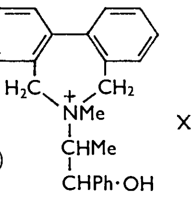
44. *Hofmann Degradation of Some Quaternary Ephedrinium Compounds.*

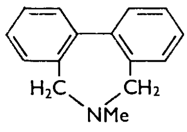
By D. Muriel Hall and Teresa M. Poole.

Hofmann degradation proceeds normally with the (+)-dibenzazepinium hydroxide (I; X = OH), to give the dibenzazepine (II) and (+)-*trans*-1-methyl-2-phenyloxiran. However, the analogous biphenyl bisquaternary dihydroxide (III; X = OH) gives an appreciable yield of the ditertiary base (IV) only if carbon dioxide is excluded; the diamine is accompanied by (—)-*N*-methylephedrine, 9-dimethylamino-9,10-dihydrophenanthrene, and the 2,7-dihydro-1,1-dimethyl-3,4:5,6-dibenzazepinium cation. Possible reaction paths are discussed.

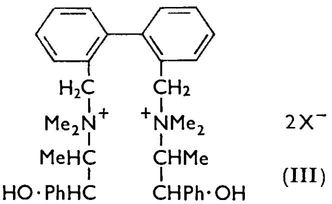
Hofmann degradation of (+)-2,7-dihydro-1-(β-hydroxy-α-methylphenethyl)-1-methyl-3,4:5,6-dibenzazepinium hydroxide [1] (I; X = OH), without special precautions to exclude carbon dioxide, proceeded normally to give 2,7-dihydro-1-methyl-3,4:5,6-dibenzazepine (II), identified as its methiodide,[2] and (+)-*trans*-1-methyl-2-phenyloxiran, the normal non-basic product from such reactions with ephedrinium compounds.[3] Similar reactions of the cyclic ephedrinium compounds containing *o*-nitro- or *o*-fluoro-groups had also given the corresponding *N*-methylazepines.[4]



(I)



(II)



(III)

However, when the unbridged compound (III; X = OH), prepared from 2,2′-bisbromomethylbiphenyl and (—)-*N*-methylephedrine in nitrobenzene at 130°, was subjected to Hofmann degradation under similar conditions (Experiment 1), *N*-methylephedrine was isolated from the basic products, suggesting that the quaternary cation was undergoing attack at the (benzyl) α-carbon atom as well as at the hydrogen of the β-hydroxyl group. A bimolecular displacement [5,6] at the α-carbon atom is the process most commonly competing with bimolecular Hofmann elimination,[7] and it has been shown [5] that the use of anions less basic than hydroxyl favours the displacement at the expense of the elimination. Thus exclusion of carbon dioxide (and hence of CO_3^{2-}) is likely to reduce the amount of the displacement by-product.[5,8]

The degradation of the bisquaternary dihydroxide (III; X = OH) was therefore repeated (Experiment 2) in an atmosphere of nitrogen (with exclusion of carbon dioxide); water was used instead of aqueous ethanol to avoid attack by alkoxide ions. The basic fraction from the products still contained some *N*-methylephedrine, but also other bases. Separation through the picrates gave the dipicrate of the expected amine (IV) as

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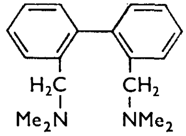
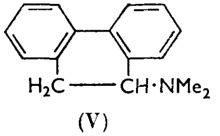
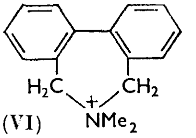
[1] Beaven, Hall, Lesslie, and Turner, *J.*, 1952, 854.
[2] Wenner, *J. Org. Chem.*, 1951, **16**, 1475.
[3] Miller, *Arch. Pharm.*, 1902, **240**, 481; Rabe, *Ber.*, 1911, **44**, 824; Emde, *Arch. Pharm.*, 1906, **244**, 241; Witkop and Foltz, *J. Amer. Chem. Soc.*, 1957, **79**, 197.
[4] Ahmed and Hall, *J.*, 1958, 3043.
[5] Hanhart and Ingold, *J.*, 1927, 997.
[6] (*a*) Ingold and Patel, *J.*, 1933, 68; (*b*) Hughes and Ingold, *J.*, 1933, 69; (*c*) Hughes, Ingold, and Patel, *J.*, 1933, 526.
[7] Cope and Trumbull, in "Organic Reactions," ed. Cope, Wiley, New York, 1960, Vol. XI, p. 317.
[8] von Braun, Teuffert, and Weissbach, *Annalen*, 1929, **472**, 121.


(IV)


(V)


(VI)

the main product, accompanied by smaller quantities of the picrate of 9-dimethylamino-9,10-dihydrophenanthrene (V).[9] Relevant ultraviolet absorption spectra are given in Table 1.

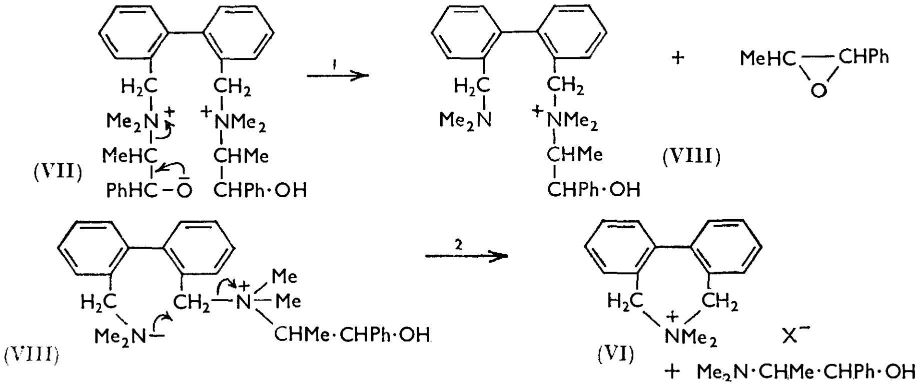
TABLE 1.

Ultraviolet absorption spectra (λ in mμ) of solutions in 96% EtOH (values in parentheses are inflections).

Compound	Short-wave band		Conjugation band		Long-wave features			
	$\lambda_{max.}$	ε	$\lambda_{max.}$	ε	$\lambda_{max.}$	ε	$\lambda_{max.}$	ε
V)	211	39,900	252	15,700	(274)	14,500		
			260	16,000	(282)	9720		
			265·5	15,900	(292)	4180		
Picrate of (V)	208	54,400	260	20,900	(270)	18,800	357·5	16,200
	212	53,500	261·5	20,800	(280)	11,800		
(II)	206	41,600	241	12,800	(281)	3030		
(VI; X = HCO_3)			248	14,000	(271)	4430		
					(281)	2380		
(VI; X = Br)			249	14,200	(275)	4270		
					(280)	3050		
(VI; X = $C_6H_2N_3O_7$)	206	51,500	245	22,700	(274)	5850	357	14,750
	212	52,900			(281)	4140	360	14,650
(XVII; X = Br),H_2O *			(233)	8980	268·5	2080		
Picric acid †			[245	10,000] †			360	16,600
Na picrate §							358	14,100

* In MeOH. † Friedel and Orchin, " Ultraviolet Spectra of Aromatic Compounds," Wiley, New York, 1951, No. 93. ‡ Not a maximum or point of inflection. § The acid in ethanol containing aqueous sodium hydroxide; Schroeder, Wilcox, Trueblood, and Dekker, *Analyt. Chem.*, 1951, **23**, 1740.

The residue from this decomposition (Experiment 2) was treated with ether and water. Evaporation of the aqueous solution, after thorough washing with ether, gave a small residue, part of which was a white solid, insoluble in chloroform. Qualitative tests and infrared bands at 834 and 1613 cm.$^{-1}$ (cf. Miller and Wilkins[10]) showed that this was a hydrogen carbonate. The ultraviolet absorption spectrum (Table 1) was typical of a



Mechanism (I): 1, Internal S_N2 by O–. 2, S_N2 by neutral N.

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[9] Hori, Abe, Yamakawa, and Fujimura, *Gifu Yakka Daigaku Kiyô*, 1958, **8**, 65 (*Chem. Abs.*, 1959, **53**, 10,148).

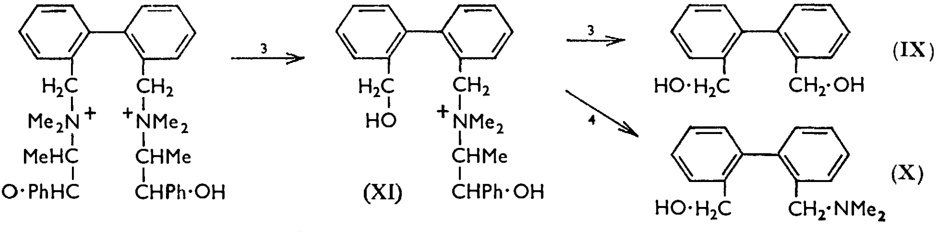
[10] Miller and Wilkins, *Analyt. Chem.*, 1952, **24**, 1253; see also Hunt, Wisherd, and Bonham, *ibid.*, 1950, **22**, 1478.

2,2′-bridged biphenyl with a seven-membered bridging ring and the compound was identified as 2,7-dihydro-1,1-dimethyl-3,4:5,6-dibenzazepinium hydrogen carbonate (VI; X = HCO_3) by conversion into the picrate, identical with that made from the corresponding bromide. (The high intensity and slight displacement of the conjugation band in the ultraviolet absorption spectrum of the picrate are due to superimposition of picrate absorption on that of the biphenyl system. Picric acid has ε 10,000 at 245 mμ in 95% ethanol[11] and the ion is probably rather similar.) The chloroform-soluble part of the residue also contained the 2,7-dihydro-1,1-dimethyl-3,4:5,6-dibenzazepinium cation and appeared (from the infrared spectrum and qualitative tests) to contain the quaternary hydroxide (VI; X = OH), which had failed to absorb dioxide during the working up.

The Hofmann degradation of compound (III; X = OH) was carried out for a third time (Experiment 3). Owing to bumping in the early stages, a little carbon dioxide was allowed to enter and a more dilute solution was used; otherwise, conditions were as in Experiment 2. The main picrate this time was that of the aminodihydrophenanthrene (V), accompanied by very small amounts of the dipicrate of base (IV). The ethereal extract of the reaction products remaining in the flask yielded phenanthrene.

Three modes of reaction * of the cation (III) with hydroxyl ions can be envisaged. (1) Proton loss at the β-hydroxyl group will give an alkoxide ion (VII), which can form the oxiran (ethylene oxide) and the ion (VIII) by an internal nucleophilic substitution. This process can occur in both side chains, in which case 2,2′-bisdimethylaminomethylbiphenyl (IV) will be formed. On the other hand, nucleophilic replacement (at the benzyl α-carbon atom) of positive (quaternary) nitrogen by neutral (tertiary) nitrogen in the ion (VIII) is the most likely route to the azepinium hydrogen carbonate (VI; X = HCO_3).

(2) Nucleophilic displacement at benzyl α-carbon atoms by hydroxyl ions (or by carbonate ions in experiments where carbon dioxide is not excluded) would lead to the diol (IX) or the hydroxy-amine (X). Cyclisation of the hydroxy-amine (X) or of the intermediate ion (XI), with loss of water, is a possible but rather unlikely route to 9-dimethylamino-9,10-dihydrophenanthrene (V).



Mechanism (2): 3, S_N2 by OH^-. 4, $-H^+$, internal S_N2 by O^-.

(3) Attack by hydroxyl ions at a benzyl methylene group may lead to proton loss rather than to substitution. This would give an ylide intermediate (XII) of a type which plays an essential part in the Stevens rearrangement. In view of the frequently observed[12] ease of 6- and 7-membered ring formation among 2,2′-substituted biphenyls it seems possible that, once formed, such an ion might preferentially attack the benzyl carbon atom attached to the other positive nitrogen, thus forming a six-membered ring, rather than a methyl or isopropyl carbon atom attached to its own nitrogen. The ion (XIII) so formed could undergo proton loss either at the β-hydroxyl group, leading to 9-dimethylamino-9,10-dihydrophenanthrene (V), or at the β-carbon atom in the saturated ring,

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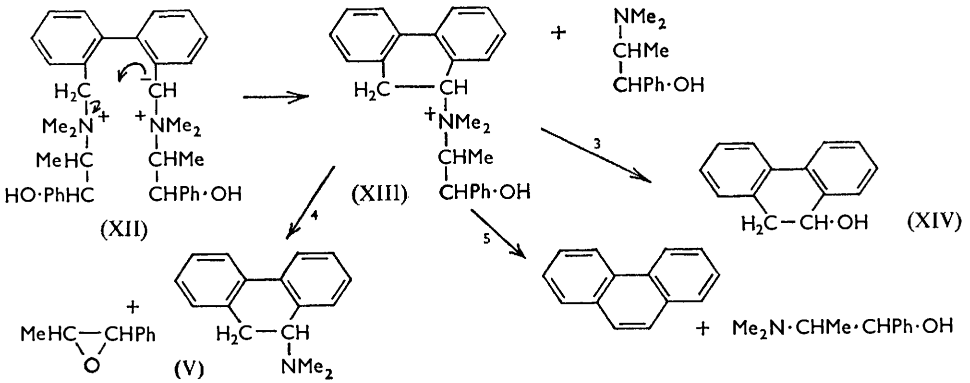
* Probable mechanisms are indicated in the reaction schemes, but in no case has a bimolecular mechanism been unequivocally proved for these particular compounds.

[11] Friedel and Orchin, " Ultraviolet Spectra of Aromatic Compounds," Wiley, New York, 1951, No. 93.

[12] Kenner, *J.*, 1913, **103**, 613; Hall, Lesslie, and Turner, *J.*, 1950, 711; Beaven, Bird, Hall, Johnson, Ladbury, Lesslie, and Turner, *J.*, 1955, 2708; Hall, Ladbury, Lesslie, and Turner, *J.*, 1956, 3475.

leading to phenanthrene; nucleophilic displacement by hydroxyl at the α-carbon atom would give 9,10-dihydro-9-hydroxyphenanthrene (XIV), which was not detected. If formed, therefore, it must have undergone ready dehydration to phenanthrene.



Mechanism (3): 3, S_N2 by OH^-. 4, $-H^+$, internal S_N2 by O^-. 5, *E*2.

The relative importance of the three modes of attack on the cation (III), and whether (2) followed by cyclisation or (3) is a source of (V), can be found by studying the effect

TABLE 2.

Products of Hofmann degradation of the dihydroxide (III; X = OH).
[Citations in parentheses are m. p.s. Others are yields in g.].

Expt.	Iodide (g.)	Condns.	Distillate		Residue		Bases present			Neutral Et_2O-sol. residue	H_2O-sol. residue (g.) (picrate,[2] m. p.)
			Bases	Picrates	Bases	Picrates	(IV)	(V)	ME[1]		
2	7·9	N_2, CO_2-free air	0·43 (solid)	0·14 (195—205°)	2·37	0·1 (170—205°) 2·17[3] (190—208°) ~0·1 (170—176°)	+	+ (less)	+	—[4]	0·4 (278—281°)
3	7·9	N_2	1·36 (liquid)	0·32 (~206°) 0·04 (168—174°)	1·60	2·31[5] (165—178°)	+	+ (more)	+	0·10[6] (60—85°)	0·38
(*a*)	3·95	N_2	0·698 (solid)	<0·01 (213°)	1·14 (solid)	1·44[7] (187—190°)	+	+	+	0·06 (71—80°)	0·60 (279—282°)
(*b*)	,,	N_2, $\not>$100° dil. soln.	—	—	0·759 (solid)	<0·01 (174—176°)	—	Trace	+	0·015	1·60[8] (285°)
(*c*)	,,	N_2, +KOH	0·353 (solid)	0·038 (206°)	0·999 (liquid)	1·67[9] (155—166°)	Trace	+	+	0·1705 (97—98°)	4·02[10] (200—320°[11])
(*d*)	,,	CO_2	0·110	—	0·664 (solid)	0·05 (212—214°) 0·84 (140—142°)[12]	Trace	—	+	0·131[13] (partly liquid)	1·215 (285°)

[1] *N*-Methylephedrine. [2] In all cases a single crystallisation raised the m. p. to 285—286°. [3] The base was distilled and only part made into the picrate. Crystallisation of this crop gave 0·90 g. of m. p. >200° and 0·37 g. of m. p. 170—174°. [4] Not isolated separately. [5] Crystallisation gave 1·64 g. of m. p. 173—176°, 0·17 g. of m. p. 169—174°, and 0·03 g. of m. p. 206°. [6] M. p. 98—100° after crystallisation. [7] Crystallisation gave 0·326 g. of m. p. 205—207°, 0·226 g. of m. p. 173—174°, 0·186 g. of m. p. 146—154°, and 0·088 g. of m. p. 143—144°. [8] Incompletely decomposed. On re-treatment with fresh Ag_2O under the conditions of (*a*) it gave 0·181 g. of bases, yielding 0·285 g. of picrate, m. p. 165—170°, and 0·90 g. of water-soluble residue. [9] Crystallisation gave 0·610 g. of m. p. 174—176°, 0·493 g. of m. p. 158—174°, and 0·206 g. of m. p. 137—142°. [10] Includes the added potassium hydroxide and its carbonate. [11] Mainly potassium picrate, melting explosively at 334° after crystallisation. [12] *N*-Methylephedrine picrate, obtained from highly concentrated mother-liquor. [13] Probably mainly 1-phenylpropan-1,2-diol (see Experimental).

TABLE 3.

Melting points of picrates used for identifications.

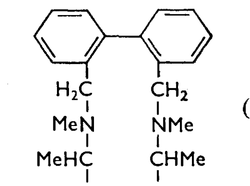
Tertiary amine	Picrate	Quaternary cation	Picrate
(II)	162°	(VI)	285—286°
(IV)	207—208	(XVII)	245
(V)	175—176		
N-Methylephedrine	143·5—144		
Trimethylamine	224		

of changes in hydroxyl-ion concentration and of added carbon dioxide on the reaction products. Change in hydroxyl-ion concentration should have little effect on process (1), since proton loss at the hydroxyl group cannot be rate-determining, but reduction in hydroxyl-ion concentration (by heating the solution under reflux instead of distilling it) might be expected to decrease processes (2) and (3), whereas added hydroxyl ions should promote them. Carbon dioxide might be expected to promote (2) at the expense of (1) and (3), since carbonate ions are nucleophilic but only weakly basic.

Accordingly, the decomposition of the quaternary hydroxide (III; X = OH) was carried out (*a*) under nitrogen, in conditions as before, (*b*) under nitrogen, but with heating under reflux without distillation, (*c*) under nitrogen with added potassium hydroxide, and (*d*) under carbon dioxide. The results are detailed in Tables 2 and 3.

The decomposition (*b*), carried out in dilute solution at 100°, gave *N*-methylephedrine, none of the base (IV) and only a trace of the aminophenanthrene (V); it was incomplete and the large residue was mainly the azepinium hydrogen carbonate (formed from the hydroxide during the subsequent working-up and evaporation). Thus, here, reaction (1) must be occurring in one side-chain, followed by nucleophilic replacement by neutral nitrogen in the other, leading to the cation of compound (VI). The weights obtained correspond to an 84% yield of *N*-methylephedrine and 113% of azepinium hydrogen carbonate, the discrepancies being partly accounted for by the presence of a little (optically active) undecomposed starting material. The residue was treated with fresh silver oxide and re-treated under conditions (*a*). Some of the amine (V) was obtained.

The presence of carbon dioxide (*d*) reduced the yields of both amines (IV) and (V) to negligible proportions. Bimolecular displacement at the benzyl α-carbon atom, followed by cyclisation, cannot, therefore, by the source of the aminophenanthrene (V) in the normal experiments. The possibility of similar reaction at one of the other α-carbon atoms (methyl or isopropyl) in *both* side chains is also eliminated, since this would give either a new tertiary amine (XV) (not observed) or (IV) (of which only a trace was obtained). However, such reaction at the isopropyl carbon atom in *one* side chain would give the ion (VIII), which could then give the azepinium ion (VI) by a replacement reaction. It is possible that this is indeed the route to (VI) under these conditions, where the basicity of the solution is so much reduced. Alternatively, there may be sufficient hydroxyl ions present to produce (VIII) by proton loss from the β-hydroxyl group, as in (*b*).



(XV)

Added potassium hydroxide (*c*) has greatly increased the yield of 9-dimethylamino-9,10-dihydrophenanthrene (V), thus providing strong support for process (3), the route involving a type of Stevens rearrangement. This rearrangement, originally[13] carried out with hydroxide or alkoxide ions on phenacylamines and later with phenyl-lithium[14,15] on compounds containing less readily ionised hydrogen, can occur during the decomposition of quaternary ammonium hydroxides of suitable structure and has been observed[6b]

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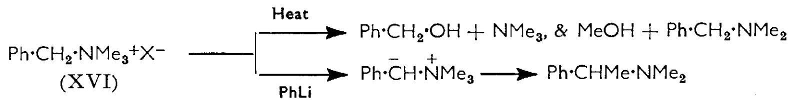
[13] Stevens, Creighton, Gordon, and MacNicol, *J.*, 1928, 3193; Stevens, *J.*, 1930, 2107.

[14] Wittig, Mangold, and Felletschin, *Annalen*, 1948, **560**, 116.

[15] Wittig and Zimmermann, *Chem. Ber.*, 1953, **86**, 629.

in, for example, the decomposition of diphenylmethyltrimethylammonium hydroxide in the presence of a high concentration of potassium hydroxide.

However, benzyltrimethylammonium hydroxide (XVI; X = OH) is decomposed when heated in aqueous solution[6b] into benzyl alcohol and trimethylamine (65% of the reaction) and methyl alcohol and benzyldimethylamine (35% of the reaction), whereas treatment of the quaternary bromide (XVI; X = Br) with phenyl-lithium in ether[14] gives the rearrangement product, *NN*-dimethyl-α-methylbenzylamine.



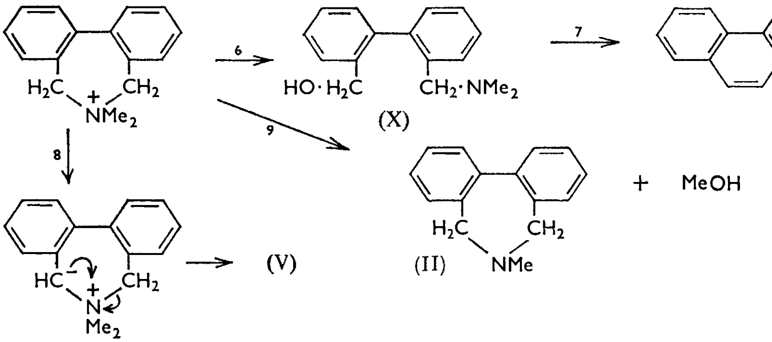
The situation of (benzyl) α-hydrogen atoms in (III) is formally rather similar to that of (benzyl) α-hydrogen atoms in (XVI), but the benzyl α-carbon atoms in the cation of (III), unlike those in (XVI), are subject to considerable steric hindrance to S_N2 reactions, since both the other part of the biphenyl system and the bulky ephedrine side-chain interfere with the formation of the transition state. If steric factors hinder nucleophilic displacements in (III), the way is open for reaction dependent upon ylide formation, even without use of a stronger base than hydroxyl ions. [Indeed the necessity to use phenyl-lithium to form an ylide from (XVI) may be only partly due to the greater basic strength of the reagent and partly due to its weak nucleophilic power.]

The diol (IX) has not been detected among the degradation products. It is stable to hot potassium hydroxide, so cannot have been formed and then destroyed. All neutral ether-soluble residues (always very small) were examined by infrared spectroscopy and in some cases phenanthrene was isolated from them. The diol was easily detectable spectroscopically in a 1 : 1 mixture with phenanthrene so that, if any was formed, it was only in very minor amount.

Thus all the evidence points to the Stevens rearrangement as the source of the aminophenanthrene (V), and to the unimportance of bimolecular displacements by hydroxyl ions at the benzyl α-carbon atoms in (III).

However, during the investigation of the quaternary hydrogen carbonate, another possible source of the 9-dimethylamino-9,10-dihydrophenanthrene (V) was revealed. The hydrogen carbonate melted with vigorous decomposition at 206°; a sample kept at 210° for 40 minutes gave 9-dimethylamino-9,10-dihydrophenanthrene. It thus appeared that at 210° the hydroxyl ion (from the decomposing hydrogen carbonate) was a sufficiently strong base to bring about a Stevens rearrangement of the cation (VI). In order to test the effectiveness of the hydroxyl ion under the conditions of the reactions described above, Hofmann degradation was carried out on 2,7-dihydro-1,1-dimethyl-3,4:5,6-dibenzazepinium hydroxide (VI; X = OH) under the conditions of experiment (*a*), the temperature not being allowed to rise above 135°. As expected, the aminophenanthrene (V) was obtained but it was accompanied by 2,7-dihydro-1-methyl-3,4:5,6-dibenzazepine (II) (the result of hydroxyl attack at the methyl α-carbon atoms) and by phenanthrene, isolated in 32—40% yield. A similar decomposition in the presence of potassium hydroxide gave a similar yield of phenanthrene (33%), and the amine (V), but none of the azepine (II). Neither the azepine nor the phenanthrene had been detected when the hydrogen carbonate was decomposed alone at 210°.

Thus the Stevens rearrangement of the azepinium ion is favoured by a high concentration of hydroxyl ions and a high temperature. Under somewhat less favourable conditions (≯135° and no added potassium hydroxide) some substitution to give azepine occurs as well. At lower temperatures and with low concentrations of hydroxyl ions no rearrangement occurs, as shown by the products of decompositions (*b*) and (*d*) (see Table 2); in (*b*) the temperature was ≯100° and the hydroxyl-ion concentration was not increased by distillation of the water; in (*d*) the temperature was higher but the hydroxyl-ion concentration was very greatly reduced by the presence of carbon dioxide.



Mechanism (4): 6, S_N2 by OH^- at CH_2. 7, ? (—$NHMe_2$). 8, —H^+. 9, S_N2 by OH^- at Me.

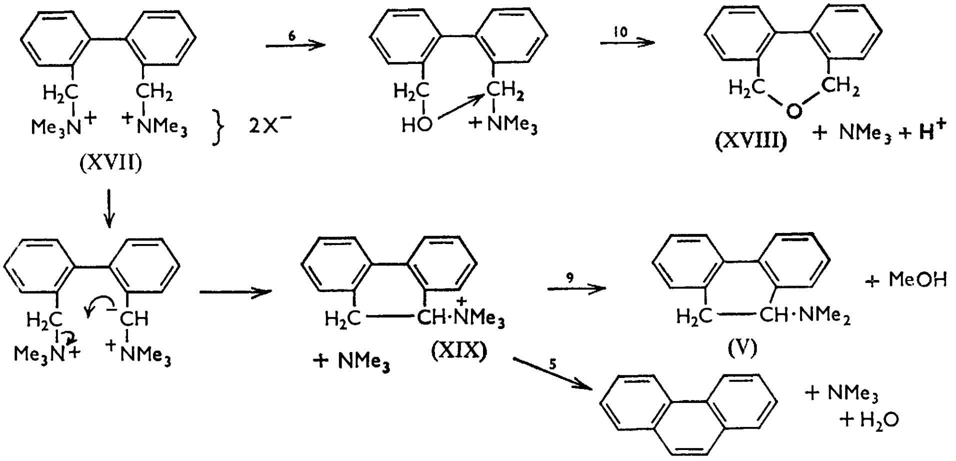
Some of the 9-dimethylamino-9,10-dihydrophenanthrene (V) produced in the other decompositions of the bisephedrinium compound (III; X = OH) may have come from the azepinium ion. However, it is considered that most of it is formed by the Stevens rearrangement on the original ion (III ⟶ XII ⟶ XIII ⟶ V), for the following reason. Any amine (V) produced *via* the azepinium ion will be accompanied by appreciable amounts of phenanthrene (and some azepine). Phenanthrene was detected among the decomposition products only in reactions where a good yield of the amine (V) was obtained but, in the most favourable case (reaction *c*; added alkali) only in 19% yield and some of this may have come from elimination reactions of compounds (XIII) or (XIV). No azepine picrate was isolated, but this is less valuable evidence since small amounts could have been missed among the other picrates.

The mode of formation of phenanthrene by the action of hydroxyl ions on the azepinium cation (VI) is not so far understood. It appears to involve elimination of dimethylamine from the benzylamine analogue (X) or from (V) and, during the decomposition, an alkaline gas (almost certainly dimethylamine) was evolved as soon as the temperature reached 80°. However, the amine (V) appeared to be stable both to heat (since it could be distilled at 183°/1 mm.) and to alkali (since the yield of phenanthrene was not increased by added potassium hydroxide). The hydroxy-amine (X) is not known; the corresponding diol is stable to hot alkali.

It is not clear why, in the original decomposition of the bisephedrinium compound (III), smaller yields of the diamine (IV) were obtained in Experiment 3 and in decomposition (*a*) than in Experiment 2. Perhaps the balance of competing reactions is very delicate and factors such as the dilution at a particular temperature (difficult to control during slow distillation at a gradually rising temperature) are of critical importance.

In view of the behaviour of the dihydroxide (III), it seemed possible that the hydroxides of other unbridged 2,2′-bisquaternary biphenyls, in which simple olefin formation would be difficult or impossible, might give bridged compounds under Hofmann degradation conditions. Accordingly, an aqueous solution of the hydroxide (XVII; X = OH) was slowly distilled under reduced pressure in an atmosphere of nitrogen. 9-Dimethylamino-9,10-dihydrophenanthrene (V) and trimethylamine were isolated as picrates. At least one other (unidentified) base was present. Non-basic products, including phenanthrene and 2,7-dihydro-3,4:5,6-dibenzoxepin (XVIII) were also obtained. The oxepin was not isolated in a pure condition but was detected spectroscopically in a mixture with phenanthrene.

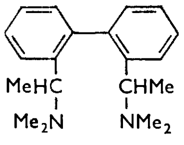
Again, several competing processes must operate. Nucleophilic displacement by hydroxyl ions at one of the benzyl α-carbon atoms, followed by cyclisation, seems the most likely route to the oxepin. Cyclisation involving alkylation of a hydroxyl group by the methylene group of $-CH_2{\cdot}NMe_3^+$ in a rather similar situation has been observed by Easton and Fish.[16]



Mechanism (5): 5, E2. 6, S_N2 by OH^- at CH_2. 9, S_N2 by OH^- at Me. 10, Internal S_N2.

Proton loss from a benzyl methylene group, followed by rearrangement, gives an ion (XIX) which can undergo either bimolecular displacement at a methyl group, giving (V), or elimination involving a β-hydrogen atom, giving phenanthrene.

The unidentified base was obtained as its picrate, m. p. 240° (decomp.); the analysis gives the formula $C_{20}H_{28}N_2,2C_6H_3N_3O_7$, if the biphenyl skeleton is still present, or $C_{10}H_{15}N,C_6H_3N_3O_7$ if it is not. The possibility that " normal " Stevens rearrangement (without cyclisation) had occurred to give the diamine (XX) was considered; decomposition of the picrate by cold alkali gave a little free base, the infrared spectrum of which showed the C–H stretching frequencies of NMe_2 (at 2760 and 2811 cm.$^{-1}$) and of CH_2 (at 2857 and 2918 cm.$^{-1}$). No peaks for C–CH_3 were found, although two slight shoulders (at 2884 and 2970 cm.$^{-1}$) on the CH_2 bands were at the CH_3 stretching frequencies. It thus appears that the base contains CH_2 groups rather than $CH{\cdot}CH_3$ groups and so cannot have structure (XX). It has not proved possible to elucidate the structure with the small amount available.



(XX)

The pure amine (IV) was obtained from its dipicrate and gave a dimethiodide identical with (XVII; X = I), prepared from 2,2′-bisbromomethylbiphenyl and trimethylamine. The ultraviolet absorption spectrum of the dimethobromide (XVII; X = Br) (Table 1) is that of a highly hindered 2,2′-disubstituted biphenyl (compare, for example, the spectrum of 2,2′-dimethylbiphenyl [17, 18]).

Infrared Spectra.—The main features of the infrared spectra of the four tertiary amines, (II), (IV), (V), and *N*-methylephedrine, are given in Tables 4 and 5. Part of the spectrum of a non-basic reference compound, 9,10-dihydrophenanthrene, is included. A sharp band at 1004—1007 cm.$^{-1}$, found in the first three compounds, is also present in the spectrum of 9,10-dihydrophenanthrene (at 1001 cm.$^{-1}$) but not in that of *N*-methylephedrine; this supports the view of Beaven and Johnson [18] that a band at 1010 cm.$^{-1}$ is characteristic of the biphenyl structure.

A few of the C–H stretching frequencies require comment. One of the CH_2 bands in 9,10-dihydrophenanthrene occurs at a rather high frequency (2874 cm.$^{-1}$ instead of the

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[16] Easton and Fish, *J. Amer. Chem. Soc.*, 1955, **77**, 2547.

[17] Beaven, Hall, Lesslie, Turner, and Bird, *J.*, 1954, 131.

[18] Beaven and Johnson, " Conference on Molecular Spectroscopy," ed. Thornton and Thompson, Pergamon Press, London, 1959, p. 78.

TABLE 4.

Infrared spectra (cm.$^{-1}$; 600—1650 cm.$^{-1}$) of some tertiary amines.

(II)	(IV)	(V)	ME *	(II)	(IV)	(V)	ME *	(II)	(IV)	(V)	ME *
605m				934m		936m	920w	1250w	1253m		1247sh
617m	619sh	619m		947m	942w	952m	956m		1261sh	1261w	1267s
632sh		627sh	630m	977w	972w		978sh		1284w	1277m	1282sh
			656m			990w	996s	1307w	1297m	1314m	1305sh
667w		667w		1006w	1007m	1004w		1333w	1337sh	1333sh	1325sh
		678m		1022m	1027s	1025s	1030sh				1355sh
	697w	699m			1041s	1041s	1041s	1366m	1361s	1361m	1368s†
			705vs	1047w		1047sh	1055s	1389w			
711w	711sh	711w		1078s	1075w		1067sh	1416sh	1401w	1404w	1418sh
730m	720sh	728sh	729sh		1095m	1096m	1095m		1439sh	1439sh	
749vs	736sh	737vs	744vs	1114sh	1107w			1443s	1449s	1451s	1447s†
	753sh			1120m				1462m	1460sh	1471sh	1460sh
	757vs	752vs		1127sh		1125w	1127s	1475m		1481s	
776m	781sh	777s	779s		1145m	1143w			1490sh	1493sh	1493sh
		790sh		1157w	1153m	1155m	1157sh	1550w		1563w	
825w	812w	814m	810m		1172m	1167s	1170s			1587sh	
833w	839sh	833w	835w	1182m	1189w	1183m		1605sh	1592w	1597w	1600w
849m	851m	861m		1195m		1200sh	1200m	1637m	1629w		1631w
870w				1235m		1238w					
885w	873m	879m	881m								

* *N*-Methylephedrine, spectrum of Nujol mull. † Nujol peak.

TABLE 5.

C–H Stretching vibrations (cm.$^{-1}$) in some tertiary amines and in 9,10-dihydrophenanthrene.

(II)	(IV)	(V)	ME *	DHP †	Probable assignment
2773s	2755s	2768s	2772s		N–CH$_3$
	2803s	2811m	2817s		N–CH$_3$
2827m				2819m	?
2859m	2843m	2851m		2874m	CH$_2$
			2867s		CH$_3$
2887sh		2884m			?CH
2924s	2927s	2930s		2921s	CH$_2$
			2941sh		
2953sh	2959sh	2956sh	2956s		?CH$_3$
			2979s		?CH$_3$
3006m	3012m	3012m	3021m	3008s	CH (arom.)
3051m	3046m	3053m	3058m	3051m	CH (arom.)
			3084sh		?CH (arom.)

* *N*-Methylephedrine, spectrum in CCl$_4$. † 9,10-Dihydrophenanthrene, spectrum of molten material.

usual [19] 2853 ± 10 cm.$^{-1}$) and one of the C–CH$_3$ bands in *N*-methylephedrine is apparently double (2956 and 2979 cm.$^{-1}$). The γ-hydroxyl group may be responsible for a shift to higher frequency in this band, although this effect is much more marked with isopropyl-O than with n-propyl-O compounds.[20]

All the amines show a strong band at 2764 ± 9 cm.$^{-1}$ and a second band (medium to strong) at 2815 ± 12 cm.$^{-1}$, which is least prominent in the azepine (II) and is also present as a weak band in 9,10-dihydrophenanthrene. A number of workers [21,22] have correlated absorption in this region with the C–H stretching vibration of an $>$NMe group, and Hill and Meakins [21] have classified the absorption pattern according to the situation of the basic group and the number of methyl groups attached to the nitrogen. With an NMe$_2$ group not directly attached to an aromatic system two bands occur in the 2825—2810 and

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[19] Fox and Martin, *Proc. Roy. Soc.*, 1938, *A*, **167**, 257; 1940, *A*, **175**, 208.

[20] Pozefsky and Coggeshall, *Analyt. Chem.*, 1951, **23**, 1611.

[21] Hill and Meakins, *J.*, 1958, 760.

[22] Braunholz, Ebsworth, Mann, and Sheppard, *J.*, 1958, 2780; Wright, *J. Org. Chem.*, 1959, **24**, 1362; Katritzky and Jones, *J.*, 1959, 3674.

2775—2765 cm.$^{-1}$ ranges. This is borne out by the spectra of the three amines containing NMe_2 (IV, V, and *N*-methylephedrine) in the present work. For amines containing an NMe group not directly attached to an aromatic system, Hill and Meakins [21] found a single band between 2805 and 2780 cm.$^{-1}$. The methylazepine (II) has a strong band just outside this range (2773 cm.$^{-1}$); the second band (at 2827 cm.$^{-1}$) is weaker than for the other amines and it is presumably due to the CH_2 groups rather than the NMe group, especially as a similar band is found in the non-basic 9,10-dihydrophenanthrene.

EXPERIMENTAL

Action of Heat on 2,7-*Dihydro*-1-(β-*hydroxy*-α-*methylphenethyl*)-1-*methyl*-3,4:5,6-*dibenzazepinium Hydroxide* (I; X = OH).—The corresponding (solvated) (+)-bromide [1] (9·1 g.) was shaken in aqueous-ethanolic solution with silver oxide for 1 hr. The filtered solution was distilled at atmospheric pressure; ethanol and water containing (+)-*trans*-1-methyl-2-phenyloxiran were collected. The residue was extracted with ether, and the ethereal solution washed with hydrochloric acid. Aqueous ammonia was added to the acid solution and the free base extracted with ether, dried (K_2CO_3), and distilled, giving 2,7-dihydro-1-methyl-3,4:5,6-dibenzazepine [2] (2·2 g., 53%), b. p. 150—160°/2 mm. [methiodide (from ethanol), m. p. 294° (decomp.), not depressed by authentic specimen (see below); *picrate*, m. p. 162° (from ethanol) (Found: C, 57·9; H, 4·25; N, 12·6. $C_{21}H_{18}N_4O_7$ requires C, 57·5; H, 4·1; N, 12·8%)].

2,2′-*Di*-[NN-*dimethylammoniomethyl*-N-(β-*hydroxy*-α-*methylphenethyl*)]*biphenyl Di-iodide* (III; X = I).—2,2′-Bisbromomethylbiphenyl (13·6 g., 1 mol.) and (−)-*N*-methylephedrine (15·8 g., 2·2 mol.) were dissolved separately in dry warm nitrobenzene (35 c.c. in all). The solutions were mixed at 120° and the temperature rose to *ca.* 150°. The mixture was kept at *ca.* 130° for 20 min. during which solid separated and the whole became very thick. It was allowed to cool and the solid filtered off and washed with dry nitrobenzene, followed by dry benzene and dry acetone. The crude quaternary dibromide (26 g.) so obtained had m. p. *ca.* 206°. In some preparations a small amount of another solid separated from the washings but was not identified. The dibromide was dissolved in a large volume of water, treated with aqueous potassium hydroxide, and extracted with benzene or carbon tetrachloride to remove any unchanged tertiary base. Addition of the benzene precipitated the dibromide in a hydrated form and much water was required to redissolve it. The aqueous solution was neutralised with hydrobromic acid and concentrated below 35° to *ca.* 1500 c.c. (Hydrated dibromide crystallised from more concentrated solutions.) A cold saturated solution of potassium iodide was added and the precipitated di-iodide was collected. Crystallisation from aqueous ethanol gave 23·8 g. (75%) of the *di-iodide*, m. p. 214—215°, $[\alpha]_{5461}^{21}$ −127·5° (*c* 1·006 in methanol) (Found: C, 54·7; H, 5·9; I, 31·8; N, 3·45. $C_{36}H_{46}I_2N_2O_2$ requires C, 54·5; H, 5·85; I, 32·0; N, 3·5%).

Action of Heat on 2,2′-*Di*-[N-(NN-*dimethylammoniomethyl*-β-*hydroxy*-α-*methylphenethyl*)]-*biphenyl Dihydroxide* (III; X = OH).—*Experiment* 2. The (−)-quaternary di-iodide (7·9 g.) was dissolved in methanol (80 c.c.) and water (40 c.c.) and shaken with freshly precipitated silver chloride for 1 hr. Methanol was removed from the filtered solution by distillation under reduced pressure. Subsequent operations were, as far as possible, carried out in an atmosphere of nitrogen or carbon dioxide-free air. Freshly precipitated silver oxide was added to the aqueous solution of the chloride, and the mixture was shaken for 1 hr. The filtered solution (chloride-free) was distilled under reduced pressure from a water-bath at 40—50°. When most of the water had been removed the bath-temperature was slowly raised to 100°, oil distilling with the water. Finally the mixture was heated at 120—125° under reduced pressure for about 10 min.

The distillate and residue in the flask were worked up separately, a procedure followed throughout the series of experiments since *N*-methylephedrine proved to be more steam-volatile than the other bases and was thus partially separated from them.

Ether was added to the distillate: water and ether were added to the residue. Both lots were separated and extracted and the ethereal layers then extracted with dilute hydrochloric acid. The resulting neutral (dextrorotatory) ethereal solutions were combined and dried ($MgSO_4$), and the ether was removed (Dufton column). The residue (1·23 g.) was mainly (+)-*trans*-1-methyl-2-phenyloxiran, together with an unidentified solid.

The two (lævorotatory) acid solutions were treated with freshly dissolved potassium hydroxide and the amines extracted with ether and dried (K_2CO_3). Removal of the ether (Dufton column) gave 0·43 g. of solid amines from the distillate fraction and 2·37 g. from the residue fraction. The latter portion was distilled under reduced pressure, giving two fractions with b. p. $<100°/2$ mm. (0·28 g.) and 100—135°/2 mm. (1·33 g.), severally. Crystallisation of the first fraction from light petroleum (b. p. 40—60°) gave *N*-methylephedrine (0·10 g.), m. p. 85—87°, raised on admixture of an authentic sample. Its identity was confirmed by its infrared spectrum and the infrared spectrum and m. p. of its methiodide, all identical with those of authentic specimens. The crystallisation mother-liquor was evaporated and the residual base dissolved in ethanol and added to a cold saturated solution of picric acid in ethanol, giving a picrate (0·10 g.), m. p. partly 170—185° and partly $>200°$. The second fraction of distilled base was partly solid but could not be crystallised and was all converted into the picrate in ethanol. It gave material (2·17 g.) of m. p. 190—208°, and a small second crop, m. p. 170—176°. Fractional crystallisation of the main crop from methanol containing some acetone separated it into two picrates, (*A*) (0·90 g.) m. p. $>200°$, and (*B*) (0·37 g.) m. p. 170—174°, together with low-melting mixtures containing picric acid. Recrystallisation of (*A*) from methanol–acetone gave 2,2′-*bisdimethylaminomethylbiphenyl dipicrate*, yellow needles, m. p. 207—208° (depending on the rate of heating) (Found: C, 49·9; H, 4·3; N, 15·35. $C_{30}H_{30}N_8O_{14}$ requires C, 49·6; H, 4·2; N, 15·4%). Recrystallisation of (*B*) from acetone gave yellow compact crystals of 9-*dimethylamino*-9,10-*dihydrophenanthrene picrate*, m. p. 175—176° (Found: C, 58·5; H, 4·6; N, 12·4; O, 25·0. $C_{22}H_{20}N_4O_7$ requires C, 58·4; H, 4·5; N, 12·4; O, 24·8%). The infrared spectrum and m. p. were identical with those of a sample prepared from the authentic base (see below).

The solid amines (0·43 g.) obtained from the distillate fraction were also treated with alcoholic picric acid and gave 0·14 g. of picrate, m. p. 195—205°. Most of the solid must therefore have been *N*-methylephedrine which gives no precipitate with alcoholic picric acid.

The aqueous solution of the original residue from the decomposition was, after the ether-extraction, optically inactive. It was evaporated to dryness and the residue (0·4 g.) extracted with benzene. Only a negligible amount dissolved. The residue was then treated with chloroform in which part dissolved, leaving a white, insoluble material (0·18 g.). This could not be crystallised but was purified by dissolution in a small volume of water, filtration from a trace of insoluble impurity, and evaporation to dryness. A hydrate was obtained and the water was only completely removed by prolonged heating *in vacuo*. The residue, 2,7-*dihydro*-1,1-*dimethyl*-3,4:5,6-*dibenzazepinium hydrogen carbonate*, had m. p. 206—207° (decomp.) (Found: C, 70·9; H, 6·65; N, 5·1; O, 17·6. $C_{17}H_{19}NO_3$ requires C, 71·6; H, 6·7; N, 4·9; O, 16·8%). Treatment of the carbonate with aqueous sodium picrate gave the *azepinium picrate*, m. p. 285—286° (from acetone or aqueous ethanol), not depressed by a sample made from the bromide (see below) (Found: C, 58·4; H, 4·4; N, 12·4. $C_{22}H_{20}N_4O_7$ requires C, 58·4; H, 4·5; N, 12·4%).

The chloroform-soluble part of the residue was not identified in this experiment; however, more of it was isolated from subsequent experiments and was shown to contain, in addition to some brown material, 2,7-dihydro-1,1-dimethyl-3,4:5,6-dibenzazepinium hydroxide and hydrogen carbonate. Chloroform was removed and the residue showed a hydroxyl band in the infrared spectrum. An aqueous solution gave, with silver nitrate, a mixed yellow and brown precipitate of silver carbonate and oxide. With potassium iodide a precipitate of the quaternary iodide, m. p. and mixed m. p. 297—303° (decomp.), was obtained and, with sodium picrate, a precipitate of the quaternary picrate, m. p. 284—285° (mixed m. p. 285—286°).

Experiment 3. The decomposition was repeated with a few minor modifications: nitrogen was used throughout instead of carbon dioxide-free air but, owing to bumping in the early stages, some air was admitted and more water was present during part of the decomposition. In this and subsequent experiments the two neutral ethereal solutions were treated separately. That from the distillate gave a purer sample (1·0 g. before distillation) of the (+)-oxide (n_D^{21} 1·5201; Fischer[23] gives n_D^{20} 1·5198), although the infrared spectrum showed that it was slightly contaminated with a compound showing hydroxyl absorption (3472 $cm.^{-1}$). The neutral ethereal solution from the residue gave a solid (0·10 g.), m. p. 98—100° (after one crystallisation from ethanol), shown by mixed m. p. and infrared spectrum to be phenanthrene.

After removal of ether from the two basic fractions, the whole of each was treated with alcoholic picric acid. Weights and recrystallisation details are given in Table 2.

[23] Fischer, *Chem. Ber.*, 1961, **94**, 893.

Experiments (a)—(d). The iodide (15·8 g.) was converted into the hydroxide *via* the chloride, and the total volume made up to 350 c.c. and divided into four lots which were decomposed under the following conditions: (*a*) the solution was slowly distilled at reduced pressure under nitrogen at 70—100° for 95 min. and finally heated at 125—130° for 15 min.; (*b*) the solution was boiled under reflux under nitrogen for 3 hr.; (*c*) potassium hydroxide (2·8 g.) was added and the solution was then treated as in (*a*); (*d*) the solution was treated as in (*a*) except that carbon dioxide was used instead of nitrogen.

In each case the smell of the methylphenyloxiran indicated that some decomposition of a "normal" type occurred. Distillate and residue fractions were treated separately [except in (*b*)]; working up as in earlier experiments gave a basic and neutral ethereal extract from each and an aqueous layer from the residue. Solvents were evaporated and the basic fractions converted into the picrates. The results are given in Table 2. 0·2 G. of the residue from the aqueous layer was in each case dissolved in water and treated with aqueous sodium picrate.

From experiment (*d*) another picrate, m. p. 140—142°, was isolated from a highly concentrated mother-liquor after removal of a trace of picrate (*A*). Analysis showed that it was *N*-methylephedrine picrate, m. p. 143·5—144° (after crystallisation from ethanol) (Found: C, 49·6; H, 5·1; N, 13·9; O, 31·7. Calc. for $C_{17}H_{20}N_4O_8$: C, 50·0; H, 4·9; N, 13·7; O, 31·3%). (Smith [24] gives m. p. 144°.)

No evidence of the presence of 2,2′-bishydroxymethylbiphenyl or 2,7-dihydro-3,4:5,6-dibenzoxepin in the ether-soluble residues was found in any of the experiments, although very small quantities of the diol, associated with larger amounts of phenanthrene, may have remained undetected. The ether-soluble residue from (*d*) showed a very intense hydroxyl band in the infrared spectrum but the substitution pattern in the 770—690 cm.$^{-1}$ region corresponded to that of a monosubstituted benzene; it seems likely that much of this residue was 1-phenylpropane-1,2-diol, formed by acid-catalysed hydration of the oxiran during the working up.

2,7-*Dihydro*-1,1-*dimethyl*-3,4:5,6-*dibenzazepinium Bromide* (VI; X = Br).—This salt, prepared from 2,2′-bisbromomethylbiphenyl and dimethylamine, had m. p. 285—287° (Wenner [2] gives 276—277°). The iodide had m. p. 294—303° (decomp.) varying with the rate of heating (Wenner [2] gives 287—288°), and the picrate had m. p. 284—286° (analysis above).

9-*Dimethylamino*-9,10-*dihydrophenanthrene*.—This base was prepared [9] by the action of phenyl-lithium on a suspension of the azepinium bromide in ether. The amine had b. p. 183°/1 mm. and gave a picrate, m. p. 176° (analysis above).

Action of Heat on 2,7-*Dihydro*-1,1-*dimethyl*-3,4:5,6-*dibenzazepinium Hydrogen Carbonate*.—Some (0·450 g. after washing with chloroform) of the water-soluble residue from experiment (*d*) was heated under reflux at 210—212° for 40 min. The resulting liquid (0·240 g., 68% for anhydrous carbonate) was 9-dimethylamino-9,10-dihydrophenanthrene (infrared spectrum and picrate, m. p. 176°). No phenanthrene was detected.

Action of Heat on 2,7-*Dihydro*-1,1-*dimethyl*-3,4:5,6-*dibenzazepinium Hydroxide* (VI; X = OH).—The azepinium bromide (4·25 g.) was shaken in aqueous solution with silver oxide for 1 hr. The filtered solution was distilled under reduced pressure, in an atmosphere of nitrogen, from a water-bath at 70—100° for 95 min. and was finally heated at 130—135° for 15 min. Ether and water were added to the residue, and ether to the distillate; the combined ethereal extracts were separated as usual into a neutral and a basic fraction. From the neutral fraction, 0·989 g. (40%) of phenanthrene, m. p. 97—99°, was obtained. The basic fraction gave 1·320 g. of a liquid, from which 2·155 g. of picrate, m. p. 163—170° with previous softening, were obtained. Crystallisation of the picrate from methanol yielded 1·185 g. of 9-dimethylamino-9,10-dihydrophenanthrene picrate, m. p. and mixed m. p. 175—176°, 0·5795 g. of 2,7-dihydro-1-methyl-3,4:5,6-dibenzazepine picrate, m. p. mainly 158—161° (slightly contaminated with the higher-melting picrate), and 0·103 g. of mixed picrates, m. p. 155—160°. Recrystallisation of the second crop from ethanol gave the picrate with m. p. 159—161°, not lowered on admixture with an authentic sample. Recrystallisation of the third crop from ethanol gave 0·055 g., m. p. 174°, softening at 155°.

In a second experiment 2·25 g. of bromide gave 0·438 g. (33%) of phenanthrene.

Action of Heat on 2,7-*Dihydro*-1,1-*dimethyl*-3,4:5,6-*dibenzazepinium Hydroxide with Added Potassium Hydroxide*.—The azepinium bromide (1·50 g.) was converted into the hydroxide, and potassium hydroxide (2·8 g.) was added. The solution was distilled as usual under reduced pressure and in an atmosphere of nitrogen. The neutral fraction (0·296 g.; 34%) was

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[24] Smith, *J.*, 1927, 2056.

phenanthrene, m. p. 100—101°. The basic fraction (0·440 g.) gave a picrate (0·852 g., 38%), m. p. 175—176°.

2,2'-Bis(trimethylammoniomethyl)biphenyl Di-iodide (XVII; X = I).—(*a*) 2,2'-Bisbromomethylbiphenyl (13·6 g.) in dry acetone (50 c.c.) was cooled to −15°. Liquid trimethylamine (25 c.c.) was added and the mixture kept (drying tube) at −15° to −10° for 3 hr., then allowed to warm to room temperature and left overnight. The quaternary *dibromide* (18 g.) was collected and crystallised from ethanol as a monohydrate, m. p. 219—221° (decomp.) (14 g., 74%) (Found: Br, 33·4. $C_{20}H_{30}Br_2N_2,H_2O$ requires Br, 33·55%). Some of the dibromide was converted (by treatment with aqueous potassium iodide) into the *di-iodide*, which crystallised from ethanol as a monohydrate, m. p. 245° (decomp.) (Found: C, 42·4; H, 5·65; I, 44·2; N, 4·9. $C_{20}H_{30}I_2N_2,H_2O$ requires C, 42·1; H, 5·65; I, 44·5; N, 4·9%). The *dipicrate* had m. p. 245° (from aqueous ethanol) (Found: C, 51·2; H, 4·5; N, 14·5. $C_{32}H_{34}N_8O_{14}$ requires C, 50·9; H, 4·5; N, 14·8%).

(*b*) 2,2'-Bis(dimethylaminomethyl)biphenyl (IV) was liberated from its dipicrate and heated with an excess of methyl iodide in nitrobenzene in a sealed tube at 100° for 5 hr. The di-iodide was collected, washed with acetone, and crystallised from ethanol: it had m. p. and mixed m. p. 245° (decomp.).

Action of Heat on 2,2'-Bis(trimethylammoniomethyl)biphenyl Dihydroxide (XVII; X = OH).—The above dibromide (9·52 g.) was converted into the dihydroxide, and the aqueous solution thereof was distilled under reduced pressure in nitrogen at 70—100° for 90 min. and finally at 125—130° for 15 min. Decomposition was accompanied by a strong smell of trimethylamine. The products were worked up as usual; a very small basic fraction (0·030 g.) and a neutral fraction (0·184 g.) were obtained from the distillate.

The basic fraction from the residue (1·476 g.) was converted into a mixture of picrates which solidified during several days. This mixture was largely intractable, crystallisation giving gums and crops melting over wide ranges, but a small quantity (0·425 g.) of 9-dimethylamino-9,10-dihydrophenanthrene picrate, m. p. 175°, mixed m. p. 175—176°, was isolated. 0·1525 G. of a new but unidentified *picrate* was also obtained. It had m. p. 240° (decomp.) (Found: C, 51·5; H, 4·7; N, 14·4; O, 29·8. $C_{20}H_{28}N_2,2C_6H_3N_3O_7$ requires C, 50·9; H, 4·5; N, 14·8; O, 29·7%).

The neutral ether-soluble fraction from the residue (1·537 g.) crystallised from ethanol and gave phenanthrene (0·335 g.), m. p. 99°, a solid (0·570 g.), m. p. 75—90° (softening at ~50°), and a liquid (0·492 g.). Both the solid and the liquid were separated (by crystallisation and chromatography on alumina) into phenanthrene and impure 2,7-dihydro-3,4:5,6-dibenzoxepin. The best sample of the oxepin had m. p. 51—67° (the pure compound [25] has m. p. 72·5—73°). Its infrared spectrum closely resembled that of the pure oxepin but still showed some phenanthrene peaks (which had decreased in intensity during the purification). One (less pure) sample had m. p. 45—55° and its analysis corresponded to a 1 : 1 mixture (Found: C, 89·4; H, 6·15; O, 4·4. Calc. for $C_{14}H_{10},C_{14}H_{12}O$: C, 89·8; H, 5·9; O, 4·3%). There was no evidence of the presence of any 2,2'-bishydroxymethylbiphenyl in any of the fractions.

The aqueous solution of the residue after ether extraction was taken down to dryness under reduced pressure in a stream of nitrogen. The residual solid (1·40 g.) gave a picrate, m. p. 245°, not depressed by the picrate of the quaternary starting material. The distillate from this operation was saturated with sodium chloride, and trimethylamine distilled off from it, collected in ethanol, and made into the picrate, m. p. 224°, isolated after evaporation of the solvent (Delépine [26] gives m. p. 216°).

Spectra.—Ultraviolet absorption spectra were measured on a Unicam S.P. 500 spectrophotometer. Infrared spectra were measured on a Grubb–Parsons GS 2A double-beam recording spectrometer.

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[25] Wittig, Davis, and Koenig, *Chem. Ber.*, 1951, **84**, 627.
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