796. *Preparation of Unsaturated Keto-acids from the Interaction of Ethylene and Acid Anhydrides.*

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Ethylene and acid anhydride–aluminium chloride complexes in ethylene chloride provide unsaturated keto-acids in low yield. With maleic anhydride 6-methyl-4-oxohepta-2 : 5-dien-1-oic acid is unexpectedly obtained. By using the corresponding half ester chlorides higher yields are obtained.

The reaction of ethylene and *cyclo*hexene with acid chloride–aluminium chloride complex in methylene or ethylene chloride has been reported.[1] This paper is concerned with the application of these solvents to the Friedel–Crafts acylation of ethylene with succinic and maleic anhydride and related compounds. Experimental procedure was complicated, partly by the low solubility of the anhydrides and their complexes and partly by polymerisation, and products were obtained in only poor yield. Higher yields were obtained by replacing the acid anhydride with the corresponding half ester chloride.

Ethylene and succinic anhydride reacted at a convenient rate at 25—30°, and reaction was essentially complete when 1 mol. of ethylene had been absorbed. The main product was 4-oxohex-5-enoic acid. Catalytic hydrogenation converted this acid into 4-oxohexanoic acid, which was identified as its oxime and semicarbazone.

$$CH_2{:}CH_2 + \overline{CO\cdot CH_2\cdot CH_2\cdot COO} \longrightarrow CH_2{:}CH\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2H$$

Ethylene and maleic anhydride reacted at 25°, but only in the presence of excess of aluminium chloride, and more than 2 mols. of ethylene were absorbed before reaction slackened. Decomposition of the mixture with hydrochloric acid and ice, esterification with diazomethane, and distillation under reduced pressure from anhydrous sodium carbonate gave a product from which methyl 6-methyl-4-oxohepta-2 : 5-dienoate was isolated.

$$2CH_2{:}CH_2 + \overline{CO\cdot CH{:}CH\cdot COO} \longrightarrow Me_2C{:}CH\cdot CO\cdot CH{:}CH\cdot CO_2H$$

Recently, Matsumoto, Hata, and Nischida [2] observed a similar reaction, acylation of ethylene with benzoyl chloride in tetrachloroethane in the presence of excess of aluminium chloride giving *iso*butenyl phenyl ketone. In absence of an excess of aluminium chloride, the expected product, phenyl vinyl ketone, was obtained. These authors carried out the reaction at 0° during 24 hr. and obtained *iso*butenyl phenyl ketone in 30—50% yield:

$$2CH_2{:}CH_2 + Ph\cdot CO\cdot Cl \longrightarrow Ph\cdot CO\cdot CH{:}CMe_2$$

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[1] Baddeley, Taylor, and Pickles, *J.*, 1953, 124.

[2] Matsumoto, Hata, and Nischida, *J. Org. Chem.*, 1958, **23**, 106.

In ethylene dichloride, ethylene was found to react readily with benzoyl chloride–aluminium chloride complex in the presence of excess of aluminium chloride at 25°, and a 40% yield of *iso*butenyl phenyl ketone was obtained in 1 hr.

The low yields obtained by using the anhydride–aluminium chloride complex suggested the use of the corresponding half ester chloride; the problem of limited solubility of the acid anhydride and its complex with aluminium chloride is then overcome. Reaction of ethylene with β-methoxycarbonylpropionyl chloride and with γ-methoxycarbonylbutyryl chloride, using 1 mol. of aluminium chloride, occurred readily at 35°, ceased sharply when 1 mol. of ethylene had been absorbed, and afforded methyl 4-oxohex-5-enoate and 5-oxohept-6-enoate, respectively, in good yield. Distillation under reduced pressure from anhydrous sodium carbonate is necessary to remove traces of chlorine. In contrast, there was no reaction between ethylene and β-methoxycarbonylacryloyl chloride.

Interaction of ethylene with acylating agents.

Acylating agent	Temp.	Product	Yield (%)
$(\mathrm{Me{\cdot}CO})_2\mathrm{O}$ [1]	−5°	$\mathrm{Me{\cdot}CO{\cdot}CH_2{\cdot}CH_2Cl}$	40
$\overline{\mathrm{CO{\cdot}CH_2{\cdot}CH_2{\cdot}COO}}$	30	$\mathrm{CH_2{:}CH{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H}$	25
Poly(adipic anhydride)	20—60	—	0
$\overline{\mathrm{CO{\cdot}CH{:}CH{\cdot}COO}}$	25	$\mathrm{Me_2C{:}CH{\cdot}CO{\cdot}CH{:}CH{\cdot}CO_2H}$	15
$\mathrm{MeO_2C{\cdot}[CH_2]_2{\cdot}COCl}$	35	$\mathrm{CH_2{:}CH{\cdot}CO{\cdot}[CH_2]_2{\cdot}CO_2Me}$	85
$\mathrm{MeO_2C{\cdot}[CH_2]_3{\cdot}COCl}$	35	$\mathrm{CH_2{:}CH{:}CO{\cdot}[CH_2]_3{\cdot}CO_2Me}$	40
$\mathrm{MeO_2C{\cdot}CH{:}CH{\cdot}COCl}$	30—60	—	0
$\mathrm{Ph{\cdot}COCl}$	30	$\mathrm{Ph{\cdot}CO{\cdot}CH{:}CMe_2}$	40

The saturated keto-acids required for identification were obtained in 40—50% yield from the corresponding dialkylcadmium and the appropriate half ester chloride, following Gilman and Nelson's method.[3] The use of the Grignard compound R·MgBr[4] was unsuccessful when applied to R = alkyl, and the alkylzinc halides [5] gave poor yields.

EXPERIMENTAL

Ethylene and Succinic Anhydride.—Powdered aluminium chloride (0·60 mole) was added with stirring to succinic anhydride (0·25 mole) in ethylene dichloride (500 ml.). The succinic anhydride–aluminium chloride complex solution was decanted from excess of aluminium chloride, and dry ethylene passed into the agitated solution at 25°; absorption ceased when 12 l. had been absorbed. The product was poured into dilute hydrochloric acid and ice, and the dried ($\mathrm{Na_2SO_4}$) organic layer distilled under reduced pressure in the presence of anhydrous sodium carbonate giving 4-oxohex-5-enoic acid (7 g.), b. p. 146—148° (Found: C, 55·9; H, 6·2. Calc. for $\mathrm{C_6H_8O_3}$: C, 56·2; H, 6·3%). A sample (2·00 g.) in ethanol (25 ml.) absorbed hydrogen (353 ml.; corr. to S.T.P. Required 350 ml.) in the presence of palladium (0·2 g.). The reduced product, b. p. 151°/10 mm., readily afforded an oxime, m. p. 72°, and a semicarbazone, m. p. 168°, which did not depress the m. p.s of the corresponding derivatives of 4-oxohexanoic acid.

Ethylene and Maleic Anhydride.—Powdered aluminium chloride (1·2 moles) was added to maleic anhydride (0·50 mole) in ethylene dichloride (400 ml.). Dry ethylene was passed into the agitated solution maintained at $<30°$. After 30 l. had been absorbed, the mixture was poured into dilute hydrochloric acid and ice, and the organic layer dried ($\mathrm{Na_2SO_4}$). Removal of the solvent gave a dark residue (36 g.). This was set aside with ethereal diazomethane [prepared from methylnitrosourea (30 g.)] for 1 hr., the ether was removed, and the residue was distilled under reduced pressure, affording a main fraction (17 g.), b. p. 95°/0·2 mm. The yellow solid, obtained by cooling at 0°, was recrystallised from light petroleum (b. p. 0—40°), giving methyl 6-methyl-4-oxohepta-2 : 5-dienoate (11 g.), m. p. 40° (Found: C, 63·9; H, 7·1. Calc. for $\mathrm{C_9H_{12}O_3}$: C, 64·2; H, 7·1%). A Kuhn–Roth estimation of terminal methyl group gave 8·1% *C*-Me. (Calc. for 1 *C*-Me 8·9%). Ozonolysis of the product, followed by decomposition of the ozonide with 2N-sodium hydroxide, afforded acetone (2 : 4-dinitrophenylhydrazone,

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[3] Gilman and Nelson, *Rec. Trav. chim.*, 1936, **55**, 518.
[4] Fieser and Dandt, *J. Amer. Chem. Soc.*, 1941, **63**, 782.
[5] Clutterbuck and Raper, *J. Biochem.*, 1925, **19**, 390.

m. p. 128°). A sample (5·00 g.) in ethanol (40 ml.) absorbed hydrogen (1310 ml., corr. to S.T.P. Calc. for $C_9H_{12}O_3$: 1333 ml.) in the presence of palladium (0·2 g.). The reduced product was hydrolysed by dilute hydrochloric acid. The acid, b. p. 112°/10 mm., readily formed a semicarbazone, m. p. 148°, which did not depress the m. p. of the semicarbazone of 6-methyl-4-oxoheptanoic acid, m. p. 148°, but did depress that of the semicarbazone of 4-oxo-octanoic acid, m. p. 155°.

Ethylene and Poly(adipic Anhydride).—Dry ethylene did not react with the poly(adipic anhydride)–aluminium chloride complex in ethylene dichloride. The addition of more aluminium chloride also had no effect.

Ethylene and β-Methoxycarbonylpropionyl Chloride.—β-Methoxycarbonylpropionyl chloride (0·25 mole) was added to a suspension of aluminium chloride (0·30 mole) in ethylene dichloride (200 ml.). The complex was decanted from excess of aluminium chloride. Dry ethylene was absorbed at a steady rate at 35° until 6 l. had been taken up. The product was then poured into dilute hydrochloric acid and ice, and the dried (Na_2SO_4) organic layer distilled twice under reduced pressure from anhydrous sodium carbonate, giving methyl 4-oxohex-5-enoate (27 g.), b. p. 96°/10 mm. (Found: C, 59·0; H, 6·9. Calc. for $C_7H_{10}O_3$: C, 59·2; H, 7·0%). The ester (5·00 g.) in ethanol (40 ml.) absorbed hydrogen (794 ml., corr. to S.T.P. Calc. for $C_7H_{10}O_3$: 788 ml.) in the presence of palladium (0·2 g.) giving methyl 4-oxohexanoate, b. p. 92°/10 mm., identified as its semicarbazone, m. p. 142°.

Ethylene and γ-Methoxycarbonylbutyryl Chloride.—γ-Methoxycarbonyl butyryl chloride (0·25 mole) was treated exactly as was β-methoxycarbonylpropionyl chloride (0·25 mole), providing methyl 5-oxohept-6-enoate (15 g.), b. p. 110°/12 mm. (Found: C, 61·3; H, 7·7. Calc. for $C_8H_{12}O_3$: C, 61·5; H, 7·7%). The product was hydrogenated to methyl 5-oxoheptanoate, identified as its semicarbazone, m. p. 106°.

Ethylene and Benzoyl Chloride.—Dry ethylene was passed into an agitated solution of benzoyl chloride (0·25 mole) and aluminium chloride (0·35 mole) in ethylene chloride (200 ml.), and the temperature kept below 30° by cooling. After 30 l. of ethylene had been absorbed the mixture was poured into dilute hydrochloric acid and ice. The organic layer was dried (Na_2SO_4) and distilled giving *iso*butenyl phenyl ketone (17 g.), b. p. 122—124°/10 mm. The product gave a 2 : 4-dinitrophenylhydrazone, m. p. 180—181° (Matsumoto, Hata, and Nischida [2] record m. p. 180—181°).

β-Methoxycarbonylpropionyl Chloride.—Succinic anhydride (1 mole) was gently refluxed with methanol (1 mole) for 30 min.; the thionyl chloride (1·2 moles) was added and the mixture refluxed for 1 hr. The excess of thionyl chloride was distilled off and the residue distilled giving β-methoxycarbonylpropionyl chloride (0·90 mole), b. p. 87°/14 mm.

γ-Methoxycarbonylbutyryl Chloride.—This was similarly prepared from glutaric anhydride. It had b. p. 98°/12 mm.

β-Methoxycarbonylacryloyl Chloride.—Fumaric acid (1 mole) was ground with phosphorus pentachloride (2 moles) and the mixture heated (water-bath) for 3 hr. The product was distilled, giving, after removal of phosphorus oxychloride, fumaroyl dichloride (0·63 mole), b. p. 62°/12 mm. Methanol (0·63 mole) was added, the mixture refluxed for 1 hr., and the product distilled. β-Methoxycarbonylacryloyl chloride (0·58 mole), b. p. 83°/12 mm., was obtained.

Saturated Keto-acids.—Powdered cadmium bromide (0·1 mole) was added to the alkylmagnesium halide (0·2 mole) in sodium-dried ether (150 ml.), and the mixture was refluxed for 3 hr. The required half ester chloride (0·2 mole) was then added and the mixture refluxed for a further 3 hr., with stirring until the product solidified. Dilute sulphuric acid was added and the organic layer was dried (Na_2SO_4). Removal of the solvent and distillation under reduced pressure afforded the methyl ester of the required keto-acid (see Table).

Keto-acid	B. p.	Ester, b. p.	Semicarbazone of acid, m. p.	Semicarbazone of ester, m. p.
$EtCO{\cdot}[CH_2]_2{\cdot}CO_2H$ …………	142°/10 mm.	91°/14 mm.	186°	142°
$PrCO{\cdot}[CH_2]_2{\cdot}CO_2H$ …………	—	102°/10 mm.	—	106°
$BuCO{\cdot}[CH_2]_2{\cdot}CO_2H$ …………	155°/10 mm.	112°/10 mm.	155°	—
$Bu^iCO{\cdot}[CH_2]_2{\cdot}CO_2H$ …………	155°/10 mm.	112°/10 mm.	148°	102°
$EtCO{\cdot}[CH_2]_3{\cdot}CO_2H$ …………	—	104°/10 mm.	—	106°

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