

The Reaction of Alkoxide Ions with Some Chlorine-substituted Norbornadienes

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The reaction of 1,2,3,4,7,7-hexachloro-5-phenylnorborna-2,5-diene with methoxide ions results in the addition of methanol to the phenyl-substituted double bond. 2,3,4,5-Tetrachlorobiphenyl, previously reported to be the reaction product, could not be detected. The reaction of ethoxide ions with 1,2,3,4,7,7-hexachloronorborna-2,5-diene affords a significant amount of 1,2,3,4,7,7-hexachloro-5-*endo*-ethoxynorborn-2-ene in addition to the major product 1,2,4,7,7-pentachloro-3-ethoxynorborna-2,5-diene reported earlier.

THE Diels–Alder addition of phenylacetylene to hexachlorocyclopentadiene was shown by McBee¹ to afford 1,2,3,4,7,7-hexachloro-5-phenylnorborna-2,5-diene (I). This diene was reported¹ to react with two molar proportions of sodium methoxide in refluxing methanol during 24 h to give 2,3,4,5-tetrachlorobiphenyl (II) (21%) *via* the intermediacy of the acetal (III). This acetal, formed by nucleophilic substitution of the bridge-chlorine atoms in (I), was neither isolated nor detected. On repeating this reaction we were unable to obtain any of either product (II) or (III); g.l.c. analysis of the reaction mixture showed that it contained starting material together with traces of two products. When eight molar proportions of sodium methoxide and a reaction time of 30 h were used, the diene (I) was largely consumed (93%) and the products (IV) (52%) and (V) (37%) of the addition of methanol to the phenyl-substituted double bond of (I) were present. Again, no 2,3,4,5-tetrachlorobiphenyl was detected.

¹ E. T. McBee, J. D. Idol, jun., and C. W. Roberts, *J. Amer. Chem. Soc.*, 1955, **77**, 6674.

² K. L. Williamson, Yuan-Fang Li Hsu, and E. I. Young, *Tetrahedron*, 1968, **24**, 6007.

³ M. Barfield and B. Chakrabarti, *Chem. Rev.*, 1969, **69**, 757.

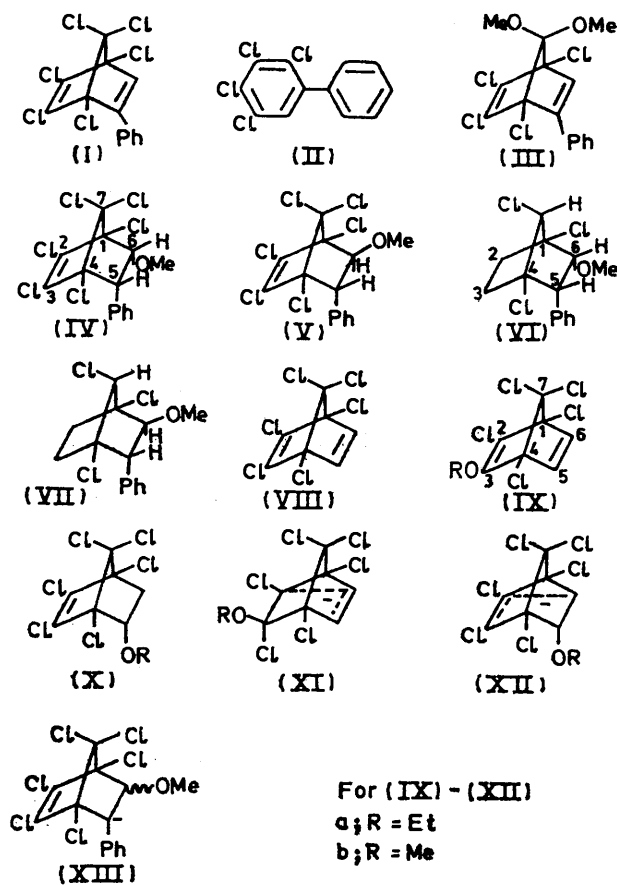
Compounds (IV) and (V) had appropriate n.m.r. spectral data (see Table), and the structures were confirmed by hydrogenolysis,² to give the norbornanes (VI) and (VII), which have definitive n.m.r. spectra (see Table) owing to the presence of 3-*exo*,5-*exo* and/or 2-*exo*,6-*exo* long-range couplings.³ The *endo*,*cis* arrangement of the phenyl and methoxy-groups in (IV) is further established by the preparation of this compound by Diels–Alder addition of hexachlorocyclopentadiene to *cis*- β -methoxystyrene. The work of Williamson⁴ on related Diels–Alder reactions makes the *endo*,*cis* structure of (IV) beyond doubt.

The reaction of potassium hydroxide in refluxing ethanol with 1,2,3,4,7,7-hexachloronorborna-2,5-diene (VIII) was reported by Mackenzie⁵ to give the 3-ethoxy-diene (IXa) as product, formed by substitution of a vinylic chlorine atom in (VIII). On repeating this experiment, using a modified procedure for product isolation, we found the product (Xa) of addition of ethanol to the unsubstituted double bond of (VIII),

⁴ K. L. Williamson, Yuan-Fang Li Hsu, R. Lacko, and Chung He Youn, *J. Amer. Chem. Soc.*, 1969, **91**, 6129; K. L. Williamson, *ibid.*, 1963 **85**, 516.

⁵ K. Mackenzie, *J. Chem. Soc.*, 1962, 457.

to be an additional product. The product (Xa) was identical with the Diels-Alder adduct of ethyl vinyl ether and hexachlorocyclopentadiene.⁶ The products



(IXa) and (Xa) are formed in the ratio 5:1, and a similar result with a product ratio of 3:1 was obtained

saturated carbon atom, Mackenzie⁵ postulated the intermediacy of the delocalised homoallylic carbanion (XIa). Since there are no activating groups for nucleophilic addition attached to the 5,6-double bond in structure (VIII) it is possible that the additional non-classical carbanion (XII) may be involved in the formation of (X). Under analogous reaction conditions the addition of methanol to ethylene or the replacement of a vinylic chlorine atom in *cis*-dichloroethylene does not take place to any appreciable extent,⁷ which suggests that intermediates of unexpected stability may be involved in the formation of compounds (IX) and (X). The addition of methanol to styrene also does not occur under these conditions,⁷ and in the formation from diene (I) of the addition products (IV) and (V) rather than the acetal (III), the intermediate carbanion (XIII) may have a non-classical nature involving the delocalisation of the carbanion centre over both the chlorine-substituted double bond and the phenyl ring.

The factors affecting the site of attack of nucleophiles on chlorine-substituted norbornadienes are very finely balanced. Sodium methanethiolate in dimethylformamide is reported to yield only products of substitution for vinylic chlorine.⁸ One reason for the failure to form addition products is the aprotic nature of dimethylformamide. It is also possible that the chlorine-substituted double bond is the favoured site for attack by nucleophiles, but in hydroxylic solvents attack additionally occurs on the unsubstituted double bond because solvation of alkoxide ions occurs. This would result in increased steric hindrance to approach to the more hindered chlorine-substituted double bond. The ability of a phenyl group to stabilise carbanion intermediates may be the cause of exclusive addition of methoxide ions to the phenyl-substituted double bond in structure (I).

N.m.r. spectra^a

| Compound | τ Values | | | | J /Hz | | | | |
|----------------------|------------------|------------------|-------------------|-------------------|----------------------------------|-----------------------------------|-----------------------------------|----------------------------------|----------------------------------|
| | 5- <i>exo</i> -H | 6- <i>exo</i> -H | 6- <i>endo</i> -H | O-CH ₃ | 5- <i>exo</i> , 6- <i>exo</i> | 5- <i>exo</i> , 6- <i>endo</i> | 6- <i>exo</i> , 6- <i>endo</i> | 3- <i>exo</i> , 5- <i>exo</i> | 2- <i>exo</i> , 6- <i>exo</i> |
| (IV) | 5.52(d) | 6.02(d) | | 6.84(s) | 7.3 | | | | |
| (V) | 5.29(d) | | 6.78(d) | 6.49(s) | | 4.4 | | | |
| (VI) ^{b,c} | 6.06(q) | 6.77(q) | | 7.03(s) | 10.0 | | | 4.0 | 2.0 |
| (VII) ^{b,d} | 5.99(q) | | 7.01(d) | 6.61(s) | | 4.5 | | 2.0 | |
| (Xa) ^e | 5.52(q) | 7.12(q) | 8.02(q) | | 7.4 | 2.5 | 12.5 | | |
| (Xb) | 5.68(q) | 7.18(q) | 8.09(q) | 6.49(s) | 7.3 | 2.5 | 12.7 | | |

^a 60 MHz spectra; CCl₄ as solvent unless stated otherwise. ^b 100 MHz spectra; CCl₄ as solvent. ^c τ 6.04(s, CHCl). ^d τ 5.74(s, CHCl). ^e τ 6.25(m, O-CH₂-CH₃) and 8.82(t, O-CH₂-CH₃). Compound (IXa) had τ 3.25(d, H-5), 3.35(d, H-6), and 5.50(q) and 8.61(t) (J 7.0 Hz, OCH₂-CH₃); $J_{5,6}$ 5.8 Hz. Compound (IXb) had τ 3.27(d, H-5), 3.47(d, H-6), and 5.88(s, O-CH₃); $J_{5,6}$ 6.0 Hz.

by replacing potassium hydroxide with sodium ethoxide. The analogous products (IXb) and (Xb) were obtained in the ratio 1:8 by use of sodium methoxide, but this product ratio is probably not significant on account of the low overall yield, and appreciable product decomposition during the reaction.

To account for the substitution of a vinylic chlorine atom, rather than a bridge chlorine attached to a

EXPERIMENTAL

The 100 MHz n.m.r. spectra were recorded by the PCMU service at Harwell; the 60 MHz spectra were obtained with a Perkin-Elmer R10 spectrometer. I.r. data were obtained with a Perkin-Elmer 257 grating spectrometer. Column chromatography (unless stated otherwise) was carried out with Wöelm neutral activity grade I alumina [light petroleum (b.p. 40–60°) as eluant]. G.l.c. analysis was carried out with a Griffin D6 Density

⁶ F. P. Sidelskovskaya, M. G. Zelinskaya, and M. F. Shostakovskii, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1961, 128.

⁷ D. R. Adams and D. I. Davies, unpublished observations.

⁸ D. I. Davies and P. J. Rowley, *J. Chem. Soc. (C)*, 1969, 288.

Balance Chromatograph, employing nitrogen as carrier gas and fitted with a 6 ft \times $\frac{1}{4}$ in column of 20% silicone oil on Chromosorb W (60–80 mesh) at 180°. 1,2,3,4,7,7-Hexachloro-5-phenylnorborna-2,5-diene (I) was prepared by the method of McBee,¹ and 1,2,3,4,7,7-hexachloro-5-endo-ethoxynorborn-2-ene by the method of Shostakovskii.⁶

Reactions of Dienes with Alkoxide Ions.—In all reactions the percentage yields of products, based on starting diene consumed, were estimated by g.l.c. The individual products were isolated as a result of repeated chromatography and recrystallisation of the crude products, and therefore quantities actually isolated are much less than the percentage yields quoted.

(a) 1,2,3,4,7,7-Hexachloro-5-phenylnorborna-2,5-diene (I) with sodium methoxide. The diene (I) (3 g, 0.008 mol) dissolved in methanol (25 ml) was added to a solution of sodium (1.5 g, 0.065 g atom) in methanol (25 ml). The mixture was boiled at reflux for 30 h, cooled, poured into water (200 ml), and extracted with carbon tetrachloride (3 \times 50 ml). The extract was dried (MgSO₄) and evaporated to yield a brown oil. Repeated chromatography and recrystallisation from light petroleum (b.p. 40–60°) gave unchanged diene (I) (0.2 g); 1,2,3,4,7,7-hexachloro-6-endo-methoxy-5-endo-phenylnorborn-2-ene (IV) (0.3 g), m.p. 84–85°, ν_{\max} 1603 cm⁻¹ (*cis*-ClC=CCl) (Found: C, 41.3; H, 2.4. C₁₄H₁₀Cl₆O requires C, 41.1; H, 2.45%); and 1,2,3,4,7,7-hexachloro-6-exo-methoxy-5-endo-phenylnorborn-2-ene (V) (0.2 g), m.p. 92–93°, ν_{\max} 1610 cm⁻¹ (*cis*-ClC=CCl) (Found: C, 41.2; H, 2.45%). Quantitative g.l.c. analysis showed the yields of (IV) and (V) were 52 and 37% respectively.

(b) 1,2,3,4,7,7-Hexachloronorborna-2,5-diene (VIII) with potassium hydroxide in ethanol (*cf.* ref. 5). The diene (VIII) (3.6 g, 0.012 mol), purified by the method of ref. 9 was added to a solution of potassium hydroxide (1.26 g, 0.0216 mol) in ethanol (5 ml), and the mixture was stirred and boiled under reflux for 4 h. After cooling the ethanol was removed by evaporation and the residue was mixed with water (100 ml) and extracted with chloroform (3 \times 50 ml). The extracts were dried (MgSO₄) and evaporated to leave an oil, which was separated after repeated chromatography [silica gel (60–120 mesh, B.D.H.)] into unchanged diene (VIII) (1.5 g), 1,2,4,7,7-pentachloro-3-ethoxynorborna-2,5-diene (IXa) (0.4 g) (properties as recorded by Mackenzie⁵), and 1,2,3,4,7,7-hexachloro-5-endo-ethoxynorborn-2-ene (Xa) (0.1 g), identical with an authentic specimen.⁶ Quantitative g.l.c. analysis showed the yields of (IXa) and (Xa) to be 55 and 11%, respectively.

(c) 1,2,3,4,7,7-Hexachloronorborna-2,5-diene (VIII) with sodium ethoxide in ethanol. The diene (VIII) (4.76 g, 0.016 mol) dissolved in ethanol (25 ml) was added to a solution of sodium (3 g, 0.13 g atom) in ethanol (50 ml). The mixture was boiled at reflux for 3 days, then evaporated; the residue was mixed with water (100 ml) and extracted with chloroform (3 \times 50 ml). The extracts were dried (MgSO₄) and evaporated to yield a brown oil, which was worked-up as before to provide unchanged diene (VIII) (0.1 g), 1,2,4,7,7-pentachloro-3-ethoxynorborna-2,5-diene (IXa) (0.6 g), and 1,2,3,4,7,7-hexachloro-5-endo-ethoxynorborn-2-ene (Xa) (1.0 g). Quantitative g.l.c. analysis showed the yields of (IXa) and (Xa) to be 66 and 21%, respectively.

(d) 1,2,3,4,7,7-Hexachloronorborna-2,5-diene (VIII) with

sodium methoxide in methanol. This reaction was carried out as for the sodium ethoxide reaction (c), and afforded unchanged diene (VIII) (0.9 g), 1,2,4,7,7-pentachloro-3-methoxynorborna-2,5-diene (IXb) (0.1 g), b.p. 70° at 0.1 mmHg, ν_{\max} 1648 cm⁻¹ [*cis*-ClC=C(OMe)-] (Found: C, 32.4; H, 2.2. C₈H₅Cl₅O requires C, 32.8; H, 1.7%); and 1,2,3,4,7,7-hexachloro-5-endo-methoxynorborn-2-ene (Xb) (0.6 g), b.p. 85° at 0.1 mmHg, ν_{\max} 1603 cm⁻¹ (*cis*-ClC=CCl) (Found: C, 28.9; H, 1.8. C₈H₆Cl₆O requires C, 29.15; H, 1.85%). Quantitative g.l.c. analysis showed the yields of (IXb) and (Xb) to be 2 and 16%, respectively. The reaction mixture was very dark; appreciable product decomposition undoubtedly took place.

Hydrogenolysis of Compounds (IV) and (V) (*cf.* ref. 2).—The norbornene (IV) or (V) (0.5 g, 0.001 mol) was added to a suspension of palladium-charcoal (10%; 0.025 g) in a solution of triethylamine (0.25 g, 0.0025 mol) in ethanol (12.5 ml), and the mixture was shaken under hydrogen. When uptake of hydrogen (80 ml) was complete (120 min) the mixture was filtered and the solvent evaporated. A solution of the residue in carbon tetrachloride was washed with water, dried (MgSO₄), and evaporated and the residue was chromatographed several times. The norbornene (IV) afforded 1,4,7-syn-trichloro-6-endo-methoxy-5-endo-phenylnorbornane (VI) (30 mg), m.p. 151–152° (after sublimation at 110–120° and 1 mmHg, and recrystallisation from light petroleum); no i.r. absorption corresponding to *cis*-ClC=CCl (Found: C, 55.0; H, 4.8. C₁₄H₁₅Cl₃O requires C, 55.2; H, 4.95%). The norbornene (V) afforded 1,4,7-syn-trichloro-6-exo-methoxy-5-endo-phenylnorbornane (VII) (36 mg), m.p. 61–62° (after sublimation at 120–130° and 0.5 mmHg, and recrystallisation from light petroleum); no i.r. absorption corresponding to *cis*-ClC=CCl (Found: C, 55.0; H, 5.05%).

cis- β -Methoxystyrene (*cf.* ref. 10).—Phenylacetylene (7.5 g, 0.066 mol) was added to a solution of sodium (2.4 g, 0.098 mol) in methanol (40 ml), and the resultant solution was heated in a sealed tube for 12 h at 120°. The solvent was evaporated and the residue was mixed with water (100 ml) and extracted with chloroform (3 \times 50 ml). The combined extracts were dried (MgSO₄) and evaporated to afford a brown oil, which was distilled to afford *cis*- β -methoxystyrene (7.0 g), b.p. 56–63° at 0.7–1.0 mmHg, n_D^{24} 1.5599 (lit.¹⁰ b.p. 210° at 760 mmHg, n_D^{20} 1.5683).

Diels-Alder Addition of *cis*- β -Methoxystyrene to Hexachlorocyclopentadiene.—Hexachlorocyclopentadiene (5 g, 0.018 mol) and *cis*- β -methoxystyrene (2.5 g, 0.018 mol) were dissolved in toluene (50 ml) and the mixture was boiled at reflux for 4 days. The toluene was removed by evaporation and the residual oil chromatographed to afford unchanged hexachlorocyclopentadiene (3.2 g) and 1,2,3,4,7,7-hexachloro-6-endo-methoxy-5-endo-phenylnorborn-2-ene (IV) (1.1 g), having properties identical with those of the product isolated from the reaction of diene (I) with sodium methoxide.

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⁹ D. I. Davies, P. Mason, and M. J. Parrott, *J. Chem. Soc. (C)*, 1971, 3428.

¹⁰ S. I. Miller, *J. Amer. Chem. Soc.*, 1956, **78**, 6091.