cooled in ice water. The contents of the ampoule were then analyzed by vpc. Each sample was analyzed at least twice and and average value was taken. The average deviation was about 0.1-0.2%. In Table II the results of the analysis are given.

TABLE II

EQUILIBRATION OF *cis*- AND *trans*-1,2-DIMETHYLCYCLOHEPTANE

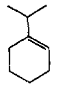
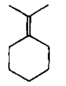
Temp, °C	Length of run, hr	Fraction 1, % trans	Fraction 2, % cis
200	336	65.72	34.27
225	144	64.98	35.02
250	72	64.60	35.40
274	24	63.94	36.06
300	24	63.38	36.62
324	24	62.99	37.01

Acid-Catalyzed Equilibration Procedure.—1,2-Dimethylcycloheptene (mixture of isomers), 0.5 g, was heated under reflux in 25 ml of olefin-free pentane containing 2 drops of concentrated sulfuric acid. Samples were occasionally withdrawn and checked by vpc. At suitable intervals, larger samples were run through the preparative vpc and fractions were isolated. The fractions were identified by infrared and nmr spectra.

Other equilibration experiments starting with 1-isopropylcyclohexene and the 1,2-dimethylcyclohexenes were carried out in a similar manner. The results are summarized in Tables III and IV.

TABLE III

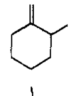
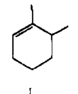
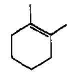
ACID-CATALYZED EQUILIBRATION OF 1-ISOPROPYLCYCLOHEXENE IN REFLUXING PENTANE (36°)

Fraction no.	Structure assigned	Retention time,[b] min	Products, % Initial concn	5 days	21 days	42 days	50 days
1		52.5	100.0	90.0	90.6	90.4	90.4
2	[a]	60.0				2.3	2.2
3		67.5		9.6	9.3	7.3	7.4

[a] Not isolated. [b] Determined at a column temperature of 110°.

TABLE IV

ACID-CATALYZED EQUILIBRATION OF SIX-MEMBERED OLEFINS I, II, AND III IN REFLUXING PENTANE (36°)

Fraction no.	Structure assigned	Retention time,[a] min	Products, % Initial concn	6 days	9 days
1		31.2	3.2		
2		35.2	30.9	15.2	15.1
3		42.5	65.9	84.8	84.9

[a] Determined at a column temperature of 110°.

Registry No.—1,2-Dimethylcycloheptanol, 37102-80-0; 1,2-dimethylcycloheptene, 20053-89-8; 1-isopropylcyclohexene, 4292-04-0; isopropylidenecyclohexane, 5749-72-4; *trans*-1,2-dimethylcyclohexane, 6876-23-9; *cis*-1,2-dimethylcyclohexane, 2207-01-4; 1-methyl-2-methylenecyclohexane, 2808-75-5; 1,6-dimethylcyclohexene, 1759-64-4; 1,2-dimethylcyclohexene, 1674-10-8.

Steric and Polar Effects in the Decarboxylation of Mercuric Salts of Unsymmetrical Aromatic 1,2-Dicarboxylic Acids (the Pesci Reaction). An Improved Procedure[1a]

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The conversion of mercury(II) salts of unsymmetrical aromatic 1,2-dicarboxylic acids to monocarboxylic acids through the intermediate anhydrohydroxymercuric acids (Pesci reaction) is discussed in terms of polar and steric effects. An improved procedure which involves heating of the mercury(II) salts in hexamethylphosphoramide containing powdered glass yields anhydrohydroxymercuric acids in higher yield and in shorter time than does the previously described procedure. The anhydrohydroxymercuric acids are rapidly and almost quantitatively converted into aromatic monocarboxylic acids by treatment with sodium borohydride.

The reaction of phthalic acid with mercury(II) acetate produces a salt (**1**) which on heating in boiling water yields anhydro-2-hydroxymercuribenzoic acid[2] (**2**) (eq 1). When the latter is refluxed for several days with aqueous hydrochloric acid benzoic acid is produced (eq 2).[2] If the mercury(II) salt of a 3-substituted phthalic acid is used, two anhydro-2-hydroxymercuric acids (**2**, **3**) and from them two substituted benzoic acids (**4**, **5**) may be formed. The object of the work herein reported was to study the effect of hydrocarbon moieties in the 3 position on the course of the Pesci reaction. During this work marked improvements in the method of decomposition of the mercury(II) phthalates, as well as replacement of mercury in the anhydro-2-hydroxymercuribenzoic acids, were made.

In earlier work, 3-chlorophthalic acid[3] (**6**), 3-bromophthalic acid[3] (**7**), 3-nitrophthalic acid[3] (**8**), and hemimellitic acid[4] (**9**) were subjected to the Pesci reaction. Each was reported to yield exclusively the corresponding meta-substituted benzoic acid (**4**). The conversion of 1,2-anthraquinonedicarboxylic acid to 2-carboxyanthraquinone was also noted.[5] Because all of

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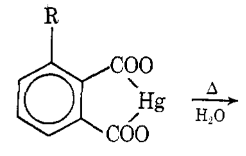
[1] (a) This work was supported by Grant 12445 of the National Science Foundation. (b) Predoctoral Research Associate.

[2] L. Pesci, *Atti Accad. Naz. Lincei*, [5] 10, I, 362 (1901); *Chem. Zentralbl.*, II, 108 (1901).

[3] F. C. Whitmore and P. J. Culhane, *J. Amer. Chem. Soc.*, **51**, 602 (1929).

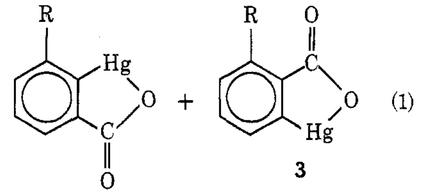
[4] F. C. Whitmore and R. P. Perkins, *ibid.*, **51**, 3352 (1929).

[5] F. C. Whitmore and F. L. Carnaham, *ibid.*, **51**, 856 (1929).



A

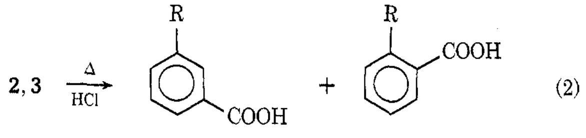
1, R = H 8, R = NO_2
6, R = Cl 9, R = COOH
7, R = Br 10, R = CH_3



3

B

2, R = H



4 5

the substituents adjacent to the carboxyl being replaced were electronegative, it was not clear whether steric or electronic factors were dominant. Work on 3- and 4-nitro-1,8-naphthalic acids[6] showed that a polar effect was operating in molecules in which no steric effect was possible (see eq 3 and 4) but no further work with other substituents has appeared. In the present study the mercury(II) salts of 3-methylphthalic acid (**10**), 1,2-naphthalic acid (**11**), and 3,4-phenanthrenedicarboxylic acid (**12**) were studied.

An alternate procedure for converting the mercury(II) salts (A) to anhydrohydroxymercuric acids (B) (eq 1) was sought because the conventional procedure calls for refluxing in water for 16 to 98 hours.

When suspensions of salts (A) in hexamethylphosphoramide (HMPA) containing powdered soft glass were heated, decarboxylation commenced at about 110° and was sufficiently rapid at about 165° that it was complete in 45 min. However, if powdered glass was not present, decarboxylation to only a minor extent occurred even on heating at 185° for 4 hr. Of other solvents tried [quinoline, ethylene glycol, tetramethylene sulfone (sulfolane), dimethylformamide, and *N*-methylpyrrolidone (NMP)] only the latter was effective, but NMP was not so good as HMPA, probably (see Experimental Section) because of the limited solubility of the mercury(II) salts in all solvents except HMPA and NMP.

The use of powdered glass was suggested by previous experience with the MacFayden–Stevens reaction.[7] Other examples of the use of powdered glass in decarbonylation[8] and decarboxylation[9] reactions are of interest.

The conversion of the anhydrohydroxymercury salts (B) to aromatic acids (**4**, **5**) was previously accomplished by long heating in aqueous hydrochloric acid[2] (eq 2). We have found that treatment of a suspension of the anhydrohydroxymercury salts (B) in ethanol with sodium borohydride[10] yields the demercurated acids in 10 min, even in the case of anhydro-4-hydroxymercuric-3-phenanthroic acid, which was not converted to 3-phenanthroic acid by the conventional procedure.[2]

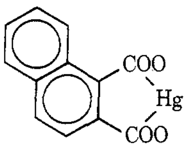
When **10**, **11**, and **12** were treated by our improved procedures, the results listed in Table I were obtained.

TABLE I
RESULTS FROM PESCI REACTIONS

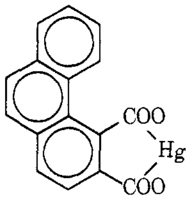
Mercury(II) salt	Products[a]	Overall yield, %
6	Methyl 3-chlorobenzoate[b]	87
8	Methyl 3-nitrobenzoate–methyl 2-nitrobenzoate (3:1)[c]	94
10	Methyl 3-methylbenzoate–methyl 2-methylbenzoate (5:1)[d]	85
11	Methyl 2-naphthoate–methyl 1-naphthoate (9:1)[d]	82
12	Methyl 3-phenanthroate[b]	98

[a] All products identified by comparison with authentic samples. [b] Purity determined by nmr and glpc. [c] Ratio determined by nmr. [d] Ratio determined by glpc.

Thus, it appears that as the steric factor is increased from an ortho methyl group to an ortho fused ring to two continuously fused rings[11] the selectivity in favor of replacement of the sterically hindered carboxyl group increases. These facts suggest the operation of a pronounced steric effect in the Pesci reaction.



11



12

The only previous study of a polar effect in the Pesci reaction was that[6] on 3-nitro-1,8-naphthalic acid (**13**), which gave mainly (after replacement of the mercury by hydrogen) 3-nitro-1-naphthoic acid (eq 3), and 4-nitro-1,8-naphthalic acid (**14**), which gave mainly 4-nitro-1-naphthoic acid (eq 4). In each case the predominant product resulted from replacement of carboxyl from the ring *not containing the nitro group*.

These results suggest that the replacement of carboxyl by mercury involves initially an opening of the ring in the cyclic[12] salt A in either of two ways

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[6] G. J. Leuck, R. P. Perkins, and F. C. Whitmore, *J. Amer. Chem. Soc.*, **51**, 1831 (1929).

[7] M. S. Newman and E. G. Caflisch, Jr., *ibid.*, **80**, 862 (1958).

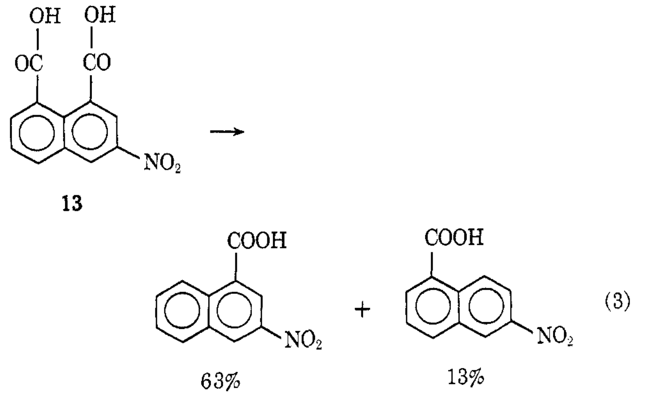
[8] W. E. Bachmann, W. Cole, and A. L. Wilds, *ibid.*, **62**, 824 (1940).

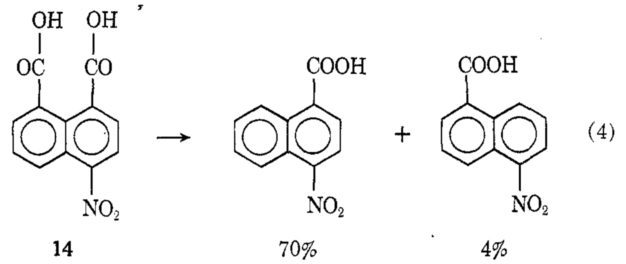
[9] D. V. Hertzler, J. M. Berdahl, and E. J. Eisenbraun, *J. Org. Chem.*, **33**, 2008 (1968).

[10] Compare H. B. Henbest and B. Nicholls, *J. Chem. Soc.*, 227 (1959), for reduction of aliphatic mercurials and F. G. Bordwell and M. L. Douglass, *J. Amer. Chem. Soc.*, **88**, 993 (1966), for conversion of phenylmercuric acetate to diphenylmercury with $NaBH_4$.

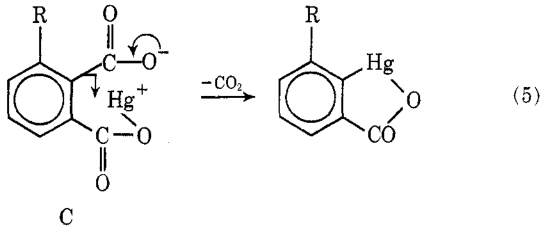
[11] For discussions of these steric effects see J. Packer, J. Vaughan, and E. Wong, *J. Amer. Chem. Soc.*, **80**, 905 (1958); M. S. Newman and H. Boden, *ibid.*, **83**, 115 (1969); and M. S. Newman and W. H. Powell, *J. Org. Chem.*, **26**, 812 (1961).

[12] The mercury(II) salts are pictured as cyclic monomeric species. However, they might be polymeric (or multimembered cyclic polymeric) salts. In any case the mechanistic arguments would be similar.





(equilibria could be involved) in an unsymmetrical case. The open dipolar ion[13] (only one form C shown) can cyclize to the anhydrohydroxymercuric acid (B) as shown (eq 5).



The products obtained from **13** and **14** may be explained by polar factors, because the electron density at position 8 would be expected to be greater than that at position 1 in each case. However, with 3-nitrophthalic acid (**8**) a mixture of about 77% of 3-nitrobenzoic acid and 23% of 2-nitrobenzoic acid is formed.[14] This result is the opposite of that expected if the reaction pictured in eq 5 is governed by polar factors similar to those operating in compounds **13** and **14**. Hence we conclude that a steric effect is involved and may be rationalized by assuming that there is a greater release of strain in expelling carbon dioxide from the transition state involving the internal carboxylate anion than that involving the external carboxylate ion.

Experimental Section

Formation of Anhydrohydroxymercuri Salts.—In a typical experiment, 1.62 g (0.01 mol) of 3-methylphthalic anhydride was added to 50 ml of 0.4 *N* sodium hydroxide. To the resulting solution was added a solution of 3.19 g (0.01 mol) of mercuric acetate in 50 ml of water and 0.5 ml of acetic acid. The colorless precipitate was collected, washed with 10 ml of alcohol, and air dried to yield 3.44 g (91%) of **10**. A suspension of this salt and 3 g of powdered soft glass[15] in 20 ml of HMPA in a 50-ml flask was placed in a silicone oil bath at 175°. The theoretical volume of carbon dioxide was collected in 60 min (for **6**, 60 min; for **8**, 25 min; for **11**, 1.5 hr; for **12**, 2 hr). The suspension was diluted with 200 ml of water and filtered. The moist solids were suspended in ethanol and stirred with 0.76 g (0.02 mol) of sodium borohydride for 15 min. After acidification with 15 ml of concentrated hydrochloric acid and dilution with 50 ml of acetone, the mixture was filtered through Celite. Removal of the solvents under reduced pressure afforded 1.22 g of a white solid which contained no neutral material. The solids were quantitatively esterified with diazomethane to yield 1.32 g (87% from 3-methylphthalic anhydride) of a clear liquid consisting of methyl 3-methylbenzoate (83%) and methy 2-methylbenzoate (17%).

Solvent Effect on Pesci Reaction.—On heating **6** and powdered glass in quinoline, ethylene glycol, sulfolane, dimethylformanide, NMP, and HMPA, at temperatures up to 200°, copious gas evolution was noted only in the case of HMPA. In order to see if solubility of the anhydrohydroxymercuri salt in the solvent concerned was the dominant factor, 5 mmol of **6**, **8**, **10**, and **12** (in separate tubes) in 10 ml of solvent was heated at 150–155° for 15 min. The solids were removed by filtration and hydrogen sulfide was passed through the filtrate. Only in the cases of NMP and HMPA did the formation of black mercury sulfide indicate appreciable solubility of the salts. In the other solvents only slight haziness was noted in a few cases. No appreciable amount of carbon dioxide was evolved in any experiment which did not include powdered glass. When powdered glass was added in similar experiments carbon dioxide evolution was appreciable *only in the HMPA case*. Thus, solubility of the salt is not alone responsible for the success of the new variation. Actually, the anhydromercuri salt from **10** is completely soluble in NMP; yet only a small amount of carbon dioxide was evolved after heating for a much longer time than that required for complete decarboxylation in HMPA.

Product Analysis.—Glpc analyses were performed on an F & M Model 500 gas chromatograph equipped with a thermal conductivity detector. A 7 ft × 0.25 in. column packed with 15% silicone gum rubber SE-30 on 60-80 mesh Chromosorb W was used. Nmr analyses were performed on a Varian A-60 spectrometer (all samples were dissolved in acetone-d_6 using TMS as internal standard).

Mercuric 3-chlorophthalate (**6**) afforded only methyl 3-chlorobenzoate, which was identified by glpc and the appearance of a single peak at δ 3.88 ppm whereas methyl 2-chlorobenzoate has a peak at 3.78.

Mercuric 3-nitrophthalate (**8**) yielded a mixture of about 77% methyl 3-nitrobenzoate (nmr methyl peak at δ 4.02) and 23% of methyl 2-nitrobenzoate (δ 3.92). Integration was effected by offsetting 200 Hz and using a 50-Hz sweep width.

The methyl ester obtained from **10**, **11**, and **12** were all separable by glpc. The product ratios given in Table I were determined from integrated peak heights. Nmr analysis of the ester from **12** confirmed that only one isomer was present (methyl 3-phenanthroate δ 4.08; only peak observed above 7.40).

Registry No.—**6**, 37102-75-3; **8**, 37102-76-4; **10**, 37102-77-5; **11**, 37102-78-6; **12**, 37102-79-7.

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[13] Since addition of galvinoxyl had no effect on the rate of decarboxylation or on the products obtained in the case of **10**, we assume that a free-radical path is not operative. The lack of effect by galvinoxyl on rates or products does not rule out a free-radical cage process; see R. C. Lamb, *et al.*, *J. Amer. Chem. Soc.*, **85**, 3483 (1963), as pointed out by a referee.

[14] Whitmore and Culhane, ref 3, report only 3-nitrobenzoic acid. However, their crude acid was recrystallized three times.

[15] Freshly ground or aged glass gave essentially the same result. Variation of the amount of glass from 0.5 to 5.0 g made no observable difference in the rate of decarboxylation. See also ref 9.