in acetic acid, sulfuric acid or a mixture of the two was added to cooled 40% peracetic acid.[28] The oxidation was allowed to proceed at room temperature. The product was determined, either directly by recrystallization of the ester, by saponification of the residue that remained after evaporating the acetic acid solvent or by saponification of the ether extract of the neutralized aqueous solution of the reaction mixture. Since the isolation procedures are commonplace and take customary advantage of the difference in acidity of phenols and acids, only in exceptional cases are more details given. References to the preparation of starting materials are given in Table 1. Common hydrolysis products and starting materials were identified by melting point and mixed melting point. Esters were identified by hydrolysis or by mixed melting point with authentic samples. Phenol was characterized as the 2,4,6-tribromide, m. p. 92-94°.

p-Methoxyphenylbenzoate.—Isolated from experiment 8, Table I, by recrystallizing from hexane the precipitate formed when the reaction mixture was diluted with water, *p*-methoxyphenylbenzoate, m. p. 87.5-88.0°, was characterized by saponification to benzoic acid, m. p. 121-122°, and *p*-methoxyphenol, m. p. 53.5-54.0° (reported[29] m. p. 53°).

Anal. Calcd. for $C_{14}H_{12}O_3$: C, 73.66; H, 5.30. Found: C, 73.56; H, 5.50.

Phenyl p-Chlorobenzoate.—Recrystallization of the crystalline material present at the conclusion of experiment 17, Table I, from hexane gave phenyl *p*-chlorobenzoate, m. p. 104-104.5°, identified by saponification to *p*-chlorobenzoic acid, m. p. 237-240°, and phenol.

Anal. Calcd. for $C_{13}H_9O_2Cl$: C, 67.11; H, 3.90. Found: C, 67.19; H, 4.01.

Oxidation of Cyclohexyl Phenyl Ketone.—The mixture resulting from the oxidation of 8.65 g. of cyclohexyl phenyl ketone[30] (expt. 30, Table I) was concentrated *in vacuo* leaving 8.41 g. of dark oil. Distillation through a small Vigreux column gave fraction A, 1.32 g., b. p. 67-136° (14 mm.) and fraction B, 4.53 g., b. p. 136-157° (14 mm.). Saponification of A gave a bicarbonate-soluble oil (0.57 g.) which was molecularly distilled to give 0.28 g. (5%) of a colorless liquid identified as cyclohexane carboxylic acid by conversion to the amide, m. p. 137-139°. On the cold finger of the apparatus, 0.28 g. (5%) of benzoic acid was obtained. The bicarbonate-insoluble portion afforded 0.22 g. (5%) of phenol. Fraction B was redistilled giving two fractions, b. p. 135-157° (19 mm.) (1.66 g.) and b. p. 157-159° (19 mm.) (2.25 g.). Saponification of the first gave 0.26 g. (6%) of cyclohexanol, micro b. p. 162°, identified as the urethan, m. p. 81-82° (reported[31] m. p. 82.5°), and 0.60 g. (11%) of benzoic acid. After being redistilled, the second fraction, which was saponifiable to cyclohexanol and benzoic acid (17%), was analyzed; $n^{23}D$ 1.5195.

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.45; H, 7.90. Found: C, 76.29; H, 8.09.

Summary

The cleavage of several unsymmetrical benzophenones with peracetic acid has been investigated. It is concluded that the migration aptitude and existence of acid catalysis support mechanisms in which the rearranging group is electron-deficient in the transition state.

NEW YORK 27, N. Y.

RECEIVED DECEMBER 7, 1949

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[28] Peracetic acid, 40%, was obtained from the Buffalo Electro-Chemical Company, Buffalo, N. Y.

[29] Hlasiwetz and Habermann, *Ann.*, **177**, 334 (1875).

[30] Prepared according to Meyer and Scharvin, *Ber.*, **30**, 1940 (1897).

[31] Bouveault, *Bull. soc. chim.*, [3] **29**, 1051 (1903).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

Reactions of Peracids. IV. The Reaction of Cyclohexylphenyl Ketone with Perbenzoic Acid

BY S. L. FRIESS AND N. FARNHAM

In a previous communication[1] in this series, it was noted that in the reaction

$$\mathrm{R{-}COCH_3 + C_6H_5CO_3H \xrightarrow[25^\circ]{CHCl_3} R{-}OCOCH_3 + C_6H_5CO_2H}$$

I, R = phenyl
II, R = cyclohexyl

compound I consumed peracid far more slowly than II. For a rough comparison, a reaction period of ten days at room temperature was observed to result in complete uptake of 1.0 mole of perbenzoic acid by II, while under identical conditions the reaction of I has progressed to the extent of only 65%. Accordingly, it was of some utility in the present study to first investigate the relative rates of reaction in a more quantitative manner, employing runs at constant temperature, in order to evaluate the effect of the degree of saturation of ring R on the rate of uptake of peracid.

A logical extension of this work was concerned with a ketone possessing both the phenyl and cyclohexyl groups in the same molecule, making possible a study in which the relative migration aptitudes of the two groups might be obtained. The cyclohexyl phenyl ketone (III) required for this objective was prepared and its rate of reaction with perbenzoic acid measured under the same conditions employed to study I and II. In addition, several larger scale runs on III were made to determine the relative proportions of the isomeric esters obtained as products, resulting from the competitive migration of the phenyl and cyclohexyl groups during some stage of the reaction.

Discussion

In the comparative rate work on compounds I, II and III, it was found that the presence of a phenyl nucleus conjugated with the carbonyl group markedly decreases the rate of reaction with peracid. In Fig. 1, for example, is shown a set of representative runs on the three ketones, with

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[1] Friess, THIS JOURNAL, **71**, 14 (1949).

uptake of peracid plotted as a function of time. It is seen that II reacts very much faster than either I or III. In turn, I and III display approximately equal speeds of reaction. All the runs indicated in Fig. 1 were made at nearly equivalent ketone concentrations and employed identical aliquots of the same stock perbenzoic acid solution, in order to keep the catalytic effect of the benzoic acid in the peracid preparation at a constant level and hence make comparisons possible.

A more quantitative estimate of the relative velocities of the runs of Fig. 1 is made possible by the data of Table I. Using second order formulations to obtain a set of rate constants (k_2) for comparison purposes, it is clear that the reaction of II with perbenzoic acid under these conditions is six to eight times faster than that of I or III.

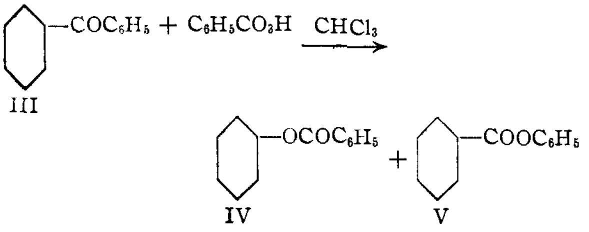
TABLE I

COMPARATIVE RATE RUNS IN PERBENZOIC ACID REACTION

Ketone	Initial concn. ketone, mole/l.	Initial concn. peracid, mole/l.	k_2, (l./mole sec.) × 10^5
I	0.3331	0.4002	1.47 ± 0.05
II	.3295	.4132	11.7 ± .5
III	.3448	.4132	1.83 ± .10

Apparently, then, an unsubstituted phenyl group bonded to the carbonyl function has a markedly decelerating effect on the rate of reaction with peracid, when compared to the completely saturated cyclohexyl or methyl groups. This result is not surprising if the reaction involves addition of the peracid (or some ionic entity derived from it) to the carbonyl group[2] in a rate-determining step, since it is known that in other reactions involving addition to the carbonyl, with semicarbazone formation[3] as an example, the conjugation of an unsubstituted aryl group with the carbonyl lowers its reactivity toward the addition step.

Somewhat more striking than this comparison of rates is the occurrence of isomeric products from III, while II was previously shown[1] to give only the single product cyclohexyl acetate. In the reaction of III with a slight excess of perbenzoic acid



the esters IV and V were found in a proportion of approximately 5:1. The determination of the ratio of esters was accomplished through the ROH fraction obtained on saponification of the mixture and separation of the phenol and cyclohexanol portions of the hydrolysate, with total ROH yields of the order of 85% being observed.

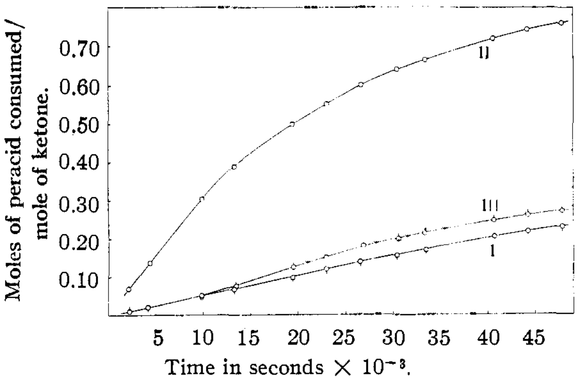
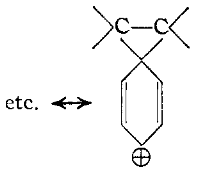


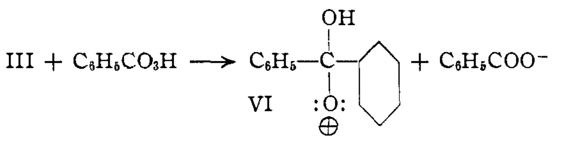
Fig. 1.—Rate runs on ketones I, II, III. See Table I for conditions.

This very unexpected product ratio indicates a fivefold factor in migration aptitude of the cyclohexyl over the phenyl group in this reaction. Although these two groups have not been compared previously as competitors in migration, in a standard pinacol rearrangement[4] for example, it was initially assumed that for a carbanion, R:$^-$, as a more or less free rearranging entity,[5] the phenyl group should migrate more readily than the cyclohexyl group. Using the pinacol–pinacolone rearrangement for illustration, the root of this reasoning lies in the stabilization of the transition state for phenyl migration by forms such as



while no such reasonable forms can be written for cyclohexyl migration.

In the present case, if the reaction of III progresses through the cationoid oxygen containing intermediate VI, as postulated for the very similar



cyclic ketone reactions,[2,6] and VI initiates the migration step, then again phenyl should preferentially migrate if it moves with an electron pair because of the relatively high stabilization of the

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(2) Friess, *ibid.*, **71**, 2571 (1949).

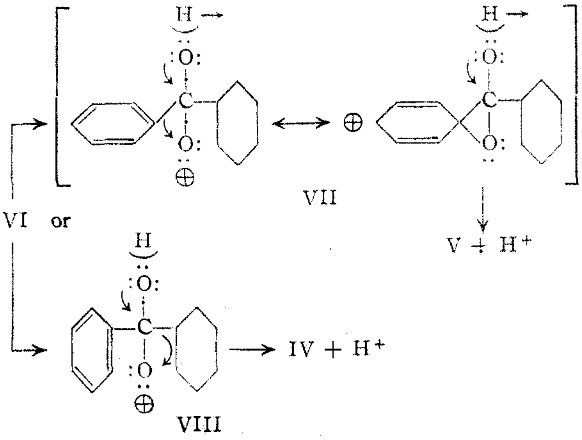
(3) (a) Conant and Bartlett, *ibid.*, **54**, 2881 (1932); (b) Westheimer, *ibid.*, **56**, 1962 (1934).

(4) The available data largely concern the migration aptitudes of substituted aryl and simple alkyl groups: see Bachmann and Steinberger, *ibid.*, **56**, 170 (1934); Tiffeneau and Levy, *Bull. soc. chim.*, **49**, 1661 (1931).

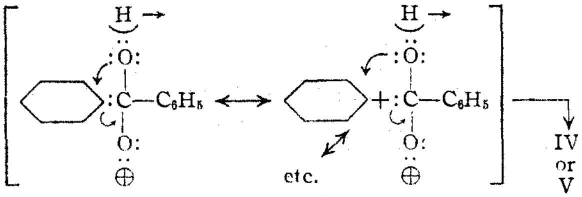
(5) This assumption is consistent with the recently observed retention of configuration of the group R during the course of reaction in the cyclohexane series; Turner, THIS JOURNAL, **72**, 878 (1950).

(6) Criegee, *Ann.*, **560**, 127 (1948).

half-reacted state VII, as compared to VIII for cyclohexyl migration

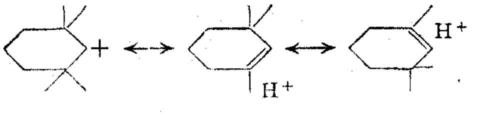


As an alternative formulation for migration in VI, it is conceivable that the migrating group R moves as a relatively positive entity, in the process pictured in IX



IX

In this case, the question of the relative stabilizations of the entities ⊕ (X) and ⊕ (XI) must be considered, not in the form of free carbonium ions but rather as relatively positive migrating groups involved in the concerted process IX. It is then possible that hyperconjugative stabilization of X through forms such as



which are impossible in XI, renders ease of migration of the cyclohexyl group much greater than that for the phenyl group, as observed experimentally.

The process pictured in IX is still consistent with the observed retention of configuration[5] in the migrating group. The nucleophilic attack of oxygen on the front face of the ring carbon, leading to retention, is formally similar to the S_N^i process involved[7] in treatment of optically active alcohols with $SOCl_2$. In the absence of other nucleophilic agents, retention of configuration is observed.

Experimental[8]

The ketones employed in this study were purified samples prepared by standard methods, and possessed the properties shown in Table II.

Table II

Compound	B. p. °C.	Mm.	M. p., °C.	Index of refraction
I	199-200[b]	750		n^{19}D 1.5338
II[a]	60-61	8		n^{27}D 1.4500
III			53-54	

[a] Prepared according to Nenitzescu and Cantuniari, *Ber.*, **69B**, 1820 (1936). [b] Uncorrected.

Perbenzoic acid in chloroform was prepared according to Braun,[9] and dried over anhydrous sodium sulfate before use. The titer of peracid solutions was determined by the usual iodimetric titration.

Rate Work.—The procedure outlined for previous rate work[2] in peracid oxidation was followed in this study. All runs were thermostated at 27.90 ± 0.05°. As in the previous studies, the presence of ketone and its reaction products stabilized the peracid in solution, leading to good precision in duplicate runs.

Preparative Scale Reaction of III with Peracid.—To 18.8 g. (0.10 mole) of III was added 250 ml. of a dried chloroform solution containing 0.110 mole of perbenzoic acid. The colorless reaction mixture was swirled at intervals, and kept in the dark at room temperature (24–26°). At the end of 239 hours, exactly 0.098 mole of peracid had been consumed by the ketone. The reaction mixture was then extracted with two 100-ml. portions of 1 *M* sodium bicarbonate solution, to remove the benzoic and residual perbenzoic acids, followed by a 50-ml. water wash. The combined aqueous phases were extracted with ether and the ether and chloroform phases combined and dried over anhydrous sodium sulfate. The solvent was then removed under reduced pressure.

The crude ester mixture was saponified by extended reflux with 30% sodium hydroxide solution, and the cyclohexanol extracted directly with ether. After removal of the ether, 7.06 g. (0.071 mole) of purified cyclohexanol, b. p. 158–159°,[10] was obtained. Treatment with α-naphthyl isocyanate gave the α-naphthylurethan of cyclohexanol, m. p. and mixed m. p. with an authentic sample, 127–128°.

The basic solution remaining after the ether extraction was saturated with carbon dioxide to liberate the free phenol. The phenol was extracted with ether. Removal of the ether gave 1.30 g. (0.014 mole) of phenol, which was converted quantitatively to 4.53 g. of tribromophenol, m. p. 93°.

In this run, the total yield of ROH product amounted to 0.085 mole, or 85% of the theoretical. The molar ratio of cyclohexanol to phenol was 5:1.

Repetition of the experiment on a smaller scale, using 0.0297 mole of ketone and 0.0442 mole of peracid, gave a molar ratio of 4.6 and an over-all ROH yield of 87%.

Summary

The rates of reaction of cyclohexyl methyl ketone, acetophenone and cyclohexyl phenyl ketone with perbenzoic acid in chloroform solution have been compared. A phenyl group adjacent to the ketone function markedly lowers the rate of reaction.

In the reaction of cyclohexyl phenyl ketone with peracid, both possible esters are formed. The ratio of products indicates a migration aptitude

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(7) (a) Kenyon, Phillips and Martin, *J. Chem. Soc.*, 382 (1931); (b) Hughes, *Trans. Faraday Soc.*, **34**, 202 (1938).

(8) Melting points are corrected; boiling points are corrected unless otherwise noted.

(9) Braun, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1947, p. 431.

(10) Lit. value 160°.

for the cyclohexyl group that is five times greater than that of the phenyl group. A possible interpretation of this point has been discussed in terms of rearrangement in an intermediate possessing cationic oxygen.

ROCHESTER, NEW YORK

RECEIVED JUNE 14, 1950

[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

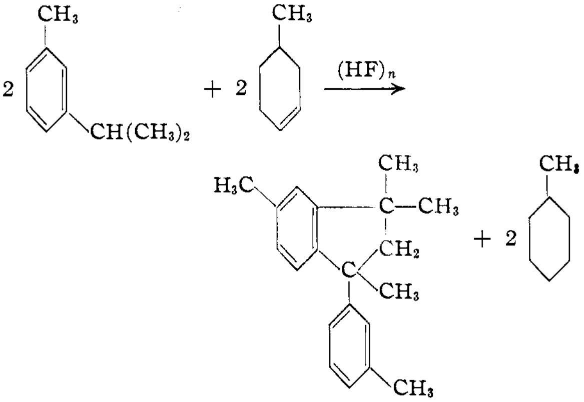
Hydrogen Transfer. V.[1] Reaction of *m*-Cymene and *o*-Cymene with Methylcyclohexene in the Presence of Hydrogen Fluoride

BY HERMAN PINES, D. R. STREHLAU[2] AND V. N. IPATIEFF

In previous studies of this series[3,4,5] it was shown that *p*-alkyl substituted toluenes reacted with 4-methylcyclohexene in the presence of either hydrogen fluoride or sulfuric acid to give mainly products resulting from hydrogen transfer.

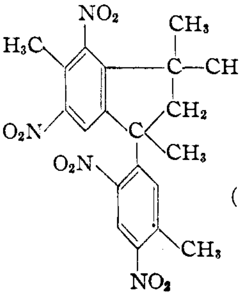
It was of interest to determine whether this type of reaction was limited only to the *p*-alkyl substituted toluenes; therefore *meta*- and *ortho*-cymene were prepared and treated with 4-methylcyclohexene at 0° in the presence of anhydrous hydrogen fluoride.

It was found that the reaction of *m*-cymene with methylcyclohexene also gave products resulting from hydrogen transfer. Of the methylcyclohexene charged, 26 mole per cent. was converted to methylcyclohexane, 7% to dimethyldicyclohexyl and 43% condensed with *m*-cymene to form an alkylated product probably 2-(1-methylcyclohexyl)-5-isopropyltoluene. Of the *m*-cymene reacted, 42 mole per cent. was isolated as the cycloalkylated product and 25% underwent a hydrogen transfer type reaction to form a compound whose elementary analysis corresponded to $C_{20}H_{24}$. In accordance with the mechanism proposed for the hydrogen transfer reactions described previously,[3,5] it was assumed that the $C_{20}H_{24}$ hydrocarbon corresponds to 1,3,3,5-tetramethyl-1-*m*-tolylindan (Compound I) formed according to the first equation shown.

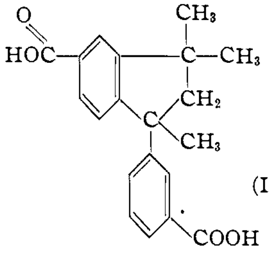


(I)

Compound I on nitration yielded a tetranitro derivative, melting at 202–203° and corresponding probably to 1,3,3,5-tetramethyl-1-(3-methyl-4,6-dinitrophenyl)-4,6-dinitroindan (Compound Ia).



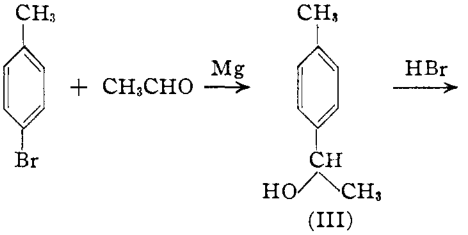
(Ia)



(Ib)

On oxidation with chromic anhydride in acetic acid, a dicarboxylic acid was obtained melting at 210° and corresponding to 1,3,3-trimethyl-1-(3-carboxylphenyl)-5 carboxyindan (Compound Ib). Compound I yielded, on destructive hydrogenation at 230° under pressure in the presence of a copper oxide–alumina catalyst, toluene and a bicyclic aromatic hydrocarbon corresponding to $C_{13}H_{18}$ which was believed to be 1,3,3,6-tetramethylindan (II). The reaction is similar to that reported previously.[3]

The bicyclic hydrocarbon obtained from the destructive hydrogenation was identical, according to its physical constants, solid derivatives and infrared absorption spectra with a synthetic sample of II prepared as shown



(III)

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(1) For paper IV of this series see H. Pines, D. R. Strehlau and V. N. Ipatieff, THIS JOURNAL, **72**, 1463 (1950).

(2) Universal Oil Products Company Predoctorate Fellow (1945–1948).

(3) V. N. Ipatieff, H. Pines and R. C. Olberg, THIS JOURNAL, **70**, 2123 (1948).

(4) H. Pines, A. Weizmann and V. N. Ipatieff, *ibid.*, **70**, 3859 (1948).

(5) H. Pines, D. R. Strehlau and V. N. Ipatieff, *ibid.*, **71**, 3534 (1949).