Metal ketyl	Solvent	Concn., wt. %	Temp., °C.	Molal susceptibility of solute, χ_M	D, %
p-Biphenyl phenylketone sodium	Benzene	9.4	27	-152×10^{-6}	1.7
p-Biphenyl phenylketone sodium	Dioxane	3.0	26	+339	41
Benzophenone sodium	Benzene	1.7	25	−195	<1.0

A result for *p*-methoxybenzophenone sodium of $D = 33\%$ at 25° and a concentration of 1.0% with benzene as the solvent was also obtained, but, because of the fact that only a small concentration of the metal ketyl could be obtained coupled with the fact that a relatively large excess of the ketone was necessary to cause reaction with the sodium, a large correction thus being made necessary, the results were considered to be not very significant. We found that α-naphthyl phenyl ketone would not form a metal ketyl in benzene solution even though sodium, potassium and sodium amalgam were tried.

Schlenk and Thal [*Ber.*, **46**, 2840 (1913)] advance as evidence that the metal ketyls are completely dissociated (at least in ether solution) the results of certain boiling point measurements. The boiling point reading of the thermometer was taken first for the pure solvent, then after the addition of a small amount of *p*-biphenyl phenyl ketone, and finally after the addition of some potassium metal. The solution was kept in contact with an atmosphere of nitrogen. Schlenk and Thal state that they observed no fall in boiling point after the addition of the potassium. We have repeated their work as nearly as possible, but have obtained quite different results. We made two runs, in each of which there was a fall in boiling point after the addition of the potassium of approximately one-half of the total rise caused by the addition of the ketone. The fall took place over a period of about an hour, and the final reading was a steady one. The fall in boiling point indicates a decrease in the number of moles of dissolved material; this decrease presumably corresponds to the formation of undissociated molecules of the sodium salt of the pinacol. We attempted the experiment also with dioxane as the solvent, but at the boiling point of this solvent (101°) the metal ketyl would not go into solution, but merely formed a protective coating on the surface of the potassium, although the latter was molten.

Sugden [*Trans. Faraday Soc.*, **30**, 18 (1934)] has recently published some results for the magnetic susceptibilities of benzophenone potassium and *p*-biphenyl phenyl ketone potassium in dioxane which show that these metal ketyls are very highly dissociated in the solutions used. His results are in qualitative but not in quantitative agreement with ours. The difference may be due to the fact that the potassium rather than the sodium salt was used. We are not continuing the work because Sugden has promised to furnish more details soon.

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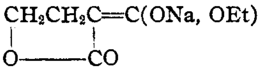
R. N. DOESCHER
G. W. WHELAND

RECEIVED AUGUST 9, 1934

THE FORMATION OF ENOLATES FROM α-LACTONIC ESTERS

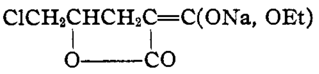
Sir:

Traube and Lehmann [*Ber.*, **34**, 1977 (1901)] treated an alcoholic solution of sodium enol malonic ester with ethylene oxide and obtained a sodium derivative of α-carbethoxybutyrolactone. In continuation of an investigation on the synthesis of lactones from malonic acid and related substances [Michael and Ross, THIS JOURNAL, **55**, 3684 (1933)] we deemed it important to prove experimentally its enolate structure, (I) [Meyer-Jacobson "Lehrb. org. Chem.," I², 641 (1913)]. We find that it can be reformed from the lactone and sodium ethoxide, that it reacts with methyl iodide to form the C-α-methyl derivative, and that treatment with iodine yields a mixture of two stereomeric dilactonic esters. These results definitely prove its enolate structure.



$$\begin{array}{l} CH_2CH_2C{=}C(ONa, OEt) \\ \vert \qquad\quad \vert \\ O \text{———} CO \end{array}$$

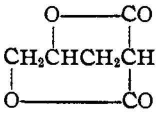
(I)

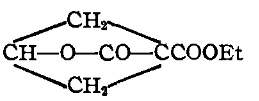


$$\begin{array}{l} ClCH_2CHCH_2C{=}C(ONa, OEt) \\ \qquad\quad \vert \qquad\quad \vert \\ \qquad\quad O \text{———} CO \end{array}$$

(II)

With epichlorohydrin, Traube and Lehmann [*loc. cit.*] isolated the enolate of α-carbethoxy-δ-chlorovalero-γ-lactone (II). On heating this compound with alcohol, and the formed viscous organic product with hydrochloric acid, Leuchs [*Ber.*, **40**, 307 (1901)] obtained a small yield of the γ,δ-dilactone (III). We find the first phase to be an intramolecular C-alkylation, leading to the cyclic tetramethylene lactonic ester (IV), which, on boiling with hydrochloric acid is converted into the γ-δ-dilactone.


(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.

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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