indicated by bands at 1559, 1540, 1377 and 1328 cm.$^{-1}$. The SO_2(str.) at 1358 and 1158 cm.$^{-1}$ is indicative of the presence of a sulfone.

No pure product could be isolated from the reaction of this compound with the sodium salt of thiophenol.

URBANA, ILLINOIS

[CONTRIBUTION FROM HAVEMEYER LABORATORY, COLUMBIA UNIVERSITY]

The Benzilic Ester Rearrangement[1]

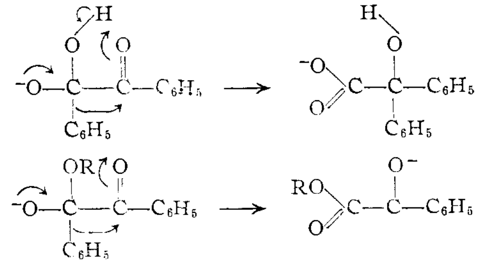
BY W. VON E. DOERING[2] AND R. S. URBAN

RECEIVED JULY 6, 1956

The benzilic ester rearrangement has been realized in the conversions of benzil to *t*-butyl benzilate and methyl benzilate with potassium *t*-butylate and methylate, respectively. The rearrangement of benzil with oxidizable alkoxide ions generally competes with the Meerwein–Ponndorf–Verley–Oppenauer equilibration and the subsequent cleavage of benzoin with alkoxide ions. So, for example, with ethoxide ion these competitions are unfavorable and no benzilic ester rearrangement can be detected. With this limitation the rearrangement is probably a general one. In benzene solution where, from freezing point measurement, it appears to be present as the tetramer, potassium *t*-butylate effects the rearrangement very rapidly in high yield in a clearly second-order reaction with a heat of activation of 19 ± 2 kcal. The condition of "specific hydroxide-ion catalysis," previously accepted as a characteristic of the benzilic rearrangement, is invalid and its mechanistic formulation as a simultaneous proton transfer is no longer *necessary* and may be incorrect. Another example of the mechanistically related, but relatively rare, alkaline tertiary ketol rearrangement has been uncovered in the reaction of benzil with mesitylmagnesium bromide to give *mesitoyl*diphenylcarbinol instead of the expected *benzoyl*phenylmesitylcarbinol.

The benzilic acid rearrangement has come to be considered a reaction specifically effected by hydroxide-ion.[3] This conviction has rested on several pieces of evidence: the formation from benzil and potassium *hydroxide* of an addition product which rapidly proceeds to benzilic acid on warming[4]; the rapid *hydroxide*-ion catalyzed exchange of oxygen-18 in benzil[5] by H_2O^{18}; the demonstrations by Westheimer[6] that the rearrangement is second order, first order each in benzil and *hydroxide* ion,[6a] that two other bases, phenolate and *p*-chlorophenolate ions, are neither catalysts nor reagents[6a] and that the intermediate is a negatively charged species[6b]; and the failure of alkoxide ion to effect the rearrangement. Illustrations of this last type are to be found in the reaction of benzil and sodium ethoxide which, alone, gives an adduct without rearrangement[4] and which, in ethanol, gives benzoic acid, ethyl benzoate, benzaldehyde and traces of benzilic acid[7]; in the reaction of the benzil-sodium methoxide adduct in benzene to give benzoin (13%) and sodium benzilate (6%)[4]; in the reaction of benzil and sodium ethoxide to give, in addition to the products isolated by Lachmann, ethyldibenzoin[8] later shown to be 1-hydroxy-3,4-diphenyl-4-benzoyltetrahydrofuran,[9] a condensation product of benzaldehyde, acetaldehyde and benzoin; and in the observation of Swan that benzil and potassium *t*-butylate in ether gives benzilic acid.[10]

The apparent failure of alkoxides to effect the benzilic acid rearrangement has been denied,[11] thought mysterious[12] and considered to support the hypothesis of "specific hydroxide-ion catalysis."[13] However, as a generally accepted characteristic of the benzilic rearrangement, specific hydroxide-ion utilization (scarcely catalysis in any sense) represented one of the conditions to be satisfied by a mechanistic hypothesis. One satisfying this condition is the Michael hypothesis[14] (restated in contemporary language here and by Clark, Hendley and Neville[15e] who, however, make reference in this connection only to Doering, Taylor and Schoenewaldt[16]) that the transition state involves simultaneously rearrangement of phenyl and neutralization of the incipient carboxyl group by a migration of a proton (A). This exothermic step can only contribute to the reaction when hydroxide ion is the rearranging base and would be precluded were alkoxide ion the rearranging agent (B).



(A)

(B)

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[1] Taken from a dissertation submitted April 1, 1949, by Richard Stephen Urban in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science of Columbia University.

[2] Sterling Chemistry Laboratory, Yale University, New Haven, Conn.

[3] C. K. Ingold, *Ann. Repts. on Progr. Chem.* (*Chem. Soc. London*), **25**, 124 (1928).

[4] G. Scheuing, *Ber.*, **56**, 252 (1923).

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

[6] (a) F. H. Westheimer, *ibid.*, **58**, 2209 (1936); (b) *J. Org. Chem.*, **1**, 339 (1936).

[7] A. Lachmann, THIS JOURNAL, **45**, 1509 (1923).

[8] M. E. Owen and F. R. Japp, *Am. Chem. J.*, **7**, 16 (1886).

[9] J. B. Garner, *ibid.*, **32**, 600 (1904).

[10] G. Swan, *J. Chem. Soc.*, 1408 (1948).

[11] M. J. S. Dewar, "Electronic Theory of Organic Chemistry," Oxford Univ. Press, London, England, 1949, p. 218.

[12] E. R. Alexander, "Principles of Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 199.

[13] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 321.

[14] A. Michael, THIS JOURNAL, **42**, 787 (1920).

[15] (a) O. K. Neville, *ibid.*, **70**, 3499 (1948); (b) C. J. Collins and O. K. Neville, *ibid.*, **73**, 2471 (1951); (c) E. C. Hendley and O. K. Neville, *ibid.*, **75**, 1995 (1953); (d) H. W. Davis, E. Grovenstein and O. K. Neville, *ibid.*, **75**, 3304 (1953); (e) M. T. Clark, E. C. Hendley and O. K. Neville, *ibid.*, **77**, 3280 (1955).

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

Rather than accept the condition of specific hydroxide-ion utilization (and have our thinking about the mechanism forced into line), we chose to remove the condition entirely by showing it to be experimentally (as well as rationally[11]) untenable. With the knowledge that benzil is an excellent oxidizing agent for alcohols in the presence of their alkoxides[17] and thinking that the rearrangement of benzil with alkoxide ion must of necessity fail whenever benzil is reduced faster by the alkoxide ion than it is rearranged, we attempted the benzilic ester rearrangement with potassium *t*-butylate where the Meerwein–Ponndorf–Verley–Oppenauer equilibration is excluded.

The fact is that benzil and *t*-butylate ion react with rearrangement in refluxing anhydrous *t*-butyl alcohol to give *t*-butyl benzilate. The yield is a mixture of the ester and free benzilic acid in 76 and 10% of theory, respectively. The mode of formation of free benzilic acid, being easily rationalized as a thermal or EN2 elimination, appeared uninteresting and was pursued no further.

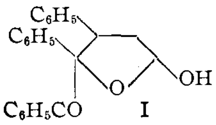
The structure assigned to *t*-butyl benzilate is consistent with the formation of benzilic acid by hydrolysis with dilute sulfuric acid, by saponification (where *t*-butyl alcohol was also isolated) and by heating a few minutes at 185°. This latter pyrolytic decomposition is quite characteristic of the esters of tertiary aliphatic alcohols.[18] *t*-Butyl benzilate was synthesized from methyl benzilate and potassium *t*-butylate in *t*-butyl alcohol by transesterification.

Phenoxide ion, found by Westheimer[6a] to have no effect on the rate of the benzilic acid rearrangement in aqueous ethanolic solution, as the slightly soluble potassium salt left benzil unchanged after refluxing for two hours in dry benzene. There seems to be no reason to alter Westheimer's explanation of the failure.

With primary and secondary alkoxide ions, the Meerwein–Ponndorf–Verley–Oppenauer equilibration becomes competitive so that the benzilic ester rearrangement will only be detectable when its rate is greater than roughly one-tenth the rate of the oxidation–reduction. An additional complication may arise if the conjugate aldehyde or ketone of the alkoxide ion undergoes aldol condensation with subsequent elimination of water. This water, which would be present largely as hydroxide ion when formed during an attempted benzilic *ester* rearrangement, could then effect the benzilic *acid* rearrangement.

Boiling, anhydrous, methanolic sodium methoxide reacts with benzil to give methyl benzilate (68% of theory resulting from the benzilic ester rearrangement), benzoin (9.6% of theory; detectable but not predominant as one of the products of the M.P.V.O. equilibration), benzilic acid (9.7% of theory; quite probably the product of a displacement reaction of methoxide ion on methyl benzilate)[19] and, in very small amount, benzaldehyde, a product also obtained by Lachmann from benzil and sodium ethoxide.[7] Previously, Scheuing[4] had heated the addition product from benzil and sodium methoxide in benzene for 15 minutes and had recovered much benzil (61%), some benzoin (13%), a little sodium benzilate (6%) but no methyl benzilate. From the closely related reaction of benzil and sodium methoxide suspended in benzene at the boiling point for 2 hr., there have now been isolated benzoic acid (8%), benzoin (13%), benzilic acid (30%) and *methyl benzilate* (18%).

Confirming the results of Lachmann,[7] we have obtained benzoic acid (18%), benzilic acid (29%) and a little benzoin (2%) from the reaction of refluxing absolute ethanolic sodium ethoxide and benzil. From a similar reaction at room temperature, the yield of benzilic acid was lower (7%) and of benzoic acid higher (36%); in addition, ethyl benzoate (10%) and ethyl dibenzoin (3%)[8,9] identified as its acetate[9] were isolated. Garner[9] has shown that benzoin reacts with absolute ethanolic sodium ethoxide to give a variety of products among which are benzoic acid and ethyldibenzoin. He has assigned the structure I to ethyldibenzoin and has proposed that it originates from the condensation of benzaldehyde, acetaldehyde and benzoin. We feel that the isolation of a small amount of benzoin and its transformation product ethyldibenzoin leaves little doubt that the M.P.V.O. equilibration also occurs in the benzil–ethanol–sodium ethoxide mixture. Combining the observations of Garner with our experiences with benzil and *t*-butylate ion, it can be concluded that the cleavage products benzaldehyde, ethyl benzoate and benzoic acid, arise much more probably from benzil.



I

The benzilic rearrangement is, therefore, not an example of specific hydroxide-ion utilization capable of producing acids alone. It can also be effected by alkoxide ions with the limitation that these must be sufficiently strong bases to effect rearrangement and must have a structure (and be employed under conditions) consistent with preventing the competitive M.P.V.O. equilibration from becoming predominant.[20]

Mechanistically the conclusion is a negative one: it is not a *necessary* condition for the benzilic rearrangement that, simultaneously with the carbon rearrangement, there be *intramolecular* transfer of a proton (A) with consequent access of the heat of neutralization (of the incipient carboxylic acid by the incipient alkoxide ion) to the energy of the transition state.

This conclusion can be countered partially by proposing that, in the transition state of the ben-

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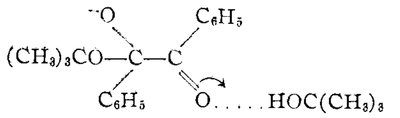
[17] H. Adkins and R. C. Franklin, THIS JOURNAL, **63**, 2381 (1941).

[18] E. Müller, "Methoden der Organischen Chemie," Vol. VIII, Georg Thieme Verlag, Stuttgart, Germany, 1952, p. 635.

[19] J. F. Bunnett, M. M. Robinson and F. C. Pennington, THIS JOURNAL, **72**, 2378 (1950).

[20] Historically it is now clear why the choice of sodium ethoxide by Lachmann failed to disclose the generality of the benzilic rearrangement. It is not so clear why Scheuing failed to isolate methyl benzilate in the reaction with sodium methoxide, nor why Swan[10] failed to detect *t*-butyl benzilate in his experiment. It might be mentioned that benzilic acid was isolated by I. Kasiwagi, *Bull. Chem. Soc. Japan*, **1**, 66 (1926), from the reaction of benzil and sodamide and that water alone and benzil produce benzilic acid [A. Jena, *Ann.*, **155**, 78 (1870); H. Klinger, *Ber.*, **19**, 1868 (1886)].

zilic *ester* rearrangement, there be simultaneous neutralization of the negative charge *intermolecularly* by molecules of alcoholic solvent (C). We chose to examine this possibility by comparing the


(C)

rates of the *t*-butylate–benzil rearrangement in benzene as an aprotic solvent and *t*-butyl alcohol as the protic one.

Solvent-free potassium *t*-butylate is surprisingly soluble in benzene (solutions as concentrated as 0.18 *M* being obtainable at room temperature) so that it is a simple matter to effect the reaction in homogeneous benzene solution. Under these conditions the yield of *t*-butyl benzilate is exceedingly good, being 90% of theory.[21]

The kinetic investigation was made at 12.5 and 25° using the absorption maximum at 386 mμ for determining the concentration of benzil. The reaction is surprisingly rapid, having a half-life of about 70 minutes at 12.5° when the base and benzil are each about 0.04 *M*.

The reaction appears to be second order, first order each in benzil and potassium *t*-butylate. Excellent straight lines are obtained when the data are plotted as second-order reactions, whereas marked curvature is shown by the lines resulting from the first-order plots. Furthermore, as can be seen in Table I, over a twofold increase in the concentration of potassium *t*-butylate, the second-order rate constant does not change within the limits of experimental error. From the rate constants at 12.5 and 25.0° a heat of activation of 19 ± 2 kcal./mole can be calculated.

TABLE I

KINETICS OF THE BENZILIC ESTER REARRANGEMENT IN BENZENE

Concn. of benzil, *M*	Concn. of $KOC(CH_3)_3$, *M*	*T*, °C.	k_2 in liter moles^{-1} min.$^{-1}$	Reacted, %
0.0384	0.0482	12.5	0.55	92
.0384	.0712	12.5	.50	84
.0385	.0790	12.5	.47	81
.0377	.0494	25.0	2.27	83

In *t*-butyl alcohol as solvent the same analytical method could not be used because an interfering, colored impurity is formed. In order to make some comparison, a reaction was run at 25.00° in which the starting concentrations of benzil and potassium *t*-butylate were 0.0381 and 0.0886 *M*, respectively. Ten aliquots were removed over a period of 211 minutes, combined and worked to recover 54% of the initial benzil. Had a similar experiment been run in benzene solution, it could be calculated from the known rate constant that only 16% of the benzil would have been recovered. It seems reasonably clear that the reaction is slower in *t*-butyl alcohol solution, despite the higher dielectric constant of this solvent and the availability of protons and that the objection raised above to the mechanistic conclusion is not a significant one.

In order to find out more about the nature of the solution of potassium *t*-butylate in benzene, measurements of the freezing point depressions were made and are reported in Table II.

TABLE II

FREEZING POINT DEPRESSIONS OF BENZENE SOLUTIONS OF POTASSIUM *t*-BUTYLATE

Concn. of $KOC(CH_3)_3$, *M*	Obs. ΔT_f	Calcd. ΔT_f[a]	Ratio $\Delta T_{\text{calcd.}}/\Delta T_{\text{obsd.}}$
0.0077	0.011	0.039	3.6
.0611	.082	.314	3.8
.0888	.116	.454	3.9
.0971	.133	.496	3.7

[a] Calculated from the molar freezing point depression of benzene assuming potassium *t*-butylate to be in the form of monomeric ion-pairs.

The average degree of polymerization of the ion-pairs is close to 4. It is an attractive, although by no means necessary, hypothesis that the polymerization stops at the tetramer stage with the four *t*-butylate ions situated symmetrically at four of the eight points of a cube. Such an arrangement having an outer coat of *t*-butyl groups might well be soluble in benzene. This type of arrangement is not possible for ions of the tetraalkylammonium type and here higher average degrees of association have been found.[22]

When small amounts of *t*-butyl alcohol are added to the solutions of potassium *t*-butylate in benzene, the freezing point depression decreases becoming almost zero when one equivalent of *t*-butyl alcohol has been added. At the same time the solution becomes very cloudy and obviously heterogeneous. As more *t*-butyl alcohol is added, the freezing point depression rises, essentially paralleling but always remaining below (*ca.* 0.3–0.6°) the freezing point curve of *t*-butyl alcohol in pure benzene. Not until roughly 10 equivalents of *t*-butyl alcohol have been added does the solution become clear again, although the freezing point depression still remains about 0.6° below that of an equal concentration of *t*-butyl alcohol in pure benzene.

The benzilic rearrangement in benzene with potassium *t*-butylate and varying amounts of *t*-butyl alcohol is complicated by the heterogeneity of the solution. In brief, there is an initial, small, rapid reaction which is then followed by a very slow second-order reaction. Even with amounts of *t*-butyl alcohol large enough to give homogeneous solutions, the rate remains much slower (*ca.* $^1/_{50}$) than that in pure benzene. When less than one equivalent of *t*-butyl alcohol is added, the rate is equal to that calculated assuming that one molecule of *t*-butyl alcohol effectively removes one molecule of potassium *t*-butylate from the reaction.

Having effected the benzilic rearrangement with alkoxide ion, we attempted to generalize the reaction further by employing Grignard reagents as the base and by treating tertiary ketols with potassium *t*-butylate.

Among the numerous examples in the literature of reactions between benzil and Grignard reagents, only one, the reaction of *o*-tolylmagnesium bromide

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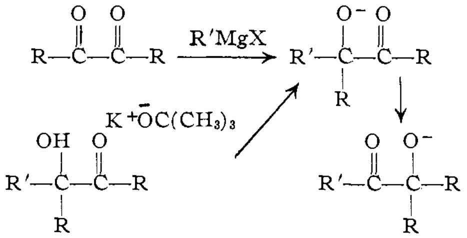
[21] A routine examination is underway to determine whether this set of conditions is generally more satisfactory than those currently in use for effecting the benzilic rearrangement.

[22] C. A. Kraus and R. A. Vingee, THIS JOURNAL, **56**, 511, 2017 (1934); **59**, 1699 (1937).



and benzil to give *o*-toluoyldiphenylcarbinol discovered by Roger and McGregor,[23] leads to rearrangement. We have now found another example in the reaction of mesitylmagnesium bromide and benzil in benzene to form mesitoyldiphenylcarbinol. At least, the product is identical with that isolated by Weinstock and Fuson[24] from phenylmagnesium bromide and phenyl mesityl diketone and can be cleaved by alcoholic alkali to benzhydrol (60%) and mesitoic acid (30%).[25]

Two other types of alkaline tertiary ketol rearrangements are reported: that of 3β,17β-dihydroxypregnan-20-one to 3β,17aβ-dihydroxy-17a-methyl-D-homoandrostan-17-one and related examples[26]; and that of α-benzhydrylbenzoin to α-hydroxydibenzhydryl ketone uncovered by Curtin and Leskowitz[27] as well as related rearrangements in the reaction of α-substituted benzoins with alkali.[28] A study of the reaction of diphenylacetylcarbinol and phenylmethylbenzoylcarbinol with potassium *t*-butylate disclosed no rearrangement but only a rapid cleavage reaction. When the former compound was treated under nitrogen, benzhydrol was isolated in 10% yield.[29] The latter compound gave benzoic acid in 82% yield when treated similarly. When the two ketols were treated separately with mesitylmagnesium bromide in ether for 5 hr., each was recovered unchanged.

In contrast to the benzilic acid and ester rearrangement where the resonance energy in the carboxylic acid and ester groups causes a large free energy decrease in the reaction and is presumably expressed in part as a lowering in the energy of the transition state, the alkaline tertiary ketol rearrangement has little or, in degenerate cases, no free energy change. Therefore, we conclude tentatively that the ketol rearrangement occurs only when the release of steric strain lowers the energy of the transition state from a value which is normally too high to permit the rearrangement being a general one.

Experimental[30]

Rearrangement of Benzil and Potassium *t*-Butylate. (a) **In *t*-Butyl Alcohol Solution.**—A solution prepared from 2.5 g. of potassium in 100 cc. of *t*-butyl alcohol (dried by distilling from sodium) in a flask protected from moisture was heated. With frequent flushing by nitrogen, 8.0 g. of benzil (m.p. 94.0–94.4°) was added quickly with stirring. After being refluxed for 2 hr., excess alcohol was removed by distillation leaving a solid residue which was hydrolyzed with sodium bicarbonate solution and extracted with ether. Acidification of the aqueous layer gave 0.85 g. of benzilic acid (9.7%), m.p. 149–150° after one recrystallization from water. The dried ether solution was concentrated to a residue which was crystallized once from carbon tetrachloride affording 8.26 g. (76%) of crude *t*-butyl benzilate, m.p. 53–55°. Further recrystallization from carbon tetrachloride gave pure material, m.p. 60.0–60.2°, very soluble in ether and ethanol and insoluble in water.

Anal. Calcd. for $C_{15}H_{20}O_3$: C, 76.0; H, 7.1. Found: C, 76.3; H, 7.4.

(b) **In Benzene Solution.**—A solution of 0.064 mole of potassium *t*-butylate (prepared by removing the last traces of alcohol at 150–160° at 2 mm. for 1 hr.) and 8.0 g. (0.038 mole) of benzil in 80 cc. of dry benzene was heated under reflux for 2 hr. Extraction with water gave an aqueous solution, acidification of which afforded 0.23 g. (2.6%) of benzilic acid. Concentration and cooling of the benzene solution gave 9.7 g. (90%) of crude *t*-butyl benzilate, m.p. 59.5–60.0°, which was recrystallized twice from carbon tetrachloride, m.p. 60–61°.

When the reaction was repeated, but with the addition of 0.038 mole of *t*-butyl alcohol, there was obtained benzilic acid (2.8%) and *t*-butyl benzilate (10.0 g., 93%), m.p. 58.5–59.0°.

Proof of Structure of *t*-Butyl Benzilate. (a) **Hydrolysis.**—Refluxing 40 mg. of *t*-butyl benzilate from the rearrangement for 2 hr. with 20% sulfuric acid gave 30 mg. of benzilic acid, m.p. 149–150°, showing no depression of m.p. on admixture with authentic material.

Saponification of 2.0 g. of ester according to the procedure of Redemann and Lucas[31] gave 1.40 g. (87%) of benzilic acid and 0.42 g. (80%) of *t*-butyl alcohol, b.p. 79.0°. For further identification the alcohol was converted to *t*-butyl chloride, b.p. 51.5°, by shaking with concentrated hydrochloric acid.

(b) **Pyrolysis.**—When a sample of the ester was heated for 12 min. at 175–185°, a gas was evolved leaving material which melted at 149–150° after crystallization from water and did not depress the m.p. of authentic benzilic acid.

(c) **Synthesis by Transesterification.**—A solution of 1.02 g. of methyl benzilate[32] and potassium *t*-butylate (from 0.20 g. of potassium and 20 cc. of *t*-butyl alcohol) was refluxed 2 hr. Removal of solvent by distillation left material which was hydrolyzed and extracted with ether. Concentration of the ether extract left an oil which crystallized from hexane on cooling. Recrystallization from hexane gave 0.28 g. (24%) of *t*-butyl benzilate, m.p. 60.0–60.5°. The various samples of *t*-butyl benzilate failed to depress each other's m.p. on admixture.

Rearrangement of Benzil and Sodium Methoxide. (a) **In Methanol Solution.**—A solution of 0.065 mole of sodium methoxide and 8.0 g. (0.038 mole) of benzil in 100 cc. of methanol (dried by distillation from magnesium methoxide) was refluxed for 2 hr. Removal of solvent gave a purple residue which on treatment with water solidified to crude methyl benzilate. The alkaline aqueous wash liquid was extracted with ether. Concentration of the ether solution gave a small residue which was shaken with sodium bisulfite and ether. From the bisulfite solution about 10 mg. of benzaldehyde was obtained, identified as the phenylhydrazone, m.p. 149–152°, showing no depression of m.p. on mixing with authentic benzal phenylhydrazone. Acidification of the alkaline aqueous wash liquid above gave 0.85 g. (9.7%) of benzilic acid, m.p. 149–150°. The crude methyl benzilate was dissolved in a small amount of ether and filtered from 0.77 g. (9.6%) of insoluble material.

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[23] R. Roger and A. McGregor, *J. Chem. Soc.*, 442 (1934).

[24] H. H. Weinstock, Jr., and R. C. Fuson, THIS JOURNAL, **58**, 1233 (1936).

[25] The possibility that the structure of the Weinstock–Fuson product and of our Grignard product is benzoylphenylmesitylcarbinol and that rearrangement occurs during the treatment with alcoholic alkali seems unlikely but is not excluded. It would nevertheless remain a fact that an alkaline tertiary ketol rearrangement had occurred in one of the two steps.

[26] L. Ruzicka and H. F. Meldahl, *Helv. Chim. Acta*, **21**, 1760 (1938); **22**, 421 (1939); **23**, 513 (1940); L. Ruzicka, K. Gätzi and T. Reichstein, *ibid.*, **22**, 626 (1939); C. W. Shoppee and D. A. Prins, *ibid.*, **26**, 185, 201, 1004 (1943); H. E. Stavely, THIS JOURNAL, **62**, 489 (1940); R. B. Turner, *ibid.*, **75**, 3486 (1953), who has studied and explained the stereospecificity of the rearrangement.

[27] D. Y. Curtin and S. Leskowitz, *ibid.*, **73**, 2633 (1951).

[28] D. B. Sharp and E. L. Miller, *ibid.*, **74**, 5643 (1952).

[29] When air is passed through, benzophenone was isolated in 68% yield in a reaction which most probably was of the type elaborated by W. von E. Doering and R. M. Haines, *ibid.*, **76**, 482 (1954).

[30] Melting points are corrected. Analyses were performed by Miss Lois May and the Clark Microanalytical Laboratory.

[31] C. E. Redemann and H. J. Lucas, *Ind. Eng. Chem., Anal. Ed.*, **9**, 521 (1937).

[32] S. F. Acree, *Ber.*, **37**, 2764 (1904).

After several recrystallizations from ethanol pure benzoin, m.p. 131–133°, showing no depression on admixture with an authentic sample, was obtained. The ether-soluble material was recrystallized from ethanol to give 6.23 g. (68%) of methyl benzilate, m.p. 70.0–70.5°, identical with a sample prepared by the method of Acree.[32]

(b) In Benzene Solution.—A suspension of 0.030 mole of sodium methoxide (dried by heating 1.5 hr. at 140–150° at 1–2 mm.) in 100 cc. of benzene was heated and stirred in a flask protected by a calcium chloride tube. A solution of 4.0 g. of benzil in 30 cc. of benzene was added slowly over 30 min. After being refluxed for 2 hr., the black solution was hydrolyzed. The aqueous layer yielded 0.13 g. (8%) of benzoic acid, m.p. 122°, and 1.30 g. (30%) of benzilic acid, m.p. 149–150°, separated by sublimation. Concentration of the benzene solution gave solid material which was fractionally recrystallized from ethanol to give 0.83 g. (18%) of methyl benzilate, m.p. 69–70°, and 0.51 g. (13%) of benzoin, m.p. 130–132°. A similar experiment using 0.035 mole of sodium methoxide, 0.047 mole of methanol and 0.019 mole of benzil in 100 cc. of benzene gave benzoic acid (8%), benzilic acid (19%), methyl benzilate (25%) and benzoin (16%).

Reaction of Benzil and Sodium Ethoxide.—Carried out like the reaction in methanol solution described above, 0.065 mole of sodium ethoxide and 8.0 g. (0.038 mole) of benzil in 100 cc. of ethanol reacted to give 4.5 g. of red tar of which only 0.21 g. distilled in a molecular still at 150–160° at 0.5 mm. Recrystallization from ethanol afforded benzoin, m.p. 127–130°. No ethyl benzilate could be isolated.

In another reaction in which the ethanol had been dried with magnesium ethoxide, benzoic acid (18%), benzilic acid (29%) and benzoin (2%) were obtained. Using ethanol dried with diethyl phthalate and sodium ethoxide, benzoic acid (18%) and benzilic acid (25%) were isolated.

An identical reaction was carried out at room temperature instead of refluxing in ethanol dried over magnesium ethoxide. After 5 days, removal of the alcohol under reduced pressure gave a residue which was treated with water and extracted with ether. Distillation of the ether-soluble material gave 0.54 g. of ethyl benzoate (10%), b.p. 70–75° at 8 mm. Acidification of the aqueous solution gave material which was separated by sublimation into benzoic acid (36%) and a residue which was partially soluble in sodium carbonate solution. The carbonate solution gave benzilic acid (7%). Several recrystallizations of the insoluble fraction from ethanol gave ethyldibenzoin (3%), m.p. 191–193°, converted to an acetate, m.p. 144.0–144.5° (reported[9] m.p. 195°; acetate, m.p. 145°).

Rate Measurements of the Benzilic Ester Rearrangement.—The ultraviolet absorption spectrum of benzil in benzene solution has a maximum at 386 mμ which obeys Beer's law over the concentration range 0.002 to 0.02 *M*.

A stock solution of potassium *t*-butylate in benzene was prepared from potassium *t*-butylate which had been freed of solvent by drying at 2 mm. and 150–160° for 1 hr. The concentration of alkoxide was determined by shaking an aliquot with water and titrating with standard hydrochloric acid. Because of the extreme sensitivity of benzene solutions of potassium *t*-butylate to moisture, all transfers were made by forcing the stock solution under a positive pressure of dried nitrogen through a glass filter stick into a dried flask from which samples were removed by a volumetric pipet with constant flushing by dry nitrogen. The reaction flask was a 300-cc. round-bottomed flask fitted with a wire stirrer pierced through a rubber stopper and a side-arm in the form of a T-tube so that nitrogen could be flushed continually whenever an aliquot was removed.

Following the addition of a known volume of the stock benzene solution of potassium *t*-butylate, the desired volume of benzene (dried by distillation and storing over sodium) was added and thereafter the desired volume of a known solution of benzil (m.p. 94.0–94.5°) in benzene. Zero time was taken after half the benzil had been added (8–10 sec. was required). The stirred flask was first equilibrated in the constant temperature bath at 12.50 ± 0.01° as were the solutions prior to addition.

To determine the quantity of benzil consumed, 10-cc. aliquots of the benzene solution were removed at intervals, transferred rapidly to a test-tube containing a slight excess of acetic acid, centrifuged to settle the precipitated potassium acetate and diluted with 90 cc. of benzene (to one-tenth the original concentration). Using the Beckman model DU ultraviolet spectrometer and a calibration curve at 386 mμ, the concentrations were determined.

Plotting $2.3/(a - b) \log [(a - x)b/(b - x)a]$ against time gave excellent straight lines from the slopes of which k_2 was calculated (a is the starting concentration of potassium *t*-butylate, b is the starting concentration of benzil and x is the concentration of products formed). The results are shown in Table I. If the function $2.3[\log b - \log (b - x)]$ is plotted against time, the lines are markedly curved and there is a big difference in the slopes between the first and third reactions in Table I.

Freezing Point Depression of Potassium *t*-Butylate and *t*-Butyl Alcohol in Benzene.—Because of the exceptional sensitivity of benzene solutions of potassium *t*-butylate to atmospheric moisture, the usual Beckman freezing point apparatus was modified by using a glass stirrer fitted with a rubber sleeve and lubricated with oil and by closing the side arm with an injection-type rubber stopper so that samples could be introduced with a hypodermic syringe. Benzene for these experiments was dried over phosphorus pentoxide. The experimental results with dry potassium *t*-butylate are shown in Table II. Since the apparent association does not vary over a 13-fold increase in concentration, one concludes that a homogeneous polymer is present.

For the determination of the effect of added *t*-butyl alcohol, small increments of *t*-butyl alcohol were added through the rubber stopper with stirring. These results are described in the text above.

Benzil and Mesitylmagnesium Bromide.—A solution of mesitylmagnesium bromide prepared from 13.0 g. of mesityl bromide and 1.6 g. of magnesium in 35 cc. of ether was added by decantation to a solution of 1.00 g. of benzil in 30 cc. of dry benzene (0.7 g. of unreacted magnesium was recovered). The ether was removed by distillation, more benzene was added and the solution was refluxed for 9 hr. After treatment with dilute sulfuric acid and drying, the benzene solution was concentrated to an oil which was evaporatively distilled at 100° at 0.3 mm. to remove mesitylene and mesityl bromide. The residue was washed with hexane and recrystallized several times to give 330 mg. of **diphenylmesitoylcarbinol** (?), m.p. 169.5–170°.

Anal. Calcd. for $C_{23}H_{22}O_2$: C, 83.6; H, 6.7. Found: C, 83.7; H, 6.9.

When the reaction was carried out in refluxing ether, the yield of carbinol was much lower; in refluxing benzene it was raised somewhat to 470 mg.

When 130 mg. of the carbinol was refluxed with 20 cc. of concentrated alcoholic potassium hydroxide for 8 hr., 50 mg. of benzhydrol, m.p. 65–66°, and 20 mg. of mesitoic acid, m.p. 153–154°, was isolated.

Reaction of Diphenylacetylcarbinol with Potassium *t*-Butylate.—A solution of 250 mg. of diphenylacetylcarbinol (prepared according to Temnikova[33]) and 0.0032 mole of potassium *t*-butylate in 26 cc. of benzene became yellow, then green on standing for 1.5 hr. After hydrolysis the benzene solution yielded 20 mg. of benzhydrol, m.p. 65.5–66°. When dry air was passed through an otherwise identical reaction, benzophenone, m.p. 47.5–49.0°, was obtained in 68% of the theoretical yield.

Reaction of α-Methylbenzoin with Potassium *t*-Butylate.—A solution of 230 mg. of α-methylbenzoin,[34] m.p. 65–65.5°, and 0.0032 mole of potassium *t*-butylate in 40 cc. of benzene became dark red after standing 1 hr. and yielded 100 mg. (82%) of benzoic acid. No benzhydrol or benzophenone could be isolated from the small neutral fraction.

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