

A New Synthesis of 2-Pyrones

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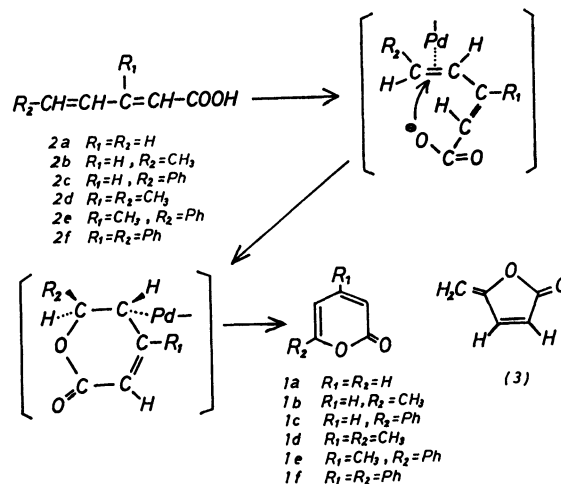
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Synopsis. The reaction of sodium salt of penta-2,4-dienoic acids with lithium chloropalladite in a polar solvent such as water led to the formation of 2-pyrone derivatives.

Numerous reports on the synthesis of 2-pyrones (**1**) have appeared in the literature.¹⁾ However, no direct cyclization of penta-2,4-dienoic acids (**2**) into **1** has yet been reported. In this report, we wish to describe an intramolecular cyclization of **2** to **1** with lithium chloropalladite in moderate yields.

The solution of sodium salt of penta-2,4-dienoic acid (**2a**) in water was stirred with lithium chloropalladite under reflux to produce 2-pyrone (**1a**) in a 72% yield. The experiment in a mixture of dioxane and water (1:1) gave also **1a** in a 67% yield. In the conversion of **2a** to **1a** with palladium(II) salt, no formation of the five-membered-ring product [protoanemonin (**3**)] was observed.

Similarly, 6-methyl- and 6-phenyl-2-pyrone (**1b** and **1c**) were synthesized from sorbic acid (**2b**) and 5-phenylpenta-2,4-dienoic acid (**2c**) respectively. The reactions carried out are summarized in Table 1. In the presence of palladium(II) salt, the reaction of nucleophile with olefins has received considerable attention;²⁾ however, only a few reports are known in the field of intramolecular oxy-palladation.³⁾ Henry and Ward,⁴⁾ have reported that the reaction of olefins with palladium(II) acetate gave products which were consistent with a *trans* acetoxy-palladation, followed by a *cis* elimination of hydridopalladium. Recently, Hosokawa *et al.*⁵⁾ have reported that, in the reaction between 2- γ -methylallylphenol and palladium(II) acetate, the processes of both *cis*- and *trans*-oxy-palladations are involved. However, in the reaction of **2** with palladium(II) salt, the reaction is explained only by a *trans*-oxy-palladation, since a *cis*-palladium-hydride elimination is a general process.^{4,6)}



Experimental

Materials. All the melting points are uncorrected. The following compounds were synthesized by the methods described in the literature: penta-2,4-dienoic acid (**2a**),⁷⁾ 5-phenylpenta-2,4-dienoic acid (**2c**),⁸⁾ 3,5-dimethylpenta-2,4-dienoic acid (**2d**),⁹⁾ 3-methyl-5-phenylpenta-2,4-dienoic acid (**2e**),⁹⁾ and 3,5-diphenylpenta-2,4-dienoic acid (**2f**).⁹⁾ Sorbic acid (**2b**) of a commercial grade was used without further purification.

General Procedure for the Preparation of 1. A solution of 10 mmol of **2** and 5 mmol of sodium carbonate in water (50 ml) or dioxane-water (1:1, 50 ml) was stirred with 10 mmol of lithium chloropalladite under reflux for 4 hr. The reaction mixture was then extracted with ether. The ether layer was washed with water and then dried over anhydrous magnesium sulfate. After the evaporation of the solvent, the product was isolated by distillation or by column chromatogram on silica gel. The structures of the products were confirmed by a

TABLE 1. REACTION OF PENTA-2,4-DIENOIC ACID (**2**) WITH LITHIUM CHLOROPALLADITE

Substrate	Solvent	Product	Yield (%) ^{a)}
2a	H ₂ O	2-Pyrone (1a)	72
2a	Dioxane-H ₂ O	1a	67
2b	H ₂ O	6-Methyl-2-pyrone (1b) ^{c)}	75
2b	Dioxane-H ₂ O	1b	70
2c	H ₂ O	6-Phenyl-2-pyrone (1c) ^{d)}	68
2d	H ₂ O	4,6-Dimethyl-2-pyrone (1d) ^{e)}	65
2e	H ₂ O	4-Methyl-6-phenyl-2-pyrone (1e) ^{f)}	65
2f	H ₂ O	4,6-Diphenyl-2-pyrone (1f) ^{g)}	68

a) Yields are based upon the lithium chloropalladite. b) Bp 102—103 °C/18 mmHg (lit.^{h)} bp 110 °C/26 mmHg). c) Bp 80—82 °C/18 mmHg (lit.^{h)} bp 80—85 °C/20 mmHg). d) Mp 67—68 °C (lit.^{h)} mp 68 °C). e) Mp 48—49 °C (lit.^{k)} mp 49—50 °C). f) Mp 88—90 °C (lit.^{h)} mp 90 °C). g) Mp 137—139 °C (lit.^{m)} mp 138—139 °C). h) H. E. Zimmerman, G. L. Grunewald, and R. M. Paufler, "Organic Synthesis," Vol. 46, p. 101 (1966). i) E. Dunkelbleum, M. Rey, and A. S. Dreiding, *Helv. Chim. Acta*, **54**, 6 (1971). j) J. Kalff, *Rec. Trav. Chim. Pays-Bas*, **46**, 596 (1927). k) K. Yamada, *This Bulletin*, **35**, 1323 (1962). l) K. E. Schulte, J. Reisch, and O. Heine, *Arch. Pharmaz.*, **294**, 236 (1961). m) A. Arndt and B. Eistert, *Ber.*, **58**, 2318 (1925).

mixed-melting-point determination, by comparing the retention times on the gas chromatogram, and by the observation of the IR and NMR spectra. The results are summarized in Table 1.

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