NOTES.

357. *Preparation of* 1-(*Halogenophenyl*)*propynes.*

By D. HAMER and W. R. MAGEE.

FIVE new 1-(halogenophenyl)propynes have been prepared by treatment of the corresponding cinnamic acid dibromides with alcoholic potassium hydroxide [1] (*ca.* 5% yield), or by acid treatment [2] of the β-bromocinnamic acid (*ca.* 10% yield). The cinnamic acids and their dibromides were obtained in yields of 65 and 45%, respectively.

Experimental.—*4-Bromo-α-methylcinnamic acid.*[3] *p*-Bromobenzaldehyde (19·4 g.), fused sodium propionate (9 g.), and propionic anhydride (45 ml.) were refluxed at 170° for 8 hr., and the mixture was digested with sodium carbonate solution at 80° for 1 hr. After cooling and washing with ether, the aqueous extract was acidified with concentrated hydrochloric acid, and the precipitate was filtered off, m. p. 173—174° (from ethanol).

4-Bromo-α-methylcinnamic acid dibromide [*αβ-Dibromo-β-(p-bromophenyl)-α-methylpropionic acid*]. 4-Bromo-α-methylcinnamic acid (10 g.) was exposed to bromine vapour (7·2 g.) in an enclosed glass vessel for 2 weeks. The acid, which was finely divided, was turned over from time to time. The material was then triturated with light petroleum (b. p. 60—80°), and filtered. The *dibromide* was obtained as a white powder, m. p. 162° (from aqueous alcohol) (Found: C, 30·1; H, 1·9; Br, 59·8. $C_{10}H_8Br_3O_2$ requires C, 29·9; H, 2·2; Br, 59·8%).

Bromination in carbon tetrachloride. 4-Bromo-α-methylcinnamic acid (4 g.) was dissolved in carbon tetrachloride (250 ml.), and the solution heated to boiling. Bromine (2·6 g.) in carbon tetrachloride (10 ml.) was added during 2 hr. Hydrogen bromide fumes were evolved during the addition. On cooling, white crystals separated out, m. p. 183° (from carbon tetrachloride) (Found: C, 37·2; H, 2·6; Br, 49·8. $C_{10}H_8Br_2O_2$ requires C, 37·4; H, 2·5; Br, 50·0%). It was therefore apparent that bromination in solution was unsatisfactory compared with bromination of the solid. In solution, hydrogen bromide is eliminated, giving products of the type, $Br{\cdot}C_6H_4{\cdot}C(Br){:}C(Me)CO_2H$.

1-(p-Bromophenyl)prop-1-yne. The dibromide of 4-bromo-α-methylcinnamic acid (26·9 g.) was added slowly to alcoholic potassium hydroxide solution (100 ml.; 50% w/v). After the initial reaction had subsided, the contents were refluxed for 3 hr. Some of the alcohol (70 ml.) was removed by distillation, water (60 ml.) was added to the residue, and the mixture was steam-distilled. The distillate was extracted with ether, and yielded a yellow oil, b. p. 64°/0·5 mm. (Found: C, 55·9; H, 3·9; Br, 40·2. C_9H_7Br requires C, 55·5; H, 3·6; Br, 41·0%), $\lambda_{max.}$ 247 and 258 mμ.

[1] Bogert and Davidson, *J. Amer. Chem. Soc.*, 1932, **54**, 334; Otto, *ibid.*, 1934, **56**, 1393.
[2] Schenkel and Schenkel-Rudin, *Helv. Chim. Acta*, 1948, **31**, 514.
[3] Sudborough and Thompson, *J.*, 1903, **83**, 666.

Substituted cinnamic acids. The following cinnamic acids were prepared by methods similar to that described above for 4-bromo-α-methylcinnamic acid. 2-Bromo-α-methyl- (Found: C, 49·6; H, 3·8; Br, 33·1. Calc. for $C_{10}H_9BrO_2$: C, 49·7; H, 3·8; Br, 33·2%), m. p. 90°. 3-*Bromo-α-methyl-* (Found: C, 49·4; H, 3·8. $C_{10}H_9BrO_2$ requires C, 49·7; H, 3·8%), m. p. 107°. 4-*Chloro-α-methyl-* (Found: C, 61·1; H, 4·6; Cl, 17·8. $C_{10}H_9ClO_2$ requires C, 61·1; H, 4·6; Cl, 18·2%), m. p. 159°. 2-*Chloro-α-methyl-* (Found: C, 61·6; H, 4·7; Cl, 18·3%), m. p. 111°. 3-*Chloro-α-methyl-* (Found: C, 61·6; H, 4·5%), m. p. 109—110°.

Dibromides of α-methylcinnamic acids. These were prepared by exposing the acids to bromine vapour. 2-*Bromo-* (Found: C, 30·8; H, 2·0; Br, 59·0. $C_{10}H_9Br_3O_2$ requires C, 29·9; H, 2·3; Br, 59·8%), m. p. 174—175°. 3-*Bromo-* (Found: C, 31·0; H, 2·5; Br, 59·6%), m. p. 175°. 4-*Chloro-* (Found: C, 33·5; H, 2·5. $C_{10}H_9Br_2ClO_2$ requires C, 33·7; H, 2·5%), m. p. 174°. 2-*Chloro-* (Found: C, 34·1; H, 2·3%), m. p. 198°. 3-*Chloro-* (Found: C, 34·0; H, 2·5%), m. p. 176°.

1-(*Halogenophenyl*)*propynes.* The following were prepared by the method described above for 1-(*p*-bromophenyl)prop-1-yne. o-*Bromo-* (Found: C, 54·4; H, 3·6; Br, 42·0. C_9H_7Br requires C, 55·5; H, 3·6; Br, 41·0%), b. p. 131°/20 mm., $\lambda_{max.}$ 244 and 255 mμ. *m*-Bromo-, all attempts to prepare this compound were unsuccessful. p-*Chloro-* (Found: C, 71·3; H, 4·9; Cl, 22·8. C_9H_7Cl requires C, 71·7; H, 4·6; Cl, 23·6%), b. p. 125°/25 mm., $\lambda_{max.}$ 246 and 256 mμ. o-*Chloro-* (Found: C, 71·9; H, 4·4; Cl, 23·1%), b. p. 233°, $\lambda_{max.}$ 242 and 253 mμ. m-*Chloro-* (Found: C, 71·7; H, 6·8; Cl, 14·0%), indicating that decomposition had taken place. In the case of this preparation an alternative method tried was decarboxylation in acid solution. After heating the dibromide in alcoholic potassium hydroxide to remove the first molecule of hydrogen bromide, acidification of the mixture yielded an acid (Equiv., 275) which was refluxed with acetic acid–2N-sulphuric acid (10 : 1, v/v). The mixture was then poured into excess of alcoholic potassium hydroxide, and the acetylene extracted in the usual way (Found: C, 71·1; H, 5·0; Cl, 24·0%), b. p. 118°/25 mm., $\lambda_{max.}$ 240 and 251 mμ.

College of Technology, Belfast 1, Northern Ireland. [*Received, January 3rd*, 1963.]

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358. *Determination of Vapour-phase Dimerization Constants from Pressure–Temperature Data.*

By Sherril D. Christian, Harold E. Affsprung, and Chii Lin.

Measurements of vapour density, pressure, and temperature are frequently used to determine association constants; however, in most vapour density experiments the relative error in the measured density is considerably greater than the relative errors in temperature and pressure. We have devised a scheme for the calculation of dimerization constants and enthalpies of dimerization from measurement of the variation of the pressure, p, with absolute temperature, T, for a given volume of gas. Density measurements are not required. The technique is illustrated with data for acetic acid, obtained using a vapour density apparatus described previously.[1]

For species which dimerize, but undergo no higher polymerization, the equilibrium constant for the dimerization reaction may be written:

$$K = A \exp(-\Delta H/RT) = (\bar{M} - M_m)M_m/(2M_m - \bar{M})^2 p, \quad (1)$$

where A is related to the entropy of dimerization, ΔH is the enthalpy of dimerization, $\bar{M}$ is the average molecular weight of the vapour, and M_m is the molecular weight of the monomer of the associating species. It is assumed that ΔH and A are constant over a range of temperatures, and that the monomeric and dimeric species individually obey the ideal-gas law. If vapour density is constant, $\bar{M}$ may be replaced by aT/p, where a is a

[1] Christian, Affsprung, and Lin, *J. Chem. Educ.*, 1963, **40**, 323.

constant of proportionality. Upon making this substitution and multiplying by T, equation (1) becomes:

$$AT \exp(-\Delta H/\boldsymbol{R}T) = \frac{(aT/p - M_m)(T/p)M_m}{(2M_m - aT/p)^2} = \frac{(ax - M_m)xM_m}{(2M_m - ax)^2}, \quad (2)$$

where x is defined as T/p, and both T and x are measurable quantities.

Taking logarithms of both sides of equation (2) and differentiating with respect to $1/T$, one obtains:

$$-(\Delta H/\boldsymbol{R} + T) = \frac{(3ax/M_m - 2)}{(ax/M_m - 1)(2 - ax/M_m)} \cdot \frac{\mathrm{d} \ln x}{\mathrm{d}(1/T)}. \quad (3)$$

Note that $\Delta H/\boldsymbol{R} + T$ is virtually constant over a considerable range of temperatures, provided that $\Delta H/\boldsymbol{R} \gg T$. (In the case of acetic acid vapours, $\Delta H/\boldsymbol{R}T \sim 25$.)

In equation (3), values of $\mathrm{d} \ln x/\mathrm{d}(1/T)$ are directly determinable from p against T measurements, and the function,

$$\frac{(3ax/M_m - 2)}{(ax/M_m - 1)(2 - ax/M_m)} = \mathrm{f}(ax/M_m),$$

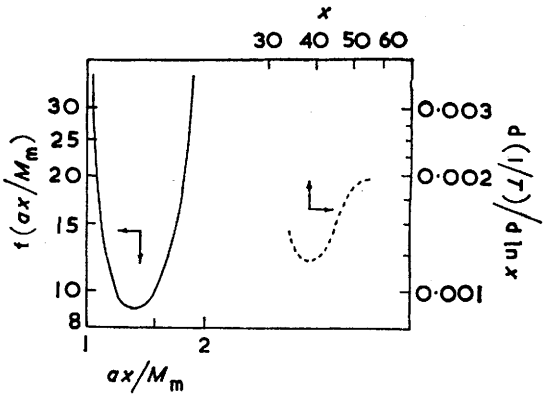
depends on the parameter ax/M_m. Plots of $\mathrm{f}(ax/M_m)$ against ax/M_m, and of $\mathrm{d}(1/T)/\mathrm{d} \ln x$ against x can be constructed on the same log-log graph, and, if $\Delta H/\boldsymbol{R} + T$ is constant, equation (3) requires that the two curves be identical in shape but translated with respect to each other. The displacement of the abscissae should be equal to $\log (a/M_m)$, and the displacement of the ordinates should be $\log (-\Delta H/\boldsymbol{R} - T)$. Thus, both a and ΔH can be determined by translation of one of the curves so that it coincides as nearly as possible with the other.

The method of curve-fitting is illustrated with the aid of the Figure. A standard curve of $\mathrm{f}(ax/M_m)$ against ax/M_m (on a log-log scale) is plotted as the solid line. Values of $\mathrm{d}(1/T)/\mathrm{d} \ln x$ (determined from a least-squares quartic fit of $\ln x$ against $1/T$ data) are plotted against x on the same graph, for acetic acid vapours, at pressures and temperatures ranging from about 5 mm. at 15° to 9 mm. at 85°. The values of the parameters determined by translation of the $\mathrm{d}(1/T)/\mathrm{d} \ln x$ curve to force it to fit as nearly as possible the standard $\mathrm{f}(ax/M_m)$ curve are: $a = 2{\cdot}06$ mm. g. °K^{-1} mole^{-1} and $-\Delta H = 15{\cdot}6$ kcal./mole. From these values, the constants in equation (1) can be evaluated. The following expression may thereby be obtained for the equilibrium constant: $\log_{10}K$ (mm.$^{-1}$) $= -11{\cdot}14 + 3410/T$. This result may be compared to the value of $-11{\cdot}789 + 3590/T$, obtained by MacDougall [2] (for temperatures and pressures ranging from 25 to 40° and 3 to 23 mm.), and to $-10{\cdot}931 + 3347/T$, reported by Taylor [3] (for temperatures and pressures ranging from 50 to 150° and 13 to 34 mm.). At 300°K our result leads to $K = 1{\cdot}70$ mm.$^{-1}$, compared with values of 1·51 and 1·71 mm.$^{-1}$ calculated from the data of MacDougall and Taylor, respectively.

It is somewhat difficult to relate errors in the measured P and T values to errors in the calculated values of ΔH and K. For the run indicated in the Figure, the average deviation of p values from values calculated using the least-squares quartic equation is 0·07 mm. From a comparison of slopes obtained graphically with those obtained by differentiation of cubic and quartic power series expressions representing the data, we estimate that, except for points near the extremities of the range of x, the approximate error in $\mathrm{d}(1/T)/\mathrm{d} \ln x$ is everywhere less than 5×10^{-5} °K^{-1}. This corresponds to a maximum uncertainty in ΔH of about 0·7 kcal. Judging from the reproducibility of values of ΔH and a obtained from repeated attempts to bring the theoretical and experimental curves

[2] MacDougall, *J. Amer. Chem. Soc.*, 1936, **58**, 2585.
[3] Taylor, *J. Amer. Chem. Soc.*, 1951, **73**, 315.

into coincidence, the curve-matching process appears to introduce an uncertainty in K at 300°K of less than 0·1 mm.$^{-1}$. The tailing off of the computed curve at large values of x



Standard $f(ax/M_m)$ against ax/M_m curve, and $d(1/T)/d \ln x$ against x curve, for acetic acid vapours.

(see Figure) is an artifact of the method of curve-fitting, and causes little difficulty in locating the position of the minimum of the derivative curve.

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DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF OKLAHOMA,
NORMAN, OKLAHOMA, U.S.A. [*Received, June 17th,* 1963.]

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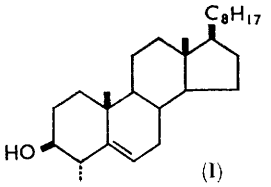
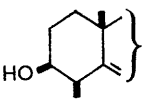
359. *The Preparation of 4α- and 4β-Methylcholest-5-en-3β-ol.*

By A. D. TAIT.

JULIA AND LAVAUX [1] have reported the synthesis of 4α- and 4β-methylcholest-5-en-3β-ols (I and II) by multistage processes. They also describe an attempted synthesis by sodium borohydride reduction of 4-methylcholesta-3,5-dien-3-yl acetate, the only product described being 4-methylcholesta-3,5-diene. We have found that this reduction gives three sterols as well as the hydrocarbon.



(I)



(II)

Methylation of cholest-4-en-3-one as described by Atwater [2] gave 4,4-dimethylcholest-5-en-3-one [3,4] (17%), 4-methylcholest-4-en-3-one [3] (51%), and unchanged material. The monomethyl compound, on acetylation, gave 4-methylcholesta-3,5-dien-3-yl acetate.[1a,2]

Reduction of this acetate with sodium borohydride, treatment of the product with ethanolic hydrochloric acid, and precipitation with digitonin gave material, found by thin-layer chromatography to have two components. Chromatography on alumina gave a partial separation and by analogy with the 4-methylcholestanones,[5] the less readily eluted

[1] (*a*) Julia and Lavaux, *Compt. rend.*, 1960, **251**, 733; (*b*) Julia, Lavaux, Moutonnier, and Decouvelaere, *Bull. Soc. chim. France*, 1961, 1997; (*c*) Julia and Lavaux, *Compt. rend.*, 1962, **254**, 3702.
[2] Atwater, *J. Amer. Chem. Soc.*, 1960, **82**, 2847.
[3] Sondheimer and Mazur, *J. Amer. Chem. Soc.*, 1957, **79**, 2906.
[4] Woodward, Patchett, Barton, Ives, and Kelly, *J. Amer. Chem. Soc.*, 1954, **76**, 2852.
[5] Beton, Halsall, Jones, and Philips, *J.*, 1957, 753.

isomer was designated as the 4β(*ax*)-methyl and the more readily eluted as the 4α(*eq*)-methyl compound. The first fractions eluted were acetylated and, on fractional crystallisation, 4α-methylcholest-5-en-3β-yl acetate was concentrated in the mother-liquor; hydrolysis gave the sterol. The less readily eluted material, similarly treated, gave 4β-methylcholest-5-en-3β-yl acetate.

Chromatography of the material which was not precipitated by digitonin gave 4-methylcholesta-3,5-diene, 4-methylcholesta-3,5-dien-3-yl acetate, 4-methylcholest-4-en-3-one, material believed to be 4α-methylcholest-5-en-3α-ol [the designation of the methyl group as "α" is based on this being the more stable (equatorial) conformation], and 4β-methylcholest-5-en-3β-ol. Comparison, by infrared spectra and mixed melting points, of 4α- and 4β-methylcholest-5-en-3β-ols and their acetates with samples provided by Dr. S. Julia substantiated the assigned structures.

There appears to be some selectivity between the 4α- and 4β-methylcholest-5-en-3β-ols in digitonide formation since the 4α-methyl-3β-ol was completely precipitated while the 4β-methyl-3β-ol was only partially precipitated.

Experimental.—Melting points were determined on a Kofler hot-stage apparatus. Optical rotations were determined for chloroform solutions at room temperature and ultraviolet spectra for ethanol solutions. Light petroleum had b. p. 40—60°.

4-*Methylcholesta*-3,5-*dien*-3-*yl acetate.* A mixture of 4-methylcholest-4-en-3-one (III) (470 mg.), acetic anhydride (1 ml.), and acetyl chloride (1 ml.) was heated on a steam-bath (nitrogen atmosphere) for 1·5 hr. Evaporation of the solution to dryness under reduced pressure and crystallisation (from chloroform–methanol and then ethanol), gave the pure enol-acetate,[1a,2] m. p. 111—114°, $[\alpha]_D$ −100° (*c* 0·60), $\lambda_{max.}$ 236 mμ (ε 20,100), $\lambda_{infl.}$ 230 and 243 mμ (ε 19,000 and 16,000); $\nu_{max.}$ (in Nujol) 1760, 1670, 1630, 1220, and 1095 cm.$^{-1}$ (Found: C, 81·5; H, 10·9. Calc. for $C_{30}H_{48}O_2$: C, 81·8; H, 11·0%).

Sodium borohydride reduction of 4-*methylcholesta*-3,5-*dien*-3-*yl acetate.* 4-Methylcholesta-3,5-dien-3-yl acetate (980 mg.) was dissolved in a mixture of ether (90 ml.) and methanol (160 ml.), and a solution of sodium borohydride (1·6 g.) in water (15 ml.) and methanol (50 ml.) was added in one portion. The mixture was stored at 5° in darkness for 10 hr. and then diluted with water and extracted with ether. The ethereal solution was washed with water, dried (Na_2SO_4), and evaporated to give a solid (948 mg.). This was dissolved in ethanol (60 ml.) containing concentrated hydrochloric acid (8 drops), and the solution was refluxed for 2 hr., then evaporated to dryness. The residue [$\lambda_{max.}$ 235 mμ ($E^{1\%}$ 180)] was dissolved in 90% ethanol (130 ml.), and a solution of dignitonin (3 g.) in 90% ethanol (150 ml.) was added. After 14 hr. at 0° the precipitated digitonide was filtered off, washed with cold ethanol and ether, and dried under vacuum. The digitonide was dissolved in the minimum volume of pyridine, the digitonin precipitated with ether, and the mixture filtered through Celite. The filtrate was washed with dilute hydrochloric acid and water, then dried and evaporated to dryness. Crystallisation of the residue from methanol gave material, m. p. 160—165°. Thin-layer chromatography showed this to have two components, R_S 1·15 and 1·20 [silica gel G was used as adsorbent, benzene–ethyl acetate (2 : 1) as solvent, and cholesterol as standard]. A portion (80 mg.) of this material was chromatographed on alumina (7 g.). Prolonged elution with 1% ether–light petroleum gave a series of fractions which were mixtures. Thin-layer chromatography of the fractions indicated that the first eluted contained mainly material with R_S 1·20 and the last fractions material with R_S 1·15. The first fractions were combined (30 mg.) and acetylated (12 hr.) at room temperature in acetic anhydride–pyridine. Fractional crystallisation from methanol gave slightly impure 4α-methylcholest-5-en-3β-yl acetate, m. p. 100—105°, $[\alpha]_D$ −29° (*c* 0·70); $\nu_{max.}$ (KCl disc) 1745, 1667, 1242, and 1042 cm.$^{-1}$, R_S 1·20 (Found: C, 81·3; H, 11·25. Calc. for $C_{30}H_{50}O_2$: C, 81·4; H, 11·4%). Hydrolysis and crystallisation gave the sterol, m. p. 165—168°, $[\alpha]_D$ −46° (*c* 0·53), $\nu_{max.}$ (KCl disc) 3448 and 1064 cm.$^{-1}$. The last fractions were combined (32 mg.) and acetylated (14 hr.) at room temperature in acetic anhydride–pyridine. The product was crystallised from methanol to give 4β-methylcholest-5-en-3β-yl acetate, m. p. 163—166°, $[\alpha]_D$ −73° (*c* 0·38); $\nu_{max.}$ (KCl disc) 1724, 1250, and 1038 cm.$^{-1}$ (Found: C, 81·1; H, 11·3. Calc. for $C_{30}H_{50}O_2$: C, 81·4; H, 11·4%). Hydrolysis and crystallisation from methanol gave the sterol, m. p. 138—140°, $[\alpha]_D$ −65° (*c* 0·35); $\nu_{max.}$ (KCl

disc) 3390, 1647, 1060, and 1024 cm.$^{-1}$ (Found: C, 83·65; H, 11·85. Calc. for $C_{28}H_{48}O$: C, 83·9; H, 12·1%). Benzoylation (benzoyl chloride–pyridine) gave the benzoate, m. p. 197—200°, $[\alpha]_D$ −38° (*c* 0·35), having infrared spectrum identical with that of the sample described below.

The filtrate from the digitonide formation was concentrated under vacuum and diluted with ether, and the digitonin filtered off (Celite) and washed with ether. Evaporation under reduced pressure gave a solid (602 mg.) which was chromatographed on alumina (60 g.). Light petroleum eluted a clear oil (87 mg.). Two crystallisations from methanol gave pure 4-methylcholesta-3,5-diene, as plates, m. p. 71—74°, $[\alpha]_D$ −88° (*c.* 1·36), $\lambda_{max.}$ 232 and 238 mμ (ε 16,200) and 19,000), $\lambda_{infl.}$ 245 mμ (ε 12,600) (Found: C, 87·65; H, 11·8. Calc. for $C_{28}H_{46}$: C, 87·9; H, 12·1%). Elution with 2% ether–light petroleum produced 4-methylcholesta-3,5-dien-3-yl acetate (8 mg.), m. p. 110—114°, having infrared spectrum identical with that of an authentic sample. Elution with 4% ether–light petroleum yielded 4-methylcholest-4-en-3-one (154 mg.), m. p. 99—102°, $\lambda_{max.}$ 251 mμ, having infrared spectrum identical with that of an authentic sample. Further elution with 4% ether–light petroleum gave 4α-*methylcholest-5-en-3α-ol* (82 mg.) (from methanol), m. p. 134—137° $[\alpha]_D$ −43° (*c* 0·78); $\nu_{max.}$ (KCl disc) 3472, 1072, 985, 975, and 949 cm.$^{-1}$ (Found: C, 83·9; H, 11·95. $C_{28}H_{48}O$ requires C, 83·9; H, 12·1%). Acetylation (acetic anhydride–pyridine) gave a gum, $[\alpha]_D$ −50° (*c* 0·62), $\lambda_{max.}$ (KCl disc) 1730, 1258 (complex band), and 1020 cm.$^{-1}$. Elution with 10% ether–light petroleum yielded 4β-methylcholest-5-en-3β-ol (109 mg.) (from methanol), m. p. 136—139°, $[\alpha]_D$ −68° (*c* 0·84), having infrared spectrum identical with an authentic sample. Acetylation (acetic anhydride–pyridine) at room temperature gave the acetate, m. p. 163—166°, $[\alpha]_D$ −74° (*c* 1·27). The *benzoate*, prepared with benzoyl chloride and pyridine, formed fine plates (from ethyl acetate), m. p. 198—200°, $[\alpha]_D$ −37° (*c* 0·88); $\nu_{max.}$ (KCl disc) 1709, 1464, 1449, 1271, 1099, and 713 cm.$^{-1}$ (Found: C, 83·7; H, 10·0. $C_{35}H_{52}O_2$ requires C, 83·3; H, 10·25%).

The author thanks Dr. R. P. Cook for his interest in this work and Dr. S. Julia for providing 4α- and 4β-methylcholest-5-en-3β-ols and their acetates. Thanks are offered to the D.S.I.R. for a maintenance grant.

Department of Biochemistry, Queen's College,
University of St. Andrews, Dundee.

[Present address: Worcester Foundation for Experimental Biology,
Shrewsbury, Mass., U.S.A.]

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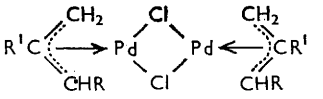
360. *The Reaction of Some π-Allylic Palladium Chloride Complexes with Carbon Monoxide.*

By R. Long and G. H. Whitfield.

The carbonylation of di-μ-halogeno-di-π-allyldinickel complexes in methanol has been reported by Fischer and Bürger [1] to give methyl methacrylate and by Chiusoli and Merzoni [2] to give methyl but-3-enoate. Recently, Heck [3] confirmed that methyl but-3-enoate is the product and discussed possible reaction mechanisms.

We had previously studied the carbonylation of three π-allylic complexes of palladium, di-μ-chloro-di-π-allyldipalladium (I; R = R^1 = H), di-μ-chloro-di-π-but-2-enyldipalladium (I; R = Me, R^1 = H), and di-μ-chloro-di-π-methallyldipalladium (I; R = H, R^1 = Me).



(I)

No reaction was evident at atmospheric pressure but when increased pressures of carbon

[1] Fischer and Bürger, *Z. Naturforsch.*, 1962, **17***b*, 484.
[2] Chiusoli and Merzoni, *Z. Naturforsch.*, 1962, **17***b* 850.
[3] Heck, *J. Amer. Chem. Soc.*, 1963, **85**, 2013.

monoxide were employed reaction occurred and hydrolysis of the products gave unsaturated acids. The identity and yield of the acid in each case is recorded in the Table.

π-Allylic palladium chloride	Product	Yield (%, w/w)
$(\pi\text{-AllylPdCl})_2$	But-3-enoic acid	65
$(\pi\text{-But-2-enylPdCl})_2$	Pent-3-enoic acid	88
$(\pi\text{-MethallylPdCl})_2$	3-Methylbut-3-enoic acid	57

It is evident that the insertion of carbon monoxide has occurred at an end carbon atom of the allyl group and that in the case of the π-but-2-enyl complex it has taken place at the least substituted end carbon atom.

Experimental.—Gas–liquid chromatography was carried out on a Griffin and George instrument having a 6 ft. column ($\frac{3}{16}$ in. i.d.) of silicone oil on "Celite," operated at a temperature of 120°. The carrier gas was nitrogen, passed at 2·5 l./hr., and the bridge current of the katharometer was 165 mA.

The carbonylation of di-μ-chloro-di-π-allyldipalladium complexes—general procedure. A suspension of the complex (10·0 g.) in benzene (60 ml.) was placed in a glass-lined 1-l. chrome-steel rocking autoclave and shaken with carbon monoxide for 5 hr. at 200 atm. and 50°. After a further 7 hr. at room temperature the mixture was discharged and agitated with water (5 ml.) for 15 min. The hydrolysed product was then filtered and the solid washed with acetone–ether (1 : 1). The filtrate and washings were evaporated under reduced pressure. The subsequent treatment varied with each complex as follows.

(a) *π-Allyl complex.* The residue was treated with ether–light petroleum (b. p. 40—60°) (1 : 1) and the mixture filtered, giving unchanged di-μ-chloro-π-allyldipalladium (0·2 g.). The filtrate was evaporated yielding but-3-enoic acid (3·0 g.), identified by comparison with a synthetic sample [4] by g.l.c. and i.r. spectroscopy. The *p-bromophenacyl ester* formed needles (Found: C, 50·4; H, 3·8; Br, 28·8. $C_{12}H_{11}BrO_3$ requires C, 50·9; H, 3·9; Br, 28·2%), m. p. 50—60° despite repeated crystallisation. The p-bromophenacyl ester prepared from the synthetic but-3-enoic acid, had m. p. 51—59°.

(b) *π-But-2-enyl complex.* The procedure described for the π-allyl complex was followed, and unchanged di-μ-chloro-di-π-but-2-enyldipalladium (0·6 g.; m. p. 136°) and an oil (4·2 g.) separated. The oil was examined by g.l.c. and i.r. spectroscopy and shown to be pent-3-enoic acid, prepared according to the method of Lane, Fentress, and Sherwood.[5]

(c) *π-Methallyl complex.* No unchanged complex was isolated, and the oily product (2·9 g.) was shown by g.l.c. and i.r. spectroscopy to be identical with 3-methylbut-3-enoic acid, prepared synthetically.[6] The *p*-bromophenacyl ester formed crystals, m. p. 43—44° undepressed in admixture with a sample of *p*-bromophenacyl ester prepared from synthetic acid; Morton *et al.*[7] record m. p. 44—44·5°.

HEAVY ORGANIC CHEMICALS DIVISION, IMPERIAL CHEMICAL INDUSTRIES LIMITED, BILLINGHAM, CO. DURHAM.

[Present address (R. L.): BOROUGH POLYTECHNIC, LONDON S.E.1.]

[*Received, September 23rd,* 1963.]

[4] Horning, "Organic Syntheses," Wiley, New York, 1955, Vol. 3, p. 851.
[5] Lane, Fentress, and Sherwood, *J. Amer. Chem. Soc.*, 1944, **66**, 545.
[6] Wagner, *J. Amer. Chem. Soc.*, 1949, **71**, 3214.
[7] Morton, Marsh, Coombs, Lyons, Penner, Ramsden, Baker, Little, and Letsinger, *J. Amer. Chem. Soc.*, 1950, **72**, 3785.

361. *The Pyrethrins and Related Compounds. Part IV.*[1] *The Ultraviolet Absorption of the Conjugated* cis-*Pentadiene in Pyrethrolone.*

By M. Elliott.

It is difficult to obtain *cis*-1,3-dienes pure, and therefore the intensity of their ultraviolet absorption is sometimes in doubt. Syntheses of compounds containing this system, involving semihydrogenation of vinylacetylenes, may give overhydrogenated products even when only one mole of hydrogen is absorbed.[2,3] *cis*-Penta-2,4-dienol [4] exemplifies this.

From degradative and synthetical evidence, naturally derived pyrethrolone is known to be (+)-4-hydroxy-3-methyl-2-(penta-*cis*-2,4-dienyl)cyclopent-2-en-1-one.[5] It forms a crystalline monohydrate [6] and is thus available pure and free from closely related alcohols (*e.g.*, cinerolone [5]). Therefore, the spectra of pyrethrolone purified in this way, and of its derivatives, have been measured to determine the absorption of the diene in these compounds.

	$\lambda_{max.}$ (mμ)	ε	Δε(diene)
(+)-Pyrethrolone [6]	225	33,500	21,700
(+)-Pyrethrolone hydrate [6]	225	33,800	22,000
Tetrahydropyrethrolone [2]	(227) [a]	11,800	
(+)-Pyrethrolone methyl ether [1]	225	31,600	21,200
Tetrahydropyrethrolone methyl ether	(225) [b]	10,400	
(−)-Pyrethrolone semicarbazone [1]	229 [c]	27,300	21,600
Tetrahydropyrethrolone semicarbazone	(229)	5,700 [d]	
(+)-Pyrethrolone 2,4-dinitrophenylhydrazone [6]	225	34,700	19,800
(+)-Cinerolone 2,4-dinitrophenylhydrazone [6]	225	14,900	
(+)-Pyrethrolone methyl ether 2,4-dinitrophenylhydrazone	225 [e]	34,900	19,200
Tetrahydropyrethrolone methyl ether 2,4-dinitrophenylhydrazone	(225) [f]	15,700	
4-Methyl-5-(penta-*cis*-2,4-dienyl)cyclopent-4-ene-1,3-diol	230·5 [g]	22,800	22,700
4-Methoxy-3-methyl-2-(penta-*cis*-2,4-dienyl)cyclopent-2-enol	230	22,000	21,900
4-Allyl-5-methylcyclopent-4-ene-1,3-diol	(230) [h]	100	

[a] Max. at 230 mμ.[2] [b] Max. at 230 mμ, ε 11,100. [c] Another max. at 265 mμ, ε 21,800. [d] Taken from graph of Gillam and West; [7] Crombie *et al.*[2] used 4300, which here gives Δε 23,000. [e] Another max. at 380 mμ, ε 27,500; inflexion at 282 mμ, ε 9300. [f] Max. at 217, 254, ε 380 mμ, 16,600, 17,700 28,300; inflexion at 290 mμ, ε 8700. [g] Determination on Optika CF4 DR recording spectrophotometer. [h] No max. 205—300 mμ.

(+)-Pyrethrolone monohydrate, obtained by processes conducted at room temperature or below (which made thermal isomerization impossible [7]), gave (+)-pyrethrolone with a higher refractive index (n_D^{20} 1·5475) and more intense absorption (see Table) than earlier naturally derived specimens [7,8] (n_D^{18} 1·5390, $n_D^{19.5}$ 1·5422, n_D^{21} 1·5410; $\lambda_{max.}$ 228 mμ, ε 27,000, 25,800, 26,700) known to contain cinerolone, and higher than unpurified (±)-*cis*-pyrethrolone [2] (n_D^{20} 1·536; $\lambda_{max.}$ 227 mμ, ε 26,800). The ultraviolet absorption of pyrethrolone is the sum of contributions from the cyclopentenolone ring and the monosubstituted conjugated diene; [7,9] Crombie, Harper, and Newman [2] estimated that the diene contributed 14,000—14,200 to $\varepsilon_{max.}$ in their synthetic *cis*-pyrethrolone (measured before purification as the semicarbazone), in contrast to 23,200—25,600 in *trans*-pyrethrolone. The value for the *cis*-diene was considered possibly low because traces of

[1] Part III, *J.*, 1964, 888.
[2] Crombie, Harper, and Newman, *J.*, 1956, 3963.
[3] Crombie, Harper, and Smith, *J.*, 1957, 2754.
[4] Boehm and Whiting, *J.*, 1963, 2541.
[5] Crombie and Elliott, *Fortschr. Chem. org. Naturstoffe*, 1961, **19**, 120.
[6] Elliott, *Chem. and Ind.*, 1958, 685; and unpublished results.
[7] Gillam and West, *J.*, 1942, 671.
[8] West, *J.*, 1945, 463.
[9] Gillam and West, *J.*, 1942, 486; 1944, 49.

saturated and mono-olenic components from overhydrogenation of acetylenic intermediates were present. The main cause for the lower $\varepsilon_{max.}$ was thought to be stereochemical, however. For the *cis*-diene, Gillam and West [7] estimated $\varepsilon_{max.}$ to be 18,600 by comparison of pyrethrolone with tetrahydropyrethrolone, and 17,700 from the difference in the spectra of the semicarbazones.

Using (+)-pyrethrolone purified through the monohydrate and its derivatives (this work), higher ε values for the diene were deduced (Table). Therefore, to measure directly the absorption of the diene, the cyclopentenolone chromophores in (+)-pyrethrolone and in (+)-pyrethrolone methyl ether were suppressed by reducing each keto-group with sodium borohydride, to give 1,4-dihydroxy- and 1-hydroxy-4-methoxy-3-methyl-2-(penta-*cis*-2,4-dienyl)cyclopent-2-ene, respectively. The extinction coefficients of these two compounds, whose high intensity absorption comes only from the *cis*-diene at the wavelength investigated, agree with the values for this system deduced by comparisons of related compounds. Thus, although the true absorption of the diene in *cis*-pyrethrolone is less intense than in *trans*-pyrethrolone, previous examinations of impure samples of *cis*-pyrethrolone have exaggerated the difference in $\varepsilon_{max.}$.

Experimental.—Ultraviolet spectra were measured in ethanol on a Unicam S.P. 500 spectrophotometer, except where stated otherwise. Infrared spectra were determined for liquid films on a Perkin-Elmer Infracord model 137 spectrometer.

2,4-*Dinitrophenylhydrazone* of (+)-*pyrethrolone methyl ether*. This compound was obtained from the parent ketone [1] in methanolic sulphuric acid, m. p. 157° (Kofler block) (from methanol) (Found: C, 58·2; H, 5·4; N, 14·7. $C_{18}H_{20}N_4O_5$ requires C, 58·1; H, 5·4; N, 15·05%).

4-*Methyl*-5-(*penta*-cis-2,4-*dienyl*)*cyclopent*-4-*ene*-1,3-*diol*. (+)-Pyrethrolone hydrate (1·38 g.) was reduced in propan-2-ol (20 ml.) at room temperature for 16 hr. with sodium borohydride (1·0 g.). Addition of saturated sodium chloride solution and isolation with ether gave the *diol* (0·40 g.), b. p. 114—116°/4 × 10^{-3} mm., n_D^{20} 1·5242, no absorption at 1715 cm.$^{-1}$ (C=O) (Found: C, 72·5; H, 9·4. $C_{11}H_{16}O_2$ requires C, 73·3; H, 8·95%), after rejection of lower boiling fractions.

4-*Allyl*-5-*methylcyclopent*-4-*ene*-1,3-*diol*. By a similar procedure, allethrolone (3·25 g.) gave the *diol* (1·62 g.), b. p. 113°/3 × 10^{-2} mm., n_D^{20} 1·5018, no absorption at 1715 cm.$^{-1}$ (C=O) (Found: C, 70·45; H, 9·6. $C_9H_{14}O_2$ requires C, 70·1; H, 9·2%).

DEPARTMENT OF INSECTICIDES AND FUNGICIDES, ROTHAMSTED EXPERIMENTAL STATION, HARPENDEN, HERTS. [*Received, October 18th*, 1963.]

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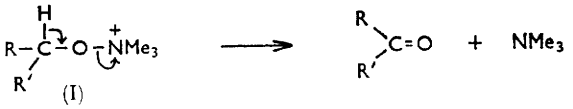
362. *A New Procedure for the Oxidation of Alcohols.*

By D. H. R. BARTON, B. J. GARNER, and R. H. WIGHTMAN.

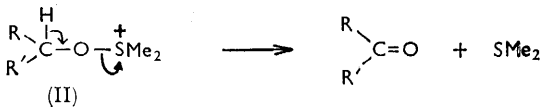
IN spite of its potential importance there is still no convenient method for the oxidation of alcohols to aldehydes and ketones under neutral conditions at room temperature. In principle, it should be possible to devise an ester which fragments [1] spontaneously into a carbonyl compound. In practice, this is illustrated by the fragmentation [2] of quaternised



trialkylhydroxylamines (I), although the reaction is, in fact, base catalysed. Kornblum

[1] *E.g.*, Grob, *Bull. Soc. chim. France*, 1960, 1360.
[2] Franzen and Otto, *Chem. Ber.*, 1961, **108**, 1360; cf. Feely, Lehn, and Boekelheide, *J. Org. Chem.*, 1957, **22**, 1135.

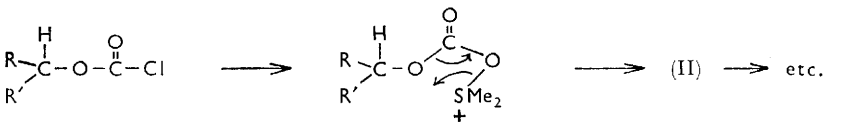
and his collaborators [3] showed that dimethylsulphoxonium salts (II) decompose into a carbonyl compound and dimethyl sulphide.



(II)

However, rather high temperatures are needed to make the salts by displacement of, say, alkyl toluene-*p*-sulphonates with dimethyl sulphoxide.

We thought that dimethylsulphoxonium salts might be easily prepared [4] by the action of dimethyl sulphoxide on alkyl chloroformates (III). In practice, mixing the reagents at room temperature or lower caused evolution of carbon dioxide and formation of an intermediate which, with a slight excess of triethylamine, rapidly gave the aldehyde or ketone and dimethyl sulphide.



There is certainly a detectable intermediate, because if the dimethyl sulphoxide and triethylamine are added together no carbonyl compound is formed. The yields of carbonyl compounds that can be obtained are illustrated in the Table. Alcohols were

Yields of carbonyl compounds (as 2,4-dinitrophenylhydrazones).

Alcohol	Yield (%)	Alcohol	Yield (%)	Alcohol	Yield (%)
n-Butyl	65	Isobutyl	70	Citronellol	46
n-Hexyl.....	68	Neopentyl	57	(−)-Menthol	26
s-Butyl	78	Butane-1,4-diol	80	Cholestanol.....	20

converted quantitatively into crude chloroformates, which gave essentially the same yields as purified chloroformates. The high yield of succinaldehyde is gratifying since this compound is not easily prepared. The yields for primary alcohols are, in general, good. The results with the cyclic alcohol (−)-menthol and cholestanol were disappointing. The yield for (−)-menthol was improved to 35% by working throughout at 10°. Benzyl and cinnamyl alcohols were not oxidised by the reagent, but gave the corresponding chlorides. Clearly the procedure has some merit for aliphatic alcohols, especially when the preparation of aldehydes is involved.

Experimental.—All 2,4-dinitrophenylhydrazones were compared with authentic specimens.

Preparation of chloroformates. The following procedure was found to be convenient. Phosgene was passed into dry ether until saturated (15—20% w/v). The alcohol (10 g.) in dry ether (50 ml.) was treated with ethereal phosgene (see above; 1·1 mol.) at room temperature until the reaction was complete (infrared control). Removal of the solvent *in vacuo* gave the chloroformate. In representative cases these compounds were purified by distillation, but this is not necessary for the subsequent oxidation. Yields on distilled and on non-distilled chloroformate oxidations were essentially identical. For the preparation of the chloroformates of hindered alcohols quinoline can be added as a catalyst, quinoline hydrochloride being subsequently removed by filtration.

Action of dimethyl sulphoxide on chloroformates. The following general procedure was adopted. The chloroformate (1—2 mmoles) was treated with dimethyl sulphoxide (10 ml.)

[3] Kornblum, Powers, Anderson, Jones, Larson, Levand, and Weaver, *J. Amer. Chem. Soc.*, 1957, **79**, 6562; Kornblum, Jones, and Anderson, *ibid.*, 1959, **81**, 4113.

[4] Cf. Boschan, *J. Amer. Chem. Soc.*, 1959, **81**, 3341; Norris, *ibid.*, p. 3346.

with stirring during 2 min. at 15° (vigorous evolution of carbon dioxide), and then stirred at ambient temperature for 15 min. Dry triethylamine (20% molar excess; redistilled) was added with cooling, and the stirring continued for a further 20 min. at room temperature (odour of dimethyl sulphide). Addition of aqueous 2,4-dinitrophenylhydrazine reagent in the usual way gave the 2,4-dinitrophenylhydrazone.

If the chloroformate is added to the mixture of dimethyl sulphoxide and triethylamine, no carbonyl compound is produced (no 2,4-dinitrophenylhydrazone).

The effect of chloroformate concentration was investigated as follows. n-Butyl chloroformate (redistilled; 500 mg.) and dimethyl sulphoxide (variable amount; see below) were stirred at room temperature until evolution of carbon dioxide was complete (6 min.). Dry triethylamine (redistilled; 2·0 ml.) was added with cooling and stirring for 5 min. (temp. not above room temperature). Distilled water (100 ml.) was added, and the solution acidified (2N-hydrochloric acid) and treated with 2,4-dinitrophenylhydrazine. The variation of yield (in parentheses) with volume of dimethyl sulphoxide (see above) was as follows: 1·0 ml. (75%), 2·0 ml. (82%), 5·0 ml. (82%), 10·0 ml. (71%), 25·0 ml. (57%).

The effect of temperature was investigated as follows. (−)-Menthyl chloroformate (500 mg.) was treated with dimethyl sulphoxide (3·0 ml.) at various temperatures for 5 min. After cooling (ice-bath) the triethylamine (2·0 ml.) was added and the reaction solution further processed as above. The variation of yield of ketone 2,4-dinitrophenylhydrazone (in parentheses) with temperature at which the reaction with dimethyl sulphoxide was carried out (see above) was as follows: 10° (35%), 20° (29%), 30° (25%), 40° (20%).

We thank the Government Grants Committee of the Royal Society, and the D.S.I.R., for financial assistance. One of us (R. H. W.) acknowledges with gratitude the award of a Fellowship from the N.R.C. of Canada.

IMPERIAL, COLLEGE, LONDON S.W.7. [*Received, October 29th*, 1963.]

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363. *The Isolation of Marrubiin from* Leonotis leonurus *R.Br.*

By D. E. A. RIVETT.

THE crystalline material obtained from an acetone extract of the leaves of *Leonotis leonurus* R.Br. (wilde dagga), when chromatographed on alumina, gave marrubiin in addition to the compounds X, $C_{20}H_{28}O_5$, and Y, $C_{20}H_{28}O_3$, previously isolated.[1] Like horehound (*Marrubium vulgare* L.), the only other source of marrubiin, *Leonotis leonurus* is also a member of the Labiatae. The structures of compounds X and Y are being investigated.

Experimental.—Melting points are corrected, and $[\alpha]_D$ values refer to solutions in chloroform. Alumina for chromatography was acid-washed, neutralised, and activated by heating at 170° for 18 hr. Infrared spectra were determined on an Infracord spectrometer in chloroform solution.

Air-dried leaves (4·5 kg.), collected in the summer months near Grahamstown, were extracted with acetone (90 l.). The extract was concentrated in a vacuum to 5 l., shaken with activated charcoal (2 × 100 g.), and filtered. The pale yellow filtrate was evaporated under reduced pressure, the residue taken up in ethanol (200 ml.), and the resulting crystalline precipitate (85 g., 1·9%) filtered off after 1 week. This precipitate (50 g.) was chromatographed in benzene on alumina (1·0 kg.). Marrubiin was isolated from benzene eluates (5 l.) in 0·4% yield based on plant. Recrystallised from benzene or ethanol it had m. p. and mixed m. p. 160° (infrared spectra also identical), $[\alpha]_D$ +33·3° (*c* 1·0) (Found: C, 72·4; H, 8·7. Calc. for $C_{20}H_{28}O_4$: C, 72·2; H, 8·4%). On hydrogenation in ethanol in the presence of 10% palladised barium sulphate, marrubiin was quantitatively converted into tetrahydromarrubiin, m. p. and mixed m. p. 123° (lit.,[2] 123·5°) (from benzene–hexane), $[\alpha]_D$ +33·2° (*c* 1·0) (Found: C, 71·2; H, 9·5. Calc. for

[1] Cragg and Little, *J.S. African Chem. Inst.*, 1962, **15**, 29.
[2] Hardy, Rigby, and Moody, *J.*, 1957, 2955.

$C_{20}H_{32}O_4$: C, 71·4; H, 9·6%). Marrubiin was converted into marrubic acid, m. p. 198° (decomp.) (Found: C, 68·4; H, 8·7%; Equiv., 354. Calc. for $C_{20}H_{30}O_5$: C, 68·6; H, 8·6%; Equiv., 350).

Further elution with 0·5% ethanol–benzene (7 l.) gave a mixture. The eluates were subjected to thin-layer chromatography on silica gel (Merck's Kieselgel G) using hexane–ethyl acetate (5 : 2) as mobile phase. The plates were sprayed with a 30% solution of chlorosulphonic acid in acetic acid, heated at 100° for 10 min, and viewed under ultraviolet light, to bring out the spots of compound X. The main fraction was re-chromatographed on alumina, elution being with benzene containing increasing amounts of ethyl acetate. Fractions of similar composition were combined to give compounds X (0·5 g.) and Y (0·5% of plant). Compound X was obtained as fine needles (from ethanol), m. p. 234°, $[\alpha]_D$ +10·6° (*c* 1·4), $\lambda_{max.}$ 214 mμ (ε 193) (Found: C, 69·5; H, 8·0. Calc. for $C_{20}H_{28}O_5$: C, 69·0; H, 8·0%). Recrystallised from ethanol, compound Y formed plates, m. p. 116°, $[\alpha]_D$ −36° (*c* 1·2), $\lambda_{max.}$ 245 and 318 mμ (ε 11,400 and 50) (Found: C, 75·8; H, 9·1. Calc. for $C_{20}H_{28}O_3$: C, 76·0; H, 8·9%).

The author thanks Professor W. Cocker for a sample of marrubiin.

RHODES UNIVERSITY, GRAHAMSTOWN, SOUTH AFRICA. [*Received, November 7th*, 1963.]

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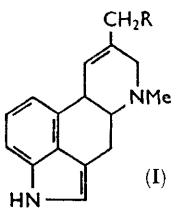
364. *Ring Cleavages of Clavine Alkaloids.*

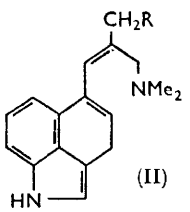
By J. P. DICKINSON, JOHN HARLEY-MASON, and J. H. NEW.

AGROCLAVINE (I; R = H) reacted readily with methyl iodide to give a well-defined quaternary salt. On treatment with hot alkali under nitrogen, Hofmann elimination occurred, giving a methine exhibiting a long-wave absorption band at 342 mμ, indicating that the new double bond was conjugated with the indole ring system. Moreover, the compound was optically inactive, showing that both asymmetric centres had been destroyed. The structure of the methine is therefore (II; R = H). Similar treatment of elymoclavine (I; R = OH) led to the methine (II; R = OH). In the complete absence of oxygen, the methines dissolved in aqueous acids to give colourless solutions; on admission of air, oxidation occurred very rapidly, giving ultimately an intensely blue solution.

On hydrogenation of the methiodides over Adams catalyst two molecules of hydrogen were smoothly absorbed without a break or inflexion in the uptake curve, giving the hydriodides of tertiary bases. Plainly, in addition to the reduction of the double bond,



(I)



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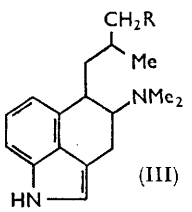
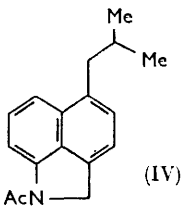


(III)



(IV)

carbon–nitrogen hydrogenolysis had also occurred, giving the seco-products (III; R = H and OH). The position of cleavage was proved as follows. The seco-compound (III; R = H) was quaternised with methyl iodide and subjected to Hofmann elimination. Trimethylamine was evolved and an oxygen-sensitive methine obtained, which, on treatment with acetic anhydride, gave 1-acetyl-1,2-dihydro-5-isobutylbenz[*cd*]indole (IV).

Similar examples of carbon–nitrogen hydrogenolysis of allylic quaternary salts have

previously been recorded, *e.g.*, the reduction of cinnamyltrimethylammonium salts [1,2] and of echitamine.[3] However, this appears to be the first example where the nitrogen atom and the double bond are in the same six-membered ring, though an Emde reduction of agroclavine and elymoclavine methiodides with sodium and liquid ammonia was recently reported by Birch and his co-workers.[4]

A further example was studied briefly. 1,2,3,6-Tetrahydro-1-methylpyridine methiodide was hydrogenated over Adams catalyst. Contrary to an earlier report,[5] 1·5 mol. of hydrogen were absorbed and the product was an approximately equimolecular mixture of *N*-methylpiperidine methiodide and *NN*-dimethylpentylamine hydriodide. Thus, in this case, simple double-bond reduction and hydrogenolysis appear to be competing processes. It is possible that, in the alkaloid cases above, the course of reaction is steered exclusively in one direction by the affinity of the indolic portion of the molecule for the catalyst.

Experimental.—Agroclavine methiodide. Agroclavine [$\lambda_{max.}$ (ethanol) 224, 282, 293 mμ (ε 26,300, 6600, 5500)] (1·7 g.) in methanol (25 ml.) was refluxed with methyl iodide (2 ml.); the *methiodide* (2·35 g., 88%) separated during the heating and formed prisms, m. p. 245° (decomp.) (from methanol) (Found: C, 53·75; H, 5·8; N, 7·35. $C_{17}H_{21}IN_2$ requires C, 53·7; H, 5·55; N, 7·35).

Elymoclavine methiodide. Elymoclavine (1 g.) in methanol (20 ml.) was refluxed for 0·5 hr. with methyl iodide (2 ml.). The cooled solution was diluted with ether (50 ml.), and the precipitated gum collected and recrystallised from water, yielding the *methiodide* (1·2 g.) as flakes, m. p. 230° (Found: C, 50·45; H, 5·6; N, 7·1. $C_{17}H_{21}IN_2O,\frac{1}{2}H_2O$ requires C, 50·2; H, 5·3; N, 6·9%).

$\Delta^{5(10)}$-*Dehydro*-6-*methyl*-5,6-*seco*-*agroclavine* (II; R = H). Agroclavine methiodide (2 g.) was dissolved in N-sodium hydroxide (10 ml.) and heated at 90° for 40 min. under nitrogen. After cooling, the precipitated solid was collected and sublimed at 130—140°/10^{-3} mm., to give the *methine* (50 mg.) as pale yellow crystals, m. p. 126° (decomp.) (Found: N, 11·4. $C_{17}H_{20}N_2$ requires N, 11·1%), $[\alpha]_D^{20}$ 0°, $\lambda_{max.}$ (ethanol), 211, 234, 342 mμ (ε 26,300, 10,700, 6000).

$\Delta^{5(10)}$-*Dehydro*-6-*methyl*-5,6-*seco*-*elymoclavine* (II; R = OH). Elymoclavine methiodide (300 mg.) was dissolved in N-sodium hydroxide (5 ml.) and heated at 90° for 10 min. under nitrogen. After cooling, the greenish gum which had separated was extracted into peroxide-free ether, the extract washed with water, and the ether removed by freeze-drying, leaving the *methine* as a pale yellow powder, m. p. 120° (decomp.) (Found: C, 74·1; H, 7·45; N, 10·15. $C_{17}H_{20}N_2O$ requires C, 73·8; H, 7·35; N, 10·1%). The compound decomposed on attempted sublimation in a high vacuum. Both methines exhibited an intense blue fluorescence in organic solvents and gave an intense purple colour with Ehrlich's reagent. The initially colourless solutions in aqueous acids rapidly absorbed aerial oxygen, giving, after a series of colour changes, an intensely blue solution.

8,9-*Dihydro*-6-*methyl*-6,7-*seco*-*agroclavine* (III; R = H). Agroclavine methiodide (2 g.) in methanol (90 ml.) and water (60 ml.) was hydrogenated over Adams catalyst (0·1 g.); 242 ml. of hydrogen (1·94 moles per mole) were absorbed during 5 hr. Filtration and evaporation of the solution gave the hydriodide of the product which, with alkali, gave the *seco*-*base*, needles, m. p. 169° (from methanol) (Found: C, 79·7; H, 9·25; N, 11·4. $C_{17}H_{24}N_2$ requires C, 79·7; H, 9·35; N, 11·4%), $[\alpha]_D^{20}$ (*c* 10 in ethanol) −84° $\lambda_{max.}$ (ethanol) 224, 283 mμ (ε 23,400, 6800).

8,9-*Dihydro*-6-*methyl*-6,7-*seco*-*elymoclavine* (III; R = OH). Elymoclavine methiodide (0·9 g.) in methanol (100 ml.) was hydrogenated over Adams catalyst (50 mg.); 107 ml. (1·96 moles per mole) of hydrogen were absorbed during 3·5 hr. Filtration and evaporation of the solution gave the hydriodide of the product which, with alkali, gave a gum, purified by sublimation at 150°/5 × 10^{-5} mm., to give the *seco*-*base* as small prisms, m. p. 136° (Found: C, 75·1; H, 9·1. $C_{17}H_{24}N_2O$ requires C, 75·0; H, 8·8%).

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8,9-*Dihydro*-6-*methyl*-6,7-*seco-agroclavine methiodide*. 8,9-Dihydro-6-methyl-6,7-seco-agroclavine (400 mg.) in ether (5 ml.) was refluxed with methyl iodide (0·4 ml.) for 1 hr., and the mixture was then evaporated to dryness. The residual gum afforded the *methiodide* as flakes, m. p. 207—210° (from water) (Found: C, 53·65; H, 7·0; N, 7·15. $C_{18}H_{27}IN_2$ requires C, 53·65; H, 6·85; N, 6·95%).

1,3-*Dihydro*-6-*isobutylbenz*[cd]*indole*. The foregoing methiodide (200 mg.) was heated at 100° under nitrogen with aqueous potassium hydroxide (10%; 6 ml.) for 1·5 hr. Trimethylamine was evolved and identified as its picrate, m. p. 216°. During the heating a greenish gum separated. After cooling, this was extracted into peroxide-free ether, the solvent removed, and the residue distilled at 100°/5 × 10^{-4} mm., affording the *dihydrobenz*[cd]*indole* as an oil (Found: N, 6·75. $C_{15}H_{17}N$ requires N, 6·65%), $\lambda_{max.}$ (ethanol) 215, 247, **351** mμ. Immediately on exposure to air the product turned bright blue owing to oxidation.

1-*Acetyl*-1,2-*dihydro*-5-*isobutylbenz*[cd]*indole* (IV). 1,3-Dihydro-5-isobutylbenz[*cd*]indole (60 mg.) was refluxed with acetic anhydride (3 ml.) for 1 hr. and the mixture then evaporated to dryness under a vacuum. Sublimation of the residue at 80°/2 × 10^{-5} mm. afforded the 1,2-*dihydrobenz*[cd]*indole* as needles, m. p. 91° (Found: C, 79·7; H, 7·8. $C_{17}H_{19}NO$ requires C, 80·6; H, 7·5%), $\lambda_{max.}$ (ethanol) 232, 320, 333 mμ (1-acetyl-1,2-dihydrobenz[*cd*]indole [6] has $\lambda_{max.}$ 233, 318, 333 mμ).

Hydrogenation of 1,2,3,6-*tetrahydro*-1,1-*dimethylpyridinium iodide*. 1,2,3,6-Tetrahydropyridine (5 g.) was added slowly, with cooling and stirring, to a mixture of methyl iodide (20 ml.) and ethanol (50 ml.). The quaternary salt was precipitated, and formed hygroscopic flakes (from ethanol). The iodide (1 g.) in ethanol (100 ml.) was hydrogenated over Adams catalyst; 140 ml. (1·52 moles per mole) of hydrogen were absorbed during 3 hr., after which uptake ceased. Filtration and concentration afforded 1,1-dimethylpiperidinium iodide (490 mg.), m. p. 357°, mixed m. p. 356—357°. The iodide was converted into the picrate, m. p. and mixed m. p. 317°. Further concentration of the mother-liquors afforded 1-dimethylamino-n-pentane hydriodide as a gum which was converted into the picrate, m. p. and mixed m. p. 101°.

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UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, November 21st,* 1963.]

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