

of the Δ_3 tetrahydro-2,6-xylic acid. This is decidedly in favor of the idea of steric hindrance as the structure of the Δ_1 acid resembles that of the xylic acid much more closely than does that of the Δ_3 acid.

10. The esterification of the $\Delta_{1,5}$ dihydro-2,6-xylic acid is less favorable to the idea of steric hindrance as being merely due to space relations.

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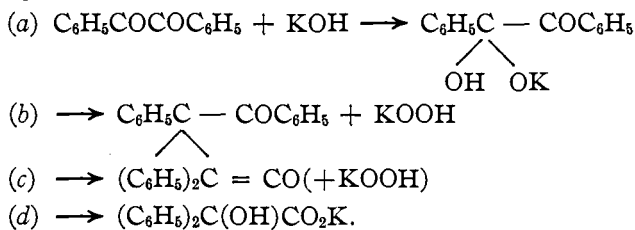
[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO.]
**THE BENZILIC ACID REARRANGEMENT. THE NON-ADDITION
OF HYDROGEN PEROXIDE TO DIPHENYL KETENE.**

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Of the molecular rearrangements that have been known for a long time one of the most mysterious is that of benzil to benzilic acid. Nef,² Schröter,³ Tiffeneau,⁴ and Michael⁵ have offered four different explanations. The first three suggest mechanisms by which the reaction may be supposed to take place, involving intermediate products, and therefore somewhat susceptible to experimental investigation. Michael discusses the reaction from the "affinity-energy-spatial viewpoint," and his hypotheses do not lend themselves very directly to the test of experiment.

Schröter's explanation, which had seemed preferable, involves the following stages:



Of these, (a) is very reasonable, and marks the starting point of all the four schemes mentioned; (c) has been well justified by Schröter, who proved that azibenzil gives good yields of nitrogen and diphenyl ketene when heated. Reactions (b) and (d), however, are highly hypothetical, and it was the purpose of the work here described, to determine whether or not hydrogen peroxide or its potassium salt would add to diphenyl ketene to form benzilic acid.

In this connection attention is called to the fact that Schröter's theory

¹ The material here presented is used by Joseph J. Pelc in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Chicago.

² Nef, *Ann.*, **298**, 372 (1897).

³ Schröter, *Ber.*, **42**, 2336 (1909).

⁴ Tiffeneau, *Rev. gen. Sci.*, **1907**, p. 585.

⁵ Michael, *THIS JOURNAL*, **42**, 812 (1920).

involves the assumption that diphenyl ketene, *in the presence of water or alcohol*, will add hydrogen peroxide or its potassium salt (KOOH), *present in only equivalent quantity, so much more rapidly than either water or alcohol that an excellent yield of benzoic acid can be obtained.*

No evidence of the addition of hydrogen peroxide to the ketene in anhydrous solvents (ether and low-boiling ligroin) could be obtained, even after 8 months of contact. When the conditions existing during the rearrangement in question are simulated as nearly as possible, by dropping the ketene-peroxide solution into an excess of hot caustic soda, there is still no evidence of addition.

It must be concluded that Schröter's scheme, *in the form given by him, at least*,¹ must be abandoned, since he specifically assumes the formation of potassium hydrogen dioxide in the reaction.

Experimental Part.

Diphenyl ketene was prepared by the method of Staudinger,² and dissolved in carefully dried ligroin of low boiling point. It was not entirely pure as on treatment with water a small amount of benzoic acid was formed, along with the chief product, diphenyl-acetic acid. The peroxide solution was made by concentrating the commercial solution, extracting with ether, and drying with sodium sulfate.

Molecular quantities of the ketene and peroxide solutions were mixed and allowed to stand for lengths of time varying from one hour to 8 months. In all cases unchanged hydrogen peroxide was still present. The solutions were worked up by treatment with water or aqueous alkali, and the melting points of the liberated acids determined. In every case benzoic acid was present, as indicated by the melting points, and this was confirmed by actually isolating it; but the amount was no greater than when the ketene itself, without the addition of peroxide, was treated in the same way. Prolonged contact of the two substances also, gave no increase in the yield of benzoic acid.

The approximate melting points (capillary tube method) of mixtures of pure benzoic and diphenyl-acetic acids are given in Table I.

¹ The present work does not show the impossibility of the formation of the radicals —OK and —OH, or of their combination with a rearrangement product of the residual portion of the molecule to give potassium benzoate. Michael, for instance (*loc. cit.*, p. 814), assumes a migration of $C_6H_5\cdot$ and H-radicals, but it would perhaps be unfair to test his theory by trying to make benzene add to benzoyl formic acid to form benzoic acid. In all these rearrangements, the possibility must not be lost sight of, that radicals of opposite sign may migrate to new positions under circumstances that give them no opportunity to combine with each other. The present paper, then, is not an attempt to prove that no modified form of Schröter's theory could fit the facts, but is merely a report of work which curiosity tempted the writers to carry out.

² Staudinger, *Ann.*, **356**, 51 (1907); if one has hydrazine available in quantity, the method of Schröter (*loc. cit.*, cf. Staudinger, *Ber.*, **44**, 1622 (1911)) is probably to be preferred.

TABLE I.
 Melting points of benzilic-acid—diphenyl-acetic acid mixtures.

Ph ₂ COHCO ₂ H. %	Ph ₂ CHCO ₂ H. %	M. p. ° C.	Ph ₂ CHOHCO ₂ H. %	Ph ₂ CHCO ₂ H. %	M. p. ° C.
100	0	150	40	60	119
90	10	139	30	70	120
80	20	128.5	20	80	125
70	30	119.5	10	90	135.5
60	40	118	0	100	146
50	50	119

Table II shows the results of various methods of working up the ketene-peroxide mixtures after varying periods of contact. In all cases, the formation of a certain amount of oil (diphenyl-acetic anhydride) which slowly hydrolyzed, on boiling, to diphenyl-acetic acid, was noted.

 TABLE II.
 Results of Working up Equimolecular Solutions of Diphenyl Ketene and Hydrogen Peroxide.

Expt.	Time.	Treatment.	M. p. of crude acid. ° C.	M. p. of crude acid mixed with 10% benzilic acid. ° C.
I	1 hour	Evaporated to dryness and taken up in excess NaOH solution.	139	129
II	1 hour		140	119 ^a
III	1 week		140	130
IV	1 hour	Dropped into excess hot NaOH solution	139	118 ^a
V	1 hour		139	119 ^a
VI	3 months		139	118 ^a
VII	8 months		140	120 ^a
VIII	1 hour	Dropped into hot water.	140.5	129
IX	3 months		140.5	129
X	1 hour	Added dil. HCl and distilled off solvent	139	119 ^a
XI	(Boiled 16 hours under reflux; dropped into excess NaOH solution).		142	132

^a Mixed with 30% benzilic acid instead of 10%.

Summary.

1. Hydrogen peroxide does not react appreciably with diphenyl ketene in anhydrous solvents, even after standing for 8 months.
2. Hydrogen peroxide does not react appreciably with diphenyl ketene in the presence of water or of alkalis.
3. The mechanism given by Schröter for the benzilic acid rearrangement, involving as it does the assumption of an addition of hydrogen peroxide or its potassium salt to diphenyl ketene, cannot be accepted.

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