Journal of Organometallic Chemistry, 80 (1974) 213—218

REACTION OF *gem*-DIBROMOCYCLOPROPANES WITH ZINC IN DIMETHYLFORMAMIDE

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(Received May 2nd, 1974)

Summary

Dehalogenation of five assorted *gem*-dibromocyclopropanes with zinc in dimethylformamide is described. Monobromocyclopropanes, allenes and fully saturated cyclopropanes are obtained. The method is of preparative value only in certain cases.

Introduction

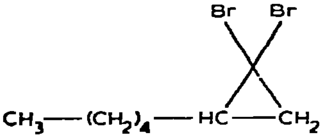
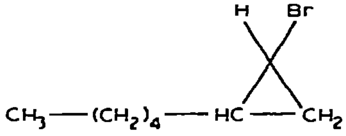
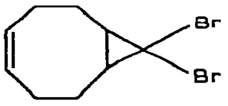
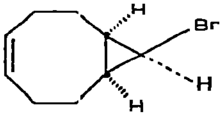
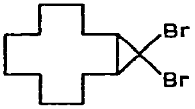
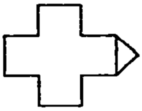
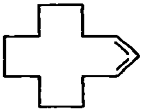
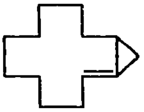
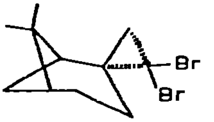
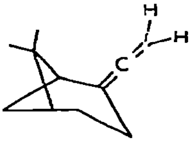
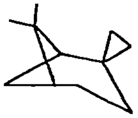
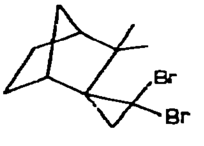
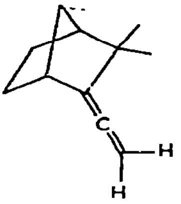
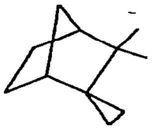
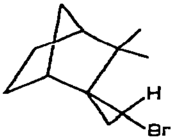
The addition of dihalocarbenes to olefins followed by subsequent reactions of the derived *gem*-dihalocyclopropanes is known to provide a convenient route to monohalocyclopropanes, fully saturated cyclopropanes and ring-expanded allenes. The reductions and α-eliminations from *gem*-dihalocyclopropanes can be brought about by a variety of reagents such as lithium aluminium hydride [1], alkyllithium in alcohol [2], organotin hydride [3], methyl sulphinyl carbanion [4], Grignard reagent [5], Na in liquid ammonia [6], zinc in ethanol [7] or acetic acid [6], chromium sulphate [8], catalytic hydrogenation [9] and electrochemical reductions [10]. Our recent observation that zinc in dimethyl formamide (DMF) is a useful combination for the non-reductive elimination of halogen from alkyl halides [11], led us to investigate the reaction of this reagent with several assorted *gem*-dibromocyclopropane compounds. The results are described here.

Results and discussion

We examined the reactions of five *gem*-dibromocyclopropane compounds I to V, derived from 1-heptene, 1,5-cyclooctadiene, cyclododecene, β-pinene and camphene, with zinc in DMF. The products and percentage yields are shown in Table 1. No particular effort was made to optimize yields. The compounds I and II gave only single products, which were readily purified by passage through a silica gel column. The dibromocarbene adducts III, IV, and V, gave a complex

TABLE 1

SUMMARY OF THE Zn—DMF REACTION OF *gem*-DIBROMOCYCLOPROPANES

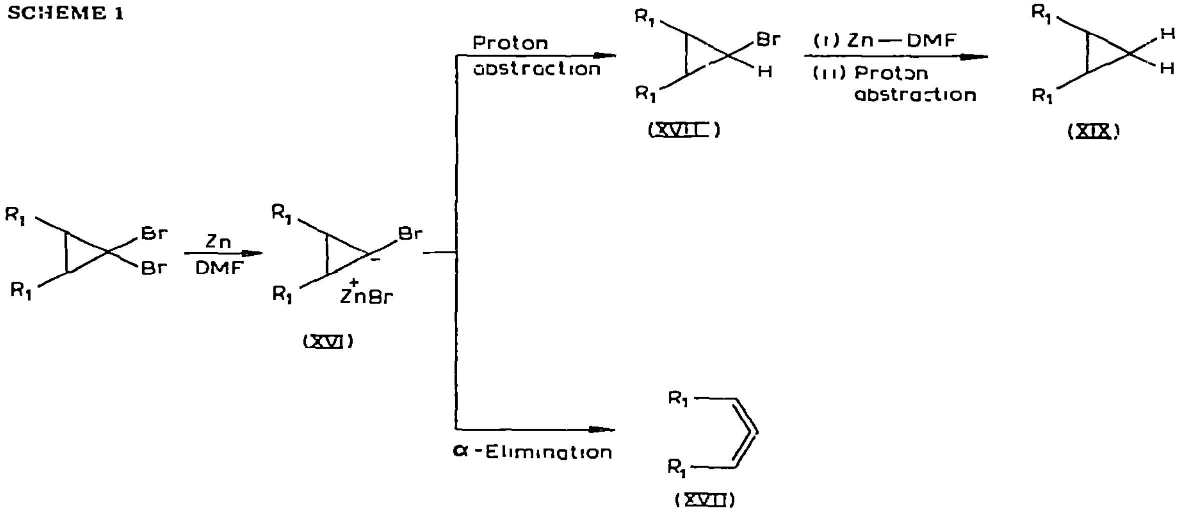
Starting *gem*-dibromo cyclopropane	Structure and composition of products
 (I)	 (VI) (60%)
 (II)	 (VII) (50%)
 (III)	 (VIII) (18%)  (IX) (31%)  (X) (15%)
 (IV)	 (XI) (58%)  (XII) (13%)
 (V)	 (XIII) (30%)  (XIV) (25%)  (XV) (13%)

mixture of products, and these were separated and purified by chromatography over silver nitrate impregnated silica gel. The structures of the products VI to XV are based on a combination of elemental analysis, complimentary spectroscopic evidence and spectral identity with authentic samples. The NMR and other spectral parameters of the compounds are described in the experimental section.

The results indicate that the *gem*-dibromocyclopropane compounds are readily reduced with zinc in DMF. The products of the reactions are, as expected, monobromocyclopropanes (VI, VII and XV), allenes (IX, XI and XIII) and fully saturated cyclopropane (VIII, XII and XIV) compounds. The type and the relative amount of the products formed from compounds I—V is dependent on the ring system of the substrate and no generalisations are possible. However, the yields of some of the products formed from *gem*-dibromocyclopropanes I—V are comparable to those obtained by other methods. For example, the yield of allenes XI and XIII in our case is 58% and 30% respectively and compare well with the yields reported in the literature [12] for the reaction of IV and V with alkyllithium reagents. Similarly, the yield (50%) of monobromocyclopropane VII is better than reported [6] for zinc—acetic acid reduction. In view of the mild reaction conditions and manipulative simplicity of the reaction, the Zn—DMF dehalogenation procedure can be effectively used in certain cases.

We propose that the dehalogenation of *gem*-dibromocyclopropanes proceeds through the initial formation of the organozinc intermediate XVI. Competitive α-elimination or proton abstraction from the medium gives the allene XVII or monobromocyclopropane XVIII. Further formation of the organozinc compound from XVIII and proton abstraction furnishes the saturated cyclopropane XIX (Scheme 1).

SCHEME 1



Experimental

Starting materials

1,1-Dibromo-2-(n-pentyl)cyclopropane (I) [13], 9,9-dibromobicyclo[6.1.0]non-5-ene (II) [14], 13,13-dibromobicyclo[10.1.0]tridecane (III) [15], 7,7-dimethyl-norpinane-2-*spiro*-1′-[2′,2′-dibromocyclopropane] (IV) [16], 2,2-dimethyl-norbornane-3-*spiro*-1′-[2′,2′-dibromocyclopropane] (V) [16] were prepared by published procedures and characterized by spectroscopic methods.

Reaction of 1,1-dibromo-2-(n-pentyl)cyclopropane (I) with zinc in DMF

A solution of 5 g of I in 25 ml of DMF was heated with 2.5 g of zinc powder and stirred overnight at 90—95°. The reaction mixture was poured into water and the precipitate was filtered and washed thoroughly with petroleum ether. The filtrate was extracted with petroleum ether (two 100 ml portions), washed with brine and dried (Na_2SO_4). Removal of solvent gave 2.1 g of an oil. This was adsorbed on silica gel (40 g) column and chromatographed. Elution with petr. ether gave 1.8 g (60%) of 1-bromo-2-(n-pentyl)cyclopropane (VI): b.p. 60—65° (bath, 10 mm), n_D^{34} 1.4565, IR (neat) 3070, 2980 cm^{-1} (cyclopropane hydrogens). NMR (CCl_4): δ 0.48 (2H, m, cyclopropane), 0.91—1.41 (12H, broad envelope). 3.08 ppm (1H, *m*, CHBr). (Found: C, 50.18; H, 7.7. $C_8H_{15}Br$ calcd.: C, 50.26; H, 7.85%.)

Reaction of 9,9-dibromobicyclo[6.1.0]non-5-ene (II) with zinc in DMF

A solution of 5 g of II in 25 ml of DMF was heated with 1.9 g of zinc powder and stirred for 4 h at 125—130°. The reaction mixture was worked up as in the above experiment and got 2.4 g of compound. This material was adsorbed on silica gel (40 g) column and chromatographed. Elution with petr. ether afforded 1.8 g (50%) *cis*-9-bromobicyclo[6.1.0]non-5-ene (VII): b.p. 80—85° (bath, 7 mm), n_D^{34} 1.5465; IR (neat) 3065, 2980 (cyclopropane hydrogens), 1650 and 855 cm^{-1} (C=C). NMR (CCl_4): δ 5.70 (2H, *m*, vinyl), 3.33 (1H, t, J = 8 Hz, CHBr) and 1.05 ppm (2H, m, cyclopropane). The spectroscopic data is well in agreement with that reported for VII [6]. (Found: C, 53.58; H, 6.23. $C_{19}H_{13}Br$ calcd.: C, 53.75; H, 6.15%.)

Reaction of 13,13-dibromobicyclo[10.0.1]tridecane (III) with zinc in DMF

A solution of 5 g of III in 25 ml of DMF was heated with 2 g of zinc powder with stirring for 4 h at 125—130°. The reaction mixture on usual work-up gave 2.4 g of an oily material. This material was adsorbed on (40 g) silica gel/$AgNO_3$ (15%) column and chromatographed. Elution with petr. ether afforded 0.5 g (18%) bicyclo[10.1.0]tridecane (VIII): b.p. 65—70° (bath, 1 *mm*), n_D^{34} 1.4795; IR (neat) 3070, 2980 cm^{-1} (cyclopropane hydrogens). NMR (CCl_4): δ 0.6 (2H, m, cyclopropane), 1.36 ppm (22H, broad envelope). Its IR spectrum was indistinguishable from the authentic sample, prepared by Na/liq. NH_3 reduction of III.

Further elution with petr. ether gave 1 g (31%) 1,2-cyclotridecadiene (IX): b.p. 65—70° (bath, 1 *mm*), n_D^{34} 1.5045. IR (neat) 1960, 870 cm^{-1} (allenic double bond), NMR (CCl_4): δ 4.98 (3H, q, J = 5 Hz, allenic), 2.08 (4H, allylic protons) and 1.36 ppm (16H, methylene).

Further elution with petr. ether gave 0.4 g (15%) *bicyclo*[10.1.0]-2-tridecene (X): b.p. 65—70° (bath, 1 *mm*), n_D^{34} 1.4798; IR (neat) 3070, 2980 (cyclopropane hydrogens), 1650 and 965 cm^{-1} (C=C). NMR (CCl_4): δ 5.28 (1H, broad singlet, >C=CH), 2.08 (2H, broad singlet, allylic), 1.28 ppm (19H, broad singlet).

Reaction of 7,7-dimethyl-norpinane-2-spiro-1'-[2',2'-dibromocyclopropane] (IV) with zinc in DMF

A solution of 5 g of IV in 25 ml of DMF was heated with 2.2 g of zinc powder and stirred overnight at 80—85°. The reaction mixture on usual work-up gave 2.2 g of an oily material. This material was adsorbed on (40 g) silica gel/$AgNO_3$ (15%) column and chromatographed. Elution with petr. ether afforded 0.3 g (13%) of 7,7-dimethyl-norpinane-2-*spiro*-cyclopropane (XII): b.p. 55—60° (bath, 10 mm), n_D^{34} 1.4690; IR (neat) 3070, 2980 cm^{-1} (cyclopropane hydrogens); NMR (CCl_4): δ 0.96 (3H, s, $CH_3{-}C\leqq$), 1.14 (3H, s, $CH_3{-}C\leqq$) and 0.6—0.84 ppm (4H, m, cyclopropane). Its IR spectrum was superimposable with that of an authentic compound prepared by Na/liq. NH_3 reduction of IV.

Further elution of column with petr. ether gave 1.4 g (58%) of 6,6-dimethyl-2-vinylidene-norpinane (XI): b.p. 55—60° (bath, 10 mm), n_D^{34} 1.5135; IR (neat) 1960, 850 cm^{-1} (allenic double bond). NMR (CCl_4): δ 0.84 (3H, s, $CH_3{-}C\leqq$), 1.2 (3H, s, $CH_3{-}C\leqq$) and 4.48 (2H, q, $J = 5$ Hz, $>C{=}C{=}CH_2$). The spectroscopic data is in good agreement with that of reported for XI [12].

Reaction of 2,2-dimethyl-norbornane-3-spiro-1'-[2',2'-dibromocyclopropane] (V) with zinc in DMF

A solution of 5 g of V in 25 ml of DMF was heated with 2.2 g of zinc powder with stirring overnight at 80—85°. The reaction mixture on usual workup gave 2.3 g of an oily material. This material was fractionally distilled, giving 1.6 g of compound at 47—54°/10 mm as first fraction and 0.5 g at 95°/10 mm as the second fraction. The first fraction material was adsorbed on (40 g) silica gel/$AgNO_3$ (15%) column and chromatographed. Elution with petr. ether afforded 0.6 g (25%) 2,2-dimethyl-norbornane-3-*spiro*-1'-cyclopropane (XIV): b.p. 50—55° (bath, 10 mm), m.p. and mixture m.p. 55—56°. Its IR was identical with that of an authentic sample prepared by the Na/liq. NH_3 reduction of V [17].

Further elution with petr. ether gave 0.8 g (30%) 2,2-dimethyl-3-vinylidene-norbornane (XIII): b.p. 50—55° (bath, 10 mm), n_D^{34} 1.5464; IR (neat) 1960 and 840 cm^{-1} (allenic double bond). The spectroscopic data are in good agreement with those of reported for XIII [12].

The second fractionated fraction was adsorbed on (15 g) silica gel column and chromatographed. Elution with petr. ether gave 0.3 g (13%) of 2,2-dimethyl-norbornane-3-*spiro*-1'-2'-bromocyclopropane (XV): b.p. 95—100° (bath, 10 mm), n_D^{34} 1.5124; IR (neat) 3070, 2980 cm^{-1} (cyclopropane hydrogens). NMR (CCl_4): δ 3.23—3.95 (1H, m, CH(Br)), 1.05 (3H, s, $CH_3{-}C\leqq$), 1.01 (3H, s, $CH_3{-}C\leqq$) and 0.83—0.75 (2H, broad envelope, cyclopropane). (Found: C, 57.48; H, 7.15. $C_{11}H_{17}Br$ calcd.: C, 57.64; H, 7.42%.)

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