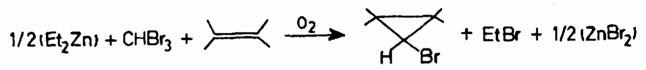
Synthesis of Monobromocyclopropanes from Olefins Using a Bromocarbenoid of Zinc

By SOTARO MIYANO*, YUKIHISA MATSUMOTO, and HARUKICHI HASHIMOTO
(*Department of Applied Chemistry, Faculty of Engineering, Tohoku University, Aramaki, Sendai* 980, *Japan*)

Summary The zinc bromocarbenoid reagent prepared from diethylzinc and bromoform in the presence of oxygen, causes conversion of olefins into the corresponding monobromocyclopropanes in good yields.

WHILE cyclopropanation of olefins with various carbene and carbenoid reagents is well known,[1] direct syntheses of monobromocyclopropanes from olefins are limited,[2,3] the conventional route being semireduction of *gem*-dibromocyclopropanes.[4] We report a convenient synthesis of monobromocyclopropanes from olefins using the zinc bromocarbenoid reagent obtained from diethylzinc and bromoform in the presence of oxygen (Scheme 1).



SCHEME 1

Dry air was passed at 10 ml min^{-1} above a mixture of diethylzinc (50 mmol) and bromoform (50 mmol) in cyclohexene (50 ml) at 35—40 °C, and a 62 : 38 mixture of *syn*- and *anti*-7-bromonorcarane was obtained (59%) in < 1 h. In the absence of oxygen, the combined yield of the norcaranes was 9·4% after 6 h at 50 °C, a large amount of

TABLE

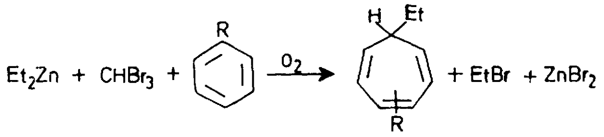
Bromocyclopropanation of some olefins with Et$_2$Zn–CHBr$_3$–oxygen[a]

Olefin	Amount of CHBr$_3$ /mmol	Amount of Et$_2$Zn /mmol	Bromo-cyclo-propane yield /%[b]	*syn* :*anti* ratio
Cyclohexene (35 ml)	35	28	84	1·9
Hex-1-ene (30 ml)	31	20	68	2·4
cis-Cyclo-octene (30 ml)	31	20	75	7·1
cis-But-2-ene[d] (15 g)	30	20	85	*syn*[c]
trans-But-2-ene[d] (12 g)	30	20	84	—
Isobutene[d] (11 g)	30	20	85	—
Styrene[e] (50 ml)	50	50	trace	

[a] Air, 10 ml min^{-1}; 1—2 h; 0—10 °C. [b] G.l.c. yield based on CHBr$_3$. [c] Negligible amounts of the *anti*-isomer were detected by g.l.c. [d] Treated in a pressure bottle in the presence of oxygen. [e] 50 °C; 8 h.

unchanged bromoform remaining. The Et_2Zn–$CHBr_3$–oxygen system was applied to the monobromocyclopropanation of various olefins (Table). All bromocyclopropanes were identified by elemental analyses and n.m.r. spectral studies. *cis*-Cyclo-octene and *cis*-but-2-ene gave *syn*-bromocyclopropanes selectively.† Styrene greatly inhibited the formation of the zinc bromocarbenoid reagent and polymerized under the reaction conditions suggesting a free-radical chain mechanism for the formation of the carbenoid reagent.[5]

The Et_2Zn–$CHBr_3$–oxygen system is also useful in the ring-expansion of alkylbenzenes[6] (Scheme 2); R, % yield, and isomer distribution (1-, 2-, and 3-position respectively) were as follows: H, 58%; Me, 42%, (59:16:25); Pr^i, 47%, (10:15:75).‡



Scheme 2

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† Preferential, but less selective formation of *syn*-9-bromobicyclo[6,1,0]nonane from *cis*-cyclo-octene has been reported with $(Me_3Si)_2NNa$–CH_2Br_2.[2]

‡ Et_2Zn, 60 mmol; $CHBr_3$, 50 mmol; PhR, 50 ml; 1 h; air, 10 ml min^{-1}; 0—5 °C.

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[6] *Cf.* S. Miyano and H. Hashimoto, *Bull. Chem. Soc. Japan*, 1973, **46**, 3257.