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REACTION OF ARYL CHROMIUM CARBENE COMPLEXES WITH ETHYL PROPIOLATE
A VERSATILE VINYL ETHER FORMATION

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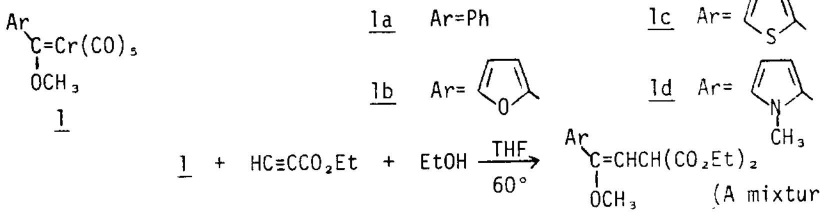
Summary: Arylmethoxychromium-carbene complexes reacted with ethyl propiolate in the presence of alcohol to form good yields of aryl vinyl ether derivatives of malonate.

The development of new uses of stable transition metal-carbene complexes[1] in organic synthesis has met with considerable success. Stereospecific reaction of $Ph(CH_3O)CCr(CO)_5$ (1a)[2] with trans methyl crotonate gave two isomeric cyclopropanes.[3] In a method of Wittig type reactions of $Ph(CH_3O)C{=}W(CO)_5$ with $CH_2{=}PPh_3$, developed by Casey,[4] the carbene complex can be viewed as an ylide with substantial $Metal^{-}$-C^{+} character. More recently a study indicated that 1a reacted with diphenyl or dialkyl acetylenes to form naphthol derivatives.[5] In the course of studies of the carbenoid chemistry of complex chromium carbonyls, we found that carbene complex (1) reacted with ethyl propiolate in the presence of alcohol to form good yields of α-aryl vinyl ether derivatives of malonate.

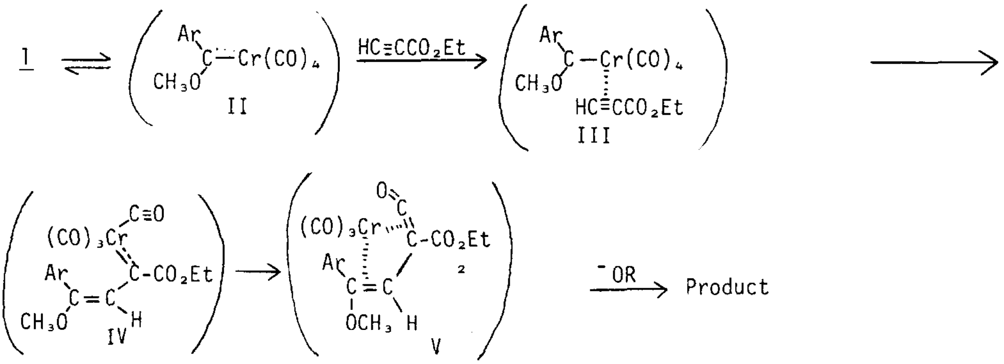


$$\underline{1} + HC{\equiv}CCO_2Et + EtOH \xrightarrow[60°]{THF} Ar(OCH_3)C{=}CHCH(CO_2Et)_2$$

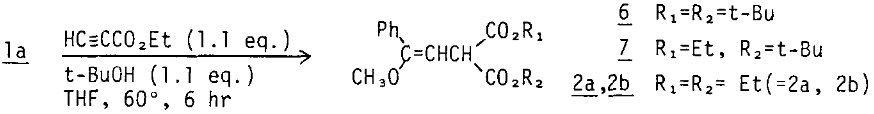
(A mixture of two isomers)

The general procedure is as follows: a tetrahydrofuran (THF) solution (100 ml) of 1a (4.8 mmole) was heated at 60°C with ethyl propiolate (1.5 eq) and ethyl alcohol (1.5 eq) under an argon atmosphere. The reaction, monitored by TLC analysis, was complete in 4-6 hr. The enol ethers were isolated as a mixture of two isomers by flash column chromatography and characterized by ir, mass, and ^1H and ^{13}C-NMR spectra analysis. The stereochemistry of the two isomers was assigned on the basis of the relative chemical shifts of the vinyl proton resonance[6] (2a, 5.01δ, J=9.1 Hz; 2b, 5.50δ, J=10.6 Hz), with the shift difference being predicted from the correlations of Fathey and Schubert.[7] This assignment was also supported by the relative chemical shifts of the carbon resonances at β-position to vinyl group (malonate carbon).[8] This method for forming vinyl ether was applied to other aryl derivatives of the chromium complex, such as α-furyl (1b),[9] α-thienyl (1c),[9] and α-(N-methyl)pyrrolyl (1d)[10] chromium-carbene complexes. Table I shows the results of the vinyl ether formation.

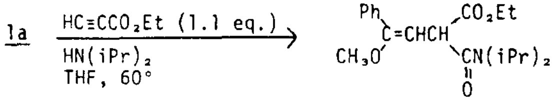
The reaction presumably proceeds by nucleophilic attack by alcohol at the ketene carbon of intermediate (V).[11]



To introduce two different ester groups in malonate, carbene (1a) was treated with ethyl propiolate (1.1 eq) and tert-BuOH in THF (20 ml/mmole); the reaction produced three vinyl ethers in 16% yield (6, E/Z=4/1), 35% yield (7, E/Z=4/1), and 18% yield (2a + 2b, E/Z=3/1), each as a mixture of two isomers.[12]

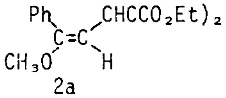
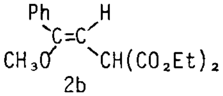
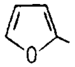
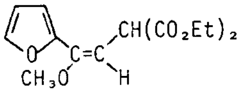
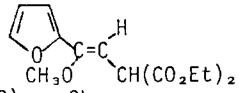
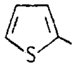
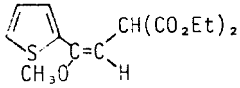
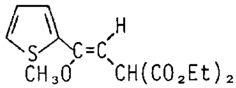
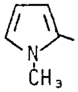
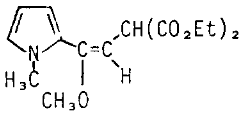


To extend the applicability of the reaction, 1a was treated with ethylpropiolate (1.1 eq) in the presence of a secondary amine (1.1 eq) under the same conditions; the corresponding amide (8) was obtained (50% yield) as a mixture of two isomers (Z>>E). The enol ethers in all cases were converted by hydrolysis (dilute HCl/THF) to the corresponding ketones, which were characterized by ir, mass and ^{1}H-NMR spectra studies.[13]



8

Table I. Reactions of Arylmethoxychromium Carbene Complexes with $HC \equiv CCO_2Et$ in the presence of EtOH

Ar	Time (hr)	Product (Ratio)[a]	Yield (%)[b]
Ph	4	 2a +  (6:1) 2b	83
	6	 3a +  (1:1.2) 3b	80
	4	 4a +  (1:2) 4b	81
	3	 5a	87

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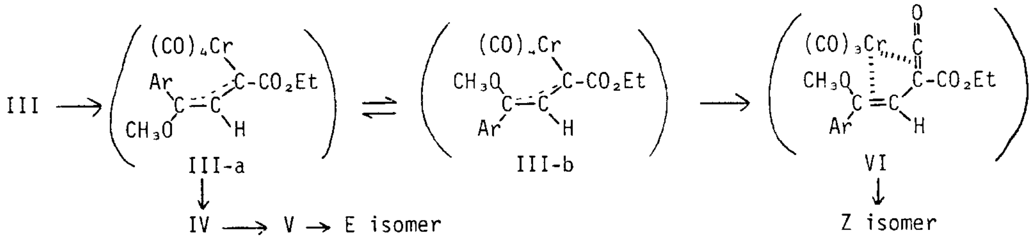
[a] Ratio of two isomers were determined by ^1H and ^{13}C-NMR spectra and gas chromatography analysis.

[b] Yield was described as combined yield of two isomers.

The ratio of two isomers varied with aryl group: 2a:2b was 6:1 while 4a:4b was 1:2. The results indicate that the presence and kind of heteroatom in the aromatic group controls the product ratio. The E and Z isomers may arise from the following equilibrium IIIa ⇆ IIIb, however, the effect of the aryl group on this equilibrium is at the present time unknown.



Experiments directed toward an explanation of these observations are currently being pursued, and further applications of this reaction with different acetylenes will be reported in due course.

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1. E.O.Fischer and A.Massböl, Angew. Chem. Int. Ed. Engl., 3 580 (1964).
2. E.O.Fischer, B.Heckl, K.H.Dötz, J.Muller and H. Werner, J. Organometal. Chem., 16 29 (1969).
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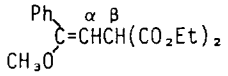
4. C.P.Casey, T.J.Burkhardt, J. Amer. Chem. Soc., 94 6543 (1972).
5. a) K.H.Dötz, Angew. Chem. Int. Ed. Engl., 14 644 (1975). b) K.H.Dötz and R. Dietz, Chem. Ber., 111 2517 (1978). c) W.D.Wulff, P.C.Tang and J.S.McCallum, J. Amer. Chem. Soc., 103 7677 (1981).
6. Chemical shifts of vinyl proton resonance of other vinyl ethers are as followed: 3a, 5.06δ, J=10.1 Hz; 3b,5.67δ, J=9.6 Hz. 4a, 5.08δ, J=10.5 Hz; 4b, 5.58δ, J=9.4 Hz. 5a, 5.19δ, J=9.0 Hz.
7. a) R.C.Fahey and C.Schubert, J. Amer. Chem. Soc., 87 5172 (1965). b) C.Pascual, J.Meir and W.Simon, Helv. Chem. Acta., 49 164 (1966).
8. S.A.Mizsak and G.Slomp, Prostaglandins, 10 3454 (1975). Chemical shifts of carbon resonance of 2a and 2b are as follows:



$$\mathrm{Ph(CH_3O)C{=}CHCH(CO_2Et)_2}$$

2a	α, 92.36 ppm; β, 51.34 ppm
2b	α, 105.03 ppm; β, 49.51 ppm

9. See Reference 3.
10. Complex (1d), thermally-stable orange crystals, was prepared by the standard method of E.O.Fischer: 2-Lithio-N-methylpyrrole, generated from the reaction of N-methylpyrrole with n-BuLi in THF at -20°C, was treated with Cr(CO)$_6$ (1.0 eq) at RT, followed by methylation with Me$_3$O.BF$_4$. 64% yield.
11. A silyl-substituted vinyl ketone from the reaction of 1a with bis(trimethyl)silylacetylene has been isolated and analyzed, and a mechanisum has been suggested. K.H.Dötz and B.Fugen-Koster, Chem. Ber., 113 1449 (1980).
12. Ratio of two isomers were determined by ^{1}H -NMR spectra and Gas chromatography analysis.
13. All ketones gave satisfactory ir, mass, ^{1}H -NMR spectra and combustion analysis.

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