968. *Hydroxylation of Olefins with Silver Iodide Dibenzoate (Prévost Reaction)*

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A study of the hydroxylation of olefins by reaction with silver iodide dibenzoate is described. The reactivity of the olefinic bond with silver iodide dibenzoate has been investigated with respect to the structure of the alkene and to the neighbouring substituent groups. *N*-Allylmorpholine undergoes rearrangement and *N*-(2-vinyloxyethyl)piperidine gives two fragmentation products, acetylpiperidine and ethane-1,2-diol dibenzoate. The action of silver iodide dibenzoate on bicyclo[2,2,1]heptadiene produced 3-*exo*,5-*endo*-dihydroxytricyclo[2,2,1,0^{2,6}]heptane dibenzoate and 3-*endo*, 5-*endo*-dihydroxytricyclo[2,2,1,0^{2,6}]heptane dibenzoate.

THE Prévost reaction for *trans*-hydroxylation of alkenes [1-3] has been the object of very little attention.[4] Its application, in its original form or according to Woodward's modified procedure,[5-7] appears to have been largely confined to the hydroxylation of long-chain alkenes.[8-11]

The structure of silver iodide dibenzoate is still uncertain,[12-15] but it is well known that complexes having the general formula $(RCO_2)_2AgX$ are capable not only of effecting hydroxylation of alkenes,[14] but also of reacting in a number of ways with aromatic compounds,[16] resulting in benzoyloxylated, halogenated, or phenylated compounds, depending upon the nature of the substituents present in the substrates. The hydroxylation is believed to proceed *via* the formation of the intermediate acyloxyhalide of the olefin.

The present work was undertaken to determine the effectiveness of the Prévost reaction

[1] C. Prévost, *Compt. rend.*, 1933, **196**, 1129.
[2] C. Prévost, *Compt. rend.*, 1933, **197**, 1661.
[3] C. Prévost and R. Lutz, *Compt. rend.*, 1934, **198**, 2264.
[4] F. D. Gunstone, *Adv. Org. Chem.*, 1960, **1**, 117.
[5] R. B. Woodward, U.S.P. 2,687,435 (*Chem. Abs.*, 1955, **49**, 14,809).
[6] R. B. Woodward and F. V. Brutcher, jun., *J. Amer. Chem. Soc.*, 1958, **80**, 209.
[7] G. W. Kenner, *Ann. Reports*, 1954, **51**, 178.
[8] H. Wittcoff and S. E. Miller, *J. Amer. Chem. Soc.*, 1947, **69**, 3138.
[9] C. Niemann and C. D. Wagner, *J. Org. Chem.*, 1942, **7**, 227.
[10] B. Loev and C. R. Dawson, *J. Amer. Chem. Soc.*, 1958, **80**, 643.
[11] F. D. Gunstone and L. J. Morris, *J.*, 1957, 487.
[12] C. Prévost, *Compt. rend.*, 1935, **200**, 942.
[13] R. G. Johnson and R. K. Ingham, *Chem. Rev.*, 1956, **56**, 219.
[14] J. Kleinberg, *Chem. Rev.*, 1947, **40**, 381.
[15] I. R. Beattie and D. Bryce-Smith, *Nature*, 1957, **179**, 577.
[16] D. Bryce-Smith and P. Clarke, *J.*, 1956, 2264.

for converting alkenes into 1,2-diols, and to determine its limitations in a number of structural situations. Particular attention has been given to substrates containing heteroatoms and fluorine atoms. In general, it was found that the course of the Prévost reaction is susceptible to steric and electronic effects.

N-Allylmorpholine reacted vigorously with silver iodide dibenzoate (preformed before addition of olefin) to give the rearranged 2-morpholinopropane-1,3-diol (I) (after saponification of the crude dibenzoate) instead of 3-morpholinopropane-1,2-diol (II), the product
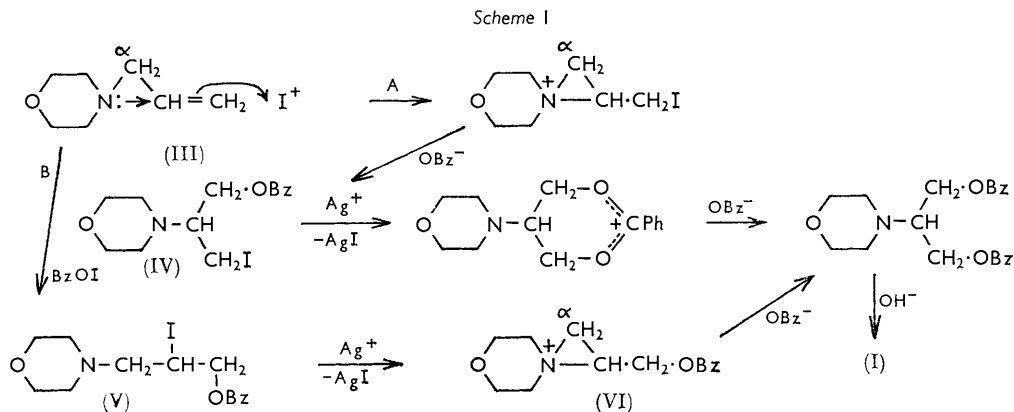
Scheme 1

of normal hydroxylation. The mechanism shown in Scheme 1 is presented only as a working hypothesis, because of the uncertainty about the structure of silver iodide dibenzoate.

Pathway A involves the concerted attack (see III) followed by attack of $PhCO_2^-$ on the α-carbon and, finally, by reaction of compound (IV) with the silver benzoate released from silver iodide dibenzoate in the first step. According to pathway B, on the other hand, the departing iodide ion would be assisted by the tertiary nitrogen in the intermediate iodohydrin (V); the second entering $PhCO_2^-$ ion would then attack the α-carbon of the resulting ethyleneimmonium ion (VI). Either sequence is clearly a case of neighbouring tertiary amine-group participation, and the first observed case of the Prévost reaction occurring with rearrangement.

Direct confirmation of either pathway was attempted by carrying out the hydroxylation with a 1 : 1 molar ratio of silver benzoate to iodine, and anhydrous carbon tetrachloride or ether as the solvent; under these conditions [17,18] one of the iodohydrin benzoates, (IV) or (V), should be the product, since their further reaction occurs much more slowly in these solvents. Unfortunately we were unable to isolate a pure product, possibly because of the inherent instability of the iodohydrin.

N(2-Vinyloxyethyl)piperidine also reacted vigorously with silver iodide dibenzoate (preformed before addition of olefin) to give two fragmentation products, acetylpiperidine and ethane-1,2-diol dibenzoate. Their amount accounted for about 40% of the starting alkene and they are to be regarded as the main reaction products. This reaction undoubtedly represents another case of participation by neighbouring tertiary amine groups, for which the mechanism illustrated in Scheme 2 is suggested. The concerted attack (VII) is analogous to the one postulated in the preceding reaction (pathway A), and here again

[17] D. C. Abbott and C. L. Arcus, *J.*, 1952, 1515.
[18] B. I. Halperin, H. B. Donahoe, J. Kleinberg, and C. A. Vanderwerf, *J. Org. Chem.*, 1952, **17**, 623.

the α-carbon is attacked by the first entering $PhCO_2^-$ with formation of the rearranged iodohydrin (VIII).

The attack of the second $PhCO_2^-$ would take place on the β-carbon with concomitant fragmentation of the ion (IX). Alternatively, proton elimination by the ion (IX) followed

Scheme 2
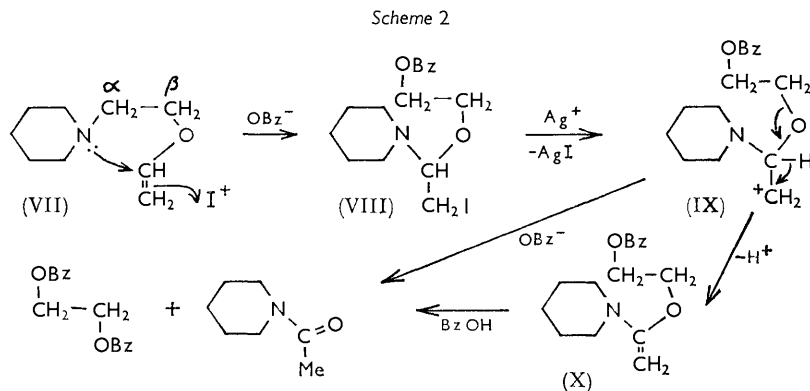
by cleavage of the resulting potential amide (X) by benzoic acid would account for the formation of the observed products; in this case also the attempted isolation of the postulated iodohydrin (VIII) was unsuccessful.

When an excess of bicyclo[2,2,1]heptadiene was treated with silver iodide dibenzoate, a diol dibenzoate of m. p. 87·5—88° was obtained in good yield. When the hydroxylation was carried out with a large excess of oxidant, a very complex mixture, which resisted chromatographic fractionation on alumina, resulted. The crude product gave a positive Beilstein test; by treatment with ethanol a very small amount of dibenzoate, m. p. 116·5—117°, crystallised after several weeks. It was soon realised that both products were derivatives of nortricyclene resulting from 2,6-homoconjugative addition, since they were not cleaved by dilute potassium permanganate at room temperature, did not add bromine, and their infrared spectra showed the characteristic C–H out-of-plane bending absorption of the cyclopropane ring at around 812 cm.$^{-1}$.

Three isomeric diols having a nortricyclenic skeleton can theoretically be formed in the hydroxylation of bicyclo[2,2,1]heptadiene with peracids or by the Prévost reaction, (XI), (XII), and (XIII).
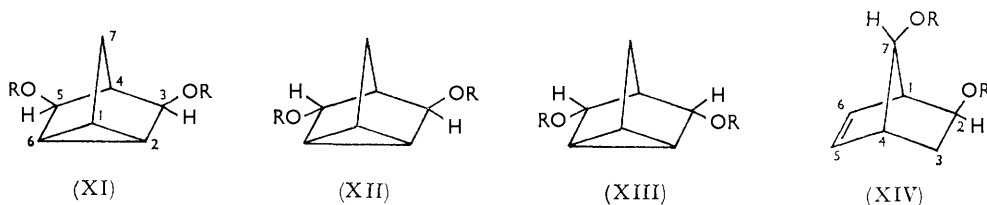
On the basis of nuclear magnetic resonance (n.m.r.) spectral evidence the 3-*exo*,5-*endo*-dihydroxy configuration (XII; R = Bz) was assigned to the low-melting isomer, and either a 3-*exo*,5-*exo*- or a 3-*endo*,5-*endo*-dihydroxy-configuration (XI or XIII; R = Bz) to the high-melting one. Subsequently, we found a discrepancy between the melting points of the diol and benzoate obtained by Schaefer [19] (m. p. 167·8—168·6° and 110—111°, respectively) to which the structures (XII; R = H and Bz) were assigned, and the melting points of the diol and benzoate of this same structure obtained by us (m. p. 175—176° and 87·5—88°, respectively) from the Prévost reaction. Moreover, the melting point of (XI; R = Bz)

[19] J. P. Schaefer, *J. Amer. Chem. Soc.*, 1960, **82**, 4091.

as reported by Schaefer [19] did not agree with that of the benzoate obtained by hydroxylation with an excess of silver iodide dibenzoate, and to which structure (XI; R = Bz) was tentatively assigned. This prompted us to repeat the hydroxylation of norbornadiene with performic acid according to the reported procedure.[19] Careful fractional crystallisation of the crude diols obtained after saponification of the mixture of isomeric hydroxy formates, and comparison of their infrared and n.m.r. spectra with the spectra of the diols from the Prévost reaction allowed us to conclude that the diol " B " referred to by Schaefer,[19] to which the structure (XII; R = H) was assigned, is a mixture of compounds (XI; R = H), m. p. 158—159°, and (XII; R = H), m. p. 175—176°. In fact, we found that these two isomers cannot be completely separated by fractional crystallisation from acetonitrile, nor by sublimation: a mixture having a constant m. p. 167—169° is obtained by crystallisation. Benzoylation of this mixture, however, resulted in the isolation of the benzoates (XI; R = Bz), m. p. 110·5—111·5° and (XII; R = Bz), m. p. 87·5—88°, thus confirming our hypothesis.

The *endo,endo*-structure (XIII; R = Bz) is assigned to the benzoate melting at 116·5—117° resulting from the Prévost reaction.

Hydroxylation of bicyclo[2,2,1]heptadiene with performic acid also afforded in our hands an unsaturated diol, which was identified as the 2-*exo*,7-*syn*-dihydroxynorbornylene (XIV; R = H), a product resulting from simple 1,2-addition.

Infrared and n.m.r. results for the four above-mentioned dibenzoates are recorded in Tables 1 and 2.

Hydroxylation with silver iodide dibenzoate of such simple mono-olefins as *cis-* and

TABLE 1

Infrared absorptions (Nujol mull; measured with a Beckman IR5A spectrophotometer, NaCl optics)

Compound	$\nu_{max.}$ (cm.$^{-1}$)
(XI; R = Bz)	3077w, 3030w, 1706s, 1447m, 1310m, 1285s, 1269s, 1263sh, 1256sh, 1174w, 1111s, 1070m, 1022m, 963s, 913w, 820m, 815sh, 808w, 803sh, 726m, 711s, 700m, 680w, 668w
(XII; R = Bz)	3077w, 3012w, 1724s, 1700s, 1450m, 1302m, 1290m, 1275s, 1250m, 1176w, 1142w, 1111s, 1070m, 1063m, 1026s, 1018m, 826w, 810m, 712sh, 707s, 692m, 683m, 670w
XIII; R = Bz)	3077w, 3030w, 1700s, 1449m, 1316m, 1287s, 1269s, 1259s, 1250s, 1170m, 1134m, 1117s, 1110sh, 1100m, 1070m, 1030s, 1000m, 956w, 927w, 823m, 816m, 740m, 706s, 684m, 678m
(XIV; R = Bz)	3077w, 3030w, 1709s, 1449m, 1330m, 1314m, 1285s, 1274s, 1227m, 1176w, 1120s, 1073m, 1033m, 1026m, 1000w, 980w, 893w, 716s, 694w, 687w, 660w

s = Strong; m = medium; w = weak; sh = shoulder.

TABLE 2

Proton magnetic resonance spectra at 60 Mc. with tetramethylsilane as internal reference

Compound	δ	Intensity	Assigned to proton(s)	δ	Intensity	Assigned to proton(s)
(XI; R = Bz) *	7·92—8·18	4	Phenyl	2·55	1	4
	7·25—7·65	6	Phenyl	2·03	2	7
	5·05	2	3-*endo* and 5-*endo*	1·72	3	Cyclopropane ring
(XII; R = Bz) *	7·92—8·18	4	Phenyl	5·08	1	3-*endo* or 5-*exo*
	7·25—7·60	6	Phenyl	2·45	1	4
	5·62	1	3-*endo* or 5-*exo*	1·50—2·25	5	7 and Cyclopropane ring
(XIII; R = Bz) *	7·75—8·05	4	Phenyl	2·69	1	4
	7·00—7·50	6	Phenyl	1·80	2	7
	5·12	2	3-*exo* and 5-*exo*	1·62	3	Cyclopropane ring
(XIV; R = Bz) †	7·46—8·00	4	Phenyl	4·77	1	2-*endo* or 7-*anti*
	6·80—7·38	6	Phenyl	3·25	1	1
	6·10	2	Vinylic	3·00	1	4
	4·90	1	2-*endo* or 7-*anti*	2·03	2	3

* Determined for *ca.* 20% solution in CDCl$_3$ with a Varian A60 spectrometer.   † Determined for 10% solution in CCl$_4$ with a Varian DP60 spectrometer.

trans-4-methylpent-2-ene resulted in the formation in good yield of the *threo*- and *erythro*-glycol dibenzoate, respectively.

Allylphenylether was successfully hydroxylated by silver iodide dibenzoate. It is noteworthy, however, that in this case iodination of the activated benzene ring, which had been experienced with another alkylphenyl ether,[10] did not occur, although a 100% excess of silver iodide dibenzoate was employed.

Attempted hydroxylation of 2-chloro-1,1,2-trifluoro-3-methyl-3-vinylcyclobutane did not go to completion, and the only pure material isolated was the iodohydrin monobenzoate (XV) in 3% yield. Unsuccessful total hydroxylation might have been caused by failure of the benzoate group in the benzoyloxyiodide intermediate (XV) to participate in the displacement of the iodide ion,[20] because of steric hindrance by the bulky substituted cyclobutane ring.
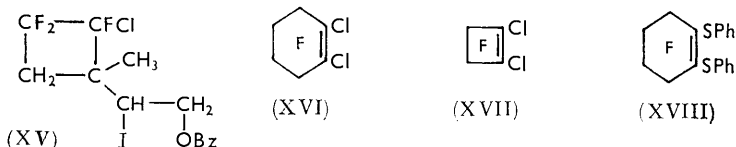
Fluorine atoms have no effect when present as ring substituents of systems such as *ortho*- and *para*-fluorostyrene and allylpentafluorobenzene since they are readily converted into the respective benzoyloxy compounds with excellent yields. On the other hand, the complete failure of 1,2-dichloro-octafluorocyclohex-1-ene (XVI) and 1,2-dichlorotetra-fluorocyclobut-1-ene (XVII) to undergo hydroxylation is probably due to the cumulative deactivating influence of the fluorine atoms. Replacement of the two chlorine atoms in the former by phenylthio-groups did not result in an increased reactivity of this system, since no reaction was observed between 1,2-bisphenylthio-octafluorocyclohex-1-ene (XVIII) and silver iodide dibenzoate.

The Prévost reaction carried out with 1-allyloxy-2-vinyloxyethane for 50 hr. resulted in incomplete hydroxylation. The crude product gave a positive Beilstein test; attempted purification by chromatography on neutral alumina failed to isolate a pure product.

Crotononitrile did not react with silver iodide dibenzoate; after 50 hr. under reflux, a large amount of oxidant was still present in the reaction mixture. Failure to react is probably due to the deactivating influence of the CN group through conjugative electron withdrawal. Incidentally, it is to be noted that usually low yields were previously experienced with acrylic systems.[1]

Osmium tetroxide failed to hydroxylate 1,2-dichloro-octafluorocyclohex-1-ene (XVI) to any appreciable extent over a period of five months, most of the oxidant being recovered unchanged. An identical result was obtained with 1,2-bisphenylthio-octafluorocyclohex-1-ene (XVIII), and the olefin was recovered unchanged. Perfluoro-olefinic systems of this type seem to be completely inert, even towards osmium tetroxide which, on the other hand, converted 2-chloro-1,1,2-trifluoro-3-methyl-3-vinylcyclobutane into the corresponding glycol in fair yield.

EXPERIMENTAL

All melting points are uncorrected and were determined in a capillary tube. All the olefins, except bicyclo[2,2,1]heptadiene and *cis*- and *trans*-4-methylpent-2-ene, were purchased from Peninsular Chem. Research, Inc., Gainesville, Florida, and used as supplied.

Hydroxylations with Silver Iodide Dibenzoate. General Procedure.—Unless otherwise specified, the hydroxylations were carried out by adding the alkene to the suspension of preformed silver iodide dibenzoate prepared by heating under reflux 2 moles of oven-dried silver benzoate and 1 mole of iodine per mole of olefin dissolved in absolute benzene; the reactions were completed by heating the mixtures under reflux for 1—10 hr. The products were washed with water, sodium carbonate, and then water. The physical properties and analytical results for the benzoates obtained by the regular course of the Prévost reaction are summarised in Table 3.

[20] S. Winstein and R. E. Buckles, *J. Amer. Chem. Soc.*, 1942, **64**, 2780.

Hydroxylation of N-*Allylmorpholine with Silver Iodide Dibenzoate.*—After a vigorous initial exothermic reaction the mixture was further refluxed for 4 hr. The crude reddish-brown oil which resulted after evaporation of the solvent could not be induced to crystallise, and could not be distilled under reduced pressure because it decomposed before the b. p. was reached. The benzoate (from another run) was then saponified with alcoholic potassium hydroxide to the diol, b. p. 117°/0·125 mm., n_D^{20} 1·4964; yield *ca.* 30% based on the starting olefin (Found: C, 52·2; H, 9·15; N, 8·8; O, 30·0%. Calc. for $C_7H_{15}NO_3$: C, 52·15; H, 9·4; N, 8·7; O, 29·8%). The structure of this diol has been previously established [21] from n.m.r. spectral measurements as 2-morpholinopropane-1,3-diol (I).

TABLE 3

Physical properties of the dibenzoates

Olefin	Diol dibenzoate	Yield (%)	M. p. or b. p./mm.	Found (%)		Formula	Calc. (%)	
				C	H		C	H
cis-4-Methyl-pent-2-ene [a]	*threo*-4-Methylpentane-2,3-diol [b]	60	143°/0·06	73·25	6·85	$C_{20}H_{22}O_4$	73·6	6·8
trans-4-Methyl-pent-2-ene [a]	*erythro*-4-Methylpentane-2,3-diol [c]	65	153/0·1	73·85	7·0	$C_{20}H_{22}O_4$	73·6	6·8
p-Fluorostyrene	2-*p*-Fluorophenylethane-1,2-diol	85	81—81·5 [d]	72·7	4·85	$C_{22}H_{17}FO_4$ [e]	72·5	4·7
o-Fluorostyrene	2-*o*-Fluorophenylethane-1,2-diol	97	98·5—99 [f]	72·4	4·7	$C_{22}H_{17}FO_4$ [g]	72·5	4·7
Allylpenta-fluorobenzene	3-Pentafluorophenyl-propane-1,2-diol	86	88—89 [f]	61·1	3·5	$C_{23}H_{15}F_5O_4$ [h]	61·35	3·35
Allyl phenyl ether	(α-Glyceryl phenyl ether [i])	37 [j]	69—70 [k]	64·5	7·15	$C_{23}H_{20}O_5$	64·3	7·2

[a] Pure grade (99 mole %) purchased from Phillips Petroleum Co., Special Products Div., Bartlesville, Okla. [b] n_D^{25} 1·5299. [c] n_D^{25} 1·5316. [d] From n-hexane. [e] Found: F, 5·15. Calc. F, 5·2%. [f] From ethanol. [g] Found: F, 5·2%. [h] Found: F, 20·8. Calc. F, 21·1%. [i] Free diol obtained by saponification of the dibenzoate. The crude ester was freed from by-product (biphenyl) by chromatography on alumina in benzene–n-hexane (1 : 1), but could not be induced to crystallise. [j] Yield of diol, based on olefin used. [k] After several sublimations.

Reaction of N-*(2-vinyloxyethyl)piperidine with Silver Iodide Dibenzoate.*—The addition of the olefin (15·5 g., 0·1 mole) to the suspension of silver iodide dibenzoate [from 45·8 g. (0·2 mole) of silver benzoate and 25·4 g. (0·1 mole) of iodine] in 250 ml. of benzene resulted in an exothermic reaction and a colloidal viscous material, containing silver iodide in suspension, was precipitated. A gentle reflux was maintained for 90 min.; the organic precipitate adsorbed on the silver iodide was dissolved, and a reddish-brown solution resulted. After removal of the silver iodide and evaporation of the benzene, a liquid (26·67 g.) was obtained which partially crystallised on standing. The whole was dissolved in warm propan-2-ol (50 ml.) from which crystalline material (10·32 g.) was separated; m. p. 73—74° after recrystallisation from propan-2-ol. This product was identified [21] as ethane-1,2-diol dibenzoate by its infrared and n.m.r. spectra and comparison with an authentic sample; yield 38%. (Found: C, 71·0; H, 5·0%; saponification equivalent, 135·5. Calc. for $C_{16}H_{14}O_4$: C, 71·1; H, 5·2%; saponification equivalent, 135·1).

The propan-2-ol mother liquor was evaporated and the liquid residue fractionally distilled *in vacuo*. Only one fraction (4·7 g.) having a constant b. p. 43°/0·1 mm. was collected. This was identified [21] by its infrared and n.m.r. spectra, and by comparison with an authentic sample, as *N*-acetylpiperidine (37%) (Found: C, 66·2; H, 10·5; N, 10·85. Calc. for $C_7H_{13}NO$: C, 66·1; H, 10·3; N, 11·0%).

The higher-boiling fraction appeared to be a complex mixture which was not further investigated.

Hydroxylation of Bicyclo[2,2,1]heptadiene (with Silver Iodide Dibenzoate and Excess of Olefin).— A mixture of silver benzoate (38·40 g., 0·167 mole) and iodine (20·32 g., 0·08 mole) in benzene (480 ml.) was stirred for a few minutes. Bicyclo[2,2,1]heptadiene * (22·08 g., 0·24 mole) was then added in one portion, and the resulting mixture was heated under reflux for 1 hr., set aside overnight, and washed in the usual way. Evaporation of the solvent afforded a thick colourless syrup. The addition of 30 ml. of ethanol caused precipitation of crystalline material (8·20 g.),

* Purchased from Matheson Coleman & Bell, Norwood (Cincinnati), Ohio. It was fractionated with a 9 in. spinning-band column shortly before use; b. p. 90·5—91°/763 mm.

[21] A. Ferretti and G. Tesi, *Tetrahedron Letters*, 1964, 2975.

m. p. 81·5—84°. Repeated recrystallisation from ethanol gave 3-exo,5-endo-*dihydroxytricyclo*-[2,2,1,0^{2,6}]*heptane dibenzoate* (XII; R = Bz) (7·50 g., 30%), m. p. 87·5—88°; (Found: C, 75·6; H, 5·6%; *M*, 336. $C_{21}H_{18}O_4$ requires C, 75·45; H, 5·45%; *M*, 334).

3-exo,5-endo-*Dihydroxytricyclo*[2,2,1,0^{2,6}]*heptane* (XII; R = H).—The above dibenzoate (7·33 g., 0·022 mole) was heated for 2 hr. under reflux with 1M-ethanolic potassium hydroxide (95 ml., 0·095 mole). The mixture was set aside overnight and the potassium benzoate was removed. The solvent was evaporated off completely, the residue was dissolved in 5 ml. of water and the solution was continuously extracted with methylene chloride for 6 days. Upon evaporation of the solvent, 2·62 g. (94%) the *diol* was obtained and was recrystallised from acetonitrile to constant m. p. 175—176° (Found: C, 66·5; H, 7·95. $C_7H_{10}O_2$ requires C, 66·65; H, 8·0%).

Hydroxylation of Bicyclo[2,2,1]heptadiene (with Excess of Silver Iodide Dibenzoate).—The reaction was carried out by adding norbornadiene (1·84 g., 0·02 mole) to the suspension of silver iodide dibenzoate obtained from 36·64 g. (0·16 mole) of silver benzoate and 20·32 g. (0·08 mole) of iodine in 200 ml. of benzene, and then heating the mixture under reflux for 7 hr. The usual working up gave a nearly colourless syrup (7·19 g.), which turned pink on standing, gave a strong positive Beilstein test, and showed a marked tendency to give up iodine under reduced pressure. Treatment with ethanol (7 ml.) and storage in a refrigerator caused slow precipitation of crystalline material (530 mg.), m. p. 115—117° over several months. This was recrystallised (ethanol) to constant m. p. 116·5—117° and identified as 3-endo,5-endo-*dihydroxytricyclo*-[2,2,1,0^{2,6}]*heptane dibenzoate* (XIII; R = Bz) (7·9%) (Found: C, 75·6; H, 5·4%; *M*, 338).

Hydroxylation of Bicyclo[2,2,1]heptadiene with Performic Acid.—Norbornadiene (46 g., 0·5 mole) was dissolved in a mixture of 97—100% formic acid (100 ml.) and ethyl acetate (125 ml.), and hydroxylated with 30% hydrogen peroxide (50 ml., *ca.* 0·5 mole) according to a previous procedure.[19] The mixture of hydroxyformates (32·4 g., 42%) was collected by distillation at 78°/0·35 mm. to 90°/ 0·40 mm.

Saponification of the Formate Mixture and Isolation of Diols (XI, XII, and XIV; R = H).—The mixture of formates (57·82 g., 0·375 mole) from two preparations was heated under reflux with 2M-ethanolic potassium hydroxide (375 ml., 0·750 mole) for 2 hr.; the solution immediately turned black. The mixture was set aside overnight, the ethanol was removed by evaporation under reduced pressure, and the potassium formate precipitated during evaporation was filtered off. Water (80 ml.) was added to the oily residue and the resulting solution was extracted continuously with methylene chloride for 6 days. Pure 3-*exo*,5-*exo*-dihydroxytricyclo[2,2,1,0^{2,6}]-heptane (XI; R = H) (15·0 g.) crystallised when the solution was cooled, m. p. 158—159° after recrystallisation from acetonitrile.

The residue obtained after evaporation of the methylene chloride was dissolved in 50 ml. of hot acetonitrile, and allowed to stand at room temperature, when 8·89 g. of material (m. p. 159—163°) crystallised out. Repeated recrystallisation of this fraction from acetonitrile afforded a product with constant m. p. 168—170°, and this was not raised even by sublimation of the product. This material is still a mixture of the two isomeric diols (XI and XII; R = H). Benzoylation with benzoyl chloride in pyridine afforded 3-*exo*,5-*exo*-dihydroxytricyclo[2,2,1,0^{2,6}]-heptane dibenzoate (XI; R = Bz), m. p. 110·5—111·5° (Found: C, 75·3; H, 5·35%), and 3-*exo*, 5-*endo*-dihydroxytricyclo[2,2,1,0^{2,6}]heptane dibenzoate (XII; R = Bz), m. p. 87·5—88° (Found: C, 75·55; H, 5·35%). The infrared spectrum of the latter was identical with that of the benzoate prepared by the Prévost reaction (with excess of olefin).

Two further portions (total 5·6 g.) of the mixture of diols (XI and XII; R = H) crystallised from the original acetonitrile mother liquor on concentration and addition of benzene.

Total evaporation of the solvent from the exhausted solution afforded a non-crystallisable residue; benzoylation resulted in the isolation of a third isomeric dibenzoate (5·0 g.), m. p. 93—94° (from ethanol) (Found: C, 75·2; H, 5·6%.) This benzoate decolourised a 2% solution of potassium permanganate, and its infrared spectrum did not display the band at *ca.* 812 cm.$^{-1}$. Saponification resulted in a diol, m. p. 136—138° after recrystallisation from light petroleum (b. p. 60—80°) and sublimation (Found: C, 66·45; H, 7·85. Calc. for $C_7H_{10}O_2$: C, 66·65; H, 8·0%.) This compound appeared to be identical to a previously reported [22] diol, and was therefore identified as 2-*exo*,7-*syn*-dihydroxynorbornylene (XIV; R = H) (lit.,[22] m. p. 135—137°). The n.m.r. spectrum and a negative test for vicinal diol further support the suggested structure.

[22] K. Alder, F. H. Flock, and H. Wirtz, *Ber.*, 1958, **91**, 609.

Hydroxylation of 2-Chloro-1,1,2,trifluoro-3-methyl-3-vinylcyclobutane with Silver Iodide Dibenzoate.—The reaction was carried out in the usual manner with 22·9 g. (0·1 mole) of silver benzoate, 12·7 g. (0·05 mole) of iodine, and 9·22 g. (0·05 mole) of olefin in 170 ml. of benzene. After 50 hr. under reflux, some unchanged silver iodide dibenzoate was still present, as was shown by the formation of a yellow-orange precipitate during the washing process.   After evaporation of the benzene, the residual oil partially crystallised from ethanol over a period of several weeks to give 0·620 g. of a white crystalline material, m. p. 118—122°; a sharp m. p. 124·5—125·5° was obtained after repeated recrystallisation from ethanol.   This product was identified as the intermediate   2-chloro-1,1,2-trifluoro-3-methyl-3-(2-benzoyloxy-1-iodoethyl)cyclobutane   (XV) (2·9%) (Found: C, 38·6; H, 2·95; F, 13·15; I, 29·2. $C_{14}H_{13}ClF_3IO_2$ requires C, 38·85; H, 3·05; F, 13·15; I, 29·35%).   The structure of the side-chain was inferred from the infrared spectrum (KBr) which displayed absorption at 1448 cm.$^{-1}$ assigned to the CH_2 bending (scissor) vibration of $-CH_2 \cdot OBz$.

Attempts to distil the uncrystallisable oily residue failed; loss of iodine was observed under reduced pressure even at 60°, and no pure fraction could be collected.   Chromatography on alumina was also unsuccessful.

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