from 95% ethanol; nmr (CF_3CO_2H) τ 6.73 (s, 4, CH_2CH_2), 2.63 (m, 6, aromatic H), 2.0 (m, 2, aromatic H); mass spectrum *m/e* (rel intensity) 488 (<0.1), 246 (2), 245 (15), 244 (100), 243 (37), 229 (10), 226 (21), 225 (22), 209 (3), 208 (3), 183 (3), 179 (20), 178 (45), 165 (15), 152 (11), 91 (9),89 (17), 77 (14).

Anal. Calcd for $C_{14}H_{13}O_2P$: C, 68.85; H, 5.37. Found: C, 69.04; H, 5.54.

B. From the Cleavage of 2 with Lithium.—The tertiary phosphine **2** (0.80 g, 2.78 mmol) was dissolved in 25 ml of dry tetrahydrofuran (THF) and treated with lithium wire (0.06 g, 9 mg-atom) by the procedure of Aguiar and coworkers.[4b] After the mixture was stirred and refluxed for 3 hr, it was cooled, hydrolyzed, and then oxidized with an excess of 3% hydrogen peroxide. The resulting solution was extracted with ether to remove any phosphine oxide formed from unreacted **2**, and the aqueous layer was acidified with hydrochloric acid and cooled. The gummy solid which separated was purified by reprecipitation from aqueous base and then dried, yield 0.70 g. Washing this substance with 10 ml of ether extracted an acidic substance discussed in the paragraph below and left as a residue 0.35 g (52%) of the desired heterocyclic phosphinic acid **1**, mp[14] 249–254° after recrystallization from 95% ethanol. This acid was identical (mixture melting point and mass spectrum) with the sample prepared *via* the fusion of **3** with sodium hydroxide.

The 10-ml ether extract mentioned in the above paragraph was evaporated to dryness, and the oily residue was converted to a solid by reprecipitation from alkaline solution: yield 0.30 g; mp 38–65°; nmr ($CDCl_3$) τ 6.43 (m, 4, CH_2CH_2), 2.55 (m, 14, aromatic H); mass spectrum displayed a base peak at *m/e* 322, which corresponds to the molecular weight of the non-heterocyclic compound **4**.

Anal. Calcd for $C_{20}H_{19}O_2P$: C, 74.52; H, 5.94. Found: C, 72.29; H, 5.79.

10,11-Dihydro-3,7-dinitro-5-hydroxy-5*H*-dibenzo[*b*,*f*]phosphepin 5-Oxide (5).—The heterocyclic phosphinic acid **1** (0.50 g) was nitrated at about 30° with 30 ml of 90% nitric acid (*d* 1.5). The reaction mixture was poured onto 250 g of crushed ice, whereupon 0.60 g (87%) of dinitro compound crystallized from solution: mp[14] 320–330° dec after recrystallization from 95% ethanol.

Anal. Calcd for $C_{14}H_{11}N_2O_6P$: C, 50.31; H, 3.32; N, 8.38. Found: C, 50.12; H, 3.42; N, 8.57.

Di-*o*-tolylphosphinic Acid.[15]—A solution of freshly distilled *o*-chlorotoluene (126.6 g, 1.00 mol) in 250 ml of dry THF was converted to *o*-tolylmagnesium chloride in the usual manner[16] and then treated with di-*n*-butyl phosphonate as in the procedure used by Crofts and coworkers[17] for the preparation of diarylphosphine oxides. After the reaction mixture was hydrolyzed with dilute hydrochloric acid and the THF was removed under reduced pressure, an aqueous solution and a supernatant yellow oil were obtained. On cooling, the oil solidified to give 72.4 g of crude di-*o*-tolylphosphine oxide: mp 94–95° after recrystallization from toluene and drying at 90° *in vacuo;* nmr ($CDCl_3$) τ 7.61 (s, 6, CH_3), 2.75 (m, 6, aromatic H), 2.35 (m, 2, aromatic H).

Anal. Calcd for $C_{14}H_{15}OP$: C, 73.03; H, 6.57. Found: C, 72.73; H, 6.71.

The crude di-*o*-tolylphosphine oxide (from 1.00 mol of *o*-chlorotoluene) was suspended in dilute sodium hydroxide and oxidized with 50 ml of 30% hydrogen peroxide. The resulting alkaline solution was filtered to remove a trace of insoluble material and then acidified with hydrochloric acid to precipitate the phosphinic acid. It was purified by recrystallization from 95% ethanol: yield 47.5 g (58% based on *o*-chlorotoluene); mp 175–177°; nmr ($CDCl_3$) τ 7.77 (s, 6, CH_3), 2.85 (m, 6, aromatic H), 2.20 (m, 2, aromatic H).

Anal. Calcd for $C_{14}H_{15}O_2P$: C, 68.29; H, 6.14; mol wt, 246. Found: C, 68.56; H, 6.35; mol wt, 244 (in 95% ethanol with a Thomas isothermal molecular weight apparatus).

Di-*o*-tolylphosphinic acid was also prepared from *o*-bromotoluene. The Grignard reagent was prepared in ether in the conventional manner and converted to di-*o*-tolylphosphine oxide by the procedure described above. Oxidation of the phosphine oxide with hydrogen peroxide gave a 74% yield of phosphinic acid.

Bis(5-nitro-2-tolyl)phosphinic Acid (6).—Di-*o*-tolylphosphinic acid (10.0 g) was nitrated with 100 ml of 90% nitric acid by the procedure described above for the nitration of the heterocyclic phosphinic acid **1**. The yield was 13.0 g (95%), mp[14] 231–241° after recrystallization from 95% ethanol (lit.[9] mp 243–245°). This compound was shown (mixture melting point and ir) to be identical with an authentic sample of **6**.[9]

Anal. Calcd for $C_{14}H_{13}N_2O_6P$: C, 50.01; H, 3.90. Found: C, 49.81; H, 4.08.

Registry No.—**1**, 30309-73-0; **2**, 30309-74-1; **3**, 30309-75-2; **4**, 30309-76-3; **5**, 30309-77-4; **6**, 30309-78-5; di-*o*-tolylphosphinic acid, 18593-19-6; di-*o*-tolylphosphine oxide, 30309-80-9.

(15) This acid was first prepared by A. Michaelis and F. Wegner, *Ber.*, **48**, 316 (1915), but they gave no information about its properties. V. M. Plets, Dissertation, Kazan, 1938 (quoted by G. M. Kosolapoff, "Organophosphorus Compounds," Wiley, New York, N. Y., 1950, p 170) reported that the compound melts at 101° and can be recrystallized from water. It should be noted, however, that a number of workers have questioned the validity of much of Plets's work; *cf.* L. D. Freedman and G. O. Doak, *Chem. Rev.*, **57**, 479 (1957), and F. A. Cotton, *ibid.*, **55**, 551 (1955). P. Haake, M. J. Frearson, and C. E. Diebert, *J. Org. Chem.*, **34**, 788 (1969), have described the mass spectrum of di-*o*-tolylphosphinic acid but have not reported its synthesis.

(16) H. E. Ramsden, A. E. Balint, W. R. Whitford, J. J. Walburn, and R. Cserr, *ibid.*, **22**, 1202 (1957).

(17) P. C. Crofts, I. M. Downie, and K. Williamson, *J. Chem. Soc.*, 1240 (1964).

A Novel Catalytic Effect in the Diaxial–Diequatorial Rearrangement of 5,6-Dibromocholesteryl Benzoate[1a]

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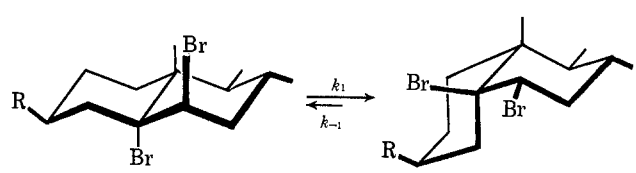
In connection with a specific project in the steroid field, we became interested in the rate of the diaxial–diequatorial rearrangement of 5α,6β-dibromocholesterol and its esters to the corresponding 5β,6α stereoisomers. This rearrangement is typical for 2,3 and 5,6 axially disubstituted steroids. It has been reviewed recently.[2] Although, in general, the reaction reaches an equilibrium, in the case of the 5,6-dibromides the thermodynamically favored 5β,6α isomers constitute not less than 80% of the rearranged product and the reaction can be utilized for preparative purposes. In



1, R = H
3, R = $OCOC_6H_5$

2, R = H
4, R = $OCOC_6H_5$

their detailed studies on 5,6-dibromocholestane, partial structure **1**, Grob and Winstein[3] attempted to discern a rate-influencing species that would be helpful in elucidating the rearrangement mechanism. The lack of a common ion effect and the insensitivity of the rate toward the addition of nucleophiles like CH_3COONa and LiBr were two of the main reasons that led them to

(1) (a) This work was supported, in part, by the National Research Council of Canada. (b) Department of Chemistry, University of British Columbia, Canada.

(2) D. N. Kirk and M. P. Hartshorn, "Steroid Reaction Mechanisms," Elsevier, Amsterdam, 1968, p 373 ff.

(3) C. A. Grob and S. Winstein, *Helv. Chim. Acta*, **35**, 782 (1952).

TABLE I

CATALYTIC EFFECT OF $HgBr_2$ ON THE RATE OF REARRANGEMENT OF 5α,6β-DIBROMOCHOLESTERYL BENZOATE TO 5β,6α-DIBROMOCHOLESTERYL BENZOATE IN BENZENE AT 40.30 ± 0.05°

Run	Vol of soln, ml	Dibromide 3		$HgBr_2$			$k_1 - k_{-1}$, sec^{-1}
		g	mol × 10^{-3}	g	mol	mol %	
1	100	1.00	1.53	0.020	5.55×10^{-5}	3.6	3.0×10^{-6}
2	100	1.00	1.53	0.050	1.38×10^{-4}	9.0	4.4×10^{-6}
3	100	1.00	1.53	0.080	2.22×10^{-4}	14.5	7.4×10^{-6}
4	100	1.00	1.53				1.0×10^{-6}

propose for this rearrangement the merged ion-pair cyclic-concerted mechanism. This concept has been recently supported by the extensive work of King, *et al.*[4] Both groups found the rearrangement rate to be solvent dependent and, in broad terms, increasing with solvent polarity. Kwart and Weisfeld[5] found that organic acids and phenols enhanced the rate of rearrangement through general acid catalysis.

In practical terms a reaction time of *ca.* 5 hr is necessary to complete the rearrangement **3** → **4** in benzene at the boiling point.[6] The rearrangement **1** → **2** requires about 10 hr in boiling heptane.[3] We were concerned with reducing this time span without resorting to the use of either organic acids and phenols[5] or polar solvents like ethanol in which substantial solvolysis takes place.[7] Concurring with the opinion of Kirk and Hartshorn[2] that the reaction may be viewed in simple terms as an internal concerted nucleophilic substitution, we were inclined to think that it could be catalyzed by metal salts, particularly Hg^{2+} salts like other nucleophilic reactions are.[8] We indeed found that in benzene solutions the rate of rearrangement of 5α,6β-dibromocholesteryl benzoate (**3**) to the 5β,6α isomer **4** is increased by the addition of $HgBr_2$. Some representative runs are summarized in Table I. The rearrangement was followed polarimetrically and the reaction constants were established graphically from first-order linear plots of the logarithm of concentration of the disappearing 5α,6β-dibromocholesteryl benzoate *vs.* time. In accordance with previous work,[3] the reaction constant is expressed as the sum of two constants corresponding to the forward and retroreaction. Viewing $HgBr_2$ as a Lewis acid permits[9] the present observation to be brought into perspective with previous work, particularly that of Kwart and Weisfeld.[5] Our data give a reasonable agreement with the acid catalysis equation $K = K_0 + K_c[HgBr_2]$ and $K_c \simeq 2.8 \times 10^{-3}\ M^{-1}\ sec^{-1}$. This catalytic constant is then in the same range of magnitude as that found by Kwart, *et al.*, for the strongest acid they studied *viz.* trichloroacetic acid. Due to our limited interest in this area we do not attempt to accommodate our results with any detailed mechanism.

(4) J. F. King and R. G. Pews, *Can. J. Chem.*, **43**, 847 (1965).

(5) H. Kwart and J. B. Weisfeld, *J. Amer. Chem. Soc.*, **78**, 635 (1956).

(6) H. Bretschneider, Z. Földi, F. Galinowski, and G. von Fodor, *Chem. Ber.*, **74**, 1451 (1941).

(7) Exploratory work in this direction was carried out by Mr. J. Hjort. In simple primary and secondary alcohols (MeOH, EtOH, *n*-PrOH, *n*-BuOH, *sec*-PrOH, *sec*-BuOH, and cyclohexanol) complete debromination of selected steroidal 5,6-dibromides took place either at reflux temperature or at 100° in higher boiling alcohols. The reaction was completed in several hours; invariably dibromides with a free 3β-OH group showed the highest rate of debromination. However, in *tert*-BuOH this solvolytic debromination was extremely slow.

(8) (a) C. K. Ingold "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1969, p 480 ff; (b) C. A. Bunton, "Nucleophilic Substitution," Elsevier, Amsterdam, 1963, p 154 ff.

(9) Thanks are due to Professor J. F. King, University of Western Ontario, for his valuable comments on our results.

Experimental Section

General.—Uncorrected melting points were taken on a Kofler hot stage. Optical rotations were measured in 0.5- or 1-dm tubes using a Carl Zeiss polarimeter whose accuracy was not less than 0.05°.

Materials.—5α,6β-Dibromocholesteryl benzoate (**3**) was prepared according to literature[6,10,11] and recrystallized from C_6H_6–CH_3OH at room temperature, mp 135–137°, $[\alpha]^{24}D$ −39° (*c* 1, C_6H_6) [lit.[10,11] mp 135–136°, $[\alpha]D$ −40° (C_6H_6)]. 5β,6α-Dibromocholesteryl benzoate (**4**) was prepared according to the literature,[6,10] and recrystallized from C_6H_6–CH_3OH, mp 162–164°, $[\alpha]^{24}D$ +100° (*c* 1, C_6H_6) [lit.[6,10] mp 163–164°, $[\alpha]D$ +102° (C_6H_6)]. Reagent grade thiophene-free benzene and mercuric dibromide (Fisher) were used directly.

Kinetic Runs.—These were carried out in volumetric flasks placed in an automatic thermoelectric water bath. Runs were followed for 50–75 hr to 30–60% completion of full rearrangement *i.e.*, to 50–80% attainment of equilibrium by the two isomers. Usually 6–8 samples per run were withdrawn at intervals of several hours and their rotation measured at 25 ± 2°. The measurement, average of eight readings, took about 5 min and we considered this time negligible in relation to the above-mentioned overall reaction time. Excellent agreement was found between runs repeated after several days. The reaction constants were established graphically using common procedures.[12] The solutions from kinetic runs with $HgBr_2$ were kept at 40° until the rearrangement equilibrium was reached and subsequently they were evaporated *in vacuo* at room temperature to dryness. The dark residue was in each case treated with cold methanol and the tan solid which separated was filtered off and recrystallized from benzene–methanol to give pure **4**, identical (melting point, ir, $[\alpha]D$, elemental analysis) with samples of **4** prepared as given above. The yields in these recoveries averaged about 80% thus indicating absence of appreciable side reactions, particularly dehalogenation, during the kinetic runs.

Registry No.—**3**, 6213-04-3; **4**, 5863-62-7.

Acknowledgment.—The technical assistance of Mrs. E. C. Fryberg is appreciated.

(10) D. H. R. Barton and E. Miller, *J. Amer. Chem. Soc.*, **72**, 1066 (1950).

(11) S. P. J. Maas, M. J. D. VanDam, J. G. De Heus, and D. Mulder, *Bull. Soc. Chem. Belg.*, **72**, 239 (1963).

(12) R. Livingston in "Techniques of Organic Chemistry," Vol. VIII, 2nd ed, part 2, S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Interscience, New York, N. Y., 1961, pp 126, 127. The usual "best fit" lines were drawn. In most runs the scattering of values plotted was negligible.

Selective Degradation of Guaiol. The Synthesis of 7-Epiguaiol

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In connection with a current project dealing with the total synthesis of the hydroazulenic sesquiterpene alco-

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