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ACYLATION OF EPOXIDES BY THE USE OF ACYLTETRACARBONYLFERRATES: SYNTHESIS OF α,β-UNSATURATED KETONES

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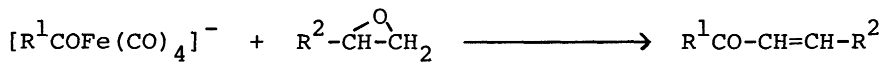
α,β-Unsaturated ketones were synthesized in high yields by the reaction of epoxides with acyltetracarbonylferrates.

α,β-Unsaturated ketones, which are useful starting materials in organic syntheses, are known to be derived from various organic compounds. However, to our knowledge, there have been no reports on the synthesis of them from epoxides. In this letter, we wish to report the facile synthesis of the enones from epoxides by the reaction with acyltetracarbonylferrates which have received considerable interest because of their wide synthetic possibilities.1)



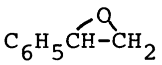
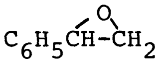
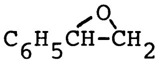
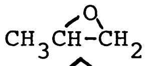
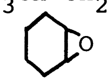
$$[R^1COFe(CO)_4]^- + R^2\text{-}\overset{O}{\overbrace{CH\text{-}CH_2}} \longrightarrow R^1CO\text{-}CH{=}CH\text{-}R^2$$

[a]

Representative reaction procedure was as follows. To a tetrahydrofuran (THF) solution (40 ml) of valeryltetracarbonylferrate, prepared *in situ* from disodium tetracarbonylferrate ($Na_2Fe(CO)_4$) (11 mmol) and valeryl chloride (11 mmol), was added 1,2-epoxy-1-phenylethane (11 mmol) by syringe and the mixture was stirred for 1 h at room temperature under argon atmosphere. Then the solution was diluted with diethyl ether, washed three times with 10% sulfuric acid, dried, and filtered, and the ether was removed with a rotary evaporator. The residue was purified by column or thin layer chromatography (silica gel-chloroform). The product was identified as 1-phenyl-1-hepten-3-one by IR, NMR, MASS, and GLC. Yield was 71% based on 1,2-epoxy-1-phenylethane.

The typical results are shown in Table 1. In these reactions, small amounts of $R^1COCH_2CH_2R^2$ were formed as by-products (R^1,R^2; see equation [a]).

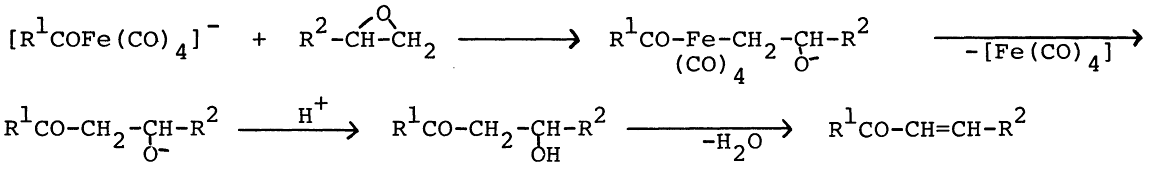
Table 1. Reaction of acyltetracarbonylferrates with epoxides[a)]

$[RCOFe(CO)_4]^-$ R	Epoxide	Method[b)]	Product	Yield(%)[c)]
$CH_3(CH_2)_3$-	 $C_6H_5\overset{O}{CH\text{-}CH_2}$	A	$CH_3(CH_2)_3COCH{=}CHC_6H_5$	71
		B		60
$CH_3(CH_2)_2$-	 $C_6H_5\overset{O}{CH\text{-}CH_2}$	A	$CH_3(CH_2)_2COCH{=}CHC_6H_5$	81
		B		70
$(CH_3)_2CH(CH_2)_2$-	 $C_6H_5\overset{O}{CH\text{-}CH_2}$	A	$(CH_3)_2CH(CH_2)_2COCH{=}CHC_6H_5$	82
		B		65
$CH_3(CH_2)_3$-	 $CH_3\overset{O}{CH\text{-}CH_2}$	A	$CH_3(CH_2)_3COCH{=}CHCH_3$	73
$CH_3(CH_2)_3$-		A	———[d)]	
		B	———[d)]	

a) At room temperature for 1 h in THF under argon atmosphere. b) Acylcarbonylferrates were prepared by two methods; method A involves a reaction between acid chlorides and $Na_2Fe(CO)_4$, and addition of a Grignard reagent to pentacarbonyliron is employed as method B. c) Isolated yield. d) 1,2-Epoxycyclohexane had a high reactivity for the ferrate but gave an intractable tarry material.

Terminal epoxides gave the unsaturated ketones in good yields but internal one (1,2-epoxycyclohexane) did not.

The overall transformation of epoxide to α,β-unsaturated ketone is assumed as follows.



$$[R^1COFe(CO)_4]^- + R^2\text{-}\overset{O}{CH\text{-}CH_2} \longrightarrow R^1CO\text{-}\underset{(CO)_4}{Fe}\text{-}CH_2\text{-}\underset{O^-}{CH}\text{-}R^2 \xrightarrow[-[Fe(CO)_4]]{} R^1CO\text{-}CH_2\text{-}\underset{O^-}{CH}\text{-}R^2 \xrightarrow{H^+} R^1CO\text{-}CH_2\text{-}\underset{OH}{CH}\text{-}R^2 \xrightarrow[-H_2O]{} R^1CO\text{-}CH{=}CH\text{-}R^2$$

References

1) a) M. Yamashita, Y. Watanabe, T. Mitsudo, and Y. Takegami, *Tetrahedron Lett.*, 1976, 1585; b) T. Mitsudo, Y. Watanabe, T. Sasaki, H. Nakanishi, M. Yamashita, and Y. Takegami, *ibid.*, 1975, 3163; c) Y. Watanabe, M. Yamashita, T. Mitsudo, M. Igami, and Y. Takegami, *Bull. Chem. Soc. Jpn.*, 48, 2490 (1975); J. P. Collman, S. R. Winter, and R. G. Komoto, *J. Am. Chem. Soc.*, 95, 249 (1973), and the references cited therein.

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