previously recorded[10] of the powerfulness of the molecular still as a tool for displacing chemical equilibria.

The description of these fragmentary experiments with bifunctional Grignard reagents is presented now because it has become necessary to suspend our work in this field.

Summary

A crystalline polydecamethylene carbinol has been prepared by the action of decamethylene dimagnesium bromide on methyl formate. Its properties are described. It is converted into a colorless, insoluble, tough, pliable mass when it is heated in a molecular still.

[10] Papers XI, XII, XIII and XIV.

WILMINGTON, DELAWARE

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d-TALONIC ACID AND GAMMA-TALONOLACTONE

BY LEONARD H. CRETCHER AND ALICE G. RENFREW

Crystalline talonic acid has been described by Hedenburg and Cretcher.[1] In common with other monocarboxylic sugar acids talonic changes slowly in aqueous solutions to an equilibrium mixture of lactone and acid. The crystalline γ-lactone was isolated for the first time during the course of this investigation.

In a study of the mutarotation of aqueous solutions of sugar acids, Levene and Sims[2] found that for several hours the change in specific rotation is determined by the dextro or levo character of the δ-lactone, which forms nearly eight times as rapidly as the γ-lactone. d-Mannonic acid with a *cis*-configuration of the fourth and fifth hydroxyl groups gave rapidly increasing dextro readings during the first four hours, and subsequently showed a slow rise in dextro values. In the case of sugar acids which have the γ- and δ-hydroxyl groups in *trans* positions, Levene and Sims[2] and Rehorst[3] have observed that the values for specific rotation pass through an early maximum or minimum, corresponding to the formation of δ-lactone.

As Rehorst has noted—in accordance with Hudson's rule and in analogy with the behavior of similarly constituted acids—d-talonic acid solutions might be expected to give a series of increasing dextro readings[4] before

[1] Hedenburg and Cretcher, THIS JOURNAL, **49**, 478 (1927).

[2] Levene and Sims, *J. Biol. Chem.*, **65**, 31 (1925).

[3] Rehorst, *Ber.*, **63**, 2279 (1930).

[4] Freudenberg and Kuhn have questioned the validity of a generalization based on these premises and have presented an extensive analysis of rotational data [Freudenberg and Kuhn, *Ber.*, **64**, 703 (1931)].

the more levo readings characteristic of the formation of γ-lactone become apparent. For most of the solutions of talonic acid studied polarimetrically, a slight increase in dextrorotation was observed. Invariably for an interval of thirty to forty-five minutes no decrease in dextrorotation was observed; the decrease, once apparent, became a constant change. The initial lag, including a slight upward trend, definitely suggests the formation of a dextrorotatory δ-lactone. However, if this lactone forms, it must be present in small quantity or must have a specific rotation little higher than the free acid. Talonic acid prepared by alkaline hydrolysis of the pure γ-lactone and liberation of the hexonic acid with hydrochloric acid, gave readings which corresponded closely to the values obtained for the crystalline acid, and showed a small dextro mutarotation during the first half-hour.

It is especially worth noting that although freshly prepared solutions of talonic acid give no evidence of γ-lactone when titrated with $N/10$ sodium hydroxide, nearly 4% of lactone was determined by titration after one hour; during this interval no comparable decrease in specific rotation was recorded. As shown in Table I, the percentages of γ-lactone calculated from titration values are definitely higher than the percentages calculated from the polarimetric readings of the same solutions during the first twenty-four hours. Such a difference in apparent percentages of γ-lactone is similar in character to the differences observed by Levene and Sims[2] for gulonic acid. The rate of formation of γ-talonolactone is of approximately the same order as the rate for γ-galactonolactone.[2]

TABLE I

CRYSTALLINE TALONIC ACID—LACTONE FORMATION

Time	$[\alpha_D]$	$(M)/100$	A % γ-lactone calcd. from optical rotation	B % γ-lactone detd. by titration
3 min.	+18.24°	+37.4°		
1 hour	+18.13	+37.2	0.2	4.8
2 hours	+17.86	+36.6	0.9	6.1
5 hours	+16.74	+34.3	3.1	9.0
7.5 hours	+15.18	+31.1	6.3	12.3
24 hours	+10.16	+20.8	16.7	19.6
55 hours	+ 1.33	+ 2.6	35.0	34.7
Pure lactone	−34.7	−61.7		

Experimental

d-**Talonic Acid.**—Talonic acid was prepared according to the method of Hedenburg and Cretcher[1] by the epimerization of galactonic acid with pyridine at 90–100°. The aqueous solution of the free acid, obtained by decomposition of the cadmium salt, was rapidly concentrated *in vacuo*. In one case the solid product began to separate from the solution before the distillation was discontinued; this product and the further concentrated mother liquor were treated with a large volume of absolute alcohol and chilled several hours before filtration. The crude talonic acid (m. p. 122–125°) was recrystal-

lized from absolute alcohol, in which it is difficultly soluble. The melting point of the recrystallized acid was 138°, and a freshly prepared 4% aqueous solution was strongly dextrorotatory as previously reported.[1] Different preparations gave $[\alpha]_D^{25}$ +18.97°, +18.24°, +19.35°, +19.65°. Talonic acid as liberated from the sodium salt had a correspondingly high specific rotation. The crystalline substance titrated as a free acid with one-half molecule of water of crystallization.

Table II gives typical readings for a solution of talonic acid. Obviously the observed increase in dextro rotation was very small, but the change was noted with most solutions by several investigators in this Laboratory. The temperature was maintained at 25° for two or more hours. As mixtures of talonic acid and lactone approach an equilibrium ratio, the specific rotation changes very slowly. It was hoped that the initial changes in the rotation of talonic acid solutions would be accentuated by conditions which might decrease the reaction velocity. However, measurements made at 9° and a study of a solution of the acid in 50% alcohol gave similar but not more striking variations.

TABLE II

MUTAROTATION DATA

Hours	$[\alpha]$ $l = 4;\ c = 4.4804$	$[\alpha]$
0.05	+3.27°	+18.24°
.083	3.27	18.24
.10	3.29	18.35
.25	3.30	18.40
.41	3.29	18.35
1.0	3.25	18.13

At intervals 2-cc. samples of the solution used for polarimetric study were titrated with $N/10$ sodium hydroxide. The specific rotations calculated for titrated solutions of acid and lactone are in all cases of a lower dextro value than the rotations actually observed. Such a deviation points to the presence of an additional dextrorotating component. Table III gives characteristic observed and calculated specific rotations, as well as the equilibrium values reached by talonic acid solutions. Similar data was obtained for other talonic acid solutions.

TABLE III

DEVIATION OF OBSERVED AND CALCULATED SPECIFIC ROTATIONS

Time	γ-lactone by titration	$[\alpha]$ Observed	$[\alpha]$ Calcd. from titration data	Deviation in $[\alpha]$
1 hour	4.8%	+18.13°	+15.7°	2.4°
2 hours	6.1	+17.86	+14.0	3.8
7.5 hours	12.3	+15.2	+11.7	3.5
55 hours	34.7	+ 1.33	− 0.1	1.4
16 days	75.5	−21.1	−21.7	0.6
Soln. heated	81.4	−24.0	−24.8	0.8

Preparation of γ-*d*-Talonolactone.—It was found that fairly pure γ-lactone could be obtained from very concentrated aqueous sirups of approximately equilibrium mixtures of talonic acid and lactone, when crystallization had been started by mechanical agitation or by seeding. The lactone crystallized from the concentrate of talonic acid solutions which had been heated several hours at 100° or four hours at 60–75°. A small amount of insoluble amorphous material formed during prolonged heating. If the sirups were seeded and allowed to stand for several days, the large hard crystals could be readily freed from the mother liquor by filtration and careful washing with 70–80% alcohol. In one case the lactone crystallized in transparent prisms from a dilute solution during the reconcentration of the alcoholic mother liquors from the preparation of talonic acid.

The lactone was recrystallized from water and from 75% alcohol. Final recrystallization from glacial acetic acid, from absolute alcohol or from water gave material melting at 132–134°. Water is not a convenient medium for recrystallization, because the solutions must be very concentrated before the lactone can be recovered.

Anal. Calcd. for $C_6H_{10}O_6$: C, 40.45; H, 5.66. Found: C, 40.44; H, 5.69.

The γ-lactone is quite stable in aqueous solutions, $[\alpha]_D^{25}$ −34.65°; $\alpha = -1.66°$; $l = 2$; $c = 2.3951$ g. No change in rotation was observed in two hours; after six hours $[\alpha] = -34.0°$; after twenty-four hours $[\alpha] = -33.5°$; and after five days $[\alpha] = -28.4°$. A solution of lactone, which had been heated for several hours at 100°, to apparent equilibrium, had a specific rotation of $[\alpha] = -28.7°$ and titrated for 11% of free acid. Although the ratio of free acid and lactone was not the equilibrium value reached by solutions of the crystalline acid, it seems probable that the difference was due to the extremely slow rate of change of solutions in this general range of concentration. Several prepared solutions of acid–lactone mixtures, containing between 11 and 18% molar proportions of crystalline acid, showed no deviation from the calculated specific rotation. These solutions changed very slowly in the direction of higher acid concentration.

The titration of a solution of talonolactone (well cooled in ice water) gave no evidence of free acid. The complete neutralization of the lactone was accomplished after heating above room temperature.

Anal. 0.1197 g. of lactone required 6.74 cc. of $N/10$ NaOH (phenolphthalein). Calcd. for $C_6H_{10}O_6$: 6.73 cc.

Classification as a γ-lactone is based on the slow change in the specific rotation of aqueous solutions, the levorotation of such solutions (Hudson's rule), and the delayed neutralization of dilute alkali.

A sample of talonic lactone was hydrolyzed with normal sodium hydroxide, and free talonic acid liberated with normal hydrochloric acid.[2] 0.9148 g. of lactone in 25 cc. is equivalent to 1.0535 g. of acid: four minutes after the addition of hydrochloric acid, $[\alpha]_D^{25}$ +18.50°; $\alpha = +3.12°$; $l = 4$; $c = 4.214$ g. The agreement in specific rotation with the values determined for solutions of the crystalline acid affords a cross-check on the purity of the two preparations. The initial dextro mutaroration of such solutions was of the same order as that observed for the crystalline acid.

Summary

1. The determination of the specific rotation of *d*-talonic acid has been repeated. The values obtained for the crystalline acid and for the acid liberated from the sodium salt are slightly higher than the specific rotation reported by Hedenburg and Cretcher.

[5] Haworth, "The Constitution of Sugars," Edward Arnold & Co., 1929, p. 14.

. 2. The shape of the mutarotation curve for talonic acid solutions is indicative of the formation of a dextro rotating δ-talonolactone, as well as a levo rotating γ-talonolactone.

3. γ-Talonolactone has been separated in crystalline form.

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THE REACTION BETWEEN ORGANIC MAGNESIUM HALIDES AND ALPHA-BROMO KETONES

BY E. P. KOHLER AND M. TISHLER

Many years ago Kohler and Johnstin[1] studied the action of organic magnesium halides on α-bromo-β,β-diphenyl propiophenone and, for reasons which seemed good at the time, represented the process with the equation

$$(C_6H_5)_2CHCHBrCOC_6H_5 + 2RMgBr = (C_6H_5)_2CHCH{=}C{\Big\langle}{\overset{\textstyle OMgBr}{\underset{\textstyle C_6H_5}{}}} + R{\cdot}R + MgBr_2$$
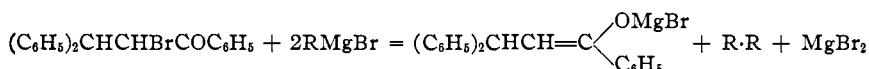
A few years later Umnowa[2] treated α-bromo-pentamethyl acetone with methylmagnesium iodide and obtained a similar result, but, for reasons which likewise seemed good at the time, represented the process in a different manner

$$(CH_3)_3CCOCBr(CH_3)_2 + CH_3MgI = (CH_3)_3CCOC(CH_3)_2 + CH_3Br$$
$$\underset{\textstyle MgI}{|}$$
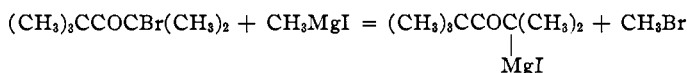
Quite recently Löwenbein and Schuster[3] rediscovered the reaction, represented their product with a formula similar to the one adopted by Kohler and Johnstin and proposed a mechanism which, in the case studied by them, was plausible

$$(C_6H_5)_2CBrCOC_6H_5 + C_6H_5MgBr \longrightarrow MgBr_2 + C_6H_5(C_6H_5{-}C_6H_5) +$$
$$\overset{\textstyle I}{}$$

$$(C_6H_5)_2\overset{|}{C}{-}COC_6H_5 \rightleftharpoons (C_6H_5)_2C{=}\overset{\textstyle O}{\overset{|}{C}}C_6H_5 + C_6H_5MgBr \longrightarrow$$
$$\overset{}{\underset{\textstyle II}{}}$$

$$(C_6H_5)_2C{=}CC_6H_5 + C_6H_5(C_6H_5{-}C_6H_5)$$
$$\underset{\textstyle OMgBr}{|}$$
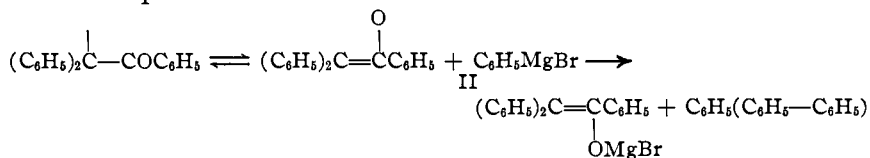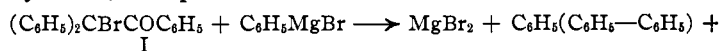
Fisher, Oakwood and Fuson,[4] who came across the same reaction when they treated tribromoacetomesitylene with alkyl magnesium halides, likewise preferred to represent their magnesium derivative as an enolate.

[1] Kohler and Johnstin, *Am. Chem. J.*, **33**, 45 (1905).

[2] Umnowa, *Chem. Zentr.*, **84**, I, 1402 (1913); *J. Russ. Phys.-Chem. Soc.*, **45**, 881 (1913).

[3] Löwenbein and Schuster, *Ann.*, **481**, 106 (1930).

[4] Fisher, Oakwood and Fuson, THIS JOURNAL, **52**, 5038 (1930).