was recrystallized from water to give long, white needles. They turned yellow on standing and melted indefinitely commencing at 136°, with a complete melt appearing only at 195° ($\lambda_{max}^{C_2H_5OH}$ 226, 306 mμ; ϵ = 24,600, 3010).

Anal. Calcd. for $C_8H_8N_2O$: C, 64.85; H, 5.4: N, 18.9. Found: C, 64.7; H, 5.2; N, 18.8.

2(1H)-Quinoxalone (IX). To a solution of 1 g. of 3,4-dihydro-2(1*H*)-quinoxalone-3-carboxylic acid, 1.5 g. of potassium carbonate, and 20 ml. of water was added a strong solution of potassium ferricyanide until a persistent green color developed. Gas was strongly evolved and a white precipitate separated from the reaction mixture. Filtration gave 0.63 g. (90%) of fine white needles, m.p. 270–271°, which were shown to be 2(1*H*)-quinoxalone by comparison with an authentic sample.

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Effect of the Alkali Cation Upon the Rate of the Benzilic Acid Rearrangement

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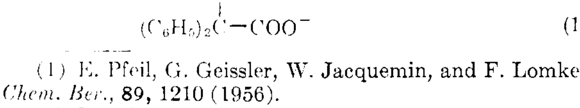
As part of a continuing investigation on the influence of the metallic cation in organic reactions, we initiated a study of the effect of varying the alkali hydroxide on the rate of the benzilic acid rearrangement. After our work had been in progress for some time, we came upon the excellent work of E. Pfeil and co-workers[1] bearing on this same field. However, as our work was concerned primarily with the alkali cation, and was done under conditions which brought out a greater magnitude of difference between lithium and the other alkali cations than was done in the former study, we felt it worthwhile to continue the project and submit the completed results.

The mechanism of the benzilic acid rearrangement has been the subject of much recent study which has shed light on a number of disputed points, but has not yet led to an undisputed mechanism. The work of Roberts and Urey[2] showing that benzil undergoes rapid exchange of carbonyl oxygen with H_2O^{18} under alkaline conditions provides the main evidence for the generally accepted mechanism[3] involving preliminary reversible addition of hydroxide ion to benzil followed by irreversible migration of a phenyl group and proton exchange (Equation 1).



$$C_6H_5COCOC_6H_5 + OH^- \rightleftarrows C_6H_5-\overset{\overset{O}{\|}}{C}-\underset{\underset{OH}{|}}{\overset{\overset{O^-}{|}}{C}}-C_6H_5 \longrightarrow (C_6H_5)_2\overset{\overset{OH}{|}}{C}-COO^- \qquad (1)$$

More recently, Doering and Urban[4] showed that the rearrangement is subject not only to specific hydroxide ion catalysis, as was long believed, but may be brought about more generally by means of certain alkoxides to yield benzilic esters as well. Hine and Haworth[5] have demonstrated that the rearrangement can not have as its rate-controlling step a mechanism involving proton transfer, since the reaction was about 85% faster with sodium deuteroxide in deuterium oxide than with sodium hydroxide in water under the same conditions. Clark, Hendley, and Neville[6] showed that in the rearrangement of unsymmetrically substituted benzils, rings containing electron-withdrawing substituents migrated preferentially to phenyl, while the reverse was true with rings containing electron-donating substituents. These workers suggested that the mechanism involving preliminary reversible addition of hydroxide ion may be incorrect, and that hydroxide ion may participate in the rate-controlling step, preferentially attacking the more reactive carbonyl group, and thus accounting for the preferred migration tendencies observed.

In view of the fact that the nature of the metallic cation has been found to play an important role in aldol condensations of esters with ketones,[7] and in certain displacement reactions[8] among others, we felt it worthwhile to study the effect of varying the alkali (and the tetramethylammonium) cation upon the rate of the benzilic acid rearrangement. The kinetic results obtained with these hydroxides

TABLE I

SECOND-ORDER RATE CONSTANTS FOR THE REACTION OF BENZIL[a] WITH ALKALI HYDROXIDES[b] IN 67% DIOXANE–33% WATER[c] AT 49.5°

Hydroxide Used	10^5k_2, l./mole^{-1}/sec.$^{-1}$
Lithium[d]	29.96 ± 0.49
Sodium[d]	9.40 ± 0.28
Potassium[d]	8.29 ± 0.38
Cesium[e]	8.76 ± 0.41
Tetramethylammonium[e]	7.98 ± 0.15
Lithium[e]	29.79 ± 0.83

[a] Initial concentrations 0.05931–0.06174*M*. [b] Initial concentrations 0.04749–0.04878*M*. [c] By volume. [d,e] These runs were carried out simultaneously in the same thermostated bath using the same reagents except for the hydroxide.

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(1) E. Pfeil, G. Geissler, W. Jacquemin, and F. Lomker, *Chem. Ber.*, **89**, 1210 (1956).

(2) I. Roberts and H. C. Urey, *J. Am. Chem. Soc.*, **60**, 880 (1938).

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

(4) W. von E. Doering and R. S. Urban, *J. Am. Chem. Soc.*, **78**, 5938 (1956).

(5) J. Hine and H. W. Haworth, *J. Am. Chem. Soc.*, **80**, 2274 (1958).

(6) M. T. Clark, E. C. Hendley, and O. K. Neville, *J. Am. Chem. Soc.*, **77**, 3280 (1955).

(7) C. R. Hauser and W. H. Puterbaugh, *J. Am. Chem. Soc.*, **75**, 1068 (1953); C. R. Hauser and W. H. Puterbaugh, *J. Am. Chem. Soc.*, **75**, 4756 (1953).

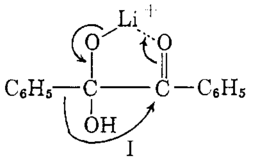
(8) W. H. Puterbaugh and C. R. Hauser, *J. Org. Chem.*, **24**, 416 (1959); W. H. Puterbaugh and R. L. Readshaw, *J. Am. Chem. Soc.*, **82**, 3635 (1960).

and benzil at 49.5° in 67% aqueous dioxane are given in Table I.

As can be seen from the Table, lithium hydroxide effected the rearrangement three to nearly four times faster than any of the others in the group. There was little significant difference in the rate constants obtained with the other four hydroxides, although it is interesting to note that the average values arrange these, with the exception of cesium hydroxide, in descending order of coordinating ability of the cation. To determine whether the reaction of benzil with lithium hydroxide was that of the rearrangement, a larger scale run employing ten grams of benzil under similar conditions as the kinetic runs was made. Products other than benzilic acid and a small amount of recovered benzil could not be found in any appreciable quantity.

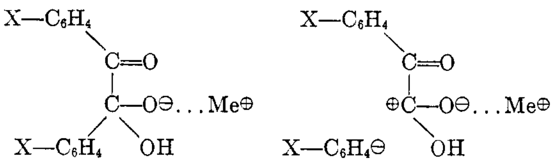
Pfeil and co-workers have similarly demonstrated[1] a dominant cation influence on the rate of this reaction using 2,2′-dichlorobenzil at 60.5° in 50% aqueous dioxane. They showed that barium hydroxide caused the rearrangement to occur about fifteen times faster than sodium hydroxide, while thallous hydroxide effected it about five times faster than barium hydroxide. They further observed that although the reaction generally follows second order kinetics with the alkali hydroxides, it is third order with thallous hydroxide and intermediate between second and third order with the alkaline earth hydroxides. However, in contrast to our results, they observed the following descending order of reaction rate with the alkali hydroxides: butyltrimethylammonium hydroxide > cesium hydroxide > lithium hydroxide > sodium hydroxide > potassium hydroxide. Moreover, the differences between these were quite small, the fastest being only about 15% more rapid than the slowest, while the half-life times for rearrangement with sodium hydroxide and lithium hydroxide were 461 and 459 minutes, respectively. Our conditions, therefore, bring out a much larger differentiation between lithium and the other alkali cations. Such a variation is in agreement with previously observed large differences in cation influence between lithium and other members of this group.[7,8] Very likely the greater differentiation observed in our experiments as contrasted with those of Pfeil is due largely to the fact that our runs were made in 67% dioxane-33% water while the latter were run in 50% aqueous dioxane. Pfeil has observed that the greater the water content of the solvent mixture, the smaller the difference in cation effect, since thallium hydroxide effected the rearrangement only six times faster than sodium hydroxide in 30% dioxane, but 110 times faster in 70% dioxane. Apparently, the more highly polar water medium obscures the cation effect.

Possibly the greater effectiveness of lithium when it is the cation accompanying the hydroxide ion may be due to greater coordinating ability which enables it to participate in a ring mechanism which facilitates migration of the phenyl group within the complex as in I below.



I

A similar mechanism could as well be proposed to account for the results of Pfeil. These workers suggest that coordination of the cation with the negative oxygen in the hydroxide ion–benzil adduct brings the neighboring carbon-phenyl bond under the influence of the strong positive field of the cation ("ionfield catalysis") which facilitates cleavage of the bond as in II below.



II

However, it is difficult to see how coordination of the cation with this single oxygen, without involving a ring mechanism, would facilitate cleavage of the carbon-phenyl bond. Instead, it might be expected to have the opposite effect and inhibit cleavage, since previous work has shown that the somewhat analogous lithium salts of β-hydroxy esters are much more stable than the sodium salts and less prone to undergo cleavage into reverse aldol products.[7] Similarly, the ease of thermal cleavage of alkali salts of hindered tertiary carbinols varies in the order potassium > sodium > lithium.[9]

While the mechanism for this rearrangement is still not unequivocal, these results, and those of Pfeil, demonstrate that any mechanism proposed should be such as will allow definite participation of the cation in the rate-controlling step.

EXPERIMENTAL

Commercial benzil was purified by washing with base and recrystallizing as described by Hine and Haworth,[5] m.p. 95.5–96.1°. Commercial dioxane was purified as described by Fieser.[10] Acetone was dried over anhydrous potassium carbonate and redistilled. Lithium, sodium, potassium, and tetramethylammonium hydroxides were the highest purity commercial grades available, and were made carbonate free by the usual methods. Cesium hydroxide was prepared by stirring a 60% aqueous solution of cesium chloride for 4 hr. with a 25% excess of thoroughly washed silver oxide precipitate, followed by filtering off the precipitated silver chloride and excess silver oxide, and standardizing the filtrate.[11]

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(9) H. D. Zook, J. March, and D. F. Smith, *J. Am. Chem. Soc.*, **81**, 1617 (1959).

(10) L. F. Fieser, *Experiments in Organic Chemistry*, 3rd ed., rev., D. C. Heath and Co., Boston, Mass., 1957, p. 284.

(11) We are indebted to Dr. C. H. Vanselow for this synthesis.

The kinetic runs were carried out essentially as described by Hine and Haworth.[5] As noted in Table I, runs were made in sets using three different hydroxides in each run to ensure comparability of results. Each hydroxide was run in duplicate samples, and two aliquots were withdrawn from each sample for titration at each time. The value obtained for k_2 at any time was thus an average of four determinations. The data for a typical run follows.

Into a nitrogen-purged, 250-ml. polyethylene bottle were placed 1.9399 g. of benzil and 100 ml. of dioxane. The solution was equilibrated in the constant temperature bath, 50 ml. of 0.1476M lithium hydroxide at the same temperature was added and the bottle vigorously shaken. Two 10-ml. aliquots were withdrawn as quickly as possible into 10 ml. of cold acetone and titrated to the phenolphthalein end-point. The time of withdrawal of samples was noted as zero time, and the base concentration given by the titration as "initial base concentration." The difference between the base concentration obtained by an analogous procedure with the omission of benzil, and the "initial base concentration" as above, was subtracted from the original benzil concentration (assuming that the partial molal volume of benzil was ideal) to correct for the reaction of benzil before zero time (maximum correction in any run, 3.3%). The result was taken as the "initial benzil concentration." Samples were then withdrawn at various times during the runs and titrated analogously to give the results shown in Table II.

TABLE II

SECOND-ORDER RATE CONSTANTS FOR THE REACTION OF BENZIL WITH LITHIUM HYDROXIDE IN 67% DIOXANE-33% WATER AT 49.5°

$[\text{Benzil}]_0 = 0.06167M$; $[\text{LiOH}]_0 = 0.04756M$

Time, sec.	[LiOH]	$10^5\ k_2$, l./mole^{-1}/sec.$^{-1}$
68,400	0.01887	30.94
86,400	0.01629	29.87
169,200	0.00881	29.17
237,600	0.00558	29.88
		29.96 ± 0.49

Larger scale run with benzil and lithium hydroxide. In a 500 ml. Erlenmeyer was placed a solution of 10.2 g. (0.0485 moles) of benzil in 260 ml. of dioxane, to which was added 0.05 mole of lithium hydroxide monohydrate dissolved in 130 ml. of water. The solution was shaken and maintained in a thermostated bath at 49.5° for 72 hr. (time required for approximately 90% reaction), after which it was transferred to a separatory funnel and extracted with several portions of ether. The solvent was removed from the dried ether solution to yield only 0.3 g. of semisolid yellow residue whose infrared spectra showed it to consist mainly of benzil. The aqueous portion from the above extraction was evaporated to a small volume under reduced pressure and then acidified to yield 9.03 g. (82%) of solid acid with a neutralization equivalent of 242 (benzilic acid = 228). Recrystallization from water yielded benzilic acid, m.p. 149.3–151° (reported[12] m.p. 150°), neutralization equivalent 231. Evaporation of the filtrates from the acidification and from the recrystallization steps gave only 0.75 g. of solid acid, neutralization equivalent 233. No other products were found.

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Fluorocarbon Sulfides. I. Synthesis of Bis(perfluoropropyl) Sulfide and Bis(perfluoroheptyl) Disulfide

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From the reaction of perfluoropropyl iodide with sulfur at 250° Hauptschein and Grosse[1] recovered bis(perfluoropropyl) disulfide and trisulfide, but at most only a trace of monosulfide, insufficient to permit isolation. They attributed this to a rapid attack by sulfur upon the (supposedly) first-formed monosulfide.[1] However, the author has now found that by carrying out the reaction at a higher temperature, 300°, an appreciable yield (11%) of the monosulfide is obtained. The mechanism suggested does not satisfactorily explain this observation, and it appears more likely that the first-formed disulfide (or perfluoropropylthiyl radical) subsequently reacts with free perfluoropropyl radicals to produce the (stable) monosulfide.

Several years after Hauptschein and Grosse's report, Haszeldine and Kidd[2] claimed that little or no reaction occurred between 1-iodo perfluoropropane and sulfur in a stainless steel autoclave at temperatures up to 350° (fourteen hours), that partial reaction occurred at 400°, and that 450° was required to convert all 1-iodoperfluoropropane to (principally) disulfide, lesser amounts of mono- and trisulfide being present in the reaction product also. It is surprising that Haszeldine and Kidd failed to recognize their error, (their reaction temperature may have been read from a Fahrenheit thermometer or themocouple chart), as Hauptschein and Grosse had reported exactly the same reaction at a much lower temperature; the latter work[1] is of course fully confirmed by the present study. The ultraviolet spectroscopic data reported by Haszeldine and Kidd for $(C_3F_7)_2S_2$ are incorrect; apparently much $(C_3F_7)_2S_3$ was in their "pure" sample.

The synthesis (by the same general method), purification, and physical properties of bis(perfluoroheptyl) disulfide are also reported. It is of interest that attempted oxidation of this disulfide by fuming nitric acid resulted in preferential elimination of higher sulfides. Such purification was apparently not achieved by simple recrystallization, for despite a good melting range, the sulfur analysis was high; formation of a solid solution is suggested.

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(1) M. Hauptschein and A. V. Grosse, *J. Am. Chem. Soc.* **73**, 5461 (1951).

(2) R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, 3871 (1955).