

Reactions of acid chlorides with ethers in the presence of iron pentacarbonyl

HOWARD ALPER¹ AND J. T. EDWARD

Department of Chemistry, McGill University, Montreal, Quebec

Received September 9, 1969

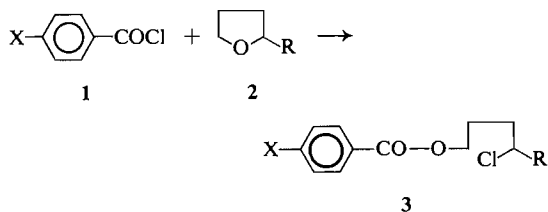
Iron pentacarbonyl catalyzes the cleavage of alkyl ethers by acid chlorides to form alkyl chlorides and alkyl esters.

On catalyse avec le pentacarbonyl du fer la rupture des éthers alkylés par les chlorures des acides carboxyliques, pour donner les chlorures et les esters alkylés.

Canadian Journal of Chemistry, 48, 1623 (1970)

Iron pentacarbonyl has proved a remarkably versatile reagent in organic chemistry, effecting deoxygenation (1), diene rearrangement (2), dehydration (3), and deoxygenation (4), and we have now found it to be effective in catalyzing the cleavage of alkyl ethers by acid chlorides. The last reaction is more effectively catalyzed by Lewis acids such as titanium, stannic, or zinc chlorides (5), but occasionally it may prove advantageous to use iron pentacarbonyl as a slower but milder catalyst.

Butyl ether was cleaved by octanoyl, benzoyl, and *p*-methoxybenzoyl chlorides in the presence of an equimolar amount of iron pentacarbonyl to give the corresponding butyl esters. (No attempt was made to isolate *n*-butyl chloride, presumably the other reaction product.) In similar fashion, benzoyl chloride (1; X = H) and *p*-methoxybenzoyl chloride (1; X = OMe) reacted with tetrahydrofuran (2; R = H) to give the chloroesters 3 (R = H, X = H, and OMe), and *p*-methoxybenzoyl chloride reacted with 2-methyltetrahydrofuran (2; R = Me) to give the chloroester 3 (R = Me, X = OMe). No



attempt was made to study the mechanism of these reactions; however, it was shown that it

did not involve catalysis by ferric chloride, produced in some way from iron pentacarbonyl, because in the presence of anhydrous ferric chloride tetrahydrofuran reacted with *p*-methoxybenzoyl chloride to give not the chloroester 3 (R = H, X = OMe), but a high-boiling oligomer. This was shown by its nuclear magnetic resonance (n.m.r.) spectrum to be produced by the reaction of several tetrahydrofuran molecules for each acid chloride molecule. In the absence of the acid chloride, tetrahydrofuran was unaffected by ferric chloride (cf. ref. 6).

Experimental

Reaction of Acid Chlorides with Butyl Ether in Presence of Iron Pentacarbonyl

A mixture of the acid chloride (20–40 mmole) and iron pentacarbonyl (1.1 mole/mole of acid chloride) in dry butyl ether (40 ml) was boiled under reflux while being stirred under nitrogen for 17 h. The mixture was cooled, filtered to remove insoluble inorganic material (shown to contain ferrous chloride by a blue coloration with potassium ferricyanide), and concentrated at 30 mm. Distillation of the residue gave the butyl ester, identified by b.p. and infrared (i.r.) spectrum; yields and b.p.'s were: butyl octanoate, 75%, b.p. 243–245° (lit. b.p. 245° (7)); butyl benzoate, 67%, b.p. 248–250° (lit. b.p. 247° (7)); butyl *p*-methoxybenzoate, 66%, b.p. 165–167° at 20 mm (lit. b.p. 186–187° at 40 mm (7)).

Reaction of Acid Chlorides with Tetrahydrofuran and 2-Methyltetrahydrofuran in Presence of Iron Pentacarbonyl

A mixture of benzoyl chloride (5.25 g; 37.3 mmole) and iron pentacarbonyl (5.52 ml; 41.1 mmole) in dry tetrahydrofuran (40 ml) was refluxed while being stirred under nitrogen for 40 h. The mixture was worked up as above, and yielded 4-chlorobutyl benzoate (3; X = R = H) (7.98 g; 86%), b.p. 142–144° at 5 mm (lit. b.p. 140–143° at 5 mm (5)).

By the same procedure, *p*-methoxybenzoyl chloride in tetrahydrofuran gave 4-chlorobutyl *p*-methoxybenzoate (3; R = H, X = OMe) (78%), b.p. 160–162° at 1 mm, positive test for Cl, ν_{max} 1717 cm^{-1} (neat liquid). Nuclear

¹Holder of NRCC Studentships, 1965–1967. Present address: Department of Chemistry, State University of New York at Binghamton, Binghamton, New York 13901, U.S.A.

magnetic resonance spectrum (in CCl_4):² triplet at δ 4.20 (CH_2 adjacent to $-\text{OCOR}$); triplet at δ 3.50 (CH_2 adjacent to Cl); multiplet at δ 1.82 (remaining CH_2CH_2).

Anal. Calcd. for $\text{C}_{12}\text{H}_{15}\text{O}_3\text{Cl}$: C, 59.4; H, 6.2. Found: C, 59.8; H, 6.4.

Similarly, *p*-methoxybenzoyl chloride in 2-methyl-tetrahydrofuran gave 4-chloro-1-pentyl *p*-methoxybenzoate (**3**; R = Me, X = OMe) (76%), b.p. 147–149° at 0.5 mm, positive test for Cl, ν_{max} 1720 cm^{-1} (neat). Nuclear magnetic resonance spectrum:² triplet at δ 4.17 (CH_2 adjacent to OCOR); multiplet at δ 4.05 (CHCl); doublet at δ 1.43 (CH_3); multiplet at δ 1.77 (remaining CH_2CH_2).

Anal. Calcd. for $\text{C}_{13}\text{H}_{17}\text{O}_3\text{Cl}$: C, 60.8; H, 6.7. Found: C, 61.1; H, 6.8.

Reaction of p-Methoxybenzoyl Chloride with Tetrahydrofuran in Presence of Ferric Chloride

A mixture of *p*-methoxybenzoyl chloride (43.9 mmole) and anhydrous ferric chloride (48.3 mmole) in dry tetrahydrofuran (40 ml) was refluxed for 40 h with stirring

²Aromatic and OMe protons gave signals at the expected frequencies.

under nitrogen and then worked up by the usual procedure. A liquid boiling at 295–298° (0.4 mm) was obtained showing an n.m.r. spectrum similar to that of **3** (R = H, X = OMe), but having weaker aromatic and OMe signals.

We are grateful to the National Research Council of Canada for financial support.

1. H. ALPER and J. T. EDWARD. *J. Org. Chem.* **32**, 2938 (1967).
2. H. ALPER and J. T. EDWARD. *J. Organometal. Chem.* **14**, 411 (1968).
3. H. ALPER and J. T. EDWARD. *Can. J. Chem.* **46**, 3112 (1968).
4. H. ALPER and J. T. EDWARD. *Can. J. Chem.* In press.
5. M. G. SYNERHOLM. *Organic synthesis*. Coll. Vol. III. Edited by E. C. Horning. J. Wiley and Sons, New York, 1955. p. 187.
6. J. SAEGASA, H. IMAI, and J. FURUKAWA. *Macromol. Chem.* **54**, 218 (1962).
7. C. D. HODGMAN (Editor). *Handbook of chemistry and physics*. Chemical Rubber Publishing Co. Cleveland, 1966.

On the occurrence of ononin in *Thermopsis rhombifolia* (Nutt.) Richards

M. H. BENN AND CHURAI WATANATADA

Environmental Sciences Centre: Kananaskis, The University, Calgary 44, Alberta

Received December 2, 1969

Ononin, formononetin-*O*- β -D-glucopyranoside, was isolated from *Thermopsis rhombifolia* (Nutt.) Richards. It seems very probable that this is the substance A which Marion and Manske isolated from this plant, and that their substance B was formononetin itself.

Canadian Journal of Chemistry, **48**, 1624 (1970)

The legume *Thermopsis rhombifolia* (Nutt.) Richards, known commonly as Buffalo- or Golden-bean,¹ is a conspicuous early-flowering prairie plant the seeds of which have long been recognized as poisonous (1), a property due to the presence of toxic quinolizidine alkaloids (2, 3).

In the course of their pioneering studies of the alkaloids of this plant, Marion and Manske described two crystalline, non-basic substances, A and B, which they isolated from dried plant tops. The two substances were characterized (2) by their solubility properties, melting points, and microanalytical data; thus A was sparingly soluble in water, but could be conveniently recrystallized from aqueous-dioxane or -pyridine,

had m.p. 218–220°, and was assigned the composition $\text{C}_{19}\text{H}_{20}\text{O}_{10}$ (no methoxyl groups); B was similarly very sparingly soluble in water, but was more soluble than A in cold dioxane, and recrystallization from aqueous dioxane afforded colorless needles, m.p. 257°, with apparent composition $\text{C}_{22}\text{H}_{16}\text{O}_6$ (one methoxyl group).

In an attempt to establish the identity of these substances,² we reexamined *Thermopsis rhombifolia*, and from fresh plant tops we isolated material which seems to correspond to Marion and Manske's substance A; we comment here on its nature, as well as on the probable identity of substance B.

Our compound, like substance A, was spar-

¹The plant blooms in spring at the time when the buffalo used to leave their wintering grounds and move out across the prairie and it is said that the Blackfoot Indians named it wudzi-eh-kay: the buffalo-flower (1).

²We hoped that, taken together with the alkaloid pattern, these compounds might provide chemical coordinates for use in a study of the effect of environment on *Thermopsis rhombifolia* populations.