, **41**, 2855 (1908)] was esterified by the method of N. B. Lorette and J. H. Brown, Jr., *J. Org. Chem.*, **24**, 261 (1959). The methyl ester boiled at 64–69°/20 mm. It was colorless or pale yellow when freshly prepared or distilled, but slowly turned dark red even when stored at about 3° in the dark. The iodo ester is a considerably more intense lachrymator than either the bromo or chloro ester. The Dow Chemical Company kindly supplied the sample of 2,2-dimethoxypropane used in the esterification procedure.

was used in place of the chloro compound and the reaction was run under gentle reflux. The ester-nitrile, 5.1 g., 33% yield, boiled at 90–117°/19 mm., n_D^{25} 1.4497. 8. Methyl methacrylate (10.0 g., 0.10 mole), α-chloropropionitrile[13] (8.9 g., 0.10 mole), sodium hydride (4.7 g., 0.10 mole), and toluene (10 ml.) were allowed to react under gentle reflux. Gas evolution was negligible even with the addition of a small amount of methanol. Apparently the chloronitrile did not react with either sodium hydride or sodium methoxide to form an anion. No product could be isolated.

1,2-Dimethyl-1,2-dicyanocyclopropane. 9. Methacrylonitrile (6.7 g., 0.1 mole), α-chloropropionitrile[13] (8.9 g., 0.10 mole), sodium hydride (4.7 g., 0.10 mole), and toluene (10 ml.) were allowed to react under gentle reflux. Gas evolution was very slight even after the addition of a small amount of methanol. After about 5 hr. of very slight gas evolution, the mixture was cooled, excess sodium hydride decomposed with methanol, and the reaction mixture was processed. A small distillate, 0.5 g., was obtained. This slowly, partially crystallized. Washing the mixture with cyclohexane gave 0.2 g. of white crystalline material, m.p. 45–48°. An analytical sample was obtained readily by sublimation, m.p. 46–48°. The infrared spectra showed no carbon carbon double bond. The dinitrile was not hydrolyzed to determine its isomeric nature.

Anal. Calcd. for $C_7H_8N_2$: C, 69.97; H, 6.71; N, 23.22. Found: C, 70.23; H, 7.04; N, 23.40.

Dimethyl 1-chloro-2-methyl-1,2-cyclopropanedicarboxylate. 10. Methyl methacrylate (20.0 g., 0.2 mole), methyl dichloroacetate (28.6 g., 0.2 mole), sodium hydride (9.4 g., 0.2 mole), and benzene (60 ml.) were allowed to react with occasional cooling of the reaction mixture.[14] Dimethyl 2-chloro-1-methyl-1,2-cyclopropanedicarboxylate, 30.5 g., 74% yield, boiled at 106–109°/12 mm., n_D^{26} 1.4581. Saponification of the diester gave a 90% yield of the diacid, m.p. 131–133.5°. An analytical sample recrystallized from nitromethane melted at 133–134°.

Anal. Calcd. for $C_6H_7O_4Cl$: C, 40.35; H, 3.95; Cl, 19.85. Found: C, 40.22; H, 4.07; Cl, 19.70.

The diacid was converted readily to the anhydride by warming with acetic anhydride. The anhydride was recrystallized from cyclohexane and then sublimed, m.p. 55–56.5°.

Anal. Calcd. for $C_6H_5O_3Cl$: C, 44.88; H, 3.14; Cl, 22.08. Found: C, 44.84; H, 3.19; Cl, 21.85.

Methyl 1-chloro-2-cyano-2-methylcyclopropanecarboxylate. 11. Methacrylonitrile (13.4 g., 0.20 mole), methyl dichloroacetate (28.6 g., 0.20 mole), sodium hydride (9.4 g., 0.20 mole), and benzene (60 ml.)[14] were allowed to react with occasional cooling of the reaction mixture. The ester-nitrile, 22.3 g., 64% yield, boiled at 110–112°/14 mm., n_D^{26} 1.4680. Hydrolysis of the ester-nitrile gave a mixture of the isomeric diacids. The *trans* diacid is very insoluble in nitromethane, but its recovery from this mixture by recrystallization from nitromethane was unsatisfactory. By treating the mixture of diacids with a limited amount of acetic anhydride so that most of the *cis* acid was converted to anhydride and recrystallization of that mixture from nitromethane, the *trans* diacid was separated readily. Recrystallization of the crude *trans* isomer gave a 4% yield of the diacid, m.p. 247–248°. An analytical sample was sublimed, m.p. 246–247°.

Anal. Calcd. for $C_6H_7O_4Cl$: C, 40.35; H, 3.95; Cl, 19.85. Found: C, 40.60; H, 4.10; Cl, 19.60.

Recrystallization of the crude mixture of diacids from nitromethane gave impure *cis* diacid in 48% yield, m.p. 123–134°. Further recrystallization did not improve the m.p., but the infrared spectrum was virtually identical with that for the pure *cis* diacid. This crude *cis* isomer was converted readily in high yield to the anhydride, m.p. 53–55°.

Methyl 2-chloro-2-cyano-1-methyl-cyclopropanecarboxylate. 12. Methyl methacrylate (10.0 g., 0.10 mole), dichloroacetonitrile[15] (11.0 g., 0.10 mole), sodium hydride (4.7 g., 0.10 mole), and benzene (30 ml.) were allowed to react with occasional cooling. The mixture became dark colored and considerable tarry material separated. No product was obtained from the processing of the reaction mixture.

1-Chloro-2-methyl-1,2-dicyanocyclopropane. 13. Methacrylonitrile (6.1 g., 0.09 mole), dichloroacetonitrile[15] (11.0 g., 0.10 mole), sodium hydride (4.3 g., 0.09 mole), and benzene (30 ml.) were allowed to react with occasional cooling. The results were the same as the preceding experiment; no product was obtained.

1-Methyl-2-phenyl-1,2-cyclopropanedicarboxylic acid. 14. Methyl methacrylate (20.0 g., 0.20 mole), methyl α-chlorophenylacetate (36.9 g., 0.20 mole), sodium hydride (9.4 g., 0.20 mole), and toluene (50 ml.) were allowed to react with occasional cooling. Work up of the reaction mixture and distillation of the toluene left the crude product, a colorless oil. Saponification of this gave the crude diacid which was digested with a small amount of nitromethane on the steam bath. The crystalline *cis* diacid so obtained melted at 157–159° dec. and was obtained in an overall yield of 38%. An analytical sample was recrystallized from acetonitrile, m.p. 157–158° dec.

Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.44; H, 5.49. Found: C, 65.55; H, 5.64.

The diacid was converted readily to the anhydride by warming with acetic anhydride. An analytical sample was sublimed, m.p. 92–93°.

Anal. Calcd. for $C_{12}H_{10}O_3$: C, 71.28; H, 4.98. Found: C, 71.14; H, 5.02.

1,2-Dimethyl-2-benzoylcyclopropanecarboxylic acid. 15. Methyl methacrylate (7.5 g., 0.075 mole), α-chloropropiophenone[16] (13.8 g., 0.075 mole), sodium hydride (3.5 g., 0.075 mole), and toluene (7.5 ml.) were allowed to react with occasional cooling to moderate the vigorous reaction. After processing the reaction mixture and removal of the toluene, a dark red, oily residue was obtained. This material was saponified and the basic solution was extracted continuously with ether for several hours; this removed a small amount of neutral material, mostly the oil from the sodium hydride dispersion. The basic solution was then acidified and again extracted continuously with ether. Removal of the ether left a viscous red oil. A volume of carbon tetrachloride equal to about one-third the volume of red oil was added. After several hours a crystalline precipitate formed. This material was recrystallized from carbon tetrachloride, m.p. 107–109°, followed by crystallization of the melt and a second m.p. 129–130°. An analytical sample was obtained by sublimation and then recrystallization from carbon tetrachloride, m.p. 108–110°, 129.5–131°.

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.68; H, 6.54.

The material with double melting point has bands in its infrared spectrum at 3.22 μ (O—H) and 5.72 μ (γ-lactone). On heating the crystals to about 115°, the material melts and then crystallizes. The new crystals have a single m.p. 129–130.5°, no longer have the infrared band at 3.22 μ, and the other band (C=O) is shifted to 5.95 μ (C_6H_5 CO, ▷—COOH). Recrystallization of these crystals from carbon tetrachloride gives the material with double

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[13] H. Backunts and R. Otto, *Ber.*, **9**, 1592 (1876). The α-chloropropionamide was generously supplied by Dr. J. J. Pappas.

[14] In runs with methyl dichloroacetate and other *gem*-dihalo compounds, considerably more solvent was used than in runs with monohalo compounds. The *gem*-dihalides are more acidic and react much more vigorously than do the monohalo compounds. Usually about one-third of the solvent was mixed with the sodium hydride and the remaining two-thirds diluted the ester (or nitrile) mixture during the addition.

[15] J. W. Wilt and J. L. Diebold, *Org. Syntheses*, **38**, 16 (1958).

[16] R. H. Baker and C. Barkenbus, *J. Am. Chem. Soc.*, **58**, 262 (1936).

melting point[17] and the original infrared spectrum. Apparently, the two materials are the isomeric lactol and keto-acid.[18] The formation of the lactol and the ready interconversion of the two isomers means the two groups are *cis.* The lactol was obtained in an overall yield of 35%.

Evaporation of the carbon tetrachloride from the first crystallization left a dark red, sticky material that could not be induced to crystallize. Its infrared spectrum was poorly defined with broad bands suggesting a mixture. It may have contained various oxides formed by Darzens-like condensations.[6] It was not examined further.

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[17] If some of the material with single melting point (keto-acid) is present and/or the melting point is taken too slowly, the first melting point may be missed or not clearly observed.

[18] The keto-acid has a single carbonyl peak in its infrared spectrum, but this is not unexpected. The carbonyl band of a benzoyl group and of a cyclopropanecarboxylic acid both would show up at about 5.95 μ and quite possibly would not or could not be resolved with the instrument used.

[CONTRIBUTION FROM THE DEPARTMENT OF INDUSTRIAL CHEMISTRY, THE FACULTY OF ENGINEERING, KYOTO UNIVERSITY]

Further Studies on the Preparation of Terephthalic Acid from Phthalic or Benzoic Acid

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The mechanism of the formation of potassium terephthalate from potassium phthalate or benzoate using cadmium or other metallic salts has been studied kinetically by C^{14}-tracer techniques. The carbon of the carboxyl group and/or the carbonates were labeled. Contrary to the Sorm-Ratusky's postulation (Scheme 2), the results obtained support our previously proposed mechanism that the reaction of phthalate is an intramolecular rearrangement and that of benzoate is a disproportionation.

B. Raecke[1] found that potassium phthalate or benzoate is convertible to potassium terephthalate by heating it with cadmium salts at 400–450°. These processes have an industrial importance for the preparation of terephthalic acid, one of the starting materials of polyester fiber.

In our previous paper,[2] the effects of various catalysts on these reactions were reported and probable mechanisms were suggested; *i.e.*, intramolecular rearrangement for phthalate and disproportion for benzoate.

Afterward, Sorm and Ratusky[3] reported on this reaction using phthalic and benzoic anhydrides with potassium carbonate–C^{14} and they postulated a mechanism involving decarboxylation-carboxylation for both reactions on the basis of a statistical isotopic exchange.

The present study was undertaken to clarify these obscurities. For this purpose, the reaction of potassium phthalate or benzoate using cadmium salt catalysts was carried out, in which the carboxyl group, cadmium carbonate or potassium carbonate, was labeled. The reactions were followed kinetically by means of radioactivity and the results were compared with those derived theoretically from these mechanisms.

EXPERIMENTAL

Materials. Barium carbonate–C^{14} was obtained from Isotope Center in Japan and diluted by normal barium carbonate to an activity of 8 μc./g. (6360 cpm. at infinite thickness). Potassium carbonate–C^{14} and cadmium carbonate–C^{14} were prepared from carbon dioxide–C^{14} produced from barium carbonate–C^{14} in a vacuum line. Benzoic-carboxy-C^{14} acid was prepared by the reaction of the appropriate Grignard reagent with carbon dioxide–C^{14} at 10^{-5}–10^{-6} mm. pressure and in glass-joint apparatus according to the Linstead procedure.[4] The activities of the acid were measured as the acid itself and also as barium carbonate after decarboxylation,[5] the specific activities being 4207 and 2720 cpm., respectively. Phthalic-carboxy-C^{14} acid was prepared by the permanganate oxidation of *o*-toluic-carboxy-C^{14} acid, prepared by the carbonation of *o*-tolylmagnesium bromide with carbon dioxide–C^{14}.[6] The specific activities of the product were 6200 and 2470 cpm. as acid and barium carbonate, respectively.

Tracer experiments. The previous procedure and apparatus[2] were used for these experiments. In the measurements of specific activity, each carbonate was converted to barium carbonate by absorbing the carbon dioxide produced by hydrochloric acid in an aqueous solution of barium acetate–potassium hydroxide. Each acid was recrystallized repeatedly until constant activity was obtained. All data are averages of duplicate experiments and they are calibrated for their background against standard barium carbonate. The activity was expressed as that of the corresponding barium carbonate even when the substance counted was the organic acid itself. Typical specific activities of the terephthalic acid obtained from labeled phthalic or benzoic acid were

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[1] German Patent **936,036** and for the review see B. Raecke, *Angew. Chem.*, 70, 1 (1958), and ref. 7.

[2] Y. Ogata, M. Tsuchida, and A. Muramoto, *J. Am. Chem. Soc.*, 79, 6005 (1957).

[3] F. Sorm and J. Ratusky, *Chem. & Ind.* (*London*), 294 1958).

[4] R. P. Linstead, "A Course in Modern Techniques of Organic Chemistry," Butterworth Publishing Co., London, 1955, p. 77.

[5] *Cf.* W. G. Dauben, J. C. Reid, P. E. Yankwich, and M. Calvin, *J. Am. Chem. Soc.*, **72**, 121 (1950).

[6] W. H. Stevens and D. A. Holland, *Science*, **112**, 718 (1950).