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THE FORMATION OF TRICARBONYL-SUBSTITUTED AROMATIC COMPOUNDS FROM CARBONYL-SUBSTITUTED OLEFINS BY PALLADIUM(II) SALTS IN THE PRESENCE OF SODIUM ACETATE

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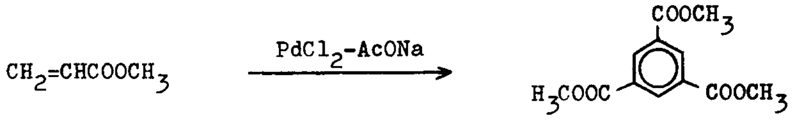
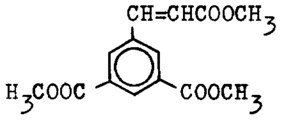
In the previous papers[1], we described the formation of cinnamic acid derivatives from saturated aliphatic acids and aromatic compounds by palladium (II) salts. In the course of further investigation of these reactions, we found that the reaction of methyl acrylate with palladium(II) chloride and sodium acetate in acetic acid at 100° gave trimethyl trimesate (I), albeit in the low yield (4.6%), along with smaller amounts of other aromatic products, such as methyl 3,5-dicarbomethoxycinnamate (II)[2], methyl 2,4,6-tricarbomethoxyphenylacetate (III)[3], trimethyl methyltrimesate (IV), tetramethyl pyromellitate (V) and dimethyl terephthalate (VI). Similarly, ethyl acrylate gave triethyl trimesate (3.1%) as a major aromatic product.



I

(1)



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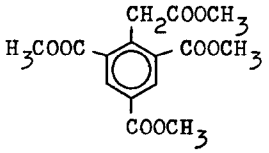

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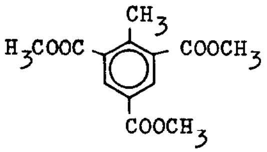

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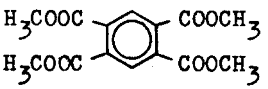

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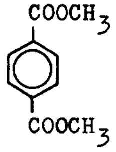
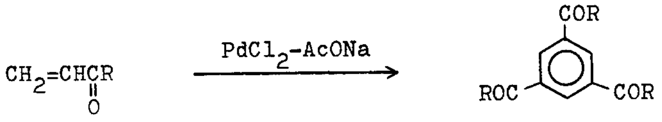


VI

Although the cyclotrimerization of acetylenic compounds with various metal complexes has been recently reported by many workers[4], the formation of aromatic compounds from the simple olefinic compounds is little known except that of triacetylbenzene from crotonaldehyde by palladium(II) chloride[5]. From this point of view, the formation of a variety of aromatic esters from acrylic acid esters is very interesting. As an extention of this work, the reaction of some carbonyl-substituted olefins, such as but-1-en-3-one and pent-1-en-3-one, with palladium(II) salts in the presence of sodium acetate has been investigated.

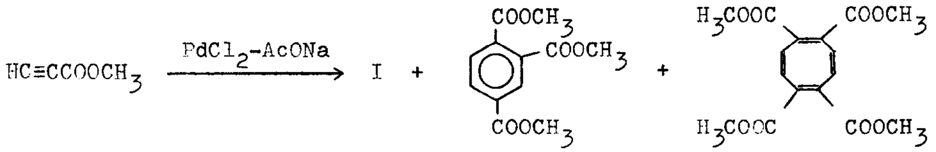
After heating a mixture of but-1-en-3-one (4.2 g, 0.06 mole), palladium(II) acetate (4.5 g, 0.02 mole) and sodium acetate (16.4 g, 0.20 mole) in acetic acid (100 ml) at 100° for 10 hr under nitrogen[6], 1,3,5-triacetylbenzene (VIIa) (25%) was isolated as a sole aromatic product, together with oily oligomers of but-1-en-3-one (0.3 g) and 4-acetoxybutan-2-one (a small amount). The similar reactions of but-1-en-3-one and pent-1-en-3-one with palladium(II) chloride in the presence of sodium acetate gave VIIa (17%) and 1,3,5-tripropionylbenzene (VIIb) (12%), respectively. The addition of cupric acetate to the former reaction increased the yield of VIIa to 30%.



VIIa R = $-CH_3$
b $-C_2H_5$

(2)

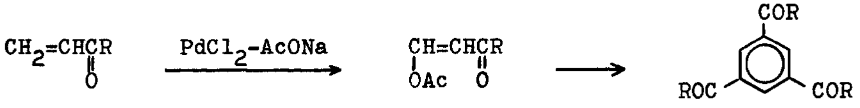
In the above reactions, palladium(II) salts may play an important role in the formation of aromatic compounds, since the absence of palladium(II) salts did not give any aromatic compounds. It has been known that various metal complexes give aromatic compounds from acetylenic compounds[7]. However, the reaction of methyl propiolate with palladium(II) chloride and sodium acetate in acetic acid at 80° gave trimethyl trimellitate (VIII) and 1,2,5,6-tetracarbomethoxycyclooctatetraene (IX) as well as I (product ratio; 63 : 8 : 29), in addition to polymeric products. The formation of VIII and IX may indicate that the present aromatization of carbonyl-substituted olefins does not proceed via an acetylenic intermediate. It is also general that the base-catalyzed aromatization of β-acetoxyolefinic compounds, such as 1-acetoxybuten-3-one[8] and methyl β-acetoxyacrylate[9], leads to the formation of 1,3,5-trisubstituted benzenes. Under the present conditions, the reaction of methyl β-acetoxyacrylate with palladium(II) chloride and sodium acetate gave almost the same result as that of the reaction of methyl acrylate. The similar reaction of 1-sodiumoxybuten-3-one gave 1,3,5-triacetylbenzene (VIIa) as a sole aromatic product. These results show that the formation of enol esters as an intermediate may be important in the formation of ester- or carbonyl-substituted olefins.



VIII IX

(3)

It is well known that the reaction of olefinic compounds with palladium (II) salt and sodium acetate gives the corresponding vinyl acetates[10]. This fact also supports that the aromatization of carbonyl-substituted olefins may principally proceed via the formation of β-acetoxyvinylketone or ester, followed by the aldol-type condensation.



(4)

R= $-OCH_3$, $-OC_2H_5$, $-CH_3$, $-C_2H_5$

References

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3. The III was identical with the authentic material in all respects of the spectral data.
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