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REDUCTION OF gem-DIBROMOCYCLOPROPANES WITH CHROMIUM(II) SULPHATE

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Abstract—*gem*-Dibromocyclopropanes I are easily attacked by chromium (II) sulphate to produce allenes (V), monobromocyclopropanes (VI) and completely reduced cyclopropanes (VII) by the scheme formulated. The product distribution (Table 1) depends on the size of the second rings fused to the cyclopropane ring. Both cyclopropyl bromides isolated (VIa and VIb) have *cis*-configuration. As shown in Table 2 certain monobromocyclopropanes (*cis*-VIa and *trans*-VIb) are hydrolysed under such reduction conditions to give the respective allylic alcohols VIIIa and VIIIb, but no completely reduced products VII are produced.

REACTION of cycloalkenes with dibromocarbene furnishes *gem*-dibromocyclopropanes I, whose debromination with alkyllithium[1] or with methylsulphinylcarbanion[2] results in ring expansion affording cyclic allenes (V) in favourable cases. On the other hand, step-wise reduction without ring cleavage gives monobromocyclopropanes (VI) and cyclopropanes (VII).[3,4] We wish to report that dibromocyclopropanes I are susceptible to the reducing action of chromium (II) sulphate to produce these products (V–VII) according to the proposed reaction scheme.

TABLE 1. PRODUCT DISTRIBUTION AS A FUNCTION OF THE SIZE OF THE SECONDARY FUSED RING[a]

Starting material	Yield (%) based on I			
	V	VI[b]	VII	VIII
Ia (X = —(CH$_2$)$_4$—)	—	25	6	16
Ib (X = —(CH$_2$)$_6$—)	30	32	25	0
Ic (X = —(CH$_2$)$_{10}$—)	85	0	0	0
Id (X = —C$_{10}$H$_{16}$—[c])	75	0	0	0

[a] For procedure of Cr(II) reduction see Experimental (aq DMF, 80°).

[b] All monobromocyclopropanes isolated were found to be the *cis* isomer, no *trans* isomer being detected.

[c] $C_{10}H_{16}$ stands for
$—CH_2CH_2CH{=}CHCH_2CH_2CH{=}CHCH_2CH_2—$.

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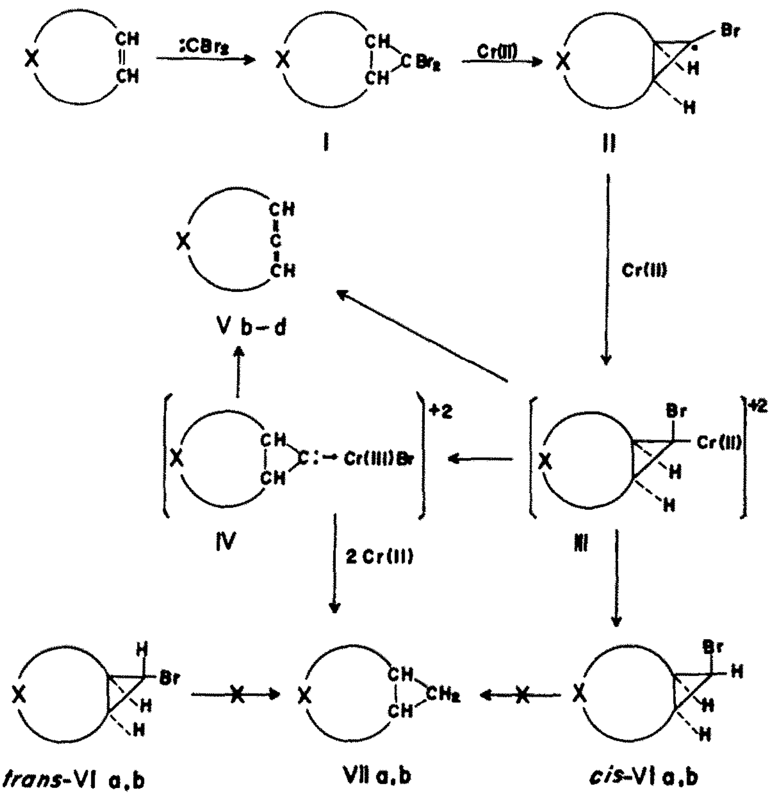
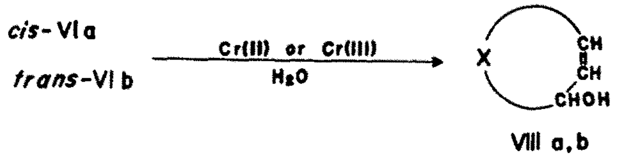
[1] [a] L. Skattebøl, *Acta Chem. Scand.* **17**, 1681 (1963); [b] W. R. Moore and H. R. Ward, *J. Org. Chem.* **27**, 4179 (1962) and refs cited therein.

[2] C. L. Osborn, T. C. Shields, B. A. Shoulders, C. G. Cardenas and P. D. Gardner, *Chem. & Ind.* 766 (1965).

[3] For example, [a] K. Hofmann, S. F. Orochena, S. M. Sax and G. A. Jeffrey, *J. Am. Chem. Soc.* **81**, 992 (1959); [b] D. Seyferth, H. Yamazaki and D. L. Alleston, *J. Org. Chem.* **28**, 703 (1963); [c] D. Seyferth and B. Prokai, *Ibid.* **31**, 1702 (1966). See also Ref. 2.

[4] Attempted reduction of Ic with methylmagnesium bromide in tetrahydrofuran, however, resulted in formation of the allene Vc in ca. 30% yield (*cf.* Ref. 3c).





a: $X = -(CH_2)_4-$ b: $X = -(CH_2)_6-$ c: $X = -(CH_2)_{10}-$

d: $X = -CH_2CH_2CH{=}CHCH_2CH_2CH{=}CHCH_2CH_2-$

Although the reduction with chromous salts has been explored,[5,6] such reactivity of *gem*-dibromocyclopropanes appears not to have been described previously.

The product distribution is influenced by the size of the second rings attached to the cyclopropane ring as shown in Table 1. The Table reveals that cyclic allenes (V)

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[5] [a] J. K. Kochi and D. D. Davis, *J. Am. Chem. Soc.* **86**, 5264 (1964); [b] J. K. Kochi and D. Buchanan, *Ibid.* **87**, 853 (1965); [c] J. K. Kochi and P. E. Mocadlo, *Ibid.* **88**, 4094 (1966) and Refs cited.

[6] [a] C. E. Castro and W. C. Kray, Jr., *J. Am. Chem. Soc.* **85**, 2768 (1963); [b] *Ibid.* **88**, 4447 (1966) and previous papers cited.

are the most favoured products with cyclopropanes (I) fused to 12-membered second rings. Rather high yields of 1,2-cyclotridecadiene (Vc)[7] or 1,2,6,10-cyclotridecatetraene (Vd)[7] imply synthetic utility of the present method of debromination. The operation involving the aqueous dimethylformamide (DMF) solution of chromium (II) sulphate is clearly more advantageous than any other known procedure including the one in the original allene synthesis reported.[1] Similar reduction of 5,5,10,10-tetrabromotricyclo[7.1.0.$0^{4,6}$]decane (IX) afforded 1,2,5,6-cyclodecatetraene (X)[1a] in 4% yield.

Hydrogenated products VI and VII were produced in the reduction of cyclohexene- and cyclooctene-dibromocarbene adducts (Ia and Ib). Remarkably, both monobromocyclopropanes isolated were found to be *cis* (*cis*-VIa and *cis*-VIb), and even a trace amount of the respective *trans* isomer (*trans*-VIa or *trans*-VIb) could not be detected. Reduction of 9,9-dibromobicyclo[6.1.0]non-4-ene (XI) gave a complex mixture, from which *cis*-9-bromobicyclo[6.1.0]non-4-ene (XII) (8% yield) and 1,2,6-cyclononatriene (XIII; 25% yield) were isolated.

The formation of an allylic alcohol (VIIIa) in a considerable amount was attributed to the hydrolysis of *cis*-VIa under the influence of chromium-(II) ion. In fact, treatment of certain cyclopropyl bromides with aqueous chromium(II) sulphate afforded the respective allylic alcohols, while reduction to hydrocarbons was never observed.[8] The results were summarized in Table 2.

TABLE 2. Cr(II)-CATALYSED HYDROLYSIS OF MONOBROMOCYCLOPROPANES[a]

Starting material	Predicted[b]		Found		
	Reactivity	Product	Reactivity	Product	Yield (%)
cis-VIa	+	2-cycloheptenol	+	2-cycloheptenol	41
trans-VIa	–	none	–[c]	none	—
cis-VIb	+	*cis*-2-cyclononenol	–[c]	none	—
trans-VIb	±[d]	*trans*-2-cyclononenol	+	*cis*-2-cyclononenol	70

[a] For reaction conditions see Experimental (aq DMF, 80°).

[b] These predictions were made on the basis of *assumed* concerted solvolysis (cf. ref 9).

[c] These halides were also inert to Ag(I)-assisted hydrolysis (aq acetone, 25°, 48 hr).

[d] The reactivity was predicted to be lower than that of *cis*-VIb.

If the ring opening and the ionization occur simultaneously, the selection rule predicts that this transformation should proceed stereospecifically in a disrotatory manner, in which substituents *trans* to the bromine atom rotate outward and those *cis* to the bromine rotate inward.[9, 10] As indicated in Table 2, the reaction of bicyclo-[4.1.0]heptane system (VIa) proceeded in accord with this rule, but anomalies were

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[7] H. Nozaki, S. Katô and R. Noyori, *Canad. J. Chem.* **44**, 1021 (1966).

[8] [a] The hydrolysis proceeded in the presence of Cr(III) ion also, but a fair amount of the starting bromides was recovered under the same conditions; [b] Cr(III) ion accelerates dehydrobromination of t-butyl bromide; L. H. Slaugh and J. H. Raley, *Tetrahedron* **20**, 1005 (1964).

[9] [a] R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.* **87**, 395 (1965); [b] C. H. DePuy, L. G. Schnack and J. W. Hausser, *Ibid.* **88**, 3343 (1966).

[10] Purely unassisted hydrolysis through classical cyclopropyl cation containing high strain would be scarcely involved if any.

encountered in bicyclo[6.1.0]nonane system (VIb). A similar discrepancy has been recorded in the acetolysis of the corresponding tosylate.[11]

All these observations are in accordance with the above reaction scheme. The attack of chromium(II) ion on the initially produced cyclopropyl radical II would probably occur at the less hindered site and the formation of organochromium intermediate III is straightforward as established by Kochi[5] and Castro.[6] Subsequent α-elimination of III, either directly or *via* chromium(III)-carbene complex IV, produces the corresponding allene V. In cases where the ring expansion is sterically inhibited, protonolysis of III occurs to afford *cis*-monobromocyclopropane (VI) which can not be further reduced to VII as shown above. The completely hydrogenated product VII would supposedly be produced from carbene complex (IV)[6b] but the direct reduction of III can not be rejected *a priori*. No partially reduced halides have been obtained in the reduction of open-chain *gem*-halides.[6b] Formation of the monobromocyclopropane derivatives would be reasonably ascribed to the larger stability of organochromium intermediate III containing cyclopropyl group. However, attempted trapping of III (or IV) with cyclohexene resulted in failure.

Finally, it should be added that similar reduction of 1,1-dibromo-2-phenylcyclopropane (XIV) proceeded smoothly at room temperature to yield a mixture of phenylcyclopropane (67% yield) and 1-bromo-2-phenylcyclopropane (18%). No phenylallene was detected.

EXPERIMENTAL

All b.ps and m.ps were uncorrected. GLC analysis and separation were performed using a 2 m column of Apiezon grease L (30%) and He as a carrier gas. NMR spectra were taken with Varian A 60 apparatus and chemical shifts were given in ppm from TMS internal standard. The aqueous soln of chromium(II) sulphate with a titer of 0·85–0·90 N was prepared by Zn dust reduction of aqueous chromium(III) sulphate,[6a] and stored below n-hexane layer. All operations involving chromium(II) sulphate soln were carried out in N_2 atmosphere.

Reduction of 7,7-*dibromobicyclo*[4.1.0]*heptane* (Ia). An aqueous soln of Cr(II) sulphate (150 ml; 130 mmoles) and freshly distilled DMF (100 ml) were placed in a 500 ml flask. A soln of Ia[12] (10·6 g; 42 mmoles) in DMF (50 ml) was added in one portion, and the mixture was subjected to vigorous stirring by means of *Vibromixer*. After 5 hr reaction at 80° the colour of the soln turned from initial sky blue to dark green, when 2·3 equivs of Cr(II) ion had been consumed. Excess Cr(II) sulphate was oxidized by aeration, and the reaction mixture was repeatedly extracted with ether. The combined ethereal extracts were washed with water, dried (Na_2SO_4) and concentrated carefully *in vacuo* at room temp. GLC separation of the residue gave following 3 products. (a) Compound VIIa (0·24 g; 6% yield) was identified by comparison of IR spectrum and retention time of GLC with ones of the authentic sample.[13] (b) Compound VIIIa[14] (0·75 g; 16% yield) showed IR (neat) absorptions at 3400, 1660, 1040 and 690 cm^{-1}, and NMR ($CDCl_3$) signals at δ 5·75 (2H, narrow multiplet, vinyl protons), 4·4 (1H, multiplet, $C\underline{H}$-OH), 2·4-1·1 (8H, multiplet, methylenes) and 2·3 (1H, singlet, OH). (Found: C, 74·5; H, 10·8. Calc. for $C_7H_{12}O$: C, 74·9; H, 10·8%.) Phenylurethane of VIIIa, m.p. 104° (lit.[14] 105·7°). (Found: C, 72·9; H, 7·3; N, 6·2. Calc. for $C_{14}H_{17}NO_2$: C, 72·7; H, 7·4; N, 6·1%). (c) Finally, *cis*-VIa (1·8 g; 25% yield) was identified by comparison of IR spectrum and retention time with ones of the authentic specimen.[3b] The absence of the *trans* isomer was established by GLC.

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[11] P. von R. Schleyer, G. W. Van Dine, U. Schöllkopf and J. Paust, *J. Am. Chem. Soc.* **88**, 2868 (1966). These authors described acetolysis of "9-*exo*-bicyclo[7.1.0]nonyl" tosylate. We understand that this is in error and actually means the reaction of "9-*exo*-bicyclo[6.1.0]nonyl" tosylate.

[12] W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.* **76**, 6162 (1954).

[13] H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.* **81**, 4256 (1959).

[14] J. E. Hodgkins and R. J. Flores, *J. Org. Chem.* **28**, 3356 (1963).

Reduction was carried out in the presence of a large excess of cyclohexene (30 mole ratio to Ia), but compounds arising from attack on the olefin were not detected among the products.

Reduction of 9,9-*dibromobicyclo*[6.1.0]*nonane* (Ib). A soln of Ib[1a] (9·3 g; 33 mmoles) in DMF (150 ml) was treated with the aq Cr(II) sulphate soln (200 ml; 175 mmoles). After 6 hr reaction at 80°, 2·2 equivts of Cr(II) ion was consumed. GLC separation of the reaction mixture yielded 3 pure components. Compound VIIb (1·0 g; 25% yield) was identified by comparison with the authentic specimen,[15] Vb (1·2 g; 30% yield) was also identified by comparison of IR spectrum with the recorded compound[1a] and *cis*-VIb (2·2 g; 32% yield) was compared with an independently synthesized sample.[3b] Neither *trans* isomer (*trans*-VIb) not allylic alcohol could be detected.

Reduction of 9,9-*dibromobicyclo*[6.1.0]*non-4-ene* (XI). Treatment of a soln of XI[1a] (10·4 g; 37 mmoles) in DMF (150 ml) with the aq Cr(II) sulphate soln (200 ml; 170 mmoles) at 80° for 4 hr yielded a complex mixture, from which XIII[1a] (1·1 g; 25% yield) and XII[16] (0·36 g; 8% yield) were isolated by chromatography on an alumina column. Both were identified by independent syntheses. About 1·5 g (30%) of an unidentified alcohol was also produced. This was found not to be 2,6-cyclononadienol.

Reduction of 5,5,10,10-*tetrabromotricyclo*[7.1.0.$0^{4,6}$]*decane* (IX). Tetrabromide IX[1a] (9·0 g; 20 mmoles) was reduced with the aq Cr(II) sulphate soln (200 ml; 175 mmoles) in DMF (150 ml). After 16 hr reaction at 80° a complex mixture was obtained. Separation of the products through an alumina column followed by distillation (0·1 mm, bath temp 80°) gave X (0·10 g; 4% yield), the IR spectrum being superimposable on the recorded one.[1a]

Reduction of 13,13-*dibromo*-cis-*bicyclo*[10.1.0]*tridecane* (Ic) *and* 13,13-*dibromo*-trans-*bicyclo*[10.1.0]-*trideca*-cis-4, trans-8-*diene* (Id). A mixture of Ic[7] (2·6 g; 7·8 mmoles), the aq Cr(II) sulphate soln (50 ml; 43 mmoles) and 50% aq DMF (100 ml) was heated at 80° under vigorous stirring in the course of 18 hr. The reaction mixture was treated with water and extracted with ether. The combined extracts were washed, dried and concentrated *in vacuo*. Distillation of the residual oil yielded Vc (1·2 g; 85% yield), b.p. 90–92°/5 mm. The IR spectrum was identical with the one of the authentic sample.[7] GLC analysis indicated the absence of cyclotridecyne.[7]

Similar reduction of Id[7] (3·1 g; 9·4 mmoles) (containing 10–15% of 13,13-dibromo-*cis*-bicyclo[10.1.0]-trideca-*trans*-4,*trans*-8-diene) with the aq Cr(II) sulphate soln (50 ml; 43 mmoles) and 50% aq DMF (100 ml) gave Vd (1·2 g; 75% yield) of about 85% purity, b.p. 125–130°/12 mm, the impurity being its stereoisomer. The structure was established by comparison with the authentic sample.[7]

Reduction of 1,1-*dibromo*-2-*phenylcyclopropane* (XIV). A mixture of XIV[17] (6·0 g; 22 mmoles), the aq Cr(II) sulphate soln (100 ml; 85 mmoles) and 50% aq DMF (100 ml) was subjected to vigorous stirring at room temp during 5 hr. Work-up followed by GLC separation afforded phenylcyclopropane[13] (1·7 g; 67% yield) and a mixture of *cis*- and *trans*-1-bromo-2-phenylcyclopropanes[3b] (0·80 g; 18% yield). Both were identified by comparison with the respective authentic specimens. Formation of phenylallene[1a] was excluded by GLC.

Hydrolysis of 7-*bromobicyclo*[4.1.0]*heptane* (VIa). A mixture of *cis*-VIa[3b] (1·1 g; 6·2 mmoles), the aq Cr-(II) sulphate soln (50 ml; 43 mmoles) and 50% aq DMF (100 ml) was heated at 80° with vigorous stirring during 16 hr. Work-up followed by GLC purification gave VIIIa (0·28 g; 41% yield) as a sole product. Identification was performed by comparison with the sample above obtained.

Attempted hydrolysis of *trans*-VIa[2] was carried out in a similar way, but no alcoholic product was obtained. The sole isolable organic material was the starting bromide (50% recovery). In both runs formation of VIIa was not observed.

Hydrolysis of 9-*bromobicyclo*[6.1.0]*nonane* (VIb). A mixture of *trans*-VIb[2] (1·1 g; 5·5 mmoles) in 50% aq DMF (100 ml) and the aq Cr(II) sulphate soln (50 ml; 43 mmoles) was maintained at 80° for 24 hr under vigorous stirring. The reaction mixture was treated with water and extracted with ether. The combined extracts were concentrated *in vacuo* to give a crystalline mass. Purification by passing through an alumina column yielded an analytical sample of cis-2-*cyclononenol* VIIIb[18] (0·54 g; 70% yield), m.p. 58–59° (from n-hexane), which showed IR (Nujol) absorptions at 3350, 1670, 1030 and 740 cm^{-1}, and NMR ($CDCl_3$)

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[15] E. LeGoff, *J. Org. Chem.* **29**, 2048 (1964).

[16] C. L. Osborn, T. C. Shields, B. A. Shoulders, J. F. Krause, H. V. Cortez and P. D. Gardner, *J. Am. Chem. Soc.* **87**, 3158 (1965).

[17] P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.* **78**, 5430 (1956).

[18] An oily mixture of *cis*, *trans* VIIIb was previously recorded by M. Santelli, M. Bertrand and M. Ronco (*Bull. Soc. Chim. Fr.* 3273 (1964)).

signals at δ 5·45 (2H, multiplet, vinyl protons), 4·0 (1H, multiplet, C$\underline{H}$-OH), 2·5–0·8 (12H, multiplet, methylenes) and 1·8 (1H, broad band, OH). (Found: C, 76·7; H, 11·6. $C_9H_{16}O$ requires: C, 77·1; H, 11·5%.) *Phenylurethane of VIIIb*, m.p. 111–112° (from n-hexane). (Found: C, 73·8; H, 8·1; N, 5·4. $C_{16}H_{21}NO_2$ requires: C, 74·1; H, 8·2; N, 5·4%). Allylic alcohol VIIIb was the sole product isolated, and no reduction product was obtained.

Similar treatment of *cis*-VIb[36] resulted in 50% recovery of the starting material. Any other product was not produced.

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