[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF LOUISVILLE]

2-Pyrones. XVII. Aryl Hydrazones of Triacetic Lactone and Their Rearrangement to 1-Aryl-3-carboxy-6-methyl-4-pyridazones. The Methyl Ether of Triacetic Lactone

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Twelve aryl diazonium salts have been coupled with triacetic lactone to yield aryl hydrazones. Under the same conditions 3-bromotriacetic lactone and methylene bis-(triacetic lactone) were found to undergo coupling and elimination reactions to yield the same products as the unsubstituted triacetic lactone. The hydrazones readily rearrange upon treatment with either aqueous base or acid to 1-aryl-3-carboxy-6-methyl-4-pyridazones. Infrared studies have shown that, contrary to previous reports, only one monomethyl ether of triacetic lactone is formed on reaction with diazomethane and that it is 6-methyl-4-methoxy-2-pyrone.

In an earlier paper of this series[2] we have treated the condensation of β-methylglutaconic anhydride with various aryl diazonium salts. The products of these reactions are tautomeric hydrazones that rearrange to 1-aryl-3-carboxy-4-methyl-6-pyridazones. In a continuing study of the reactions of 2-pyrones with aryl diazonium salts we have treated triacetic lactone (I)[3] with twelve diazonium salts to give 3-arylhydrazonotriacetic lactones (II). The unsubstituted phenylhydrazone has been previously prepared and assigned a phenylhydrazone structure because it reacted with additional phenylhydrazine to yield an osazone.[4] The phenylhydrazone structure is confirmed by the observed ultraviolet absorption maxima at 410 mμ which is associated with such structures.[2]

Data characterizing twelve 3-arylhydrazonotriacetic lactones are given in Table I. These materials are precipitated upon adding a solution of the diazotized amine to a cold alkaline solution of triacetic lactone that contains a few drops of pyridine. The color of these materials varies from golden yellow to brown. α-Naphthylamine, 4-aminobiphenyl and 2-amino-3,5-diiodobenzoic acid were diazotized as their hydrochlorides in glacial acetic acid. The reaction of 3-bromotriacetic lactone and methylene bis-(triacetic lactone) with various diazonium salts, listed in Table I, gave products which were identical with those obtained from triacetic lactone itself by elimination of the 3-substituent. Elimination reactions occurring in aliphatic compounds when coupled with a diazonium salt are known,[5,6] but to our knowledge this is the first case of such phenomena occurring in the pyrone series.[6a]

Upon treatment with either aqueous base or acid the arylhydrazones rearrange to 1-aryl-3-carboxy-6-methyl-4-pyridazones (III). This type of rearrangement has been reported before using the isomeric 4-methyl-6-hydroxy-2-pyrones (β-methylglutaconic anhydrides[2]) but this is the first time the rearrangement has been applied to the 6-methyl-4-hydroxy-2-pyrone (triacetic lactone) types. These 4-pyridazones represent a new structural class isomeric with the 6-pyridazones previously reported.[2] The structure of the product is confirmed by the infrared absorption of 1-phenyl-3-carboxy-6-methyl-4-pyridazone which shows absorption maxima in the carbonyl region quite distinct from those of the isomeric 1-phenyl-3-carboxy-4-methyl-6-pyridazone. The 6-pyridazone shows strong maxima at 1750 cm.$^{-1}$ (5.75 μ) attributable to the acid carbonyl and at 1650 cm.$^{-1}$ (6.05 μ) attributable to the amide carbonyl. The 4-pyridazone shows a broad absorption band over the 1660–1720 cm.$^{-1}$ (5.8–6.0 μ) region with shoulders attributable to an overlapping of the ketonic and carboxylic carbonyl groups. The maxima for the OH stretching frequency in the 4-pyridazone is at 3350–3500 cm.$^{-1}$ (2.8–3.0 μ) shifted from the normal position as a probable result of hydrogen bonding in the β-keto acid structure.[7] Absorption in this region for the 6-pyridazone consists of a broad maxima overlapping the C–H stretching frequencies so as to obscure individual contributions of the component structural features.

In our investigations of the reactions of triacetic lactone derivatives with aryl diazonium salts we became aware of the confusion in the literature regarding the structure of the methyl ether obtained from triacetic lactone. It has been reported that it is a 2-methoxy-4-pyrone,[8] m.p. 86°, on the basis of its formation of an ether-insoluble hydrochloride. It has also been reported that the methylation of triacetic lactone with diazomethane gives a physical mixture of the 4-methoxy-2-pyrone (IV) and the 2-methoxy-4-pyrone (V).[9]

This physical mixture was reputedly separated by precipitation of the ether-insoluble hydrochloride of one of the pair which was then assigned the structure of the 4-pyrone on the assumption that this structure explained the increased basic character. The melting points of these compounds separated by this method were reported to be 92–94° (IV) and 88–89° (V). We have repeated the preparation of the ether by the action of diazomethane on triacetic lactone and the procedure outlined for separation of the hydrochlorides. The

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[1] National Science Foundation Predoctoral Research Assistant.

[2] R. H. Wiley and C. H. Jarboe, THIS JOURNAL, **77**, 403 (1955).

[3] The *Chemical Abstracts* systematic name for this compound is 6-methyl-2H-pyran-2,4(3H)-dione. It is indexed under triacetic lactone.

[4] A. Tamburello, *Chem. Zentr.*, **76**, I, 348 (1905); A. Tamburello and E. Carapelle, *Gazz. chim. ital.*, **37I**, 564 (1907).

[5] G. T. Morgan and J. Reilly, *J. Chem. Soc.*, **103**, 810 (1913).

[6] H. v. Pechmann, *Ber.*, **25**, 3175 (1892).

[6a] NOTE ADDED IN PROOF.—Apparently this is the first observation of a Japp–Klingemann reaction in which a halogen or an alkyl rather than one of the acyl groups is eliminated. This peculiar loss of halogen or alkyl is consistent with the failure of dehydroacetic acid to undergo coupling since in this compound an acyl group, available for elimination, is not eliminated.

[7] R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, THIS JOURNAL, **71**, 1068 (1949).

[8] F. Arndt and S. Avan, *Ber.*, **84**, 343 (1951).

[9] S. Janiszewska-Drabarek, *Roczniki Chem.*, **27**, 456 (1953).

precipitated hydrochloride was converted to the free pyrone, m.p. 89°, by treatment of a dry ether slurry of the salt with triethylamine. The ether-soluble material was found to be a mixture of triacetic lactone and the methyl ether, m.p. 89°, which could be separated by extraction with petroleum ether. The two products were found to be identical. The mixed melting point was 89° and the infrared spectra were identical. On the basis of these findings we believe that the "soluble" ether previously described is a mixture of unreacted lactone with the same methyl ether which precipitates as an insoluble hydrochloride, but we are unable to account for the difference in melting points of the two products previously reported.

These observations establish that only one methyl ether is formed in this reaction and the infrared absorption spectra provide the data needed for a conclusive assignment of the structure of the ether. The methyl ether shows very strong carbonyl absorption at 1720 cm.$^{-1}$ (5.8 μ) and a strong absorption at the C–O stretching frequency at 1250 cm.$^{-1}$ (8.0 μ). These maxima occur at the same wave lengths as do the carbonyl absorption maxima observed with a variety of 2-pyrones.[10] The absorption at 1660 cm.$^{-1}$ (6.0 μ) is typical of the absorption at carbonyl frequencies observed with 4-pyrones[11] and with α,β-α',β'-unsaturated ketones.[12] There is no absorption at the carbon–oxygen stretching frequency shown in the spectra for the 4-pyrone structure. These comparisons are so conclusive as to establish without further doubt the structure of the methyl ether as that of the 4-methoxy-2-pyrone.

Comparison of the infrared spectrum for triacetic lactone with that of 4-methoxy-2-pyrone provides additional evidence that the lactone also has the 2-pyrone structure. The absorption maximum at 1720 cm.$^{-1}$ (5.8 μ) characteristic of the 2-pyrone carbonyl absorption and the maximum at 1250 cm.$^{-1}$ (8.0 μ) characteristic of the C–O stretching frequency clearly differentiate the absorption characteristics of triacetic lactone from those of 4-pyrones. The absorption maximum at 6.08 μ is possibly a carbonyl absorption shifted to this position by intermolecular hydrogen bonding. These observations confirm previous studies[13] of the reaction of triacetic lactone with ethyl acetylenedicarboxylate which were interpreted as establishing the 2-pyrone structure for the lactone. Our attempt to use this reaction with the methyl ether gave no conclusive results. We have also observed that the methyl ether fails to couple with diazonium salts. This also is inconsistent with the 4-pyrone structure, which is known to couple,[14] but is consistent with the 2-pyrone structure which has never been observed to couple in the absence of some activating influence such as a 3,4- or 6-hydroxy substituent.

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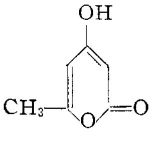

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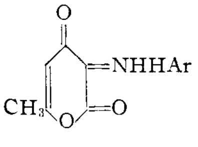

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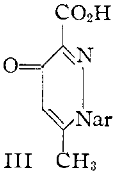

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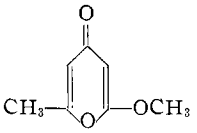

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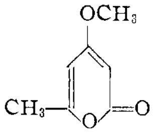

V

Experimental

Triacetic lactone,[15] m.p. 188°, methylene bis-(triacetic lactone),[16] m.p. 247°, and 3-bromotriacetic lactone,[8] m.p. 214°, were prepared by methods previously described.

3-Arylhydrazonotriacetic Lactones (II) from Triacetic Lactone and its Derivatives.—The procedure followed will be illustrated with the coupling of triacetic lactone and diazotized *m*-chloroaniline to give 3-(*m*-chlorophenylhydrazono)-triacetic lactone.

A solution of 0.6 g. (0.005 mole) of triacetic lactone in 25 ml. of water containing 5 drops of pyridine and 8.0 g. of potassium carbonate was cooled to 5°. To this solution was added a cold solution of 0.8 (0.006 mole) of diazotized *m*-chloroaniline. After one hour at 5°, the precipitated solid was collected on a filter, dried, and recrystallized from benzene to give 1.2 g., 92.5%, of yellow needles, m.p. 233°.

The coupling reactions with derivatives of triacetic lactone and with other anilines were run using similar molar quantities and the same procedure. The solvents used for recrystallization, the yields obtained, the melting points, and analytical data characterizing the products are given in Table I.

1-Aryl-3-carboxy-6-methyl-4-pyridazones (III) from Triacetic Lactone Arylhydrazones (II).—The procedure followed will be illustrated with the details of the rearrangement of 3-phenylhydrazonotriacetic lactone (II, Ar = phenyl) to 1-phenyl-3-carboxy-6-methyl-4-pyridazone (III, Ar = phenyl).

A solution of 0.5 g. (0.0025 mole) of 3-phenylhydrazonotriacetic lactone in 50 ml. of 12 *N* hydrochloric acid was refluxed for 3 hours. The color of the solution is discharged during this time. The precipitated product formed on cooling the reaction mixture was recrystallized from water to give 0.4 g., 80%, of long white needles, m.p. 173°.

4-Methoxy-6-methyl-2-pyrone.—Five grams of carefully recrystallized triacetic lactone were stirred with 50 ml. of anhydrous ether while approximately 6 g. of diazomethane in 300 ml. of dry ether was added. During this time the reaction mixture was held at 0–5°. The triacetic lactone gradually dissolved to give a clear yellow solution. Evaporation left 5.5 g. of white needles. This product, just as obtained from the reaction, was redissolved in ether to give a colorless solution and treated with dry hydrogen chloride for 4 hours. The precipitated solid was collected, suspended in ether, and treated with 10 ml. of triethylamine. The amine hydrochloride was separated and the remaining solution evaporated to give 1.4 g. of a solid. Recrystallization from petroleum ether (30–60°) gave white needles, m.p. 89°. Evaporation of the mother liquor remaining from the hydrochloride separation gave 3.0 g. of product which was

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[10] A comprehensive study of the infrared absorption characteristics of a variety of 2-pyrones has been made in our laboratories and will be reported elsewhere. The authors are indebted to Mrs. Ellen V. Mochel for having assisted in these studies.

[11] L. L. Woods, THIS JOURNAL, **77**, 3161 (1955).

[12] H. Gilman, "Organic Chemistry—An Advanced Treatise," Vol. III, Second Edition, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 152.

[13] K. Alder and H. F. Rickert, *Ber.*, **70**, 1354 (1937).

[14] R. T. Muller and W. H. Crowe, *J. Chem. Soc.*, 1753 (1927).

[15] F. Arndt, *Ber.*, **68**, 1574 (1935).

[16] W. Dieckmann and F. Breest, *ibid.*, **37**, 3387 (1904).

extracted with boiling petroleum ether. On cooling, the petroleum ether solution deposited 2.0 g. of white crystals, m.p. 89°. This product shows no depression of melting point when mixed with that obtained by the hydrochloride. The petroleum-ether-insoluble material (m.p. crude *ca.* 155–160°) was recrystallized from water to give a pure product, m.p. 188°, which showed no depression of melting point when mixed with triacetic lactone. The total yield of the 4-methoxy-6-methyl-2-pyrone, m.p. 89°, was 3.4 g., 60%.

Absorption Data.—The ultraviolet absorption measurements were made using 1.0-cm. silica cells and 95% ethanol solutions in a Beckman DU spectrophotometer. The infrared absorption measurements were made using potassium bromide pellets and a Baird double beam recording infrared spectrophotometer. 3-Phenylhydrazonotriacetic lactone shows absorption maxima at 248 mμ (log ϵ 1.33), 325 mμ (log ϵ 0.88) and 410 mμ (log ϵ 1.82).

Table I

3-Arylhydrazonotriacetic Lactones

Aryl	Color	M.p., °C.	Yield, %	Recrys.[a] from	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Phenyl	Rusty orange	193[b]	87	B				
o-Toluyl	Orange	217	90	B	11.47[c]	11.63[c]		
p-Biphenyl	Yellow-orange	281	93.5	B	70.58	70.75	4.61	4.66
2-Methyl-4-nitrophenyl	Yellow fibrous	255	93	B	54.18	54.07	3.83	3.61
2,4-Diiodo-6-carboxyphenyl	Brown	239	74.5	E,P[d]	49.25[e]	48.82[e]		
2,5-Dimethoxyphenyl	Red brown	185	55	B	57.93	58.14	4.86	4.76
m-Chlorophenyl	Yellow	233[f]	92.5	B	54.45	54.48	3.47	3.46
p-Chlorophenyl	Golden	248	96	B	54.45	54.78	3.47	3.52
o-Methoxyphenyl	Rust brown	193	84.5	E	59.99	60.01	4.65	4.77
p-Methoxyphenyl	Burned orange	199	92.5	B	59.99	60.26	4.65	4.68
1-Naphthyl	Rust brown	233	71.5	B	68.56		4.32	
2-Naphthyl	Orange	241[g]	85.7	E,G[h]	68.56	68.73	4.32	4.14

[a] B, benzene; E, ethyl acetate; P, petroleum ether; G, glacial acetic acid. [b] Obtained also from 3-bromotriacetic lactone (yield 50%). [c] Analysis for nitrogen. [d] A mixture of 3 parts ethyl acetate and 1 part petroleum ether, at −20° for one month. [e] Analysis for iodine. [f] Obtained also from 3-bromotriacetic lactone (yield 60%) and methylene bis-(triacetic lactone) (yield 80%). [g] Obtained also from 3-bromotriacetic lactone (yield 45%) and methylene bis-(triacetic lactone) (yield 70%). [h] A mixture of 2 parts glacial acetic acid and 8 parts ethyl acetate.

Table II

1-Aryl-3-carboxy-6-methyl-4-pyridazones

Aryl group	M.p., °C.	Recrys.[a] from	Yield, %	Analyses[b] Calcd.	Analyses[b] Found
Phenyl[c]	173	W	80	N, 12.15	12.11
m-Chlorophenyl	193	EG	60	N, 10.60	10.51
o-Methoxyphenyl	170	EG	50	C, 59.99	60.00
				H, 4.65	4.65
2-Methyl-4-nitrophenyl	246	G	30	N, 14.53	14.39
p-Toluyl	154	EG	70	C, 63 92	64.03
				H, 4.95	4.87

[a] E, ethyl acetate; G, glacial acetic acid; W, water; EG, 50% glacial acetic acid and 50% ethyl ether. [b] C, carbon; H, hydrogen; N, nitrogen. [c] Neutralization equivalent 229, calcd. 230.

Louisville 8, Ky.

[Contribution from the Chemical and Physical Research Laboratories, The Firestone Tire and Rubber Co.]

cis- and *trans*-Polyesters Formed by Condensation of Geometric Isomers of 2-Butene-1,4-diols and Ethene-1,2-dicarboxylic Acids

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Synthetic all-*cis* and all-*trans* polymers have not been reported. Low molecular weight polyesters of both *cis*- and *trans*-2-butene-1,4-diol with maleic and fumaric acid were synthesized and characterized. The monomers and polymers hydrogenate at significantly different rates. Only the all-*trans* polymer was crystalline by X-ray methods. The all-*cis* polymer was successfully crosslinked to give a clear film. No isomerization of the all-*cis* and all-*trans* polymers was indicated by chemical, X-ray and infrared analyses.

Introduction

Hevea and balata occur in nature in all-*cis* and all-*trans* configurations, respectively, but no exclusively *cis* or *trans* synthetic polymers were known. We have achieved the synthesis of such polymers.

In considering methods for the preparation of all-*cis* or all-*trans* polymers, we felt that ester interchange polyesterification offered the best possibility of success owing to the comparative mildness of such reactions over conventional esterification methods.

We therefore prepared pure *cis*- and *trans*-2-butene-1,4-diols and carried out their transesterification with methyl and ethyl maleate and fumarate, respectively. Diols of the highest possible purity are essential. The transesterification proceeded smoothly with methyl and ethyl maleate and with methyl fumarate in the presence of magnesium metal. Ethyl fumarate reacted sluggishly and required sodium as a catalyst. Identical *cis* or *trans* polymers resulted from either methyl or ethyl esters. Polymer yields were practically quantitative. At higher polymerization temperatures, insoluble cross-linked polymers resulted.

The all-*cis* and all-*trans* natures of the polymers

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