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REACTION OF ETHYL 3-OXOBUTANOATE AND ETHYL 4-BROMO-3-OXOBUTANOATE WITH BENZENE IN THE PRESENCE OF ALUMINUM CHLORIDE

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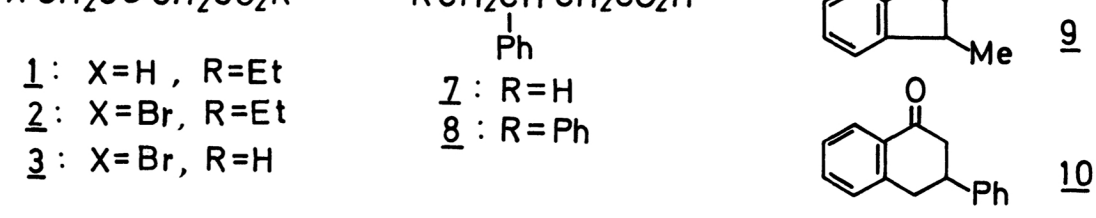
Refluxing of ethyl 3-oxobutanoate (1) in benzene in the presence of aluminum chloride gave ethylbenzene (4), 9,10-dimethylanthracene (5), 3-phenylbutanoic acid (7), and 3-methyl-1-indanone (9). Similar reaction of ethyl 4-bromo-3-oxobutanoate (2) yielded 4, 5, 4-bromo-3-oxobutanoic acid (3), 3,4-diphenylbutanoic acid (8), and 3-phenyl-1-tetralone (10).

While investigating some potential uses of diketene, we have studied reactions of 4-halo-3-oxobutanoate which is most easily prepared from diketene.[1] In the present paper, we wish to report its Friedel-Crafts reaction. Concerning this reaction Labunskii reported the reaction between ethyl 3-oxobutanoate (1) and benzene in the presence of aluminum chloride to give ethylbenzene (4), 9,10-dimethylanthracene (5), and phenylacetic acid (6).[2]

First, we reinvestigated this reaction and obtained some variant results. According to the procedure reported by Labunskii,[2] two equivalents of aluminum chloride were added gradually in portions to a solution of the ester (1) in benzene with stirring. After heating at 70-80° for 3 hr, the reaction mixture was poured into cold HCl, and the benzene layer was fractionally distilled to give ethylbenzene (4) (35%), bp 130-133°, and the starting ester (1) (1%), bp 75-80° (20 mmHg). The residue was dissolved in ether, and the ether solution was washed with 5% $NaHCO_3$. The $NaHCO_3$ washing was acidified with 10% HCl to give 3-phenylbutanoic acid (7) (1%) bp 107-109° (1 mmHg) (lit[3] bp 113-115° (2 mmHg)). The ether layer was purified by silica gel column chromatography to give 9,10-dimethylanthracene (trace) (5), mp 177-178° (lit[4] mp 180°). When the reaction was carried out in the presence of five equivalents of aluminum chloride, products obtained were 4 (9.4%), 5 (29%), 7 (41.5%), and 3-methyl-1-indanone (9) (50%), bp 80° (1 mmHg) (lit[5] bp 118-119° (11 mmHg)). Phenylacetic acid (6) was not detected.



Next, Friedel-Crafts reaction of ethyl 4-bromo-3-oxobutanoate (2) was carried out. To a boiling suspension of aluminum chloride in dry benzene, was added dropwise a solution of the bromoester (2) in benzene. After additional refluxing, the reaction mixture was poured into a mixture of conc. HCl and ice with stirring. The benzene layer separated was washed with 10% Na_2CO_3. The aqueous layer was acidified to give 3,4-diphenylbutanoic acid (8), mp 93-94° (lit[6] mp 96-97°), and 4-bromo-3-oxobutanoic acid (3), mp 66-67° (lit[7] mp 69-69.5°). The benzene layer was distilled to give ethylbenzene (4), and the residue was purified by silica gel column chromatography to give 9,10-dimethylanthracene (5), and 3-phenyl-1-tetralone (10), mp 64-65° (lit[8] mp 65°). The results are summarized in Table I.

Table I Reaction of ethyl 4-bromo-3-oxobutanoate (2) with benzene

Benzene	2	$AlCl_3$	Reaction Time(hr)	Reaction Temperature(°C)	Yield(%) 2	3	4	5	8	10
20 ml	2.1 g (0.01mol)	1.34 g (0.01mol)	3	20	71	+a)	+b)	–	–	–
20 ml	2.1 g (0.01mol)	1.34 g (0.01mol)	3	80	52	+a)	9	+a)	–	–
20 ml	2.1 g (0.01mol)	2.68 g (0.02mol)	1	80	46	15	12	+a)	–	–
20 ml	2.1 g (0.01mol)	2.68 g (0.02mol)	3	80	–	–	+b)	2	11	+a)
20 ml	2.1 g (0.01mol)	4.0 g (0.03mol)	3	80	–	–	+b)	28	47	5
20 ml	2.1 g (0.01mol)	6.7 g (0.05mol)	3	80	–	–	+b)	29	38	41

a) These compounds were identified by silica gel thin layer chromatography.
b) This compound was identified by gas chromatography on a 2 m×2.5 mm silicon OV-17 (5% on Chromosorb AW-HMDS) column at 100°.

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