recalled that variations of αn_a are also observed when complexation with gelatin is very unlikely (see the case of zinc tetrammine ion).

Conclusion

The present investigation suggests that the presence of gelatin affects the kinetics of electrode processes at the dropping mercury electrode. Modification of the shape of irreversible waves can be interpreted on the basis of a variation of the product αn_a (α transfer coefficient, n_a number of electrons involved in the rate-determining step). This was shown in an experiment—the reduction of zinc tetrammine ion—in which the formation of a complex with gelatin was rather improbable. Thus, the adsorption of gelatin on the electrode can be interpreted quantitatively in terms of a variation of the product αn_a. The free energy of activation is affected to a lesser extent than αn_a.

It should be emphasized that it is not implied here that binding of gelatin with the substance reacting at the electrode is to be disregarded. There is substantial proof[14] that such binding may affect the polarographic characteristics for an electrode process. Such an effect of the binding by gelatin, however, should not be regarded as responsible for the effect of gelatin in all cases.

What has been said for irreversible electrode processes involving large overvoltages can be extended to quasi-reversible electrode reactions, since the present interpretation is valid regardless of the degree of irreversibility of the reaction. The method of interpreting the wave which was used here, however, is not applicable to quasi-reversible waves. The validity of the present interpretation in the case of quasi-reversible waves is strengthened by the interesting results obtained by Wiesner[15] in the reduction of 1,2-naphthoquinone-4 sulfonate in presence of eosin. Finally, it should be added that the present conclusions can be extended to other maximum suppressors. It was indeed observed by Meites and Meites[1] that various maximum suppressors cause effects similar to those obtained in presence of gelatin.

Acknowledgment.—This work was supported (J. E. S.) by a Frederick Gardner Cottrell grant of the Research Corporation to which the authors wish to express their gratitude. The coöperation of Mr. T. J. Adams in some phases of this investigation is gladly acknowledged.

BATON ROUGE, LOUISIANA

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[14] For a bibliography, see ref. 1.

[15] K. Wiesner, *Collection Czechoslov. Chem. Communs.*, **12**, 594 (1947).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY, GLASGOW]

Aromatic Hydrocarbons. LXIII. Resonance Restriction and the Absorption Spectra of Aromatic Hydrocarbons[1]

BY E. CLAR AND D. G. STEWART

RECEIVED NOVEMBER 27, 1951

A systematic study has shown that in uniplanar aromatic hydrocarbons the ratio of the frequencies of the α- and β-bands is constant $\nu\alpha:\nu\beta = 1:1.35$. In the case of hydrocarbons with a high degree of overlapping of hydrogen atoms, the loss of resonance energy in the strained molecule becomes apparent by a decrease in this ratio.

The absorption bands of aromatic hydrocarbons have been classified into α-, β- and para-bands.[2]

(1) para-Bands are those which shift most strongly to the red with linear annulation, *i.e.*, fusion of benzene rings. They are, for example, the long wave bands in anthracene and the higher acenes, and the second group of bands in benzene and naphthalene. They shift to the red with falling temperature. The red shift, in going from the gaseous state to the solution in alcohol or hexane, amounts to -900 cm.$^{-1}$. (2) α-Bands, which are less intense, shift to the red on linear and angular annulation in the acene and phene series and are hidden, or partly hidden, by the more intense *p*-bands in the higher acenes, beginning with anthracene. These bands shift very little to the violet with falling temperature. The red shift, in going from the gaseous state to the solution in alcohol or hexane, amounts to -250 cm.$^{-1}$. The α-bands form the first group in the absorption spectra of benzene, naphthalene, phenanthrene and the higher phenes. (3) β-Bands, which are the most intense, show the same annulation effect as the α-bands and lie more in the ultraviolet. They shift considerably to the red with falling temperature. The difference between the gaseous state and the solution in alcohol or hexane amounts to -900 cm.$^{-1}$.

A systematic study has shown that in uniplanar aromatic hydrocarbons, the ratio of the frequencies of the α- and β-bands is constant: 1:1.35. This rule only applies if the hydrocarbons are uniplanar and there is no overlapping of H atoms, *e.g.*, in anthracene and pyrene. In diphenyl and in phenanthrene there is some degree of overlapping, but the loss of resonance energy in these cases is too small to be detected by the ratio $\nu\alpha:\nu\beta$. In these and similar cases low temperature absorption spectrography indicates deformation of the molecules.[3]

Owing to greatly increased overlapping (marked with X), a much higher degree of twisting, or another type of strain, can be assumed in 3,4-benzphenanthrene than in chrysene, Fig. 1) and the resulting loss of resonance energy becomes apparent in the ratio $\nu\alpha:\nu\beta$ which decreases to 1:1.324. In

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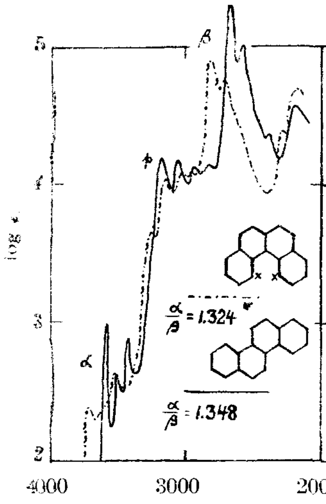
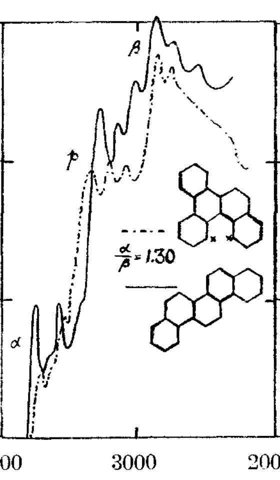
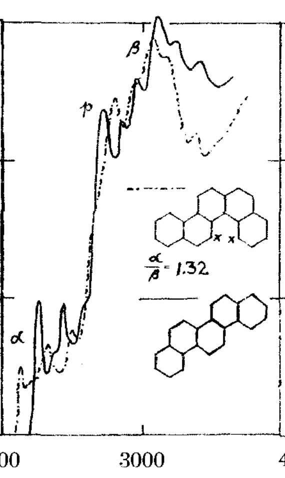
[1] Presented at the Diamond Jubilee of the American Chemical Society in New York, 1951.

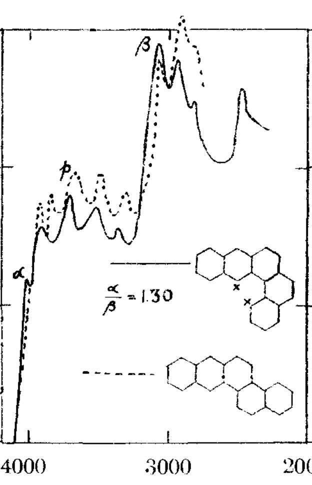
[2] E. Clar, *J. Chem. Phys.*, **17**, 741 (1949); *Chem. Ber.*, **82**, 495 (1949); *Spectrochim. Acta*, **4**, 116 (1950).

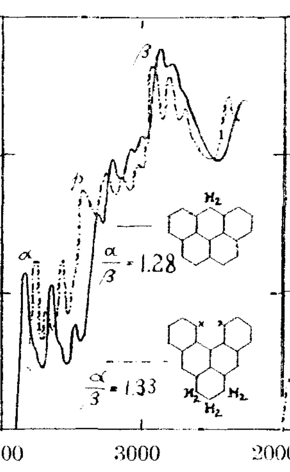
[3] E. Clar, *ibid.*, **4**, 116 (1951).











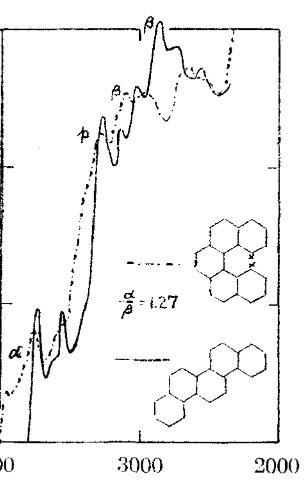


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Fig. 1. Fig. 2. Fig. 3. Fig. 4. Fig. 5. Fig. 6.

Fig. 1.—Absorption spectrum of 3,4-benzphenanthrene (-.-.-.-) in ethanol. Band maxima in Å. with log ε in parentheses: α 3720 (2.38), 3530 (2.64); *p*, 3255 (3.68), 3150 (4.06), 3030 (4.07), 2950 (4.08); β 2810 (4.90), 2720 (4.76); 2290 (4.36); β' 2180 (4.70). Absorption spectrum of chrysene (———) in ethanol. Band maxima in Å. with log ε in parentheses: α 3600 (3.00), 3510 (2.62), 3435 (2.88); *p*, 3190 (4.20), 3060 (4.18), 2950 (4.14), 2830 (4.14); β 2670 (5.14), 2590 (5.00); 2410 (4.36); β' 2200 (4.56).

Fig. 2.—Absorption spectrum of 1,2-benzchrysene (-.-.-.-) in ethanol. Band maxima in Å. with log ε in parentheses: α 3710 (2.47), 3520 (3.85); *p*, 3340 (3.94), 3210 (3.99), 3080 (3.96); β 2860 (4.78), 2765 (4.76). Absorption spectrum of picene in chloroform (———). Band maxima in Å. with log ε in brackets: α 3760 (2.98), 3640 (2.60), 3575 (3.95); *p*, 3285 (4.36), 3140 (4.28), 3030 (4.56); β 2865 (5.04), 2750 (4.86), 2575 (4.70).

Fig. 3.—Absorption spectrum of 5,6-benzchrysene (-.-.-.-) in ethanol. Band maxima in Å. with log ε in parentheses: α 3860 (2.50), 3670 (2.66), 3490 (2.78); *p*, 3205 (4.46), 3060 (4.60); β 2925 (4.90), 2810 (4.76); 2610 (4.20). Absorption spectrum of picene in chloroform (———).

Fig. 4.—Absorption spectrum of 1,2-benztetraphene (———) in ethanol. Band maxima in Å. with log ε in parentheses: α 4010 (3.08), 3910 (3.56); *p*, 3720 (3.80), 3540 (3.70), 3380 (3.54); β 3080 (4.88), 2950 (3.76), 2840 (4.48); β' 2480 (4.56). Absorption spectrum of 3,4-benztetraphene (- - - -) in benzene. Band maxima in Å. with log ε in parentheses: α 3930 (3.76), 3850 (3.80); *p*, 3670 (3.96), 3490 (3.96), 3310 (3.82); 3070 (4.80); β 2910 (5.10).

Fig. 5.—Absorption spectrum of 4',5-methylene-3,4-benzphenanthrene in ethanol (———). Band maxima in Å. with log ε in parentheses: α 3750 (3.22), 3690 (2.85), 3565 (3.22); *p*, 3410 (3.76), 3260 (3.87), 3120 (3.83), 3020 (3.93); β 2910 (4.64), 2800 (4.56), 2700 (4.34); β' 2360 (4.40). Absorption spectrum of 1,10-trimethylene-3,4-benzphenanthrene in ethanol (-.-.-.-). Band maxima in Å. with log ε in parentheses: α 3830 (3.13), 3640 (3.06), 3470 (2.76); *p*, 3320 (3.57), 3210 (3.96), 3080 (4.04), 3010 (4.13); β 2870 (4.75), 3780 (4.66).

Fig. 6.—Absorption spectrum of 3,4;5,6-dibenzphenanthrene (-.-.-.) in ethanol. Band maxima in Å. with log ε in parentheses: α 3950 (2.38), 3760 (2.80); *p*, 3290 (4.26); β 3100 (4.54), 3000 (4.52); β' 2670 (4.70). Absorption spectrum of picene in chloroform (———).

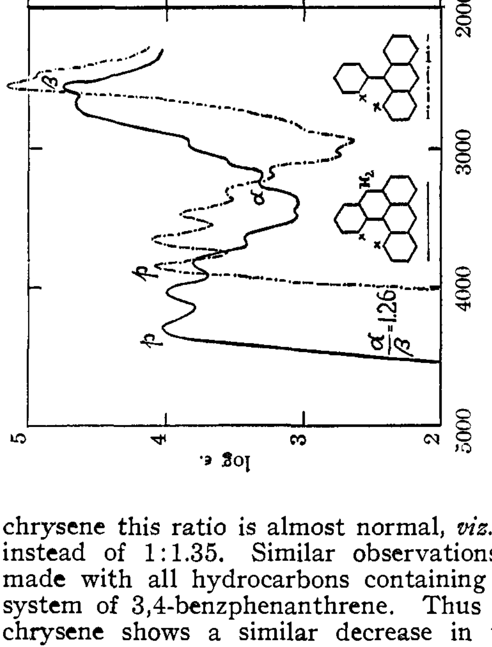

Fig. 7.

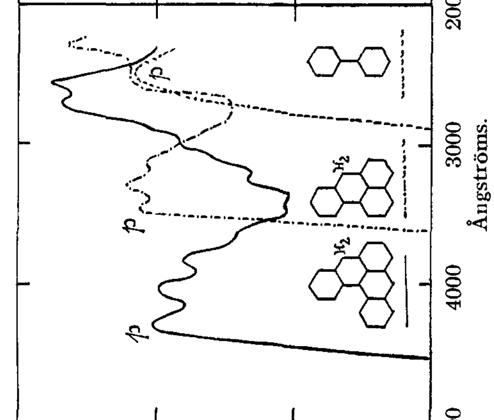

Fig. 8.

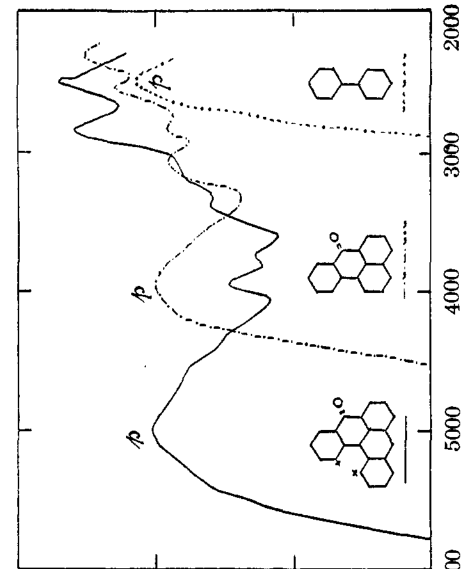

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Fig. 9.

Fig. 7.—Absorption spectrum of coeranthrene in alcohol (———). Band maxima in Å. with log ε in bracket: *p*, 4280 (4.02), 4040 (3.98), 3830 (3.80), 3650 (3.43); α 3240 (3.34), 2990 (3.84); β 2690 (4.66), 2570 (4.74). Absorption spectrum of 9-phenylanthracene in alcohol (-.-.-.). Band maxima in Å. with log ε in parentheses: *p*, 3840 (4.08), 3645 (4.10), 3465 (3.90), 3305 (3.56), 3160 (3.24), 3020 (2.75); β 2555 (5.16).

Fig. 8.—Annulation in the diphenyl series. Absorption spectrum of diphenyl in alcohol (- - - - -). Band maxima at 2500 Å., log ε 4.24. Absorption spectrum of benzanthrene in alcohol (-·-·-·-·). Band maxima in Å. with log ε in parentheses: *p*, 3440 (4.13), 3290 (4.22), 3120 (4.08); β 2500 (4.20); β′ 2280 (4.64). Absorption spectrum of coeranthrene in alcohol (———).

Fig. 9.—Annulation effect in the diphenyl series. Absorption spectrum of diphenyl in alcohol (– – – – –). Absorption spectrum of benzanthrone in alcohol (-·-·-·-·). Band maxima in Å. with log ε in parentheses: *p*, 3950 (4.01); α 3060 (3.90), 3830 (3.90); β 2530 (4.30), β 2300 (4.52). Absorption spectrum of coeranthrone in alcohol (———). Band maxima in Å. with log ε in parentheses: *p*, 4970 (4.01); α 3930 (3.48), 3740 (3.28); α′ 3280 (3.60), 3140 (3.80); β 2840 (4.58); β′ 2500 (4.70).

chrysene this ratio is almost normal, *viz.*, 1:1.348 instead of 1:1.35. Similar observations can be made with all hydrocarbons containing the ring system of 3,4-benzphenanthrene. Thus 1,2-benzchrysene shows a similar decrease in the ratio $\nu\alpha:\nu\beta$ to 1:1.30. Compared with the spectrum of picene, a considerable loss of intensity and vibrational structure of the α- and β-bands is observed in 1,2-benzchrysene (Fig. 2). The same feature is apparent in the comparison of 5,6-benzchrysene with picene (Fig. 3). The ratio $\nu\alpha:\nu\beta$ amounts to 1:1.32 in 5,6-benzchrysene. Since picene has 3 positions with the same degree of overlapping of H atoms as has phenanthrene, an appreciable degree of strain in the molecule distributed over three regions would be expected. The ratio $\nu\alpha:\nu\beta$ is in fact 1:1.32 with chloroform as solvent.[4] Since picene is almost insoluble in alcohol and the β-bands shift more than the α-bands when chloroform is used, this ratio is too low for an exact comparison with the hydrocarbons in Figs. 2, 3 and 6.

The absorption spectrum of 1,2-benztetraphene is shown in Fig. 4 compared with that of 3,4-benztetraphene. The former contains the ring system of 3,4-benzphenanthrene and in accordance with expectation the ratio $\nu\alpha:\nu\beta$ falls to 1:1.30.

An interesting comparison of the spectra of 4′,5-methylene-3,4-benzphenanthrene and 1,10-trimethylene-3,4-benzphenanthrene (dihydrocoeranthrene) is shown in Fig. 5. A considerable difference in the low ratios $\nu\alpha:\nu\beta$ is observed.

There is a much higher degree of overlapping of H atoms in 3,4,5,6-dibenzphenanthrene than in 3,4-benzphenanthrene and the ratio $\nu\alpha:\nu\beta$ decreases accordingly to 1:1.27 (Fig. 6). The loss of intensity and vibrational structure when compared with picene is striking.

It is known that in *meso*-phenylanthracenes the phenyl rings are perpendicular to the plane of the anthracene radical, owing to overlapping of H atoms in the positions marked with X. In the hitherto unknown coeranthrene, which we have now prepared, the methylene group tends to restore uniplanarity. Therefore the *p*-bands shift strongly to the red (Fig. 7) and show the annulation effect in the series diphenyl, benzanthrene and coeranthrene (Fig. 8). The wave length of the first bands (2500, 3440 and 4280 A., resp.) are approximately proportional to 6^2, 7^2, 8^2, as required by the annulation principle.[5] Since coeranthrene like perylene has 20 π-electrons its first *p*-band (4280 Å.) should be at the same wave length as the first *p*-band of perylene (4340 Å.) which fits better into the annulation series. The reason for the divergence is probably that coeranthrene is not completely uniplanar, an assumption which is supported by the fact that the ratio $\nu\alpha:\nu\beta$ = 1:1.26, a rather low value.

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(4) Mayneord and Roe, *Proc. Roy. Soc.* (*London*), **A152**, 319 (1935).

(5) E. Clar, *Ber.*, **69**, 607 (1936); **82**, 495 (1949).

Another annulation series is given in Fig. 9. Here the methylene group in the former series is substituted by the carbonyl group. The π-electrons in the latter contribute to the aromatic resonance system so that an additional red shift equivalent to half a benzene ring is produced. The wave lengths of the first *p*-bands of diphenyl (2500 Å.), benzanthrone (3950 Å.) and coeranthrone (4970 Å.) are thus proportional to 6^2, $(7\frac{1}{2})^2$ and $(8\frac{1}{2})^2$. Only small distortion of the molecular plane in coeranthrone could be deduced from the deviation of the annulation principle.

Experimental

9-(*o*-Carboxyphenyl)-anthracene.—This was prepared from benzophenone-2,2'-dicarboxylic acid dilactone (20 g.) following the synthesis of Scholl and Donat.[6] Crystallization from acetic acid gave 6 g. of yellow needles, m.p. 241–242° (lit. m.p. 242–243.5°).

Coeranthrone.—The procedure followed was a modification of that used by Bradsher and Vingiello.[7] 9-(*o*-Carboxyphenyl)-anthracene (6 g.) in 100% orthophosphoric acid (250 cc.) was heated at 200° for two hours, and a dark green solution obtained, which, after cooling was poured into water. The red precipitate, after thorough extraction with hot dilute ammonium hydroxide solution, was sublimed and recrystallized from acetic acid to give 4.5 g. (80%) of dark red needles, m.p. 175–176° (lit. m.p. 178–179°).

Coeranthrene.—Coeranthrone (3 g.) and zinc dust (15 g.) were added to a 10% sodium hydroxide solution (100 cc.) covered with a layer of octyl alcohol (15 cc.). After refluxing for six hours, the octyl alcohol was distilled off, and the hot solution filtered into concentrated hydrochloric acid. The precipitate was collected, washed with hot water and dried in a vacuum. The powdered product was decomposed by heating in a vacuum (0.5 mm.) and the orange-red sublimate obtained was dissolved in benzene and chromatographed (alumina). On developing the chromatogram with a benzene–petroleum ether (b.p. 40–60°) mixture, a clear yellow eluate with a blue fluorescence was obtained, which after concentration and cooling yielded large orange-yellow plates (1 g.), m.p. 138–139°. Coeranthrene dissolved readily in concentrated sulfuric acid to give a yellow solution which rapidly changed to green on standing.

Anal. Calcd. for $C_{21}H_{14}$: C, 94.70; H, 5.30. Found: C, 94.66; H, 5.23.

1,10-Trimethylene-3,4-benzphenanthrene.—The coeranthrone (0.75 g.), red phosphorus (1 g.) and 55% hydroiodic acid (10 cc.) were covered with xylene (10 cc.) and after refluxing for 48 hours, the mixture was diluted with water and filtered, the excess phosphorus being well washed with hot xylene. The xylene layer after drying and concentration was passed through a chromatographic column (alumina), a benzene–petroleum ether (b.p. 40–60°) mixture being used as eluant. A colorless, violet-blue fluorescent eluate was obtained, which on concentration and cooling gave long flat colorless prisms (0.5 g.), m.p. 116–117°, which did not dissolve readily in concentrated sulfuric acid. On warming however a green solution was obtained.

Anal. Calcd. for $C_{21}H_{16}$: C, 93.99; H, 6.01. Found: C, 94.08; H, 6.13.

Acknowledgment.—The authors wish to thank Prof. J. W. Cook, F.R.S., for a sample of 3,4,5,6-dibenzphenanthrene, and Dr. C. L. Hewett for samples for 1,2-benzchrysene, 5,6-benzchrysene and 1,2-benztetraphene.

GLASGOW, SCOTLAND

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[6] Scholl and Donat, *Ann.*, **512**, 1 (1934).

[7] Bradsher and Vingiello, *J. Org. Chem.*, **13**, 786 (1948).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Preparation, Reactions and Kinetics of Reactions of Epicholesteryl *p*-Toluenesulfonate[1]

BY L. CARROLL KING AND M. JEROME BIGELOW

RECEIVED JULY 11, 1952

Epicholesteryl *p*-toluenesulfonate was prepared and its reactions with pyridine, piperidine, methanol and ethanol were studied. Kinetic studies were made of the solvolysis of epicholesteryl *p*-toluenesulfonate in ethanol and in methanol.

Epicholesterol (I) was prepared from cholesterol in over-all yield of 37%. Cholesterol was converted to 3-β-5-α-cholestandiol (II) by a modification of the method of King and Campbell.[2] Compound II was then converted to I by a modification of the procedure of Plattner and Lang.[3] Epicholesteryl *p*-toluenesulfonate (III) was then prepared from I. A description of these preparations, and evidence as to identity and homogeneity of products is given in the Experimental part of this paper.

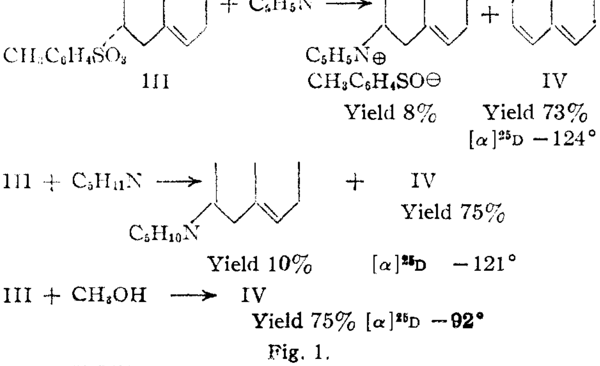

Fig. 1.

Epicholesteryl *p*-toluenesulfonate (III) reacted with pyridine to give cholestadiene (IV) in 80% yield and 6–10% of 3-β-cholesterylpyridinium *p*-toluenesulfonate.[4] With piperidine III gave a 75% yield of IV and 10% of 3-β-cholesterylpiperidine (VI).[4] When III was allowed to react with methanol or ethanol, or with ethanol containing ethoxide ion, a 75% yield of a cholestadiene was obtained. These reactions are summarized in the diagram.

Details for preparation, separation and identification are given in the Experimental part.

A kinetic study was made of the solvolysis of III

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[1] Paper No. 22, Organic Division American Chemical Society, Chicago Meeting, 1950.

[2] L. C. King and J. A. Campbell, THIS JOURNAL, **71**, 3556 (1949).

[3] P. A. Plattner and W. Lang, *Helv. Chim. Acta*, **27**, 1872 (1944); P. A. Plattner, T. Petrzilka and W. Lang, *ibid.*, **27**, 518 (1944).

[4] The 3-β-structure for this compound is discussed in a recent paper; L. C. King and M. J. Bigelow, THIS JOURNAL, **74**, 3338 (1952).