Journal of Organometallic Chemistry, 262 (1984) 85–88
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

REACTION OF ETHYL DIAZOACETATE WITH HALOGENOETHYLENES IN THE PRESENCE OF RHODIUM(II) PIVALATE

DAVID J. MILNER

Imperial Chemical Industries PLC, Process Technology Department, Organics Division, Blackley, Manchester (Great Britain)

(Received September 1st, 1983)

Summary

In the presence of rhodium(II) pivalate, ethyl diazoacetate reacted with vinylidene chloride, vinyl bromide and *cis*-1,2-dichloroethylene to afford the corresponding cyclopropane carboxylates, but tetrachloroethylene, trichloroethylene and *trans*-1,2-dichloroethylene did not undergo cyclopropanation. These results indicate that cyclopropane carboxylates were accessible only from those halogenoethylenes having an unsubstituted end or side.

Introduction

Various cyclopropane carboxylates are prepared conveniently by treating an appropriate olefin with ethyl diazoacetate (EDA) in the presence of a catalyst. Copper catalysts have been used most often but the use of certain rhodium(II) species has proved advantageous, giving both high yields [1] and useful stereoselectivity [2]. Both the copper and the rhodium catalysts work well with alkenes, but they are reported to give low yields with electron poor olefins [3,4]. This pattern of reactivity is consistent with the intermediacy of electrophilic carbenemetal species [4].

By contrast, molybdenum hexacarbonyl and palladium(II) acetate are effective catalysts for the cyclopropanation of electron deficient olefins, such as acrylates, bearing one electron-withdrawing group but not of cyclohexene [5,6]. There appear to be no reports of even moderate yields of cyclopropane carboxylates from olefins bearing two electron-withdrawing groups. Cyclopropane carboxylates have now been formed from EDA and various electron poor halogenoethylenes, some having two halogen atoms, in the presence of rhodium(II) pivalate, with yields much greater than those suggested either by literature precedence or by comparative reactions using copper bronze as catalyst.

0022-328X/84/$03.00

TABLE 1

REACTIONS OF HALOGENOETHYLENES WITH EDA IN THE PRESENCE OF RHODIUM(II) PIVALATE AND COPPER CATALYSTS

Reactants (mmol)		Catalyst (mg atom)	Solvent (ml)	Temperature (°C)	Cyclopropane carboxylate produced			
Olefin	EDA				mmol	Yield[a] (%)	m/e	^{1}H NMR (δ, ppm)
cis-1,2-Dichloroethylene (1000)	(118)	Rh^{II} (0.33)	CH_2Cl_2 (100)	25	38	32	109 (2 ^{35}Cl), 137 (2 ^{35}Cl) 147 (1 ^{35}Cl), 119 (1 ^{35}Cl)	4.25m (2.2H), 3.65d (2.0H), 2.15t (1.0H), 1.3t (3.3H)
cis-1,2-Dichloroethylene (100)	(11.8)	Cu^0 (20)	CH_2ClCH_2Cl (10)	80	0.16	1.4		
trans-1,2-Dichloroethylene (100)	(118)	Rh^{II} (0.33)	CH_2Cl_2 (100)	25	1.8	1.5		
Vinylidene chloride (360)	(76)	Rh^{II} (0.33)	None	25	58	76	182 (2 ^{35}Cl), 154 (2 ^{35}Cl) 137 (2 ^{35}Cl), 109 (2 ^{35}Cl)	4.2q (2.0H), 2.4m (0.9H), 2.0m (1.7H), 1.3t (3.0H)
Vinylidene chloride (36)	(7.6)	Cu^0 (47)	CH_2ClCH_2Cl (10)	80	1.5	20		
Vinyl bromide (374)	(77)	Rh^{II} (0.10)	CH_2ClCH_2Cl (20)	25	48	62		4.15m (2.0H), 3.2m (1.2H), 1.5q (2.0H), 2.0m (1.1H), 1.3t (3.0H)
Vinyl bromide (see ref. 5)		Cu^{II}		100		9		
Trichloroethylene (100)	(10)	Rh^{II} (0.03)	None	60	0	0		
Tetrachloroethylene (100)	(10)	Rh^{II} (0.03)	None	60	0	0		

[a] Mol product/mol EDA consumed. GLC mass spectroscopy was carried out using a 2 m column of 5% carbowax 20M at 130°C.

Discussion

The results are tabulated (Tab. 1). Trichloroethylene and tetrachloroethylene were resistant to cyclopropanation. However, fair to good yields of cyclopropane carboxylates were obtained, using EDA and rhodium(II) pivalate, from those halogenoethylenes bearing no more than two halogen atoms, namely vinylidene chloride, vinyl bromide and *cis*-1,2-dichloroethylene.

An exception was *trans*-1,2-dichloroethylene. The strikingly different reactivities of *cis*- and *trans*-1,2-dichloroethylene towards rhodium(II)/EDA has an interesting parallel in their Friedel–Crafts reactions. Schmerling found that treatment of *cis*- and *trans*-1,2-dichloroethylene with 2-chloro-2-methylpropane in the presence of aluminium chloride gave 1,1,2-trichloro-3,3-dimethylbutane in yields of 75 and 2%, respectively [7]. With 2-chloropropane Schmerling found that the difference in the reactivities of the 1,2-dichloroethylene isomers was less marked. These observations indicate that the lower reactivity of the *trans*-isomer under Friedel–Crafts conditions is due to a steric effect, and steric factors probably also operate during the cyclopropanation.

Steric effects are not solely responsible for the differing reactivities of olefins towards the rhodium(II)/EDA systems, however; electronic factors are even more important. The Van der Waals radii of a methyl group and of a chlorine atom are 2.0 and 1.8 Å, respectively [9], yet 1,1-dichloro-4-methylpenta-1,3-diene was cyclopropanated almost exclusively across the 3,4-positions [2]. Similarly, 2,3-dimethylbut-2-ene [1], but not tetrachloroethylene, afforded the corresponding cyclopropane carboxylate in good yield.

Apparently, three vinylic halogen substituents effectively deactivate an olefin towards rhodium(II)/EDA. With the dihalogenoethylenes, cyclopropanation by the rhodium (II)/EDA system can occur when one end (as in vinylidene chloride) or one side (as in *cis*-1,2-dichloroethylene) is unsubstituted. Even those halogenoethylenes which give good yields of cyclopropane carboxylates are probably much less reactive towards rhodium(II)/EDA than are electron rich olefins. Thus, treatment of *cis*-1,2-dichloroethylene (100 mmol) together with 2,5-dimethylhexa-2,4-diene (50 mmol) with EDA (23 mmol) in the presence of rhodium(II) pivalate (0.033 mg atom Rh) gave ethyl chrysanthemate (16 mmol, 69% yield), but no ethyl 2,3-dichlorocyclopropane carboxylate was detected.

All these results accord with the idea of a ethoxycarbonylcarbene-rhodium intermediate which transfers the carbene preferentially to an electron rich olefin or, less readily, to an unhindered halogenoethylene.

Experimental

Rhodium(II) pivalate was formed by treatment of rhodium trichloride, ethanol, sodium pivalate and pivalic acid [8]. The products were filtered, ethanol was removed from the filtrate and the residue was dissolved in methylene chloride. Excess pivalic acid was removed by washing with 5% aqueous sodium bicarbonate. Olefins were freed from stabilisers by washing successively with 1% sodium hydroxide, 1% hydrochloric acid and water. They were dried ($MgSO_4$) and distilled. The EDA (Aldrich) was added dropwise to the stirred olefin and catalyst over a period of 2 h.

References

1 A.J. Hubert, A.F. Noels, A.J. Anciaux, and P. Teyssie, Synthesis, (1976) 600.

2 D. Holland and D.J. Milner, J. Chem. Res (S), (1979) 317.

3 F.W. Breitbeil, D.T. Dennerlein, A.E. Fieling and R.E. Kuznicki, J. Org. Chem., 33 (1968) 3389.

4 A.J. Anciaux, A.J. Hubert, A.F. Noels, N. Petiniot amd P. Teyssie, J. Org. Chem., 45 (1980) 695.

5 K.B. Wiberg, R.K. Barnes and J. Albin, J. Amer. Chem. Soc., 79 (1957) 4994; M.P. Doyle and J.G. Davidson, J. Org. Chem., 45 (1980) 1539.

6 M.W. Majchrzak, A. Kotelko and J.B. Lambert, Synthesis, (1983) 469.

7 L. Schmerling, J. Amer. Chem. Soc., 68 (1946) 1655.

8 P. Legzdins, R.W. Mitchell, G.L. Rempel, J.D. Ruddick and G. Wilkinson, J. Chem. Soc., A, (1970) 3322.

9 L. Pauling, The Nature of the Chemical Bond, 1st. Ed., Cornell University Press, 1948, p. 189.