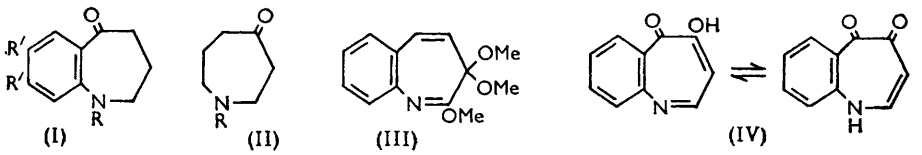
631. *Azatropolones.*

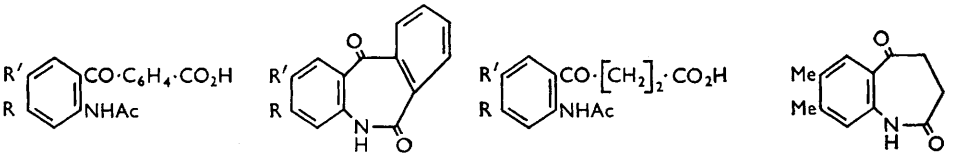
By A. H. Rees.

Succinylation * of *N*-acetyl-3 : 4-xylidine and subsequent deacetylation give an amino-acid which can be cyclised to 2 : 3 : 4 : 5-tetrahydro-7 : 8-dimethyl-2 : 5-dioxobenz[*f*]azepine in 30% overall conversion. From this compound a variety of new compounds has been made including two which are formally azatropolones. Evidence has been obtained, however, that these are not heteroaromatic.

Since Dewar [1] postulated the aromatic tropolone system there has been much speculation as to the existence and nature of heterocyclic analogues and in recent years the chemistry of compounds containing a seven-membered nitrogenous ring has expanded appreciably.[2] Ketones such as (I; R = Me and *p*-$C_6H_4Me{\cdot}SO_2$, R′ = H) and (II; R = H and CH_2Ph),



though reported,[3] have not yet been used to afford azatropolones. The nearest approach has been 2 : 3 : 3-trimethoxybenz[*f*]azepine [4] (III) but demethylation caused ring contraction to give methyl quinaldate. Although the tropolone-like compound (IV) remains to be synthesised, two related compounds have been obtained in this study. From substituted anilides Kränzlein [5] obtained 2-phthaloyl derivatives (V) which, when boiled with mineral acid gave the amino-acids and thence the lactams (VI). The Friedel–Crafts reaction of anilides with succinic anhydride is now described.



It has been reported that *N*-acetyl-*p*-toluidine cannot be acetylated,[6] and attempted succinylation failed, owing perhaps to the opposing effects of the methyl and acetamido-groups. The *meta*-isomer was however converted into its β-carboxypropionyl derivative, which by analogy with the orientation of the phthaloyl-anilide (V; R = Me, R′ = H) and the fact that acetylation of *N*-acetyl-*o*-toluidine occurs *para* to the methyl group,[7] was thought to have structure (VII; R = Me, R′ = H). However, the free amino-acid did not yield a lactam; on deamination it gave β-*o*-toluoylpropionic acid,[8] so it must be 4-β-carboxypropionyl-3-methylacetanilide.

* In this paper, "succinylation" denotes introduction of a $HO_2C{\cdot}CH_2{\cdot}CH_2{\cdot}CO$– group.

[1] Dewar, *Nature*, 1945, **155**, 50.
[2] Lyle, U.S.P. 2,683,145/1954; Leonard, Fox, and Oki, *J. Amer. Chem. Soc.*, 1954, **76** 5708; Bertho, *Chem. Ber.*, 1957, **90**, 29; Butenandt, Biekert, and Neubert, *Annalen*, 1957, **603**, 200; Lloyd, Matternas, and Horning, *J. Amer. Chem. Soc.*, 1955, **77**, 5932.
[3] (*a*) Astill and Boekelheide, *ibid.*, p. 4079; (*b*) Braunholtz and Mann, *J.*, 1957, 4174; Proctor and Thomson, *ibid.*, p. 2312; Yokoo and Morosawa, *Bull. Chem. Soc. Japan*, 1956, **29**, 631.
[4] Look, *Diss. Abs.*, 1957, **17**, 36.
[5] Kränzlein, *Ber.*, 1937, **70**, 1952.
[6] Mehta, Sacha, and Patel, *J. Indian Chem. Soc.*, 1950, **33**, 867.
[7] Sacha and Patel, *ibid.*, p. 129.
[8] Dauben and Tilles, *J. Org. Chem.*, 1950, **15**, 785.

Since it appeared desirable to block the position *para* to the acetamido-group, *N*-acetyl-3 : 4-xylidine and 2-naphthylamine were next studied and the product (VII; R = R′ = Me) from the former, being formed in better yield, was used for further work. Hydrolysis with acid gave the amine salt and though this did not give a lactam, the free amino-acid could be cyclised thermally with or without a solvent to 2 : 3 : 4 : 5-tetrahydro-7 : 8-dimethyl-2 : 5-dioxobenz[*f*]azepine (VIII) which was characterised as carbonyl derivatives.

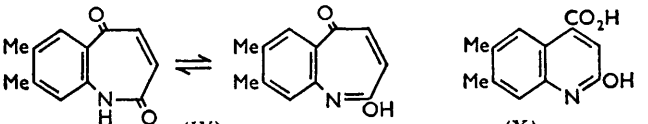
N-Arylsuccinamic acids, prepared for attempts at shortening this synthesis, cyclised, not on to the ring as desired, but back on to the nitrogen atom to give *N*-arylsuccinimides. The latter could not be converted into keto-lactams under the conditions used for rearranging diacetylaniline to *p*-acetylacetanilide.[9]

The ultraviolet spectrum of the keto-lactam (VIII) is tabulated below and the infrared spectrum confirmed the structure (CO band 5·97 μ). The keto-lactam, with selenium dioxide under the conditions for the oxidation of oxindole to isatin,[10] did not yield a definite product. An attempt at protecting the NH group by acetylation gave a compound which still contained one active hydrogen atom and was probably the enol acetate. The acid (VII; R = R′ = Me) could not be cyclised to the *N*-acetyl derivative of the keto-lactam.

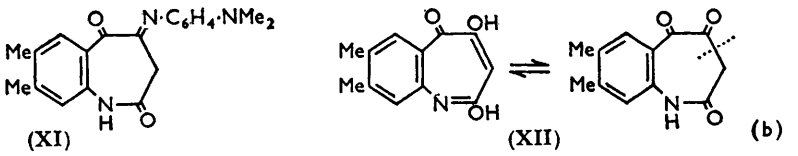
log ε	5·55	4·95	4·90	4·55	4·00	2·40	2·30
$\lambda_{max.}$	235	265		320		430	
$\lambda_{min.}$			255		288 *		410

* Shoulder at 362—370 mμ (log ε 3·65—3·55).

The keto-lactam was then brominated, and a derivative was obtained from which the halogen acid was easily eliminated giving 2 : 5-dihydro-7 : 8-dimethyl-2 : 5-dioxobenz[*f*]-azepine (IX) which was examined briefly. It was stable to dilute mineral acid, in contrast to the keto-lactam whose ring was opened thereby. The infrared spectrum showed no true carbonyl band and a dinitrophenylhydrazone could not be obtained. It was not possible to decide between OH and NH bands in the higher-frequency region though an NH group was indicated by a band at 1660 cm.$^{-1}$. The compound (IX) was not soluble in



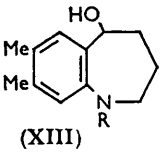
cold dilute aqueous alkali. Hot alcoholic alkali caused a reaction: though this is not yet fully understood, a tropone type of ring contraction [11] did not occur; 2-hydroxy-6 : 7-dimethylquinoline-4-carboxylic acid (X) was not found as a product and it is thought that the seven-membered ring was opened at the 3 : 4-double bond. This double bond could not be introduced into the keto-lactam (VIII) by dehydrogenation which should be easy if the compound (IX) were aromatic.



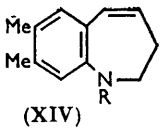
Of greater interest is 2 : 3 : 4 : 5-tetrahydro-7 : 8-dimethyl-2 : 4 : 5-trioxobenz[*f*]-azepine (XII) which was prepared from the keto-lactam (VIII) by condensation with *NN*-dimethyl-*p*-nitrosoaniline followed by acid-hydrolysis of the intermediate anil (XI). The

[9] Chattaway, *J.*, 1904, **85**, 386.
[10] Giovannini and Portmann, *Helv. Chim. Acta*, 1948, **31**, 1396.
[11] Bartels-Keith, Johnson, and Langemann, *J.*, 1952, 4461.

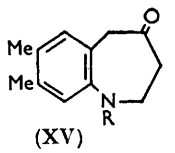
trione (XII) was alkali-soluble but prolonged action gave two products, the acid (X) and 5 : 6-dimethylisatin. It is considered that the common precursor was *N*-acetyl-4 : 5-dimethylisatic acid formed by ring opening of form (XIIb) as indicated. Thus from chemical evidence a heterotropolone behaviour and nature for (XII) is excluded. The infrared spectra of compounds (XI) (as hydrochloride) and (XII) conform to the same type as that of (IX), indicating mainly the existence of tautomerism.



(XIII)



(XIV)



(XV)

In a compound such as (IV), lactam–lactim tautomerism would be impossible, except perhaps by the vinylogous system, NH·CH:CH·CO $\rightleftharpoons$ N:CH·CH:C(OH). In preliminary attempts to prepare starting material, reduction of the keto-lactam (VIII) by lithium aluminium hydride gave the hydroxy-amine (XIII; R = H). Acetylation [12] and oxidation [13] then gave 1-acetyl-2 : 3 : 4 : 5-tetrahydro-7 : 8-dimethyl-5-oxobenz[*f*]azepine (I; R = Ac, R′ = Me) and thence the free amino-ketone. Attempts at preparing the isomeric 4-ketone (XV) failed. Dehydration [3a] of the hydroxy-amine (XIII; R = H) gave 2 : 3-dihydro-7 : 8-dimethylbenz[*f*]azepine (XIV; R = H). After acetylation, the 4 : 5-double bond was oxidised with perbenzoic acid but a polymer resulted. Addition of bromine to the double bond gave a dibromide, but with silver acetate this afforded an undistillable oil which when hydrolysed [14] gave only traces of ketone.

Experimental

Succinylation of N-*Acetyl*-m-*toluidine*.—By reaction as in the succinylation of acetanilide,[15] 4-β-*carboxypropionyl*-3-*methylacetanilide*, m. p. 192° (from alcohol), was obtained in 47% yield with 39% recovery (Found: C, 62·6; H, 6·1; N, 5·3. $C_{13}H_{15}O_4N$ requires C, 62·6; H, 6·1; N, 5·6%).

Acetyl-*p*-toluidine was not acylated under these conditions or after 12 hr. in nitrobenzene at 140°.

4-β-*Carboxypropionyl*-3-*methylaniline*.—Its *N*-acetyl derivative (above; 16·5 g.) was heated for 3 hr. on a steam-bath with 40% sodium hydroxide solution (20 ml.), then left to cool. Adding 6N-hydrochloric acid to pH 6 precipitated the *amino-acid* (12·9 g.), m. p. 158° (from aqueous alcohol) (Found: C, 64·05; H, 6·4; N, 7·1. $C_{11}H_{13}O_3N$ requires C, 63·75; H, 6·3; N, 6·8%).

The base (6·6 g.) gave, by Kornblum and Iffland's method,[16] β-*o*-toluoylpropionic acid (5·7 g.), m. p. 101° (from light petroleum), identical with a sample kindly provided by Professor Dauben [8] (Found: C, 68·9; H, 6·3. Calc. for $C_{11}H_{12}O_3$: C, 68·7; H, 6·3%).

Succinylation of N-*Acetyl*-3 : 4-*xylidine*.—The powdered amide (32·6 g.) was added to a suspension of succinic anhydride (30 g.) in carbon disulphide (350 ml.). Powdered aluminium chloride (200 g.) was then added with stirring. After the initial reaction had subsided the mixture was refluxed until a dark red complex was formed. The supernatant liquor was decanted and the residue decomposed with ice, dilute hydrochloric acid, and wet benzene. Filtration left 2-β-*carboxypropionyl*-4 : 5-*dimethylacetanilide* (VII; R = R′ = Me) which was triturated with benzene, then water, and dried [yield, 50%, 26·4 g.; m. p. 179° (from aqueous alcohol) (Found: C, 64·2; H, 6·7; N, 5·1. $C_{14}H_{17}O_4N$ requires C, 63·9; H, 6·5; N, 5·3%). From the benzene liquors, the starting amide (40%) was recovered.

Succinylation of N-*Acetyl*-2-*naphthylamine*.—By the above method the 1-β-*carboxypropionyl derivative* was obtained in poor yield, with m. p. 229° (from alcohol) (Found: C, 67·05; H, 5·35; N, 4·8. $C_{16}H_{15}O_4N$ requires C, 67·35; H, 5·3; N, 4·9%).

[12] Synge, *Biochem. J.*, 1939, **33**, 1290.
[13] Poos, Arth, Beyler, and Sarett, *J. Amer. Chem. Soc.*, 1953, **75**, 422.
[14] Newhall, Harris, Holly, Johnston, Richter, Walton, Wilson, and Folkers, *ibid.*, 1955, **77**, 5646.
[15] English, Clapp, Cole, and Krapcho, *ibid.*, 1945, **67**, 2263.
[16] Kornblum and Iffland, *ibid.*, 1949, **71**, 2141.

2-β-*Carboxypropionyl*-4 : 5-*dimethylaniline*.—The crude acetyl derivative (VII; R = R′ = Me) (28·7 g.) was refluxed for 3 hr. with 6N-hydrochloric acid (110 ml.). Charcoal (0·5 g.) was added and after filtration the *hydrochloride monohydrate* (20·2 g.), m. p. 172° (from dilute hydrochloric acid), separated (Found: C, 52·1; H, 6·55; N, 5·1; Cl^-, 12·7. $C_{12}H_{15}O_3N,HCl,H_2O$ requires C, 52·3; H, 6·6; N, 5·1; Cl^-, 12·9%). The salt (17·7 g.) was ground in a mortar with addition of N-sodium hydroxide until the pH rose to 7—8. After being collected and washed with water the free *amino-acid* (13·7 g.), m. p. 137° (from aqueous alcohol), was left (Found: C, 65·0; H, 6·85; N, 6·4. $C_{12}H_{15}O_3N$ requires C, 65·1; H, 6·83; N, 6·3%).

Cyclisation of the Amino-acid.—The amino-acid was heated in a vacuum at about 180°/0·1 mm. pressure; the keto-lactam (VIII) was obtained as a white sublimate, m. p. 199° (from tetrahydrofuran).

Alternatively the amino-acid (16·2 g.) was refluxed for 6½ min. in tetralin (55 ml.). On cooling, the *keto-lactam* crystallised (13 g.) (Found: C, 70·8; H, 6·7; N, 6·8. $C_{12}H_{13}O_2N$ requires C, 70·9 H, 6·45; N, 6·9%). The red *dinitrophenylhydrazone* had m. p. 300° (decomp.) (from acetic acid) (Found: C, 56·2; H, 4·5; N, 18·2. $C_{18}H_{17}O_5N_5$ requires C, 56·2; H, 4·5; N, 18·3%). The *oxime* prepared under neutral conditions had m. p. 226° (from alcohol) (Found: C, 65·6; H, 6·4; N, 13·1. $C_{12}H_{14}O_2N_2$ requires C, 66·0; H, 6·5; N, 12·8%). The infrared spectrum of the keto-lactam (in Nujol) had peaks at 3220w, 3110w, 2960s, 1675s, 1615m, 1575w, 1495m, 1460m, 1445m, 1415s, 1385w, 1370w, 1330w, 1305w, 1265w, 1245w, 1215w, 1180w, 1150w, 1025w, 995w, 965w, 925w, 905w, 875w, 820w, and 740w cm.$^{-1}$.

Preparation of N-*Arylsuccinamic Acids*.—Solutions of the aniline and succinic anhydride (1 equiv.) in dioxan were mixed and heated for 10 min. on a steam-bath. On cooling, the anilide was deposited. Thus were prepared *N*-phenylsuccinamic acid and its 3-methyl, m. p. 133° (from water), and 3 : 4-*dimethyl derivative*, m. p. 143° (from aqueous alcohol) (Found: C, 65·1; H, 6·8; N, 6·3. $C_{12}H_{15}O_3N$ requires C, 65·15; H, 6·8; N, 6·3%).

Cyclisation of Arylsuccinamic Acids.—Phenylsuccinamic acid (4 g.) and aluminium chloride (7 g.), warmed to 170° in *o*-dichlorobenzene (40 ml.), gave after steam-distillation an aqueous suspension of *N*-phenylsuccinimide (1·5 g.). In absence of a solvent [17] hydrolysis took place. Boron trifluoride–ether complex gave the imide in improved yield.

By use of an excess of boron trifluoride–ether at 125°, *N*-*m*-tolylsuccinamic acid gave *N*-*m*-tolylsuccinimide [18] and some diethyl succinate.

Attempted Rearrangement of N-*Arylsuccinimides*.—The imide (3·5 g.) was heated with anhydrous zinc chloride (1·2 g.) for 20 hr. at 180°. On addition of water and filtration, the imide was recovered. At higher temperatures decomposition began. Rearrangement did not occur on use of boron trifluoride, aluminium chloride in *o*-dichlorobenzene, or molten sodium chloride–aluminium chloride.[19]

Acetylation of the Keto-lactam.—The keto-lactam (3 g.), refluxed for ½ hr. with excess of acetyl chloride, gave on concentration an *acetyl derivative* (1·5 g.), m. p. 212° (from acetic acid) (Found: C, 68·8; H, 6·25; active H; 0·44; N, 5·7. $C_{14}H_{15}O_3N$ requires C, 68·8; H, 6·2; active H, 0·41; N, 5·7%). From the mother-liquor an *isomer* was obtained having m. p. 225° (depressed by the acetyl derivative) (Found: C, 68·9; H, 6·2; active H, 0·49; N, 5·5%).

Bromination of the Keto-lactam.—Chloroform solutions of bromine (0·25 ml.) and the keto-lactam (1 g.) were mixed and when the colour had faded the solution was concentrated at 40°. Benzene was then added and after decantation from some tar the solution was rapidly washed until neutral, dried, and set aside; the yellow *bromo-keto-lactam* deposited had m. p. *ca.* 135° (decomp.) (Found: C, 51·5; H, 4·4; N, 5·05; Br, 28·0. $C_{12}H_{12}O_2NBr$ requires C, 51·1; H, 4·3; N, 5·0; Br, 28·3%).

Dehydrobromination of the Bromo-keto-lactam.—To a chloroform solution of the bromo-compound was added hydrated sodium acetate. On shaking, filtration, and storage, yellow 2 : 5-*dihydro*-7 : 8-*dimethyl*-2 : 5-*dioxobenz*[f]*azepine* (IX), m. p. 258° (from propanol), was deposited (0·55 g.) (Found: C, 71·55; H, 5·9; N, 7·05. $C_{12}H_{11}O_2N$ requires C, 71·6; H, 5·5; N, 6·95%). The compound was not stable in borneol, the molecular weight decreasing.

A dinitrophenylhydrazone, obtained slowly as a red oil from alcohol solution, became tarry and dark and may not have been that of the dione.

The infrared spectrum (in Nujol) had peaks at 3240m, 3170m, 3110m, 2930s, 1665m, 1615s,

[17] Norris and Klemka, *J. Amer. Chem. Soc.*, 1940, **62**, 1432.
[18] Miolati and Longo, *Rend. Accad. Lincei*, 1896, [v], **4**, I, 357.
[19] Bruce, Sorrie, and Thomson, *J.*, 1955, 2403.

1585s, 1490w, 1460s, 1415m, 1375m, 1345w, 1280w, 1265w, 1230m, 1185m, 1150w, 1025w, 990w, 915w, 875m, 800w, 755w, and 745w cm.$^{-1}$.

Action of Alkali on the Dione (IX).—The dione (0·5 g.) in dioxan (5 ml.) was refluxed for ½ hr. with 2N-sodium hydroxide (0·9 ml.) and water (2 ml.). On cooling, dione (0·25 g.) and a black tar were obtained.

To the dione (0·5 g.) in alcohol (60 ml.) was added potassium hydroxide (1 g.) in water (20 ml.). A stable red colour developed. After 24 hr., and 1 hr. on a steam-bath, the solution was evaporated to small bulk and filtered. The residue was suspended in water and acidified; it changed from brown-red to yellow-brown. After collection, washing, and drying it had no m. p. below 400°. The alkaline filtrate when acidified gave a brown solid (0·3 g.), insoluble in sodium hydrogen carbonate solution and soon becoming virtually insoluble in caustic alkali solution. The sticky solid could not be recrystallised and it gave an unstable dinitrophenylhydrazone.

Preparation of 6 : 7-*Dimethyl*-2-*oxoquinoline*-4-*carboxylic Acid* (X).—The method given in *Org. Synth.*[20] gave the acid apparently unaccompanied by the isomer obtained in its original preparation.[21] The higher m. p. recorded for material crystallised from acetic acid has now been shown to be due to the formation of a *monoacetate*, m. p. 360° (Found: C, 60·6; H, 5·6; N, 5·05. $C_{12}H_{11}O_3N,CH_3{\cdot}CO_2H$ requires C, 60·6; H, 5·45; N, 5·0%). The infrared spectrum of the intermediate 1-acetyl-5 : 6-dimethylisatin was taken for reference, peaks (Nujol) being at 3110w, 3050w, 2940s, 2870m, 1760s, 1735s, 1720s, 1620s, 1580m, 1475s, 1455m, 1425w, 1390s, 1325s, 1285m, 1230s, 1195w, 1185w, 1160m, 1105w, 1045w, 1025w, 1015w, 1000w 960w, 905m, 810w, and 805w cm.$^{-1}$.

Condensation of the Keto-lactam with p-*Nitrosodimethylaniline*.—The nitroso-compound (1·5 g.) and the keto-lactam (1 g.) were dissolved in hot methanol, and 2N-alkali (2 ml.) was added. The mixture was set aside and deposited 4-p-*dimethylaminophenylimino*-2 : 3 : 4 : 5-*tetrahydro*-6 : 7-*dimethyl*-2 : 5-*dioxobenz*[f]*azepine* (XI), m. p. 316° (from dimethylformamide) (Found: C, 71·5; H, 6·35; N, 12·3. $C_{20}H_{21}O_2N_3$ requires C, 71·6; H, 6·3; N, 12·5%). The red anil gave a yellow-green hydrochloride which regenerated the base with alkali. The salt was not easily purified as the anil was hydrolysed by acid, but a sample had m. p. 265° (in block at 250°) (Found: N : Cl, 1·19. $C_{20}H_{22}O_2N_3Cl$ requires N : Cl, 1·20), $\nu_{max.}$ (in Nujol) 3300s, 2940s, 2520w, 2450w, 1650s, 1625s, 1590s, 1560m, 1515m, 1485s, 1445m, 1375m, 1345w, 1320w, 1305w, 1230w, 1180m, 1140m, 1115w, 965w, 890w, 855w, 840w, 810w, 790w, 755w, and 740w cm.$^{-1}$.

Acid Hydrolysis of the Anil (XI).—The anil (1·2 g.) was refluxed for ½ hr. with concentrated hydrochloric acid (10 ml.), a dark suspension being obtained. The solid was collected and washed with water, hot alcohol, benzene, and acetone,[22] then dried, giving 2 : 3 : 4 : 5-*tetrahydro*-7 : 8-*dimethyl*-2 : 4 : 5-*trioxobenz*[f]*azepine* (XII) (0·5 g.), yellow-green, m. p. 290° (decomp.) (Found: C, 66·1; H, 5·05; N, 6·5. $C_{12}H_{11}O_3N$ requires C, 66·35; H, 5·1; N, 6·45%), $\nu_{max.}$ (in Nujol) 3280m, 3120w, 2940s, 1660s, 1620m, 1590s, 1570s, 1485w, 1460s, 1430m, 1375m, 1360m, 1340m, 1260w, 1255w, 1225m, 1185m, 1140s, 1015w, 955w, 890w, 875w, 855w, 800w, 755w, and 740w cm.$^{-1}$.

Action of Alkali on the Trione (XII).—The trione (0·25 g.) in 2N-sodium hydroxide was heated for ¾ hr. on a steam-bath. On acidification an acid was precipitated which, recrystallised from acetic acid, had m. p. 360° alone or mixed with the acetate of the acid (X). The aqueous mother-liquor slowly gave a mixture of a buff-coloured with a red solid. Addition of sodium hydrogen carbonate to pH 8 left only the red solid (5 : 6-dimethylisatin), as needles, m. p. 210°, raised to 212° (m. p. and mixed m. p.) by crystallisation from benzene.

Reduction of Keto-lactam (VIII) *by Lithium Aluminium Hydride*.—To the hydride (7 g.) in tetrahydrofuran (100 ml.) was added rapidly a solution of the keto-lactam (10 g.) in the same solvent (200 ml.). After 2 days' stirring with refluxing, ethyl acetate (10 ml.) and water (25 ml.) were added dropwise. Filtration and evaporation gave a base (6·6 g.) which solidified. A portion, rapidly distilled at low pressure from a retort, then recrystallised from methanol, had m. p. 127° or 132—135° (bath pre-heated to 120°). This was 2 : 3 : 4 : 5-*tetrahydro*-5-*hydroxy*-7 : 8-*dimethylbenz*[f]*azepine* (XIII; R = H) (Found: C, 75·05; H, 8·6; N, 7·25. $C_{12}H_{17}ON$

[20] Marvel and Hiers, in *Org. Synth.*, Coll. Vol. I, 2nd edn., p. 327; Jacobs, Winstein, Linden, Robson. Levy, and Seymour, *Org. Synth.*, Coll. Vol. III, 1955, p. 456.
[21] King and Wright, *Proc. Roy. Soc.*, 1948, *B*, **135**, 271.
[22] Ityerrah and Mann, *J.*, 1958, 467.

requires C, 75·35; H, 8·95; N, 7·3%). Solvent extraction of the alumina gave more of the hydroxy-amine (3 g.). Use of acid or alkali in the work-up caused dehydration to 2 : 3-*dihydro*-7 : 8-*dimethylbenz*[f]*azepine* (XIV; R = H), m. p. 89° (from alcohol) (Found: C, 83·3; H, 8·7; N, 7·8. $C_{12}H_{15}N$ requires C, 83·2; H, 8·7; N, 8·1%). Both bases gave the same *picrate*, m. p. 174° (decomp.) (from alcohol) (Found: N, 13·7. $C_{18}H_{18}O_7N_4$ requires N, 13·9%). The unsaturated base was the stronger and reduced alcoholic silver nitrate. Both bases, with acetic acid–anhydride, gave 1-*acetyl*-2 : 3-*dihydro*-7 : 8-*dimethylbenz*[f]*azepine* (XIV; R = Ac), m. p. 95° (from ether) (Found: C, 77·8; H, 7·95; N, 6·5. $C_{14}H_{17}ON$ requires C, 78·1; H, 8·0; N, 6·5%).

Preparation and Oxidation of 1-*Acetyl*-2 : 3 : 4 : 5-*tetrahydro*-5-*hydroxy*-7 : 8-*dimethylbenz*[f]-*azepine* (XIII; R = Ac).—To the hydroxy-amine (XIV; R = H) (0·96 g.) were added 2N-sodium hydroxide (5 ml.) and acetic anhydride (1 ml.), dropwise at $<5°$. The mixture was shaken in an ice-bath for several hours, then extracted with benzene, giving on evaporation of the extract a neutral solid (1 g.) which could not be satisfactorily purified; a sample triturated with methanol had m. p. 136°, depressed on admixture with the hydroxy-amine.

Chromic oxide (1·3 g.) in pure pyridine (15 ml.) was mixed with the crude *acetyl compound* (1 g.) in pyridine (8 ml.) and left overnight. Then water was added and the mixture extracted with 1 : 1 ether–benzene (3 × 33 ml.). Evaporation of the dried extracts left a solid (0·7 g.). Crystallisation from methanol gave 2 : 3 : 4 : 5-*tetrahydro*-7 : 8-*dimethyl*-5-*oxobenz*[f]*azepine* (I; R = H, R′ = Me), m. p. 106° (Found: C, 76·35; H, 7·9; N, 7·4. $C_{12}H_{15}ON$ requires C, 76·15; H, 8·0; N, 7·4%). This ketone was acid-soluble and gave a very poor yield of a dinitrophenylhydrazone, m. p. 205°, probably as a rather soluble hydrochloride.

The ketone mother-liquor, when worked up, gave the N-*acetyl-ketone* (I; R = Ac, R′ = Me), m. p. 105° (Found: C, 72·5; H, 7·1; N, 6·2. $C_{14}H_{17}O_2N$ requires C, 72·7; H, 7·4; N, 6·05%). Its dinitrophenylhydrazone was very soluble and deacetylation was suspected. The *semicarbazone*, obtained from alcohol, had m. p. 206° (Found: N, 19·3. $C_{15}H_{20}O_2N_4$ requires N, 19·4%).

1-*Acetyl*-4 : 5-*a bromo*-2 : 3 : 4 : 5-*tetrahydro*-7 : 8-*dimethylbenz*[f]*azepine*.—To the unsaturated amide (XIV; R = Ac) (1 g.) in chloroform was added bromine (0·24 ml.). Evaporation of the rapidly decolorised solution left the *dibromo-compound*, m. p. 173° (from methanol) (Found: C, 45·1; H, 4·5; N, 3·0; Br, 44·0. $C_{14}H_{17}ONBr_2$ requires C, 44·8; H, 4·7; N, 3·7; Br, 43·0%).

The author acknowledges the benefit of discussions with Professors F. Bergel and C. W. L. Bevan and thanks Dr. D. H. Irvine for the ultraviolet spectrum and Messrs. Roche Products Ltd. for gifts of xylidine and Dr. A. A. Wagland for infrared spectra.

UNIVERSITY COLLEGE, IBADAN, NIGERIA. [*Received, February 27th,* 1959.]