Journal of Organometallic Chemistry, 124 (1977) 131—134

ALCOHOLS AS SOLVENT FOR THE GENERATION AND REACTION OF ALLYLIC ZINC HALIDES WITH ALDEHYDES AND KETONES

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(Received June 28th, 1976)

Summary

Alcohols can serve as solvent for the generation and addition of allylic zinc halides to aldehydes and ketones. In the absence of a reactive carbonyl compound reactive allylic halides undergo coupling when treated with zinc and ethanol.

We wish to report that alcohols ** can serve as solvent for the generation and addition of allylic zinc halides to aldehydes and ketones. The allylic zinc halides have generally been prepared in ether or THF and show a reactivity comparable with Grignard reagents. Thus slow addition (20—30 min) of allyl bromide (0.11 mol) to a stirred slurry of "activated" zinc dust (0.11 g-atom) ***, an aldehyde or ketone (0.1 mol) and 25 ml of 95% ethanol or t-butyl alcohol at a bath temperature of 78—95° gave the products listed in Table 1 in yields comparable in some instances with those obtained in aprotic solvents [3]. The reaction of zinc with allyl bromide in t-butyl alcohol has an induction period of 10—60 min. A small amount of allyl bromide is added to the reaction mixture and care is taken to insure the reaction has started before adding more bromide. Failure to observe this precaution may lead to an uncontrollable reaction when initiation does take place. When 0.1 equivalent of zinc bromide is added at the outset the reaction with allyl bromide is immediate and proceeds smoothly.

In the case of ketones the less acidic t-butyl alcohol seems to be preferable as solvent. The yield of alcohol diminishes as the reactivity of the ketone decreases. The yield from pinacolone in t-butyl alcohol is low (22%), but can be improved

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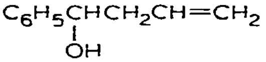
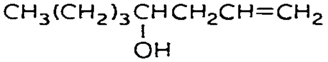
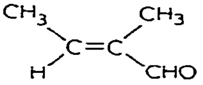
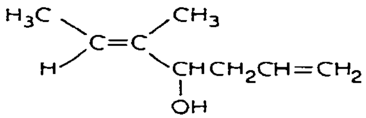
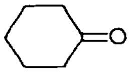
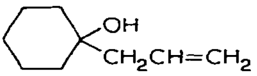
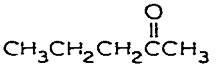
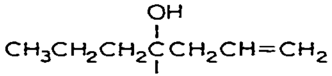
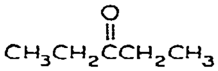
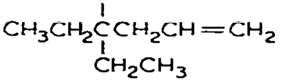
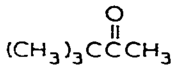
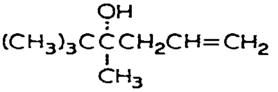
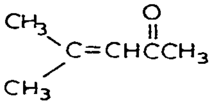
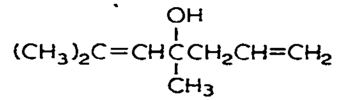
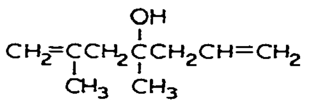
** For the reaction of organozinc compounds with alcohols see ref. 1. Aqueous alcohol is the solvent of choice for converting 1,3-halides with zinc to cyclopropane derivatives [2].

*** Technical grade zinc dust in 100 g batches was activated by washing with 5% HCl aq. ethanol and ether and then dried by heating at 80°C in a stream of nitrogen. The activated zinc dust was stored under nitrogen.

(37%) by employing two equivalents of allyl bromide and zinc. Isophorone, esters, nitriles, and orthoesters are too unreactive to compete with the solvent for allylzinc bromide and only protonolysis to propene was observed.

TABLE 1

REACTION OF ALLYL BROMIDE AND ZINC WITH ALDEHYDES AND KETONES IN ALCOHOLS AS SOLVENT

Reactant	Product	Yield (%)[a] in 95% EtOH (78°C)	in t-BuOH (95°C)
C_6H_5CHO	 $C_6H_5\underset{OH}{C}HCH_2CH{=}CH_2$	66	71
$CH_3(CH_2)_3CHO$	 $CH_3(CH_2)_3\underset{OH}{C}HCH_2CH{=}CH_2$	39[b]	33[b]
		43[c]	24[c,d]
		42	63
 $CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3$	 $CH_3CH_2CH_2\overset{OH}{\underset{CH_3}{C}}CH_2CH{=}CH_2$	23	61
 $CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_3$	 $CH_3CH_2\overset{OH}{\underset{CH_2CH_3}{C}}CH_2CH{=}CH_2$	9	46
 $(CH_3)_3C\overset{O}{\overset{\|}{C}}CH_3$	 $(CH_3)_3C\overset{OH}{\underset{CH_3}{C}}CH_2CH{=}CH_2$	trace	22
	 $(CH_3)_2C{=}CH\overset{OH}{\underset{CH_3}{C}}CH_2CH{=}CH_2$	6[e]	—
	 $CH_2{=}\underset{CH_3}{C}CH_2\overset{OH}{\underset{CH_3}{C}}CH_2CH{=}CH_2$	—	6[f]

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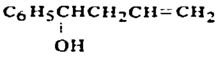
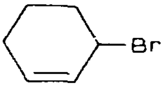
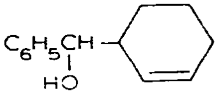
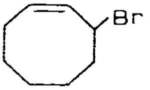
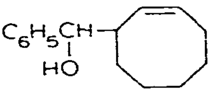
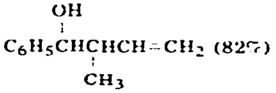
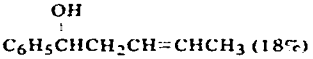
[a] Based on product isolated by distillation. The purity of each distillation fraction was checked by GLC. The identity of products was determined by examination of IR and NMR spectra. [b] The major products are unidentified higher boiling liquids. [c] Gas chromatographic analysis of distillation fractions. [d] 6-t-Butoxy-5-methyl-1,4-heptadiene was also isolated. [e] 6-Ethoxy-4,6-dimethyl-1,4-heptadiene was also obtained. [f] The major product (39%) was a mixture of 2,4-dimethyl-1,3,6-heptatriene and 2,4-dimethyl-2,4,6-heptatriene.

TABLE 2

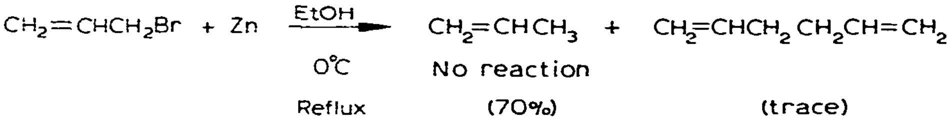
REACTION OF ALLYLIC HALIDES WITH ZINC AND BENZALDEHYDE IN 95% ETHANOL

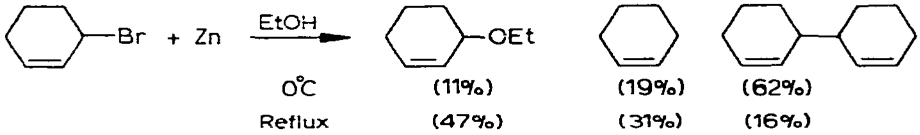
Halide	Bath temperature (°C)	Product	Yield (%)
$CH_2{=}CHCH_2Br$	90	 $C_6H_5CH(OH)CH_2CH{=}CH_2$	66
	0		24
	90		48
$CH_3CH{=}CHCH_2Br$[a]	90	 $C_6H_5CH(OH)CH(CH_3)CH{=}CH_2$ (82%)  $C_6H_5CH(OH)CH_2CH{=}CHCH_3$ (18%)	60

[a] For typical products derived from crotylzinc bromide see ref. 4.

A variety of allylic bromides were successfully combined with zinc and benzaldehyde in 95% ethanol to give the results illustrated in Table 2.

When the reaction of allylic halide with zinc in 95% ethanol was carried out at 0°C in the absence of a carbonyl compound, no reaction is observed with allyl bromide after 8 hours whereas coupling is the major event observed for 3-bromocyclohexene. In contrast, protonolysis predominated with allyl bromide to afford propene at the reflux temperature * [6], whereas solvolysis and coupling as well as protonolysis were observed with 3-bromocyclohexene. 3-Bromocyclooctene gave 80% of coupled product when treated with zinc and 95% ethanol at ambient temperature.





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* For the action of zinc on crotylbromide in aqueous ethanol see ref. 5.

To insure that allylzinc bromide is actually involved as an intermediate in these reactions a sample was prepared in THF. A 20 ml portion of a 1.2 $\overline{\text{M}}$ THF solution of allylzinc bromide was added to 0.02 mol of benzaldehyde in 12 ml of 95% ethanol, while a similar portion of allylzinc bromide solution was added to 0.02 mol of benzaldehyde in 12 ml of THF. The yield of 1-phenyl-3-buten-1-ol was 60 and 80%, respectively.

Many attempts to generate and add isopropylzinc bromide to benzaldehyde in ethanol as solvent failed and in every instance a high yield of propane was obtained. This is not surprising in view of the extremely slow reaction that occurs between isopropylzinc bromide and benzaldehyde *. At ambient temperature in THF approximately 21 days are required to bring the reaction to completion, whereas one day is needed at reflux. The major products are phenyl isopropyl ketone and benzyl alcohol resulting from a redox reaction of benzaldehyde and the zinc salt of phenylisopropylcarbinol (which is observed to build up and then disappear as the reaction proceeds).

References

1 M. Ishimori and T. Tsuruta, Makromol. Chem., 64 (1963) 190; R.J. Herold, S.L. Aggarwal and V. Neff, Can. J. Chem., 41 (1963) 1368; G.E. Coates and D. Ridley, J. Chem. Soc., (1965) 1870; J.M. Bruce and D.W. Farren, Polymer, 6 (1965) 509; H.M. Shearer and C.B. Spencer, Chem. Commun., (1966) 194; G. Allen, J.M. Bruce, D.W. Farren and F.G. Hutchinson, J. Chem. Soc. B, (1966) 799; J.M. Bruce, B.C. Cutsforth, D.W. Farren, F.G. Hutchinson, F.M. Rabagliatti and D.R. Reed, J. Chem. Soc. B, (1966) 1020; M.H. Abraham and J.A. Hill, J. Organometal. Chem., 7 (1967) 23; G.E. Coates and P.D. Roberts, J. Chem. Soc. A, (1967) 1233; J.G. Noltes and J. Boersma, J. Organometal. Chem., 12 (1968) 425; A. Deffieux, M. Sepulchre and N. Spassky, J. Organometal. Chem., 80 (1974) 311: S. Inoue, M. Kobayashi and T. Tozuka, J. Organometal. Chem. 81 (1974) 17; and G. Emptoz and F. Huet, J. Organometal. Chem., 82 (1974) 139.

2 H.B. Hass, E.T. McBee, G.E. Hinds and B.W. Gluesenkamp, Ind. Eng. Chem., 28 (1936) 1178; J.B. Bartleson, R.E. Burk and H.P. Lankelma, J. Amer. Chem. Soc., 68 (1946) 2513.

3 M. Gaudemar, Bull. Soc. Chim. Fr., 974 (1962): M. Gaudemar, ibid., (1963) 1475; D. Abenhaim, E. Henry-Basch and P. Freon, C.R. Acad. Sci. Ser. C, 264 (1967) 1313; D. Abenhaim, E. Henry-Basch and P. Freon, Bull. Soc. Chim. Fr., (1969) 4038.

4 B. Gross and C. Prevost, Bull. Soc. Chim. Fr., (1967) 3610; B. Mauze, C. Nivert and L. Miginiac, J. Organometal. Chem., 44 (1972) 69; F. Gerald and P. Miginiac, C.R. Acad. Sci., Ser. C, 275 (1972) 1129; B. Mauze and L. Miginiac, Bull. Soc. Chim. Fr., (1973) 1832.

5 E. Charon, Ann. Chim. Phys., 17 (1899) 197; W.G. Young and S. Winstein, J. Amer. Chem. Soc., 58 (1936) 441; W.G. Young, J.F. Lane, A. Loshokoff and S. Winstein, J. Amer. Chem. Soc., 59 (1937) 2441; W.G. Young and M. Eisner, J. Amer. Chem. Soc., 63 (1941) 2113.

6 J. Nosek, Coll. Czech. Commun., 29 (1964) 597.

7 H. Meerwein, G. Hinz, H. Majert and H. Sonke, J. Prakt. Chem., 147 (1936) 226; H. Gilman and J.F. Nelson, J. Amer. Chem. Soc., 61 (1939) 741; G.E. Coates and D. Ridley, J. Chem. Soc. A, (1966) 1064; B. Marx, E. Henry-Basch and P. Freon, C.R. Acad. Sci. Ser. C, 264 (1967) 527; B. Marx, ibid., 266 (1968) 1646; D. Abenhaim, ibid., 267 (1968) 1426; B. Eistert and L. Klein, Chem. Ber., 101 (1968) 900; P.R. Jones, E.J. Goller and W.J. Kauffman, J. Org. Chem., 34 (1969) 3566: M. Chastrette and R. Amouroux, Tetrahedron Lett., (1970) 5165; P.R. Jones, W.J. Kauffman and E.J. Goller, J. Org. Chem., 36 (1971) 186; S. Inoue and Y. Yokoo, J. Organometal. Chem., 39 (1972) 11; E.C. Ashby, L.C. Chao and J. Laemmle, J. Org. Chem., 39 (1974) 3258.

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* For reactions of alkylzinc derivatives with aldehydes and ketones see ref. 7.