CHEMISTRY LETTERS, pp. 337-338, 1979. Published by the Chemical Society of Japan

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

Tetsuzo KATO* and Hitoshi KIMURA
Pharmaceutical Institute, Tohoku University, Aobayama, Sendai 980

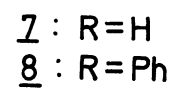
Refluxing of ethyl 3-oxobutanoate (1) in benzene in the presence of aluminum chloride gave ethylbenzene (4), 9,10-dimethylanthracene (5), 3-phenylbutanoic acid (7), and 3-methyl-1-indanone (9). Similar reaction of ethyl 4-bromo-3-oxobutanoate (2) yielded 4, 5, 4-bromo-3-oxobutanoic acid (3), 3,4-diphenylbutanoic 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) (lit3) 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° (lit4) 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) (lit5) bp 118-119° (11 mmHg)). Phenylacetic acid (6) was not detected.

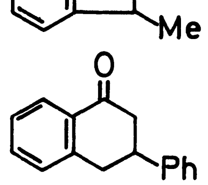
$XCH_2COCH_2CO_2R$

1: X=H, R=Et
2: X=Br, R=Et
3: X=Br, R=H

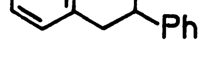


$RCH_2\underset{Ph}{CH}CH_2CO_2H$

7: R=H
8: R=Ph



9



10

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°.

References

1) F. Chick and N. T. M. Wilsmore, *J. Chem. Soc.*, 97, 1978 (1910).
2) I. P. Labunskii, *J. Gen. Chem. USSR*, 31, 1467 (1961).
3) K. Bott, *Chem. Ber.*, 100, 2791 (1967).
4) C. S. Gibson and J. D. A. Johnson, *J. Chem. Soc.*, 1931, 753.
5) J. v. Braun and G. Kirschbaum, *Ber.*, 46, 3041 (1913).
6) L. L. McCoy and A. Zagalo, *J. Org. Chem.*, 25, 824 (1960).
7) K. J. Boosen, Brit. Pat., 209 725 (1969).
8) S. Ruhemann, *J. Chem. Soc.*, 97, 460 (1910).

(Received February 16, 1979)