

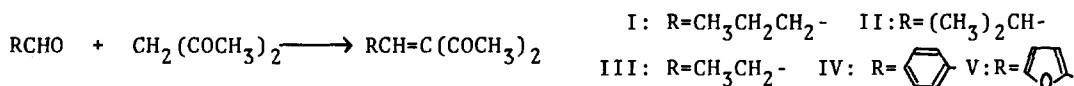
THE REACTION OF TETRACARBONYLHYDRIDOFERRATE WITH THE KNOEVENAGEL
CONDENSATES OF 2,4-PENTANEDIONE WITH ALDEHYDES. A NEW SYNTHETIC
ROUTE OF ALKYL METHYL KETONES FROM ALDEHYDES

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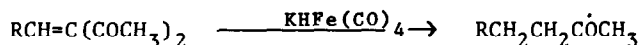
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Many works have been reported on the syntheses of ketones using organo-metallic compounds and iron carbonyl complexes are also employed for this purpose.¹⁾ In this communication, we wish to report a new synthetic route of alkyl methyl ketones from aldehydes via the Knoevenagel condensates using tetracarbonylhydridoferrate.

General procedure was as follows. The Knoevenagel condensates I-V were easily obtained from 2,4-pentanedione and the corresponding aldehydes.²⁾ To



an alcoholic solution of tetracarbonylhydridoferrate (22 mmol),³⁾ an alcoholic solution of the condensate (11 mmol) was added and the reaction mixture was stirred for 5 hr at room temperature under argon. After the solvent was evaporated, the residue was extracted with ether and the ether layer was washed twice with water and dried over sodium sulfate. The solvent was removed in vacuo and the liquid remained was then subjected to fractional distillation. The products were identified by NMR, IR and glpc using authentic samples. The results are listed in Table 1. The only isolated products were monomethyl



ketones, but the corresponding saturated diketones were not obtained.⁴⁾ In this reaction, deacylation and hydrogenation of the condensates readily occurred.⁵⁾

Table 1. Reaction of the Knoevenagel condensate with $\text{KHFe}(\text{CO})_4$

Condensate	Product	Yield(%) ^{a)}
I	n-Amyl methyl ketone	69 (89) ^{b)}
II	iso-Amyl methyl ketone	60
III	n-Butyl methyl ketone	71 (92)
IV	Benzylacetone	76 (90)
V	Furfurylacetone	82

a) Isolated yields based on the condensates. b) Yields in parentheses were determined by glpc using internal standards.

High yields of the products and the facility of the reaction procedure make it possible to utilize this reaction for the syntheses of methyl ketones which have three more carbons than the starting aldehydes. Further studies on the mechanistic aspect and development of this reaction are currently underway.

REFERENCES AND NOTES

- 1) For example; J. P. Collman, S. R. Winter, D. R. Clark, J. Amer. Chem. Soc., 94, 1788 (1972); B. F. G. Johnson, J. Lewis, D. J. Thompson, Tetrahedron Lett., 3791 (1974)
- 2) The Knoevenagel condensates were prepared by the improved method of the literature;⁶⁾ After an equimolar mixture of 2,4-pentanedione and an aldehyde was cooled in an ice-bath, 0.4-0.5 mol% of piperidine was added drop by drop, and the mixture was stirred for 5 hr at 0°C and then at room temperature for 5 hr. The reaction mixture was then subjected to fractional distillation. Yields were 60-75% in all cases.
- 3) Y. Takegami, Y. Watanabe, T. Mitsudo, and H. Masada, Bull. Chem. Soc. Japan, 42, 202 (1969)
- 4) In the reaction of usual α,β -unsaturated carbonyl compounds with $\text{KHFe}(\text{CO})_4$, the corresponding saturated ketones are formed; R. Noyori, I. Umeda, and T. Ishigami, J. Org. Chem., 37, 1542 (1972)
- 5) Such behavior was also observed when the condensate of ethyl acetoacetate with n-butyraldehyde was treated with the ferrate and the corresponding ester, ethyl capronate, was obtained in rather low yield.
- 6) K. Uehara, T. Matsumura, T. Nishi, A. Tamura, and J. Murata, Kogyo Kagaku Zasshi, 69, 2027 (1966)