trans-N-Isopropyl-2-phenylcyclopropylamine hydrochloride. A mixture of 13.3 g. (0.1 mole) *trans*-2-phenylcyclopropylamine and 7.0 g. (0.12 mole) of acetone in 300 ml. of benzene was stirred at room temperature for 1 hr. and then refluxed azeotropically for 1.5 hr. The solution was concentrated *in vacuo*. The residual oil was dissolved in 100 ml. of ethanol and 0.3 g. of platinum oxide was added. The mixture was hydrogenated at room temperature under 50 p.s.i. of hydrogen. After 1 hr., the mixture was filtered and the filtrate concentrated. The yellow oil was converted to a *hydrochloride* in ethanol. Two recrystallizations from butanone gave 17.9 g. (85%) of colorless crystals, m.p. 155–157°.

Anal. Calcd. for $C_{12}H_{18}ClN$: C, 68.07; H, 8.57. Found: C, 67.98; H, 8.52.

trans-N-Isopropyl-2-phenylcyclopropylamine was also prepared in 70% yield from *trans-N*-(2-phenylcyclopropyl)-trifluoroacetamide and isopropyl iodide in the same manner as described for the preparation of *trans-N*-methyl-2-phenylcyclopropylamine from the trifluoroacetamide derivative.

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Products from the Reaction of 2-Bromo-4'-phenylacetophenone with Powdered Sodium Hydroxide in Ether

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Under heterogeneous conditions 2-bromo-4'-phenylacetophenone reacts with powdered sodium hydroxide in anhydrous ether to give *p*-phenylbenzoic acid (4%) and neutral polymerization products which could not be identified. Addition of 0.5% water to the reaction medium increases the yield of *p*-phenylbenzoic acid to 22% and also gives *p*-phenylmandelic acid (12%) and *p*-phenylacetophenone (8%). Careful exclusion of ether peroxides from the reaction medium and use of a nitrogen atmosphere markedly decreases the quantities of *p*-phenylbenzoic and *p*-phenylmandelic acids and increases the quantity of *p*-phenylacetophenone formed. Increase in the amounts of added water up to a maximum of 5%, at which point the reaction medium becomes homogeneous, results in almost complete quenching of the reaction and recovery of a high per cent of unchanged starting material.

Acidic products containing the same number of carbon atoms[3-7] and containing fewer carbon atoms,[5,8] have been reported from reactions of nucleophilic bases with α-halo ketones containing no enolizable α'-hydrogen atoms *via* quasi-Favorski rearrangements and cleavage processes, respectively. The present paper reports the results of investigations into the nature of the products obtained from the reaction of 2-bromo-4'-phenylacetophenone with sodium hydroxide in ether under heterogeneous conditions.

The experimental results summarized in Table I were obtained from the reaction of 2-bromo-4'-phenylacetophenone (I) with approximately a twofold excess of solid sodium hydroxide in ether with variations in conditions as indicated. Each run was agitated vigorously with a Morton Hi-Speed stirrer for ten hours at room temperature. Preliminary experiments using anhydrous ether indicated that the yield of crude acid approached a maximum in ten hours. The sodium hydroxide was added as pellets which were pulverized in a few minutes by the action of the stirrer.

The reaction of I with powdered sodium hydroxide in anhydrous ether using normal precautions against moisture yielded a small amount of *p*-phenylbenzoic acid (II) as the only acidic product. Approximately one half of the starting material was recovered unchanged. The identity of the *p*-phenylbenzoic acid was rigorously established by means of ultraviolet spectra, equivalent weights, and by mixed melting point determinations involving the isolated acid and its *p*-phenylphenacyl derivative with synthetic *p*-phenylbenzoic and 4-biphenylacetic acids and their *p*-phenylphenacyl derivatives, respectively. The isolated acid and the synthetic *p*-phenylbenzoic acid showed absorption maxima in the ultraviolet at about 271 mμ with similar extinction coefficients, while the 4-biphenylylacetic acid showed an absorption maximum at 252 mμ with a much lower extinction coefficient.

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TABLE I

SUMMARY OF REACTION PRODUCTS[a]

Run No.	Reaction Conditions[b]	Br^- Produced, %	Unchanged 2-Bromo-4′-phenylacetophenone, %	p-Phenylbenzoic Acid, %	p-Phenylmandelic Acid, %	p-Phenylacetophenone, %
1	Sodium-dried ether	38.4	48	3.6	0.0	0.0
2	0.5% H_2O in ether	87.3	0	22.2	12.1	8.3
3	1% H_2O in ether	85.6	0	7.7	Trace	0.0
4	3% H_2O in ether	43.0	27	1.4	0.0	0.0
5	5% H_2O in ether	20.0	56	3	0.0	0.0
6	0.5% H_2O in ether, N_2 atm.	95.3	0	7.7	6.0	16.8
7	0.5% H_2O in redistilled ether, N_2 atm.	98.2	0	8.4	7.7	29.3
8	0.5% H_2O in ether	22.4	71	3.9	1.9	0.4

[a] All calculated yields of organic compounds are in terms of mole % of chromatographed and recrystallized material with the exception of the *p*-phenylbenzoic acid in Run No. 5 which was based on the amount of crude product. The observed melting ranges for the various substances in the different runs are comparable. [b] The reaction period was ten hours with the exception of Run No. 8 for which it was 0.29 hours.

A careful search for 4-biphenylylacetic acid (III), the product expected from a quasi-Favorski rearrangement of I, among the reaction products was unsuccessful. Smissman and Hite[7] reported that no acid resulting from a quasi-Favorski rearrangement was formed from the reaction of (−)-1-methyl-3-benzoyl-3-chloropiperidine with powdered sodium hydroxide in ether or petroleum ether (b.p. 00–00°), but that a 7% yield of the acid was obtained in refluxing anhydrous xylene or Skellysolve A. Stevens and Farkas[5] observed that in the reaction of α-chlorocyclohexyl phenyl ketone with powdered sodium hydroxide, the yield of rearranged acid increased from 8 to approximately 50% when the solvent was changed from ether to refluxing xylene or toluene. In the present investigation the use of boiling toluene as the solvent in the reaction of I with powdered sodium hydroxide increased the yield of pure *p*-phenylbenzoic acid from 4 to 22% but again no rearrangement acid (III) could be detected among the products. Considerable formation of tar also resulted from this higher reaction temperature.

The formation of *p*-phenylbenzoic acid from I was shown conclusively to occur by cleavage of the C-1:C-2 bond with no rearrangement involved by using I labeled in the side chain with C^{14} in the C-1 (the keto carbon) and in the C-2 positions. The results, summarized in Table II, show that the cleavage acid from I-2-C^{14} was essentially inactive while that from I-1-C^{14} retained the activity. All attempts to identify the active single carbon cleavage fragment from the I-2-C^{14} were unsuccessful. A careful search was made for methanol and methyl bromide as possible hydrolytic cleavage products and for formaldehyde and carbon dioxide as possible oxidative cleavage products. The possibility that formic acid might be the cleavage product has not as yet been investigated.

TABLE II

DETERMINATION OF RADIOACTIVITIES

	Counts per Min. per 100 Mg.
1. 2-Bromo-4′-phenylacetophenone-1-C^{14}	2473
2. *p*-Phenylbenzoic acid from 2-bromo-4′-phenylacetophenone-1-C^{14}	3895
3. 2-Bromo-4′-phenylacetophenone-2-C^{14}	1044
4. *p*-Phenylbenzoic acid from 2-bromo-4′-phenylacetophenone-2-C^{14}	24

It has been suggested[5,7,8] that the formation of acidic products containing fewer carbon atoms than the parent compound in reactions of this type results from conversion of the α-halo ketone to the α-hydroxy ketone which subsequently undergoes hydrolytic or oxidative cleavage. Loftfield and Schaad[8] demonstrated that in a homogeneous sodium methoxide–methanol medium the amount of acidic cleavage product can be greatly diminished by extreme attention to the exclusion of water in reactions involving both chloromethyl cyclohexyl ketone and hydroxymethyl cyclohexyl ketone. In the present investigation the addition of 0.5% water by volume to the anhydrous ether increased the amount of cleavage acid II to 22% but also yielded *p*-phenylacetophenone (IV, 8%) and *p*-phenylmandelic acid (V, 12%).

Numerous attempts to identify 2-hydroxy-4′-phenylacetophenone (VI) as one of the ether-soluble products from the reaction of the α-halo ketone (I) with powdered sodium hydroxide were unsuccessful. In one run (No. 8, Table I) the reaction time was decreased from ten hours to seventeen minutes to determine whether the hydroxy ketone VI might

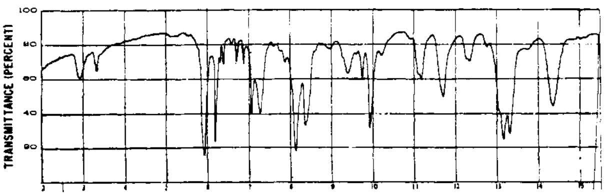

Fig. 1. Infrared absorption spectrum of Fraction B (potassium iodide pellet)

be present in the early stages of the reaction period in sufficient concentration to permit identification. Only the reaction products previously indicated could be isolated. The amounts of these products were much smaller but were in roughly the same ratio as in the runs with a ten-hour reaction period. In anhydrous ether VI was shown to react with powdered sodium hydroxide to give the cleavage acid II in about 5%.

When the reaction was run under a nitrogen atmosphere in place of air (run No. 6, Table I), and using a nitrogen atmosphere and ether which had been freshly distilled to remove any traces of peroxides (run No. 7, Table I), the yields of *p*-phenylmandelic and *p*-phenylbenzoic acids were decreased to one half and one third of the normal amounts, respectively. The yield of *p*-phenylacetophenone was increased to two and three times the normal amount under the conditions of each of the two runs, respectively. The decrease in acidic products with decreasing oxygen content in the reaction vessel is consistent with the observations of Stoll and Hulstkamp[9] with regard to the effect of oxygen on the products obtained in the preparation of cyclic acyloins.

An increase in the amount of water added to the ether to 1% or higher markedly affected the course of the reaction of I with sodium hydroxide. Contrary to expectations the yield of cleavage acid II dropped off rapidly with increasing water content and essentially no *p*-phenylmandelic acid or *p*-phenylacetophenone could be isolated from any of these runs. No unchanged starting material I could be isolated from the runs with either 0.5 or 1% added water but 27 and 56% recovery of I was possible in the runs with 3 and 5% water, respectively. The amount of bromide ion liberated decreased with increasing water content. The total amount of bromine accounted for as bromide ion and unchanged I was much lower (70 and 76%) in the runs with 3 and 5% added water than in the runs with less added water (approximately 85%). In the reactions under a nitrogen atmosphere essentially quantitative formation of bromide ion was observed. The reaction mixture with 5% added water is completely homogeneous, and a relatively large fraction of the sodium hydroxide is dissolved in the mixture with 3% added water. The drastic changes in the nature of the reaction products can undoubtedly be best explained on the basis of a change from heterogeneous to homogeneous reaction conditions. The experimental results indicate that the primary reaction of the 2-bromo-4′-phenylacetophenone with the base must take place far more rapidly at the hydrated surface of the powdered sodium hydroxide particles[7] than by attack of OH^- under homogeneous conditions. Further work is in progress in this laboratory to elucidate the mode of formation of the observed products under the heterogeneous conditions indicated.

In the experimental results summarized in Table I the material unaccounted for in each run is to a small extent material lost in purifying each of the listed products but is mainly in the form of neutral polymerization products. From the runs in anhydrous ether two fractions, "A" (m.p. 215–225°) and "B" (m.p. 308.5–311°) were separated and investigated extensively but not identified. No similar substances could be isolated from the polymerization products from the runs in aqueous ether. Consideration of the ultraviolet spectra and the elemental analyses of Fractions A and B showed conclusively that neither material was the product of a Darzens condensation similar to that leading to the formation of bromodiphenacyls[10] from the reaction of 2-bromo-acetophenone with sodium alkoxides. Neither Fraction A nor B contained bromine and the ultraviolet absorption spectra of A (λ_{max} 305 mμ) and B (λ_{max} 293 mμ) were quite different from those of the bromodiphenacyls (λ_{max} 252 and 250 mμ). Although the calculated empirical formula, $C_{14}H_{10}O$, for Fraction B suggested that it might be di-*p*-phenylbenzoylethylene, a product which could be easily rationalized[11] under the reaction conditions used, a synthetic sample of *trans*-di-*p*-phenylbenzoylethylene and Fraction B were shown to differ markedly in physical and chemical properties, in ultraviolet spectra (λ_{max} 318 and 296 mμ in ethyl acetate, respectively), and in infrared spectra (Fig. 1). Attempts to convert *trans*-di-*p*-phenylbenzoylethylene into Fraction B by reductive dimerization[12] and by reaction with powdered sodium hydroxide in anhydrous ether under the reaction conditions used in the present investigation were also unsuccessful.

EXPERIMENTAL

2-Bromo-4′-phenylacetophenone (I). Commercially available material was recrystallized from ethanol to give white crystals, m.p. 126.3–127.3°. Chromatography on silicic acid using benzene–petroleum ether (b.p. 65–70°) (1:1) as

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[9] M. Stoll and J. Hulstkamp, *Helv. Chim. Acta*, **30**, 1815 (1947).

[10] H. H. Wasserman, N. E. Aubrey, and H. E. Zimmerman, *J. Am. Chem. Soc.*, **75**, 96 (1953).

[11] M. S. Kharasch, W. Nudenberg, and E. K. Fields, *J. Am. Chem. Soc.*, **66**, 1276 (1944).

[12] R. E. Lutz, L. Love, and F. S. Palmer, *J. Am. Chem. Soc.*, **57**, 1953 (1935).

the developing solvent gave only one band from the purified I. A mixture of *p*-phenylacetophenone and I was shown to separate completely into two bands under the same conditions.

p-Phenylbenzoic acid (II) *and 4-biphenylylacetic acid* (III). *p*-Phenylbenzoic acid (m.p. 224–226°, ultraviolet spectrum in 95% ethanol, λ_{max} 270 mμ, ϵ 22,500) and 4-biphenylylacetic acid (m.p. 161–162°, ultraviolet spectrum in 95% ethanol, λ_{max} 252 mμ, ϵ 19,300) were prepared from biphenyl by standard procedures. The *p*-phenylphenacyl derivatives of *p*-phenylbenzoic acid, m.p. 250–253°, and of 4-biphenylylacetic acid, m.p. 147.5–149°, were prepared by the standard procedure.[13]

Anal. Calcd. for $C_{27}H_{20}O_3$: C, 82.63; H, 5.14. Found: C, 82.83; H, 5.20.

Anal. Calcd. for $C_{28}H_{22}O_3$: C, 82.73; H, 5.46. Found: C, 82.98; H, 5.41.

The above *p*-phenylphenacyl derivatives are completely separable in 5–10 mg. quantities on a 200 × 8 mm. silicic acid column using benzene–petroleum ether (1:1) as the developing solvent by the technique of Kirchner, Prater, and Haagen-Smit.[14] The *p*-phenylphenacyl ester of *p*-phenylbenzoic acid emerges from the column first.

Reaction of 2-bromo-4′-phenacetophenone (I) *with sodium hydroxide in anhydrous ether.* A mixture of 3.00 g. (0.011 mole) of I, 1.0 g. (0.025 mole) of sodium hydroxide pellets, and 300 ml. of sodium-dried ether was stirred at approximately 2500 r.p.m. in a Morton[15] type Hi-speed stirrer for 10 hr. at room temperature. The pellets were completely pulverized within a few minutes. The reaction mixture became yellow and then orange near the end of the run and a reddish yellow precipitate appeared as the reaction progressed.

The precipitate was collected by filtration, and the ether filtrate was reduced to one fifth of its original volume by evaporation under reduced pressure. A yellow precipitate (Fraction A) was isolated from the ether concentrate and recrystallized from benzene to give 10 mg. of colorless crystals, m.p. 215–225°. Further recrystallization did not improve the melting point.

The ether solution remaining after removal of Fraction A was dried over anhydrous sodium sulfate, filtered, and evaporated to dryness. The solid residue was dissolved in a small amount of benzene–petroleum ether (2:1), transferred to a 200 × 8 mm. silicic acid column and the chromatograph was developed using the same solvent mixture. Only one band appeared which, after elution, gave 1.3 g. (48%) of unchanged 2-bromo-4′-phenylacetophenone, m.p. 124–126°, no depression in mixed m.p. with pure starting material. Thorough extraction of the silicic acid column with acetone after removal of the above band, gave only a trace of resinous material which could not be crystallized.

The precipitate from the original reaction mixture was extracted with 500 ml. of water. The water-insoluble fraction was recrystallized from acetone three times to give 80 mg. of colorless needles (Fraction B), m.p. 308.5–311° dec. Not all of the water-insoluble material was soluble in acetone.

The aqueous extract was acidified with nitric acid. The precipitated solid acids were collected by filtration and dried. The acidic material was dissolved in a small amount of a mixed solvent of benzene, petroleum ether, and ether (2:2:1). This solution was transferred to a 200 × 8 mm. silicic acid column, and the chromatograph was developed using the same solvent mixture. The acidic material, which emerged as a single band, was recrystallized from ether–petroleum ether to give 78 mg. (3.6% yield) of white needles, m.p. 224–226°; *p*-phenylphenacyl derivative, m.p. 250–253°; equiv. wt., 194, 192 (calcd. for $C_{13}H_{10}O_2$ 198); ultraviolet spectrum in 95% ethanol, λ_{max} 270 mμ, ϵ 23,500. Mixed melting points of synthetic *p*-phenylbenzoic acid and its *p*-phenylphenacyl derivative with the isolated acid and its *p*-phenylphenacyl derivative, respectively, showed no depressions. Chromatography of the *p*-phenylphenacyl ester of the isolated acid with the derivative of *p*-phenylbenzoic acid on silicic acid using 1:1 benzene–petroleum ether as the developing solvent gave only one band, while cochromatography of the derivative of the isolated acid with the derivative of 4-biphenylylacetic acid gave two distinct bands.

Three grams of solid silver nitrate were added to the aqueous solution remaining after removal of the precipitated acids. The precipitate of silver bromide was collected on a sintered glass funnel, washed, and dried at 130° to constant weight. The 0.7806 g. of silver bromide was calculated to contain 38.4% of the bromine contained in the original 3.00 g. of 2-bromo-4′-phenylacetophenone.

Check for presence of 4-biphenylylacetic acid (III). The crude acidic fraction isolated from a run in anhydrous ether was recrystallized to remove a large per cent of the *p*-phenylbenzoic acid. The combined mother liquors were evaporated to dryness, the solid residue converted into the *p*-phenylphenacyl derivative and chromatographed as described above. Only one band, identified as the derivative of *p*-phenylbenzoic acid, was obtained. No evidence for the presence of any of the derivative of 4-biphenylylacetic acid was observed.

Investigation of fractions A and B. The materials in these fractions did not contain bromine, gave no ash on ignition, were insoluble in 5% sodium hydroxide or 5% hydrochloric acid, were soluble in concd. sulfuric acid, and gave negative tests for a carbonyl group with 2,4-dinitrophenylhydrazine or hydroxylamine reagents. Fraction B did not absorb bromine in chloroform solution. Determination of the molecular weight of Fraction A by the Rast method using camphor gave values of 488, 558, 572, and 578 on separate trials. Attempted molecular weight determinations on Fraction B were unsuccessful using camphor or cyclohexanol due to insolubility of the material and also using pinene dibromide due to its interaction with the solute.

An attempt to determine a saponification equivalent for Fraction A by heating a suspension of 20 mg. of the material in 50 ml. of 1*N* potassium hydroxide in diethylene glycol at 130° for 1 hr. was unsuccessful due to the low solubility of the solute in the solvent. A small amount of acidic material, m.p. 200–218°, which appeared to be impure *p*-phenylbenzoic acid was isolated from the reaction mixture.

The ultraviolet spectra gave λ_{max} 305 mμ ($E^{1\%}_{1\,cm.}$ 6.31) for Fraction A in 95% ethanol and λ_{max} 293 ($E^{1\%}_{1\,cm.}$ 6.82) and λ_{max} 296 mμ ($E^{1\%}_{1\,cm.}$ 292) for Fraction B in 95% ethanol and ethyl acetate, respectively. Combustion analyses gave the following data: Fraction A. Found: C, 79.24; H, 4.81. Fraction B. Found: C, 86.61, 86.23; H, 5.29, 5.22.

2-Hydroxy-4′-phenylacetophenone (VI). A mixture of 3.7 g. of *p*-phenylphenacyl acetate (m.p. 110–111°), 50 ml. of 95% ethanol, and 1 ml. of concd. sulfuric acid was refluxed for 3 hr. The reaction mixture was cooled in an ice bath and the yellow crystalline material collected by filtration. The crude product was recrystallized twice from ethanol to give 1.9 g. (63%) of 2-hydroxy-4′-phenylacetophenone as white crystals, m.p. 129–131°.

Reaction of 2-hydroxy-4′-phenylacetophenone (VI) *with sodium hydroxide in anhydrous ether.* A mixture of 1.8 g. of 2-hydroxy-4′-phenylacetophenone, 0.6 g. of sodium hydroxide, and 300 ml. of anhydrous ether was stirred as previously described. Isolation of the acidic fraction gave 80 mg. (4.8%) of crude acid which was recrystallized several times from ether-petroleum ether mixture to give colorless needle crystals, m.p. 223–225.5°; equiv. wt. 198

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[13] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, 4th ed., J. Wiley and Sons, Inc., New York, p. 200.

[14] J. G. Kirchner, A. N. Prater, and A. J. Haagen-Smit, *Ind. Eng. Chem., Anal. Ed.*, 18, 31 (1946).

[15] A. A. Morton and L. M. Redman, *Ind. Eng. Chem.*, 40, 1190 (1948).

(calcd. for $C_{13}H_{10}O_2$; 198); *p*-phenylphenacyl derivative m.p. 249–252°, no depression in m.p. when mixed with *p*-phenylphenacyl *p*-phenylbenzoate. The neutral fractions from the reaction mixture were not investigated.

Reaction of 2-bromo-4′-phenylacetophenone (I) *with sodium hydroxide in ether containing 0.5 volume per cent water.* A 5.0-g. sample of I, 500 ml. of anhydrous ether to which was added 2.5 ml. of distilled water, and 1.6 g. of dry sodium hydroxide pellets were carried through the procedure as previously described with the exceptions indicated in the following.

At the end of the reaction period, after filtration to remove the precipitate, the ether phase was washed twice with 50 ml. portions of water which were then added to the aqueous phase containing the sodium salts of the acids. The crude acid mixture obtained from this aqueous phase as previously described, was separated into two components by chromatography on silicic acid. The material from the fastest moving band was recrystallized from ether–petroleum ether to give 0.80 g. (22.2%) of *p*-phenylbenzoic acid as colorless needles, m.p. 224–226°; no depression on mixed m.p. with synthetic *p*-phenylbenzoic acid. The material from the slower moving band was recrystallized from ether–petroleum ether to give 0.50 g. (12.1%) of *p*-phenylmandelic acid as white crystals, m.p. 202–204° (lit.[16] m.p. 201–203°); acetate derivative, m.p. 140.5–141.2°; equiv. wt. 220, 224 (calcd. for $C_{14}H_{12}O_3$, 228).

Anal. Calcd. for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30. Found: C, 73.43; H, 5.42.

Concentration of the ether phase from the initial reaction mixture to one fifth of the original volume gave no precipitate. Complete removal of the ether and chromatography of the yellow residue on silicic acid gave no unchanged I but resulted in the separation of a band containing 0.41 g. of yellowish white solid which was recrystallized from petroleum ether to give 0.30 g. (8.3%) of *p*-phenylacetophenone as white crystals, m.p. 119–121°. No depression was observed on mixed m.p. with synthetic *p*-phenylacetophenone.

Anal. Calcd. for $C_{14}H_{12}O$: C, 85.70; H, 6.16. Found: C, 86.10; H, 6.79.

Additional runs also were made using 3.0 g. of I, 1.0 g. of sodium hydroxide, and 300 ml. of 0.5% aqueous ether with the following changes made individually on separate runs: (i) a nitrogen atmosphere was used, (ii) a nitrogen atmosphere was used and the anhydrous ether was redistilled immediately before use, and (iii) the reaction time was decreased from 10 hr. to 17 min. The analytical results for all of these runs are summarized in Table I. No material comparable to Fraction A was obtained in these runs with 0.5% aqueous ether, but a certain amount of yellow resinous material could always be recovered from the chromatographic column by washing with acetone after the *p*-phenylacetophenone band had been eluted out. Varying amounts of material insoluble in ether and dilute base which were similar to but not identical with Fraction B were always obtained.

A careful check for the presence of 2-hydroxy-4′-phenylacetophenone among the ether soluble neutral reaction products from the run with a 17-min. reaction time was made as follows. Chromatography of the neutral fraction on silicic acid permitted the separation of 2.14 g. (71%) of the unchanged starting material (I) and 10 mg. (0.4%) of *p*-phenylacetophenone in pure form. All the remaining neutral material, including the resinous material obtained by washing the dried silicic acid column with acetone, was dissolved in anhydrous ether and an excess of acetyl chloride added. After several hours the solution was evaporated to dryness, the residue placed on a silicic acid column and developed with a mixture of benzene and petroleum ether (2:1). No *p*-phenylphenacyl acetate could be isolated from the column.

Reaction of 2-bromo-4′-phenylacetophenone (I) *with sodium hydroxide in ether containing one, three or five volume per cent water.* The reactions were carried out using 3.0 g. of I, 1.0 g. of sodium hydroxide, and 300 ml. of the appropriate mixture of anhydrous ether and distilled water in the same manner as described for the runs with 0.5% aqueous ether. The reaction mixture containing 5% water was completely homogeneous from the start. No *p*-phenylmandelic acid nor *p*-phenylacetophenone could be isolated from the reaction products. Varying amounts of material insoluble in both ether and dilute base which were similar to but not identical with Fraction B were obtained. The analytical results from these runs are summarized in Table I.

2-Bromo-4′-phenylacetophenone-1-C^{14}. Fifty μc of sodium acetate-1-C^{14} was added to 6 g. of unlabeled sodium acetate in 20 ml. of water; the solution was stirred thoroughly and carefully evaporated to dryness. The sodium acetate was mixed with 24 g. of benzoyl chloride in a small flask and distilled to give 4.0 g. (70%) of pure acetyl chloride-1-C^{14}. The 4.0 g. of acetyl chloride-1-C^{14} reacted with 17.5 g. of biphenyl and 10 g. of anhydrous aluminum chloride in carbon disulfide by the usual Friedel-Crafts procedure to give 7.0 g. (70%) of *p*-phenylacetophenone-1-C^{14}, m.p. 119–120°. The 7 g. of *p*-phenylacetophenone-1-C^{14} was dissolved in 70 ml. of chloroform and 5 g. of bromine in 35 ml. of chloroform was gradually added. After standing overnight, the bromine color had disappeared leaving a clear yellow solution. The chloroform was removed by evaporation leaving a yellow solid which was purified by chromatography on silicic acid using benzene–petroleum ether (2:1) as the developer and then recrystallized from ethanol to give 1.8 g. (18%) of colorless crystalline 2-bromo-4′-phenylacetophenone-1-C^{14}, m.p. 125–127°.

2-Bromo-4′-phenylacetophenone-2-C^{14}. Fifty μc of sodium acetate-2-C^{14} were carried through the same process as described above to give 3.5 g. (17.3%) of 2-bromo-4′-phenylacetophenone-2-C^{14}, m.p. 125–127°.

Reaction of 2-bromo-4′-phenylacetophenone-1-C^{14} and 2-bromo-4′-phenylacetophenone-2-C^{14} with sodium hydroxide in ether. Each of the labeled bromo compounds was carried through the reaction with sodium hydroxide in ether containing 0.5% water and the *p*-phenylbenzoic acid from each run was collected and purified as previously described. The activities of the two bromo compounds and of the *p*-phenylbenzoic acid samples obtained from them were measured by placing a weighed sample of each in a planchet and determining the radioactivity using a flow gas type Geiger counter. The counts per minute listed in Table II are the average of 3-min. counts after subtraction of a background of 21 counts per minute.

Attempted identification of C-2 cleavage product from the reaction of 2-bromo-4′-phenylacetophenone-2-C^{14} with sodium hydroxide. At the end of the initial reaction period a liquid air trap was connected to the reaction flask in place of the Dry Ice condenser, and the flask was purged with a stream of dry nitrogen for 30 min. while the reaction mixture was stirred. The ether fraction collected in the liquid air trap contained no radioactivity and did not give a solid derivative when treated with 2,4-dinitrophenylhydrazine reagent.

After filtration to remove the precipitate from the reaction mixture, 50 ml. of *n*-propyl alcohol (b.p. 97.8°) was added to the ether solution and the mixture carefully distilled using a center-rod all-glass fractionating column. After removal of the ether a 1.0-g. fraction boiling from 38–97° was collected. No evidence for the presence of methanol in this fraction could be obtained. Conversion of a portion of the fraction to the 3,5-dinitrobenzoate and chromatographic investigation of the derivative[17] gave only one band which contained *n*-propyl 3,5-dinitrobenzoate, m.p. 72–73°.

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The precipitate from the original reaction mixture was treated with water and filtered. The filtrate was acidified with concd. hydrochloric acid and purged with nitrogen gas through a washing bottle containing 100 ml. of saturated barium hydroxide solution for 15 min. No precipitate of barium carbonate appeared in the barium hydroxide solution.

Di-p-phenylbenzoylethylene (*trans*). Twelve grams of fumaryl dichloride, b.p. 44–45° (3 mm.), was added to a tenfold excess of diphenyl in carbon disulfide under standard conditions for a Friedel-Crafts reaction with anhydrous aluminum chloride as the catalyst. The crude reaction product was dried, powdered, and washed with hot petroleum ether. The orange residue was recrystallized three times from benzene to give 10 g. (33%) of *trans*-di-*p*-phenylbenzoylethylene as yellow needles, m.p. 248–250° (lit.[18] m.p. 247.5–248°), ultraviolet spectrum in ethyl acetate, λ_{max} 318 mμ, ϵ 24,070.

Anal. Calcd. for $C_{28}H_{20}O_2$: C, 86.60; H, 5.18. Found: C, 86.43; H, 5.42.

The *trans*-di-*p*-phenylbenzoylethylene reacted slowly with 2,4-dinitrophenylhydrazine reagent to give a small amount of colored precipitate after standing overnight and slowly absorbed bromine in chloroform solution.

The reaction of 500 mg. of *trans*-di-*p*-phenylbenzoylethylene with 1.0 g. of dried sodium hydroxide in 500 ml. of anhydrous ether as previously described gave no material corresponding to Fraction B but did give a very small amount of *p*-phenylbenzoic acid, m.p. 224–226°.

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Addition of Ethylenic Compounds to Tetracyclones

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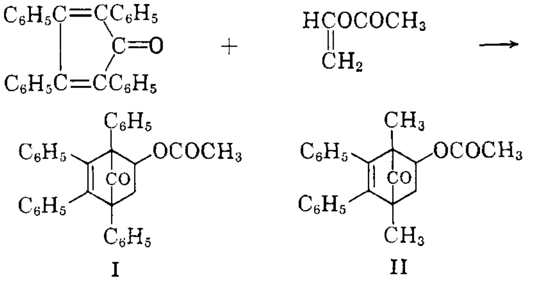
Ethylene and simple vinyl esters add to cyclopentadienones without accompanying decarbonylation, provided a low temperature is employed. An excess of the ethylenic component is essential for good yields. Anhydrous aluminum chloride catalyzes the addition of ethylene. The same catalyst also brings about a rearrangement of 1,2,3,4-tetraphenylbenzene to the 1,2,4,5-isomer, but the rate is too slow to be a complicating factor.

It has long been known that unsaturated compounds having the double bond activated by conjugation will add to cyclopentadienones.[2a,2b] Less attention has been devoted to simpler ethylenes such as allyl and vinyl compounds. Abramov and his group[3-8] described products obtained by heating cyclones and ethylenes in sealed tubes at 150–200°. As would have been expected, the conditions were so drastic that decarbonylation and aromatization usually occurred. However, adducts were obtained in six instances from allyl compounds and acecyclone and from vinyl ethers and esters and the very reactive phencyclone.

Since it seemed likely that the conditions employed previously had been too severe, a temperature of 100° was tried in these Laboratories fifteen years ago. After 24 hr., it was found that vinyl acetate added smoothly and quantitatively to tetracyclone and to the dissociating dimer of dimethyldiphenylcyclopentadiene,[9] giving the adducts I and II.



I II

Attention was next turned to ethylene itself. In benzene solution, when only one equivalent of ethylene was employed under 100 lb. pressure at 105°, there was no detectable reaction. Using a high pressure (200 lb.) of ethylene at 180°, decarbonylation occurred as expected even in the presence of added carbon monoxide (400 lb.), giving rise to the dihydrobenzene (III) as well as to the completely aromatized 1,2,3,4-tetraphenylbenzene (IV). There was no appreciable reaction at 100° until anhy-

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