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# REACTION OF ALDEHYDES WITH 1,3-DICARBONYL COMPOUNDS IN THE PRESENCE OF POTASSIUM CARBONATE. A CONVENIENT SYNTHESIS OF α,β-UNSATURATED CARBONYL COMPOUNDS VIA DEACYLATION[1)]

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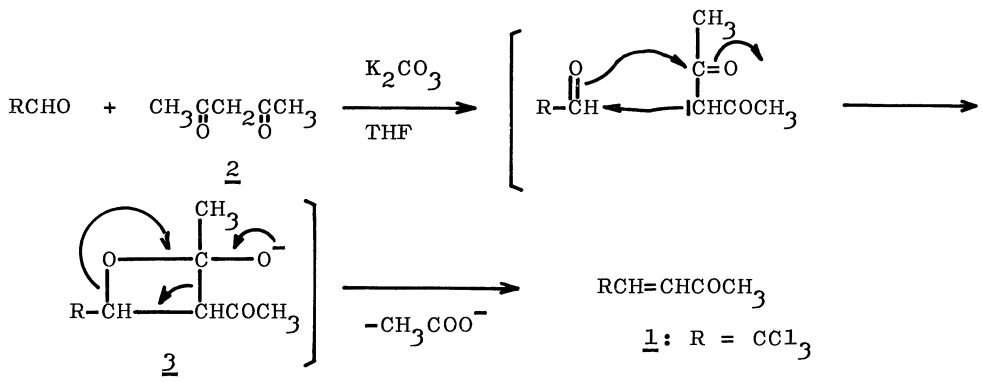
Condensation of aldehydes with 1,3-dicarbonyl compounds such as 2,4-pentanedione (2), ethyl 2-chloro-3-oxobutanoate (4), 3-chloro-2,4-pentanedione (5), and α-acetyl-γ-butyrolactones, catalyzed by potassium carbonate proceeded via deacylation under mild conditions to give α,β-unsaturated ketones and esters in one step.

In the course of our studies on the allylic rearrangement of vinylogs of α-haloketones we needed 5,5,5-trichloro-3-penten-2-one (1).[3,4,5)] In addition, this ketone became important in our laboratory as a starting material for the synthesis of the analog of chrysanthemic acid. Ketone 1 can be prepared by Salkind's method[6)] that involves the dehydration of chloralacetone derived from the base-catalyzed condensation of chloral with ethyl acetoacetate. However, this method[6)] is not suitable for a large scale preparation of 1 because a large quantity of concentrated sulfuric acid is used in the dehydration. We have recently found out a new, simple, convenient method for the synthesis of 1 by the reaction of chloral with 2,4-pentanedione (2) in the presence of anhydrous potassium carbonate at room temperature. Furthermore we have extended this method to syntheses of other α,β-unsaturated carbonyl compounds. In this communication we report an experimentally simple and convenient synthesis of α,β-unsaturated ketones as well as esters by the reaction of aldehydes with 1,3-dicarbonyl compounds proceeding via deacylation under mild conditions.

Ketone 1 was obtained in one step by using inexpensive reagents under mild conditions. A typical experiment consisted of adding anhydrous potassium carbonate (4.14 g, 30 mmol) all at once [7)] to a stirred solution of 2,4-pentanedione (2.0 g, 20 mmol) and chloral (3.53 g, 24 mmol) in 16 ml of dry tetrahydrofuran (THF) at 20-35°C. After stirring for one day, the reaction mixture was diluted with 50 ml of water and extracted with ether. After removal of the solvent, the residue was distilled to give 2.77 g (74%) of 1: bp 88-89°C/16 Torr; mp 20°C (lit.[6)] bp 93-94°C/20 Torr; mp 25-26°C). Both NMR and IR spectra were identical with those of an authentic sample.[6)]

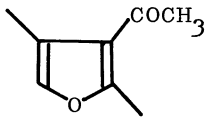
The formation of 1 can be explained by the same mechanism as that proposed in our previous paper on the base-catalyzed condensation of α-haloaldehydes with α-acetylcyclopentanones,[8)] as shown in Scheme 1. Enolate anion of 2 attacks the



Scheme 1.

aldehyde to give an intermediate 3, in which the acetyl group leaves as an acetate anion after its combination with the oxygen of chloral. In this double bond formation, the acetyl group works like phosphine in the Wittig reaction. This mechanism was strongly suggested by the isolation of acetic acid from the reaction mixture. Ueno et al. have independently proposed the same mechanism in the reaction of formaldehyde with 1,3-dicarbonyl compounds catalyzed by butyl lithium.[9]

In order to establish the generality of this reaction we investigated reactions of aldehydes with other 1,3-dicarbonyl compounds such as ethyl 2-chloro-3-oxobutanoate (4), 3-chloro-2,4-pentanedione (5), and α-acetyl-γ-butyrolactones. Table 1 summarizes the results obtained with several representative aldehydes. In general, reactive aldehydes such as chloral, dichloroacetaldehyde, and 2,2-dichloropropanal reacted with 1,3-dicarbonyl compounds, giving the desired products in moderate yields. However, α-chloropropanal reacted with 2,4-pentanedione to give no expected compound but 2,4-dimethyl-3-acetylfuran (6) in 25% yield. The reaction of chloral with ketone 5 resulted in the formation of a



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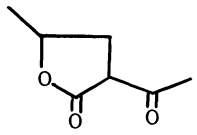
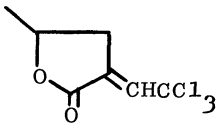
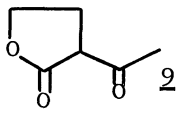
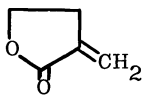
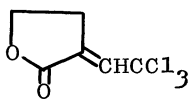
mixture of 3,5,5,5-tetrachloro-3-penten-2-one (7) and 1,1,1,5,7,7,7-heptachloro-5-hepten-4-on-2-ol (8), which seems to have been derived from 7.

The reaction of aldehydes with chlorinated 1,3-dicarbonyl compounds such as 4 and 5 gave cis olefins predominantly. However the reactions of aldehydes with acetylacetone and α-acetyl-γ-butyrolactones gave trans products exclusively. The stereochemistry seems to depend on the trans orientation between bulky groups in the intermediate 3. For the synthesis of α-chloro-α,β-unsaturated ester our simple, economical method seems to be superior to the known methods involving the use of tertiary phosphine[10,11] and lithio tert-butyl trimethylsilyl-α-chloroacetate.[12]

Table 1. Products from the Reaction between Aldehydes and 1,3-Dicarbonyl Compounds

| Aldehydes R in RCHO | 1,3-Dicarbonyl Compounds | Products | Bp, °C/Torr (mp, °C) | Yield[a] % | Ratio[b] of Z/E |
|---|---|---|---|---|---|
| $CCl_3$- | $CH_3COCH_2COCH_3$ (2) | $CCl_3CH=CHCOCH_3$ (1) | 88-89/16 | 74 | 0/100 |
| $CH_3CCl_2$- | 2 | $CH_3CCl_2CH=CHCOCH_3$ | 77-80/6[c] | 52 | 0/100 |
| Et- | 2 | $EtCH=CHCOCH_3$ | 80-90/32[d, e] | (3) | |
| $CCl_3$- | $CH_3COCHCO_2Et$ (4) Cl | $CCl_3CH=CCO_2Et$ Cl | 124-125/20 | 83 (92) | 100/0 |
| $CHCl_2$- | 4 | $Cl_2CHCH=CCO_2Et$ Cl | 114-115/19 | 67 | 100/0 |
| Et- | 4 | $EtCH=CCO_2Et$ Cl | 182-183 | 50 | 75/25 |
| n-$C_6H_{13}$- | 4 | n-$C_6H_{13}CH=CCO_2Et$ Cl | 140-141/20[f] | 41 | 71/29 |
| $CCl_3$- | $CH_3COCHCOCH_3$ (5) Cl | $CCl_3CH=CCOCH_3$ (7) Cl | 113-114/24 | 26 | 100/0 |
| | | and $CCl_3CH=CCOCH_2CHCCl_3$ Cl OH (8) | (53-54) | 51 | 100/0 |
| $CHCl_2$- | 5 | $Cl_2CHCH=CCOCH_3$ Cl | 99-100/17 | 56 | 100/0 |
| Et | 5 | $EtCH=CCOCH_3$ Cl | 162-163[g] | 37 | 87/13 |
| n-$C_6H_{13}$- | 5 | n-$C_6H_{13}CH=CCOCH_3$ Cl | 123-124/24 | 34 | 100/0 |
| $CCl_3$- |  |  | 132-134/4 | 50 | 0/100 |
| H |  9 |  | 120/7[d, h] | 21 (33)[i] | |
| $CCl_3$ | 9 |  | 135-140/0.2[d] (51.5-52.5) | 74 (82) | 0/100 |

[a] Isolated yields by distillation. In parenthesis are given crude yields by NMR analysis. [b] Estimated from the ratio of intensity of NMR signals due to olefinic protons. [c] Reported in our previous paper: reference 5. [d] Bath temperature on a short path distillation. [e] Lit. 122-124°C : H. Pringsheim and J. Leibowitz, Chem. Ber., 56, 2034 (1923). [f] Lit. 127-

(Continued)

(Table 1 is continued.)

130°C/12 Torr: H. Gault, Ann. Chim., [2] 6, 247-275 (1951); Chem. Abstr., 45, 9475g (1951). [g] Lit. 65-66°C/30 Torr: A. A. Petrov and N. P. Sopov, Zh. Obshch. Khim., 23, 1034 (1953); Chem. Abstr., 48, 8182d (1954). [h] Lit. 57-60°C/2 Torr: C. J. Cavallito and T. H. Haskell, J. Am. Chem. Soc., 68, 2332 (1946). [i] Ueno et al. also prepared in 74% yield by using butyl lithium as a base. See reference 9.

## REFERENCES AND NOTES

1) Presented in part at the 24th Annual Meeting of the Chemical Society of Japan, Abstr. No. 20414, Osaka, April 1971.
2) Present address: Okayama-ken Agricaltural Experiment Station, Sanyo-cho, Akaiwa-gun, Okayama-ken 709-08.
3) A. Takeda and S. Tsuboi, J. Org. Chem., 35, 2690 (1970).
4) A. Takeda, S. Tsuboi, T. Moriwake, and E. Hirata, Bull. Chem. Soc. Jpn., 45, 3685 (1972).
5) A. Takeda and S. Tsuboi, J. Org. Chem., 38, 1709 (1973).
6) (a) I. Salkind, J. Russ. Phys. Chem. Soc., 30, 906 (1898); (b) H. Gault and G. Mennicken, C. R. Acad. Sci., Paris, 229, 1239 (1949).
7) On large scale preparation, potassium carbonate should be added in several portions from the flask connected with rubber tube.
8) A. Takeda, S. Tsuboi, F. Sakai, and M. Tanabe, J. Org. Chem., 39, 3098 (1974).
9) Y. Ueno, H. Setoi, and M. Oogawara, Abstr. No. 3D34, the 37th Annual Meeting of the Chemical Society of Japan, Yokohama, April 1978.
10) D. J. Burton and J. R. Greenwald, Tetrahedron Lett., 1967, 1535.
11) G. Lavielle, J-C. Combret and J. Villieras, C. R. Acad. Sci., Ser. C, 272, 2175 (1971).
12) T. H. Chan and M. Moreland, Tetrahedron Lett., 1978, 515.

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