bromination of II in acetic acid) was not depressed. The infrared spectra were also identical.

3-Acetoxy-2-bromoindene (VIII).—This enol acetate was prepared in 23% yield from III, following exactly the procedure outlined for the preparation of V. When excess acetyl chloride was added to the ether solution of the enolate ion, the reaction mixture turned deep purple and sodium chloride precipitated. During removal of the ether, a solid crystallized. A small amount of petroleum ether (b.p. 30–60°) was added and the solid was filtered. Recrystallization of this solid from petroleum ether (b.p. 30–60°) gave an average yield of 1.6 g. of 2,2-dibromo-1-indanone[16] (X), m.p. 130–131.5° (recorded 132–133°),[13] from several 10 g. runs of III. A mixture melting point determination with an authentic sample of X which was prepared by the bromination of III was not depressed.

Crystallization of the original petroleum ether extract yielded colorless prisms of VIII, m.p. 80–81°. An average of 2.25 g. (23%) was obtained from several 10-g. runs.

Anal. Calcd. for $C_{11}H_9BrO_2$: C, 52.20; H, 3.59; Br, 31.58. Found: C, 52.05; H, 3.67; Br, 31.40.

Bromination of 3-Acetoxy-2-bromoindene (VIII).—Following the procedure outlined for the bromination of VII a crude yield of 88% (2.6 g.) of 2,2-dibromo-1-indanone (X), m.p. 126–130°, was obtained from 2.53 g. of VIII. Recrystallization from petroleum ether (b.p. 30–60°) yielded prisms, m.p. 131–132°.

1-Caproxy-2-chlorocyclohexene (XI).—An ether slurry of anhydrous, powdered sodium methoxide was prepared, following the directions used for the preparation of V; the volume of ether was 300 ml. Increasing the volume of ether increases the tendency for the enolate salt of 2-chlorocyclohexanone (IV) to precipitate. The temperature of the reaction mixture was lowered to −50° by means of a Dry Ice–chloroform bath. IV (13.2 g., 0.1 mole) was added in one portion. When the reaction mixture became homogeneous (2 minutes), an excess (15 g.) of caproyl chloride was added. After centrifugation of the salts and removal of the ether, the oil which remained was fractionally distilled. After a lower-boiling forerun, XI distilled as a colorless oil at 86–87° (0.05 mm.), n^{25}_D 1.4707. The yield was 8 g. (29%).

Anal. Calcd. for $C_{12}H_{19}ClO_2$: C, 62.46; H, 8.30; Cl, 15.36. Found: C, 62.56; H, 8.34; Cl, 15.56.

Oxidation of 1-Caproxy-2-chlorocyclohexene (XI).—XI (1.4 g., 0.006 mole) was dissolved in 40 ml. of reagent-grade acetone. To this solution, a water solution (40 ml.) containing an equivalent of potassium permanganate (0.98 g.) was added. Although the permanganate was decolorized rapidly, the reaction mixture was allowed to stir for two hours at room temperature. A few crystals of sodium sulfite were then added to decompose any unreacted permanganate. The inorganic material was removed by filtration and the water–acetone solution was made basic by the addition of sodium carbonate. The reaction mixture was extracted three times with 50-ml. portions of ether. The ether extracts were combined and dried over anhydrous sodium sulfate. The sodium sulfate was removed by filtration and the ether was removed *in vacuo*.

The remaining oil was dissolved in 7 ml. of 95% ethanol, and phenylhydrazine (1.3 g.) was added. Distilled water was added dropwise until the solution became turbid. Acetic acid was then added dropwise until the solution became clear. The reaction mixture was heated on a steam-bath for 3 hours and allowed to stand overnight whereupon yellow needles of the osazone of cyclohexane-1,2-dione, m.p. 145–148°, crystallized in a yield of 42% (0.75 g.) based on the starting enol caproate XI. Recrystallization from ethanol gave yellow needles,[17] m.p. 150–151° (recorded 152–153°).

Anal. Calcd. for $C_{18}H_{20}N_4$: C, 73.94; H, 6.90. Found: C, 74.06; H, 7.01.

DETROIT, MICHIGAN

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[16] C. Revis and F. S. Kipping, *Trans., J. Chem. Soc.*, **71**, 243 (1897). The disproportionation of an α-bromoketone into an α,α-dibromoketone and an unbrominated ketone in the presence of base has been noted recently by Lyle and Covey, ref. 2.

[17] O. von Wallach, *Ann.*, **437**, 174 (1924).

[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF OAK RIDGE NATIONAL LABORATORY]

C^{14}-Tracer Studies in the Rearrangements of Unsymmetrical α-Diketones. V.[1] Substituted Benzils[2]

BY MARION T. CLARK,[3a] EDWARD C. HENDLEY[3b] AND O. KENTON NEVILLE[1]

RECEIVED APRIL 1, 1954

Four unsymmetrically substituted benzils, each labeled with carbon-14 in the carbonyl group adjacent to the unsubstituted phenyl ring have been studied to determine the migration preferences of the aryl group. The percentages migration of the substituted groups as opposed to phenyl were found experimentally to be: *p*-methoxyphenyl, 31.3; *p*-methylphenyl, 38.8; *p*-chlorophenyl, 67.2; *m*-chlorophenyl, 81.2. The migration ratios, corrected for isotope effect, were found to be capable of correlation by the Hammett equation. These data emphasize the importance of the point of attack of hydroxyl ion in determining the course of the reaction and cast doubt on the postulation that the attack is reversible.

The benzilic acid rearrangement, though apparently the earliest recognized[5] organic rearrangement and though much discussed since its discovery, is still poorly understood mechanistically. The confusion is apparently due equally to the dearth of experimentation and to the wealth of discussion, for the tendency has prevailed to force this reaction into a common class with others to which it bears only the faintest resemblance.[6]

The present paper, which presents the results obtained in the study of four unsymmetrically substituted carbon-14 labeled benzils, records no solution to the question of the mechanism of this reaction but rather indicates the need for a new interpretation of the accumulated evidence.

The transformation of benzil to benzilic acid is known to occur in aqueous solution in the absence of base,[7] and in certain basic media in the absence

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[1] Previous paper in this series: E. C. Hendley and O. K. Neville, THIS JOURNAL, **75**, 1995 (1953).

[2] This document is based upon work performed under contract W-7405 eng. 26, for the Atomic Energy Commission at the Oak Ridge National Laboratory.

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[4] Nuclear Instrument and Chemical Corporation, 223 West Erie, Chicago, Ill.

[5] J. von Liebig, *Ann.*, **25**, 27 (1838).

[6] J. U. Nef, *ibid.*, **298**, 372 (1897); G. Schroeter, *Ber.*, **42**, 2341 (1909); M. Tiffeneau, *Rev. Gen. Sci.*, 585 (1907); H. Staudinger and A. Binkert, *Helv. Chim. Acta*, **5**, 703 (1922); A. Michael, THIS JOURNAL, **42**, 813 (1920); F. C. Whitmore, *ibid.*, **54**, 3274 (1932).

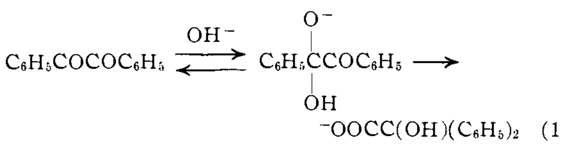
[7] H. Klinger, *Ber.*, **19**, 1868 (1886); A. Jena, *Ann.*, **155**, 78 (1870).

of water[8] but is apparently not subject to general base catalysis. This is indicated by the failure of sodium ethoxide to induce the reaction[9] in dry alcohol as well as by the finding that phenolate or *o*-chlorophenolate ion does not change the rate of the reaction in aqueous ethanol solution.[10] The reaction is apparently induced specifically by the hydroxyl ion.[11]

The reaction in aqueous ethanol solution has been found to be homogeneous, unaffected by added peroxide and of the second order (first order each in benzil and hydroxyl ion) over a sevenfold concentration change.[10]

Benzil has been shown to undergo rapid complete exchange of its carbonyl oxygen atoms, with O^{18}-enriched water in the presence of alkali, much more slowly in neutral solution and to an imperceptible extent in the presence of acids.[12]

On the basis of these data, the rearrangement has been postulated[12] to occur by the preliminary reversible addition of hydroxyl ion to one carbonyl group followed by irreversible migration of an aryl group to the adjacent carbon atom.



$$C_6H_5COCOC_6H_5 \xrightleftharpoons{OH^-} C_6H_5\overset{O^-}{\underset{OH}{C}}COC_6H_5 \longrightarrow {}^-OOCC(OH)(C_6H_5)_2 \quad (1)$$

Since this presentation gives no picture of the shape of the activated complex, no prediction can be made as to which of two aryl groups would migrate if they were dissimilar. Previous work in this Laboratory[13] and elsewhere[14,15] has demonstrated that in those cases in which the carbonyl group reactivities would be expected to be quite different (due to the nature of the adjacent R-group), the R-group adjacent to the (presumed) most active carbonyl group undergoes migration to the exclusion of the other. If the difference in R-group influence is more subtle, as by the presence of a substituent group in one aromatic nucleus, the course of the migration would be expected to be influenced similarly but to a less pronounced degree. Such results have been reported for *p*-methoxybenzil[15] and more recently for a series of chlorophenanthraquinones.[16]

In the present work, four benzils, each bearing a substituent in one aromatic ring and each labeled with carbon-14 in the carbonyl carbon atom adjacent to the unsubstituted phenyl group were prepared and subjected separately to the conditions of the rearrangement. The resultant substituted benzilic acid was isolated in each case and degraded to carbon dioxide and the respective benzophenone.

The ratio of the millimolar radioactivity of the benzophenone to that of the benzilic acid (or a precursor) multiplied by 100 gives the percentage migration of the substituted phenyl group. The ratio of the millimolar radioactivity of the benzophenone to that of the carbon dioxide[17] gives the migration ratio of the substituted and unsubstituted phenyl groups uncorrected for isotope effect—the relative case of breaking the C^{12}–C^{12} and C^{12}–C^{14} bonds. This correction has been reported to be approximately 11% for benzil[18] and approximately the same for substituted phenanthraquinones.[16]

Table I shows the experimentally determined percentage migrations of the substituted phenyl groups in the rearrangements of *p*-methoxy-, *p*-methyl-, *p*-chloro- and *m*-chlorobenzil. Column 3 shows the calculated migration ratios, column 4 has the migration ratios corrected for an 11%[19] isotope effect and column 5 the corrected percentage migrations of the substituent group.

TABLE I

PERCENTAGE MIGRATIONS AND MIGRATION RATIOS OF SUBSTITUTED PHENYL GROUPS IN REARRANGEMENTS OF C_6H_5COCOR

1 R	2 Migration R, %	3 Migration R *vs.* phenyl	4 Adjusted migration R	5 Adjusted % migration R
p-Methoxyphenyl	31.3	0.456	0.406	28.9
p-Methylphenyl	38.8	0.634	0.564	36.0
p-Chlorophenyl	67.2	2.05	1.82	64.6
m-Chlorophenyl	81.2	4.10	3.65	78.5

It is apparent from these results that phenyl groups carrying electron-donor substituents migrate to a lesser extent than phenyl, while those with electron-attracting substituents move to a greater degree. This is the reverse of the results reported for symmetrical pinacols[20] but similar to those for unsymmetrical pinacols.[21]

These results are supported by the report of Smith and Ott[16] that the percentages migration of the substituted rings in the alkaline rearrangements of 2-, 3- and 7-chlorophenanthraquinone-9-C^{14} were found to be 83.1, 66.8 and 79.8, respectively, surprisingly close to the corresponding benzil results.

If the corrected migration ratios of Table I

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[8] G. Scheuing, *Ber.*, **56**, 252 (1923); T. Evans and W. Dehn, THIS JOURNAL, **52**, 252 (1930).

[9] A. Lachman, *ibid.*, **44**, 330 (1922); **45**, 1509 (1923).

[10] F. H. Westheimer, *ibid.*, **58**, 2209 (1936); see also *J. Org. Chem.*, **1**, 339 (1936).

[11] A possible exception is the preparation of benzilic acid by the reaction of benzil with sodamide in toluene and treatment of the resultant mixture with water; M. Kasiwagi, *Bull. Chem. Soc. Japan*, **1**, 66 (1926); *C. A.*, **20**, 2491 (1926). The identity of the products prior to treatment with water is not reported, however.

[12] I. Roberts and H. C. Urey, THIS JOURNAL, **60**, 880 (1938).

[13] (a) O. K. Neville, *ibid.*, **70**, 3499 (1948); (b) C. J. Collins and O. K. Neville, *ibid.*, **73**, 2471 (1951); (c) H. W. Davis, E. Grovenstein and O. K. Neville, *ibid.*, **75**, 3304 (1953).

[14] W. E. Doering, T. I. Taylor and E. F. Schoenewaldt, *ibid.*, **70**, 455 (1948).

[15] J. D. Roberts, D. R. Smith and C. C. Lee, *ibid.*, **73**, 619 (1951).

[16] D. G. Ott and G. G. Smith, *ibid.*, **77**, 2325 (1955).

[17] In practice, the carbon dioxide from such a degradation is usually found to be low in specific activity because of contamination from normal carbon dioxide introduced from the air, by reagents and from side oxidations. Since the handling and assay of organic materials is much more reliable, the migration ratio is better calculated by dividing the percentage migration as obtained from such assays by one hundred minus this percentage. The ratios herein recorded are so calculated. Such migration ratios are relatively less precise than the percentage figures, since a 1% error in the determination of the percentage results in an approximate 6% error in the ratio.

[18] W. H. Stevens and R. W. Attree, *J. Chem. Phys.*, **18**, 574 (1950).

[19] This correction assumes that the isotope effect is the same for all of the reactions, a simplification which is necessary in the absence of further information.

[20] W. E. Bachmann and F. H. Mosher, THIS JOURNAL, **54**, 1124 (1932).

[21] W. E. Bachmann and H. Sternberger, *ibid.*, **56**, 2081 (1934).

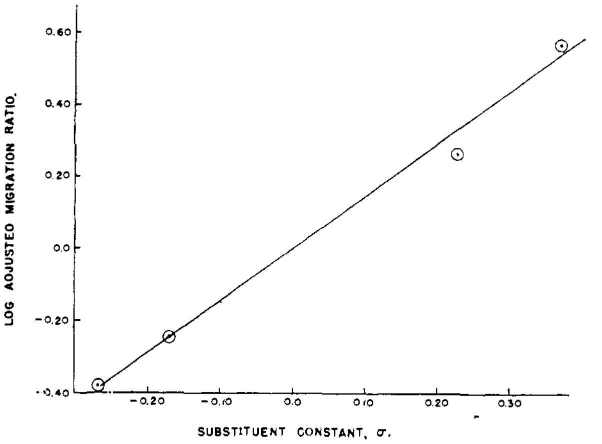


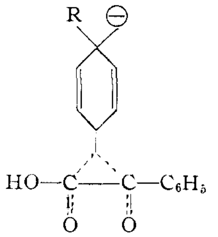
Fig. 1.

are plotted in the form of their logarithms against the respective substituent constant, σ, as tabulated by Hammett,[22] a straight line is obtained whose slope (reaction constant, ρ) is found to be approximately 1.43.

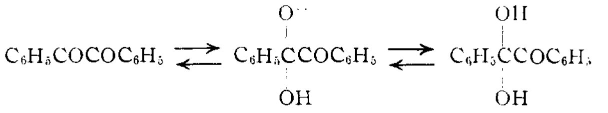
These results, regardless of the exact interpretation, add reinforcement to the previously reported[13–15] apparent importance of the relative carbonyl group reactivities in determining the course of the rearrangements.

Roberts, Smith and Lee[15] have accepted the mechanism pictured in equation 1 and have explained the inferior migration of *p*-methoxyphenyl as opposed to phenyl in the rearrangement by the assumption that the equilibrium constant ratio for the formation of the two possible ionic intermediates must be very much larger than the rate constant ratio of the succeeding migration. Such an explanation almost necessarily implies that the reaction rates of *p*-methoxybenzil and of *p*-methylbenzil must be greater than for benzil itself. Although no evidence is available for *p*-methoxybenzil, Blanksma and Zaaijer[23] have reported that *p*-anisil rearranges much more slowly than benzil itself. More recently, Black[24] has confirmed these results and in addition has shown that the bimolecular rate constant for the rearrangement of *p*-methylbenzil is 0.206 as compared with 0.488 for benzil, both expressed as liters per mole per hour and determined in aqueous dioxane solution. Similarly, the rate constant for 3-methylbenzil was determined to be 0.273 and for *p,p'*-diaminobenzil, 0.023. In view of these results one must conclude that either the presumed intrinsic migratory aptitudes of the groups have little play in the present reaction or are the reverse of those found in other reactions.[20,25]

For example, to account for the present results in terms of the picture shown in equation 1 the postulation is possible that the group which can better stabilize a negative charge will migrate preferentially. An important characteristic of the presumed transition state could be represented as[26]



A second possibility is that the proposed mechanism[12] involving preliminary *reversible* addition of hydroxyl ion is *incorrect*. The data herein reported and its correlation by the Hammett equation strongly suggest the intervention of hydroxyl ion directly in the rate-controlling step, the point of attack of hydroxyl ion being conclusive in directing the course of rearrangement of an unsymmetrical benzil. To account for the rapid O[18] exchange between benzil and water requires that this reaction be relegated to a side issue insofar as the rearrangement is required, the reversible reaction being probably the base-catalyzed conversion to the hydrate, possibly through the negative ion.



$$C_6H_5COCOC_6H_5 \rightleftarrows C_6H_5\underset{OH}{\overset{O^-}{C}}COC_6H_5 \rightleftarrows C_6H_5\underset{OH}{\overset{OH}{C}}COC_6H_5$$

The second-order rate dependence, the correlation of the present data by the Hammett equation, and the value of the slope, ρ, indicate a possible similarity in mechanism of the benzilic acid rearrangement to the base-catalyzed hydrolysis of esters. Indeed, Bender[27] has recently reported that O[18]-carbonyl labeled benzoate esters undergo oxygen exchange with the basic aqueous media during hydrolysis, the exchange reaction being slower than the hydrolysis by approximately a factor of 10. These results were interpreted as indicating the presence of a hydrated intermediate state in the hydrolysis reaction. If the analogy with the benzilic acid rearrangement is valid, the exchange might better be interpreted as due to a competing hydration reaction, slower than that found with benzil because of the difference in ester and diketone carbonyl group reactivities.

A serious failing of this attempted analogy appears to lie in the specificity of hydroxyl ion as the reagent for the benzilic acid rearrangement as compared with the larger number of anionic reagents which can displace the alkoxyl group from an ester. A possible explanation, which must be regarded as pure speculation in the absence of confirming data, is derived by an examination of molecular models. Such a study indicates that an important contribution to the transition state of the benzil reaction might well be a hydrogen bound *quasi*-ring[28] below in which the hydroxyl hydrogen

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[22] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 188.

[23] J. H. Blanksma and W. H. Zaaijer, *Rec. trav. chim.*, **57**, 883 (1938).

[24] M. L. Black, Doctoral thesis, University of Tennessee, December, 1949.

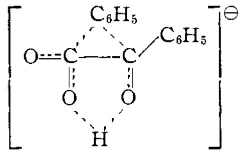
[25] J. G. Burr, Jr., and L. Ciereszko, THIS JOURNAL, **74**, 5426, 5431 (1952). These articles summarize and give references to migratory aptitude data from various sources.

[26] The suggestion as to the possible intervention of such forms in the transition state was made by Dr. J. D. Roberts in private communication.

[27] M. L. Bender, THIS JOURNAL, **73**, 1626 (1951).

[28] Doering, Taylor and Schoenewaldt, ref. 14, have postulated the contribution of such a form to the transition state of the phenylglyoxal reaction.

is passed intramolecularly to the adjacent oxygen simultaneously with phenyl group migration. When such a ring is formed deliberately with a model of



the negative ion (equation 1), the hydrogen atom is found to lie very close to the adjacent carbonyl oxygen and the phenyl groups are relatively unhindered. The formation of such a ring also is possible with phenanthraquinone models, such an arrangement being in fact encouraged by the tie bond between the aromatic rings.

Addenda such as methoxide, ethoxide and phenolate do not fit well in such an arrangement,[29] and would not be expected to permit intramolecular migration of a group coincident with phenyl migration.

Regardless of the bearing of the present data on the mechanistic interpretation, the correlation of these data by the Hammett equation makes possible the prediction of the migration ratios of other *meta*- and *para*-substituted unsymmetrical benzils for which σ-values are available. Since the available data[16] on substituted phenanthraquinones are so nearly identical with those for corresponding benzils, it would seem reasonable that predictions of migration ratios for other phenanthraquinones could also be made from the same Hammett plot.

In conclusion, the relative ease and precision of studies involving labeled benzils and other α-diketones would seem to offer real advantages for the direct comparison of carbonyl group reactivities uncomplicated by many of the problems which accompany rate determinations.

Experimental

Radioactivity Measurements.—Radioactivity assays were carried out by wet combustion of 5- to 20-mg. samples of purified organic compounds or by acidification of barium carbonate samples and determination of the ion current of the carbon dioxide in a 250-ml. ion chamber.[13a] The ion current was measured with a vibrating reed electrometer by direct comparison with a standard chamber which had been calibrated in terms of the carbon dioxide derived from sodium carbonate solution supplied by the National Bureau of Standards. Prior to each assay, the background ion current was measured and subtracted from that for the gas sample except where it was negligibly small.

Organic samples were purified in each case to constant specific activity and were assayed in replicate, the criterion of acceptable purity being that the deviation of the mean of the millimolar radioactivities of all compounds in a synthetic series in which no dilution or division of activity had occurred should be no larger than ±1% calculated for the 95% confidence interval. The migration percentages reported are therefore subject to an error of less than ±2%.

Benzamide-*carbonyl*-C^{14}.—The carbonyl-labeled benzamide, from which three of the substituted benzils were prepared, was made by carbonation of the phenyl Grignard reagent with carbon-C^{14} dioxide and conversion of the resultant benzoic acid to benzamide through the acid chloride. The radiochemical yield of the conversion which resulted in 22.9 g. of product, m.p. 121.5°, 5.3 μc./mmole, was 76.2%. The material was diluted with non-radioactive benzamide for use in the syntheses below.

***p'*-Chlorodesoxybenzoin-*carbonyl*-C^{14}.**—Three of the substituted desoxybenzoins were prepared by slight modifications of a method described by Jenkins.[30] One such preparation will be described in detail.

In a 100-ml., 3-necked flask, equipped with a stirrer, a nitrogen inlet tube, an addition funnel and a reflux condenser was prepared *p*-chlorobenzylmagnesium chloride from 16.0 g. of *p*-chlorobenzyl chloride[31] and 2.4 g. of magnesium in 50 ml. of dry ether. After the bright green reagent had formed (about one hour) a small Soxhlet extractor, containing 3.0 g. of dry benzamide-*carbonyl*-C^{14}[32] was placed between the reactor flask and the condenser. The ether solution was heated under reflux with constant stirring for three days during which time the benzamide was extracted completely into the solution. A constant pressure of dry nitrogen was maintained over the reaction mixture. After hydrolysis of the reaction complex with aqueous hydrochloric acid, the ketone was recovered from the ether solution and recrystallized repeatedly from ethanol-water solution. The yield of white crystals was 4.5 g. or 78% of the theoretical amount; m.p. 132°[33]; radioactive assay, 5.38 × 10^{-3} μc. per mg.

***m'*-Chlorodesoxybenzoin-*carbonyl*-C^{14}.**—Similarly, 3.57 g. (58.5%) of *m'*-chlorodesoxybenzoin-*carbonyl*-C^{14}, m.p. 44°,[34] was prepared from 3.2 g. of benzamide-*carbonyl*-C^{14} and 22.0 g. of *m*-chlorobenzyl chloride; radioactive assay, 4.27 × 10^{-3} μc./mg.

***p'*-Methyldesoxybenzoin-*carbonyl*-C^{14}.**—From 5.0 g. of benzamide-*carbonyl*-C^{14}, 36.1 g. of *p*-methylbenzyl chloride, and 20 g. (an excess) of magnesium was prepared 3.7 g. (38.9%) of *p*-methyldesoxybenzoin-*carbonyl*-C^{14}, m.p. 96°[35]; radioactive assay, 2.53 × 10^{-3} μc./mg.

***p'*-Methoxydesoxybenzoin-*carbonyl*-C^{14}.**—The preparation of this substituted desoxybenzoin by the Grignard reaction failed due to preferential coupling of the reagent.

The desired desoxybenzoin was prepared successfully through a reaction scheme previously described[13d] involving the rearrangement of *p*-methoxybenzylidene-(aceto-1-C^{14})-phenone oxide and decarboxylation of the resultant 2-hydroxy-2-phenyl-3-(*p*-methoxyphenyl)-propionic acid. The over-all radiochemical yield from acetophenone-*carbonyl*-C^{14} was 32.3%, m.p., 70°[36]; radioactive assay, 2.38 × 10^{-3} μc./mg.

***p*-Chlorobenzil-C^{14}.**[37]—One gram of *p'*-chlorodesoxybenzoin was dissolved in 4 ml. of acetic anhydride to which was added 0.86 g. of selenium dioxide. The solution was heated at 140° for three hours, removed from the precipitated selenium with a micropipet and heated with 5 ml. of water and 0.1 g. of charcoal. Removed by filtration from the chilled solution, the yellow crystalline material was recrystallized from aqueous ethanol and dried *in vacuo*. The yield was 1.2 g. or 96% of theoretical; m.p. 73°[38]; radioactive assay, 5.03 × 10^{-3} μc./mg.

***m*-Chlorobenzil-C^{14}.**—Following the procedure above 2.31 g. of *m'*-chlorodesoxybenzoin-*carbonyl*-C^{14} was converted by 1.66 g. of selenium dioxide in acetic anhydride solution to 2.3 g. (95%) of *m*-chlorobenzil, m.p. 86°. *Anal.* Calcd. for $C_{14}H_9O_2Cl$: C, 68.71; H, 3.68. Found: C, 68.64; H, 3.73; radioactive assay, 4.06 × 10^{-3} μc./mg.

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[29] The amido group is found to fit in such a quasi-ring but would not be expected to allow migration of a hydrogen atom. It seems possible that in this case an intermediate structure might be formed which is converted to benzilic acid by the addition of water. A stable intermediate of unknown structure is known to be capable of formation in the presence of potassium hydroxide and pyridine.[8]

[30] S. S. Jenkins, THIS JOURNAL, **55**, 703 (1933).

[31] The *p*-chloro-, *m*-chloro- and *p*-methylbenzyl chlorides used in the syntheses were prepared by lithium aluminum hydride reduction of the correspondingly substituted benzoic acids and treatment of the resulting substituted benzyl alcohols with phosphorus trichloride.

[32] The benzamide prepared as described above was diluted with non-radioactive benzamide and recrystallized before further use.

[33] *Cf.* K. Petrenko and M. Kritshenko, *Ber.*, **25**, 2240 (1892).

[34] S. S. Jenkins, THIS JOURNAL, **55**, 2896 (1933).

[35] M. Tiffeneau, *Bull. soc. chim.*, **49**, 1595 (1888).

[36] The value of 132–134° previously reported[13d] is incorrect, an error called to our attention by Dr. C. J. Collins who suggested the present preparative method and gave valuable help and advice in its methodology.

[37] These unsymmetrical benzils labeled in the carbonyl group adjacent to the unsubstituted phenyl ring are difficult to designate without resort to a somewhat involved name such as *p*-chlorobenzoyl-(formyl-C^{14})-benzene or 1-phenyl-2-*p*-chlorophenylethanedione-1-C^{14}.

[38] *Cf.* H. H. Hatt, A. Pilgrim and W. Hurran, *J. Chem. Soc.*, 93 (1936).

p-Methylbenzil-C^{14}.—Similarly 2.3 g. of p'-methyldesoxybenzoin-*carbonyl*-C^{14} was treated with 1.82 g. of selenium dioxide in 3.5 ml. of acetic anhydride, to give 1.72 g. (70.2%) of p-methylbenzil, m.p. 31°[38]; radioactive assay, 2.38 × 10^{-3} μc./mg.

p-Methoxybenzil-C^{14}.—Acetic anhydride was found to be a poor solvent for the selenium dioxide oxidation of p'-methoxydesoxybenzoin, tending to give non-crystallizing oils. The oxidation was successful when 1.66 g. of the material was treated with 0.7 g. of selenium dioxide in 12 ml. of dioxane for three hours, to give 1.54 g. (87%) of p-methoxybenzil, m.p. 62.0°[39]; radioactive assay, 2.27 × 10^{-3} μc./mg.

p-Chlorobenzilic-C^{14} Acid.[40]—A 0.9-g. portion of p-chlorobenzil was added to 10 ml. of water and 5 ml. of ethanol to which had been added 4 g. of sodium hydroxide. Nitrogen was bubbled through the solution to remove air, and the solution was allowed to stand at room temperature for three days being stirred slowly with a magnetic bar. The solution was extracted with ether, acidified and re-extracted. The solid acid residue after evaporation of the ether was recrystallized several times from aqueous ethanol and dried *in vacuo*. The white crystalline product, m.p. 130°,[41] weighed 0.68 g., or 70% of the theoretical amount; radioactive assay, 4.76 × 10^{-3} μc./mg.

m-Chlorobenzilic-C^{14} Acid.—Following a similar procedure 1.0 g. of m-chlorobenzil was converted in alkaline aqueous alcoholic ethanol to 0.56 g. (52.1%) of white crystalline m-chlorobenzilic acid, m.p. 98°; radioactive assay, 3.74 × 10^{-3} μc./mg. *Anal.* Calcd. for $C_{14}H_{11}O_3Cl$: C, 64.11; H, 4.19. Found: C, 64.15; H, 4.21.

p-Methylbenzilic-C^{14} Acid.—Similarly, 0.383 g. of p-methylbenzil was converted to 0.2737 g. (66.2%) of p-methylbenzilic acid, m.p. 133°[38]; radioactive assay, 2.22 × 10^{-3} μc./mg.

p-Methoxybenzilic Acid.—By a similar procedure 440 mg. of p-methoxybenzil was converted to 200 mg. (42.3%) of p-methoxybenzilic acid, m.p. 148°[42]; radioactive assay, 2.08 × 10^{-3} μc./mg.

Degradation of p-Chlorobenzilic Acid.—All of the benzilic acid degradations were carried out similarly in an apparatus consisting of a 25-ml. reaction vessel with additional funnel and nitrogen inlet tube—connected to a short reflux condenser which was in turn connected to two traps containing barium carbonate solution. Before the barium hydroxide tubes were attached, the solid benzilic acid and dry chromic anhydride were added to the reaction vessel and the system was swept with dry nitrogen. The barium hydroxide tubes were connected, and a few ml. of glacial acetic acid was allowed to flow into the reaction flask. The reaction was allowed to proceed at room temperature with occasional gentle warming and constant magnetic stirring until barium carbonate began to form in the second trap. (The first trap contained an amount of barium hydroxide calculated to react with 90% of the released carbon dioxide.) This required about an hour and a half. The barium carbonate was collected by centrifugation, washed with carbonate-free water and dried at 100° *in vacuo*. The reaction mixture was diluted, neutralized and extracted to isolate the substituted benzophenone, which was purified by crystallization or converted to a derivative for radioactive assay.

In this way 432 mg. of p-chlorobenzilic acid was oxidized with 144 mg. of chromic anhydride in 3 ml. of acetic acid to yield 160 mg. of p-chlorobenzophenone (74%), m.p. 76°[43]; radioactive assay, p-chlorobenzophenone, 3.85 × 10^{-3} μc./mg.; barium carbonate, 2.0 μc./mg.

Degradation of m-Chlorobenzilic Acid.—A 300-mg. sample of m-chlorobenzilic acid was oxidized with 86 mg. of chromic anhydride to give 185 mg. (85.7%) of m-chlorobenzophenone, m.p. 84°[44]; radioactive assay, m-chlorobenzophenone, 3.70 μc./mg.; barium carbonate, 0.865 × 10^{-3} μc./mg.

Degradation of p-Methylbenzilic Acid.—A 99.49-mg. sample of p-methylbenzilic acid was oxidized with 31 mg. of chromic anhydride in one ml. of acetic acid to give 77 mg. (93%) of p-methylbenzophenone, m.p. 55°[45]; radioactive assay, p-methylbenzophenone, 2.08 × 10^{-3} μc./mg.; barium carbonate, 1.63 × 10^{-3} μc./mg.

Degradation of p-Methoxybenzilic Acid.—A 60-mg. portion of p-methoxybenzilic acid was oxidized by 16 mg. of selenium dioxide in 3 ml. of acetic acid to 39 mg. (79%) of p-methoxybenzophenone, m.p. 61°[46]; radioactive assay, p-methoxybenzophenone, 0.797 × 10^{-3} μc./mg.; barium carbonate, 1.57 × 10^{-3} μc./mg.

Acknowledgment.—We wish to acknowledge helpful and stimulating discussions with Dr. J. D. Roberts of the California Institute of Technology, Dr. Walter M. Lauer of the University of Minnesota, Dr. H. C. Urey and Dr. Weldon G. Brown of the University of Chicago and Dr. G. G. Smith of Washington State College.

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[39] *Cf.* A. McKinsie, E. M. Luis, E. M. Tiffeneau and P. Weill, *Bull. soc. chim.*, **45**, 414 (1929).

[40] The development of a proper nomenclature is difficult for a labeled compound such as this which is actually a mixture of unequal amounts of three kinds of molecules (actually many more than three, if the normal C^{-13} content is taken into account). It seems wiser to treat such compounds as mixtures, which are usually nameless in the absence of a trivial name. The C^{-14} is added to the name for cataloging purposes.

[41] A. H. Ford-Moore, *J. Chem. Soc.*, 952 (1947).

[42] E. Christie, A. McKensie and A. Richtie, *ibid.*, 153 (1935).

[43] *Cf.* R. Montagne, *Rec. trav. chim.*, **26**, 263 (1907).

[44] *Cf.* A. Hantzsch, *Ber.*, **24**, 57 (1891).

[45] *Cf.* T. Zincke, *Ann.*, **161**, 108 (1867).

[46] *Cf.* T. J. Peterson, *Am. Chem. J.*, **46**, 335 (1911).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF NOTRE DAME]

The Reaction of Some Diketones with Sodium Acetylide

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RECEIVED NOVEMBER 22, 1954

A number of diketones were treated with sodium acetylide in liquid ammonia: acetonylacetone, diacetyl, benzil, acetylacetone, allylacetylacetone and diallylacetylacetone. The preparation of allylacetylacetone and diallylacetylacetone is described. It was also found that diacetone alcohol reacted with sodium acetylide to produce 3-methyl-3-hydroxy-1-butyne.

Milas and co-workers[2] and more recently Papa and co-workers[3] added sodium acetylide to acetonylacetone and diacetyl to produce diacetylenicdiols. The purpose of our investigation was to study the reaction of sodium acetylide with a number of diketones.

Sodium acetylide added to acetonylacetone and diacetyl, the former giving 3,6-dimethyl-3,6-dihydroxy-1,7-octadiyne (I) in 34% yield, and the latter, 3,4-dimethyl-3,4-dihydroxy-1,5-hexadiyne in the form of the hemihydrate II in 23% yield. Our results were interesting in that other workers[2,3] isolated compound II in the anhydrous form.

The structures of the products I and II were verified by tests for terminal acetylenic bonds, by char-

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[1] Rev. Ralph B. Davis, C.S.C.

[2] N. A. Milas, R. J. Brown and O. Phillips, THIS JOURNAL, **70**, 2862 (1948).

[3] D. Papa, F. J. Villani and H. F. Ginsberg, *ibid.*, **76**, 4116 (1954).