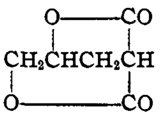
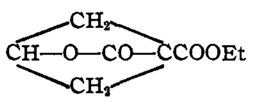

(III)


(IV)

Evidently, the negative carbethoxy and lactonic groups have so loosened the affinity of the tetramethylene α- and β-carbon atoms that the linkage between them is hydrolyzed by the acid and the formed δ-hydroxy-carboxylic acid group undergoes lactonization. Results with other α-lactonic esters and dilactones, containing mobile α-hydrogens, indicate that enolate formation is a general property of such derivatives.

Recently, Tschelinzev [*Ber.*, **67,** 960 (1934)] assumed that enolates containing an α-hydrogen react with carbonyl derivatives by intermolecular aldolization, involving the respective hydrocarbon and carbonyl groups. In accordance monoalkylated malonic and acetoacetic ester enolates do not condense with ethylene oxide. Tschelinzev overlooked that the surmized aldolization process was proved experimentally years ago and that his generalization is untenable. Enolates with an α-hydrogen unite with phenyl isocyanate with intermolecular migration of that hydrogen, forming well neutralized enolates [Michael, *Ber.*, **38,** 22 (1905); *Ann.*, **363,** 64 (1908)]: with sodium enol methyl acetoacetic and methyl malonic esters deep-seated decompositions occur, giving the well neutralized salt of a complicated acid [*loc. cit.*, p. 24]. Sodium enol methyl malonic ester adds to $\Delta^{-\alpha,\beta}$-esters by migration of the methyl group to the $\Delta^{-\alpha}$ carbon atoms [Michael and Ross, THIS JOURNAL, **52,** 4592 (1930); **53,** 1633 (1931)] and, finally, Bennett [*J. Chem. Soc.*, **127,** 1278 (1925)] found that ethylene oxide condenses with (I), which contains no α-hydrogen to give bis butyrolactone α,α-spiran. The subject is evidently complicated, but the reactions always proceed with the maximal possible neutralization of the metal.

CONVERSE MEMORIAL LABORATORY
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ARTHUR MICHAEL
NATHAN WEINER

RECEIVED AUGUST 22, 1934

THE POSSIBILITY OF SEPARATING HEAVY WATER BY FRACTIONAL FREEZING

Sir:

On the basis of the fact that D_2O has m. p. 3.8°, the possibility of separating it from H_2O by fractional freezing was taken into consideration. Admitting that the two oxides are isomorphous and form a continuous series of solid solution, the possibility of the separation clearly depends on the relative positions of the *liquidus* and *solidus* curves.

Some graduated fractional freezings were executed, on my suggestion, by Dr. M. Strada, starting from ordinary distilled water. From density measurements made by Dr. Strada it was deduced that the final fractions contained up to 4 per mille of D_2O. Similar results were found from water obtained from old electrolytic cells of a hydrogen plant. A short paper was consequently published by myself and M. Strada in *Rend. Accad. Lincei*, **19,** 433 (1934).

Doubts having arisen of the reliability of the above experiments, I asked my friend and Assistant Professor A. Quilico to repeat the whole operations, during which the greatest care to eliminate sources of error, or to estimate their influence, was taken. Professor Quilico started again from 4000 liters of common water, which, by a nine-step fractional freezing, he reduced to 280 cc. To the water 6% of sodium chloride was added each time in order to obtain ice as minute crystals and at each step about one-third of the whole was sharply separated by centrifugation, as ice. The final fraction was distilled eight times in quartz apparatus, four times alone and four with the usual chemical reagents.

On the liquid thus obtained nine independent density measurements were made, every time in comparison with the original water and four times also with the water coming from the fifth freezing. The influence of temperature was particularly considered. The uniform result was that the former determinations were entirely untrustworthy. The density differences now found were in both directions and never exceeded the possible error of the measurement.

To eliminate the doubt that the chemical treatment might originate total or partial destruction of D_2O, five more density determinations were made on samples purified by distillation only. The results were the same.

The conclusion to be drawn is that *if* a fractionation takes place, it amounts certainly to less than 1/10,000, and probably less than 1/100,000 when the original mass is reduced to 1/14,300.

This behavior is probably due to the fact that the crystal lattice of both D_2O and H_2O is substantially formed by the O-atoms while the H-resp. D-atoms do not materially affect its dimensions and both waters thus practically crystallize as a single body. This circumstance had formerly been pointed out by myself, but the absolute impossibility of a stepwise fractionation could not be postulated *a priori*.

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G. BRUNI

RECEIVED AUGUST 23, 1934

OXYGEN A FACTOR IN THE BROMINATION OF CINNAMIC ACID

Sir:

We have found that bromine and cinnamic acid combine rapidly in the dark at room temperature when dissolved oxygen has been removed from the solution. When the oxygen has not been removed, the reaction is very slow in the dark, but it proceeds rapidly in the light. Apparently the many previous investigators of the photobromination of cinnamic acid, including ourselves [Bauer and Daniels, THIS JOURNAL, **56,** 378 (1934)] have been dealing with an oxygen-inhibited reaction.

The experimental apparatus and materials were as described before, except that a side arm containing a magnetic hammer and a sealed-off bulblet of bromine was fused to the quartz reaction cell. The cell was filled with a solution of cinnamic acid in carbon tetrachloride and boiled under reduced pressure at room temperature. The cell was then chilled and sealed off. When the cell had reached 20°, the bromine cell was broken in the dark. In every case the bromine reacted and the solution became colorless so rapidly that the rate of reaction could not be measured conveniently.

Under the same conditions, when a bulblet of oxygen was broken before the bromine bulb was broken, the solution retained its reddish color until exposed to bright light, behaving qualitatively as observed in the earlier investigation when air had not been removed.

Similar results were obtained using simpler apparatus and unpurified materials. An inverted U-tube of Pyrex was provided with a stopcock and tilted in such a way that one leg was partially filled with a carbon tetrachloride solution of cinnamic acid and the other with a carbon tetrachloride solution of bromine, care being taken to prevent bromine from getting into the cinnamic acid solution. Evacuation was continued until the solutions had boiled away to about half of their volumes. The stopcock was closed and on mixing the two solutions the bromine faded out within a few minutes. Admission of air practically stopped the reaction.

These results are in agreement with the findings of Kharasch [Kharasch and Mayo, THIS JOURNAL, **55,** 2468 (1933)] that peroxides affect the addition of hydrobromic acid to the double bond, with those of Schultze [*ibid.*, **56,** 1552, (1934)] that the rate of bromination of cyclopentadiene is affected by oxygen, and with those of Dickinson and Leermakers [*ibid.*, **54,** 3852 (1932)] that oxygen inhibits the photochlorination of tetrachloroethylene.

Experiments in this Laboratory indicate that the influence of oxygen on reactions of this type may be quite general.

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RECEIVED AUGUST 24, 1934

NEW BOOKS

A Comprehensive Treatise on Inorganic and Theoretical Chemistry. By J. W. MELLOR, D.Sc., F.R.S. Vol. XIII. **Iron.** Longmans, Green and Co., 55 Fifth Ave., New York. 1934. ix + 948 pp. 559 figs. 15.5 × 25 cm. Price, $20.00.

This volume continues the discussion of iron and its compounds. Specifically it covers the physical and chemical properties of the free element and the occurrence, preparation and properties of its oxides.

There are many special chapters of great interest and merit; for instance (18) The Mechanical—(19) The Thermal—(20) The Optical—(21) The Electrical—and (22) The Magnetic Properties of Iron and Iron Carbon Alloys; (24) The Corrosion of Iron and Steel; (26) The Passivity of Iron; (31) and (32) Hydrated Ferric Oxide-Hydrosol and-Hydrogel.

An extraordinary amount of information has been assembled in this volume in compact and accessible form, and as tested in a few restricted fields familiar to the reviewer, this information appears to be surprisingly complete. There is certainly no other treatise on this subject in our language which can compare with it in these respects.