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RADIATION-INDUCED REDUCTION OF AROMATIC CARBOXYLIC ESTERS IN ALCOHOLIC SOLUTIONS

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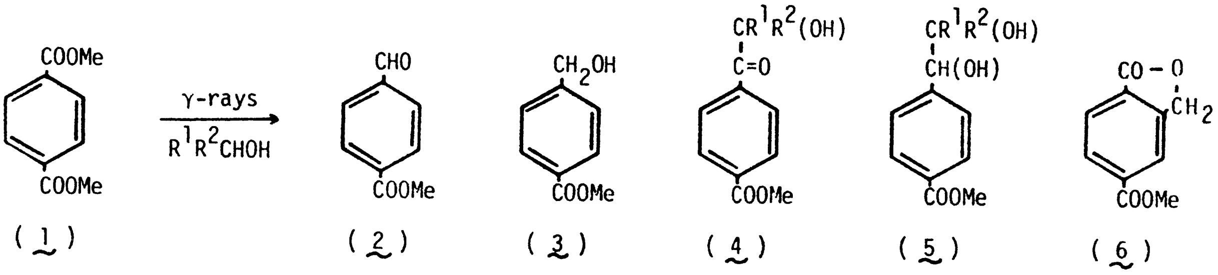
Gamma-irradiation of aromatic carboxylic esters in alcoholic solutions brings about the reduction of the ester group to aldehyde, alcohol, α-ketoalcohol, and 1,2-glycol. The reduction is effected by solvated electrons and solvent-derived hydroxyalkyl radicals.

Although the radiation-induced reactions of some simple carboxylic esters in pure form have been investigated,[1,2] a few studies have been made on the behavior of carboxylic esters in solution under ionizing radiation. The intermediates formed in the radiolysis of carboxylic esters have been studied by means of ESR,[3] but the mechanism of the radiation-induced reactions has not been discussed on the basis of product analysis. We report here several types of radiation-induced reduction of aromatic carboxylic esters in alcoholic solutions, comparing the radiation-induced reactions with the photochemical reactions,[4] and with the radiation-induced reactions of pyridinecarboxylic esters.[5]

Aromatic carboxylic esters (1.0×10^{-2} mol dm^{-3}) in alcoholic solutions were irradiated under nitrogen by Co-60 γ-rays (dose rate, 5×10^{5} rad h^{-1}; dose, 1.0×10^{7} rad). The products were separated by means of TLC and identified by IR, NMR, and MS. G-values of the products were determined by means of gas-chromatographic analyses.

Although benzoic and isophthalic esters give only substitution products in small G-values, terephthalic and phthalic esters give several types of reduction products when they are irradiated with Co-60 γ-rays in alcoholic solutions. For example, in the γ-irradiation of dimethyl terephthalate in 2-propanol, four types of reduction products were identified.6)



a, $R^1 = R^2 = H$; b, $R^1 = Me$, $R^2 = H$; c, $R^1 = R^2 = Me$

In methanol a lactone(6) which was formed probably in the course of separation from the substitution product, dimethyl 2-hydroxymethylterephthalate, was also obtained.

The G-values of the products are summarized in Table 1.

Table 1. Radiation-induced reactions of dimethyl terephthalate in alcoholic solutions
[Dimethyl terephthalate] = 1.0×10^{-2} mol dm^{-3}
Dose rate, 5×10^5 rad h^{-1}; Dose, 1.0×10^7 rad.

Alcohol	Additive	G-values of products				
		2	3	4	5	6
MeOH $R^1=R^2=H$	——	0.002	0.004	*	0.12	0.009b)
	N_2Oa)	0.002	0.003	*	0.07	0.016b)
EtOH $R^1=Me$, $R^2=H$	——	0.002	0.003	*	0.19	*
	N_2Oa)	0.001	0.003	*	0.08	*
i-PrOH $R^1=R^2=Me$	——	0.024	0.054	0.26	0.30	*
	N_2Oa)	0.013	0.050	0.23	0.57	*

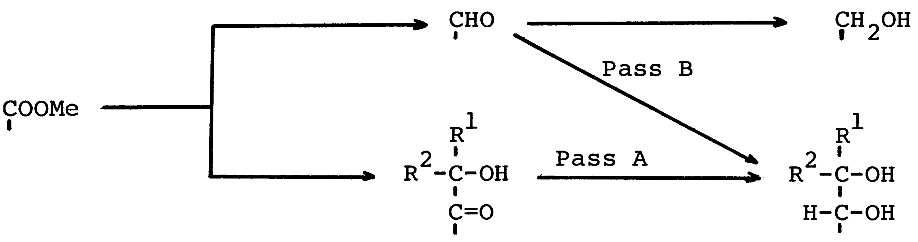
* Not determined.

a) N_2O was saturated at room temperature before irradiation.

b) Isolation yield

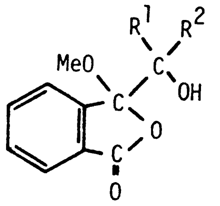
In addition to the alcohol(**3**), the similar compounds of which were found in the radiation-induced reactions of pyridinecarboxylic esters,[5)] aldehyde(**2**), α-ketoalcohol(**4**), and 1,2-glycol(**5**) are obtained in considerable G-values.

The following sequence of reactions could be postulated.



The radiation-induced reaction of methyl p-formylbenzoate(**2**) in 2-propanol gives **3** , **5c** , and 1,2-bis(4-methoxycarbonylphenyl)-1,2-ethanediol in the G-values of 0.06, 0.03, and 0.27, respectively. G-values for **5c** from **2** is smaller than the value for **5c** from **1** . This fact excludes the exclusive formation of **5c** from **2** . Therefore, Pass A and B are operating simultaneously.

In the radiation-induced reaction of dimethyl phthalate in alcohols, 1-hydroxyalkyl-1-methoxyphthalides (**7**)[7)] were obtained as main products, G(**7a**) in methanol, G(**7b**) in ethanol, and G(**7c**) in 2-propanol being 0.12, 0.13, and 0.27, respectively. Compound **7** is equivalent to α-ketoalcohol **4** . It is noteworthy that the compound of the structure similar to **4** and **7** were obtained in the photoreaction of dimethyl phthalate and tetramethyl benzenetetracarboxylate in isopropylbenzene.[4)]



(**7**)

a, $R^1=R^2=H$
b, $R^1=Me$, $R^2=H$
c, $R^1=R^2=Me$

As the reducing species formed in the radiolysis of the system, solvated electrons, hydrogen atoms, and hydroxyalkyl radicals are conceivable. As is seen in Table 1, effects of N_2O on the reduction are small. In the presence of N_2O solvated electrons are converted efficiently to hydroxyl radicals, which attack alcohols to give hydroxyalkyl radicals. Small effects of N_2O suggest that the hydroxyalkyl radicals bring about the reduction as effectively as solvated electrons. The role of the hydroxyalkyl radicals for the reduction is supported by the results on the UV-irradiation of dimethyl terephthalate in 2-propanol-acetone

(1.35 mol dm^{-3}) solutions, in which 1-hydroxy-1-methylethyl radicals should be formed. The UV-irradiation of the system with a high pressure mercury lamp gives the reduction products, **2** , **3** , **4c** , and **5c** .

References and Notes

1) P.Ausloos and C.N.Trumbore, J. Am. Chem. Soc., 81, 3866 (1959).

2) R.W.Hummel, Trans. Faraday Soc., 56, 234 (1960).

3) Y.Nakajima, S.Sato, and S.Shida, Bull. Chem. Soc. Jpn., 42, 2132 (1969).

4) K.Fukui, K.Senda, Y.Shigemitsu, and Y.Odaira, J. Org. Chem., 37, 3176 (1972).

5) K.Nakamura, Y.Morita, T.Suzuki, T.Sugiyama, and A.Sugimori, Bull. Chem. Soc. Jpn., 52, 488 (1979).

6) Methyl p-formylbenzoate(**2**) was identified by comparison with the authentic sample synthesized from p-methoxycarbonylbenzoyl chloride by Rosenmund reduction according to the synthesis of benzaldehyde from benzoyl chloride (E.B.Hershberg and J.Cason, Org. Synth., Coll. Vol.III, 623 (1955)).
Methyl p-hydroxymethylbenzoate(**3**) was identified by comparison with the authentic specimen prepared by the catalytic hydrogenation of **2** over U-Ni-B catalyst.
1-(4-Methoxycarbonylphenyl)-2-hydroxy-2-methyl-1-propanone(**4c**) mp 44-45 °C; IR(KBr disc) 3500(OH), 2980(CH), 1760(C=O), 1700(C=O), and 1680 cm^{-1}(C=O); NMR($CDCl_3$) δ= 1.60(6H, s, CH_3-C), 3.93(3H, s, CH_3-O), and 8.03(4H, ring H). Found: C, 64.98; H, 6.50%. Calcd. for $C_{12}H_{14}O_4$: C, 64.85, H, 6.35%.
1-(4-Methoxycarbonylphenyl)-2-methyl-1,2-propanediol(**5c**) liquid; IR 3450(OH) and 1705 cm^{-1}(C=O); NMR($CDCl_3$) δ= 1.05(3H, s, CH_3-C), 1.20(3H, s, CH_3-C),1.48(2H,OH), 3.89(3H, s, CH_3-O), 4.54(1H, s, $C\underline{H}$-OH), 7.40 and 7.93 (each 2H, d, J = 8.0 Hz, ring H). The compound was obtained by the catalytic hydrogenation of **4c** over Raney Co catalyst.

7) 1-(1-Hydroxy-1-methylethyl)-1-methoxyphthalide(**7c**) mp 86-87 °C; IR(KBr disc) 3500(OH) and 1755 cm^{-1}(lactone C=O); NMR($CDCl_3$) δ=1.05(3H, s, CH_3-C), 1.46 (3H, s, CH_3-C), 2.40(1H, s, OH), 3.07(3H, s, CH_3-O). and 7.66(4H, m, ring H); MS(70 eV), m/e(rel. intensity) 191(2), 175(16), 164(78), 163(53), 159(100), 135(13), 105(27).
Found: C, 64.87; H, 6.70%. Calcd. for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35%.

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