777. *Azabenzocycloheptenones. Part III.** 2,3,4,5-*Tetrahydro*-5-*oxo*-1-*toluene*-p-*sulphonylbenz*[b]*azepine.*

By G. R. Proctor.

The title compound, now available in good yield, cannot be dehydrogenated by bromination–dehydrobromination procedures, but it can be oxidised to an α-diketone which gives an enol acetate. Although this represents a partial dehydrogenation, the toluene-*p*-sulphonyl group could not be extruded nor could the amino-diketone (V; R = H) be obtained by standard methods. The basic ketone (II; R = H) can be obtained by hydrolysis of the toluene-*p*-sulphonyl derivative.

The most promising routes to azatropolones such as (I; R = OH) appear to require, as starting materials, ketones (II; R = toluene-*p*-sulphonyl, R′ = R″ = H) in which the carbonyl group is separated from the nitrogen atom by at least two carbon atoms. Closer proximity of these functions leads to the formation of lactams.

We have described [1] the synthesis of (II; R = toluene-*p*-sulphonyl, R′ = R″ = H) and now record the results of some experiments designed to convert it into the azatropolone (I; R = OH) and into the azatropone (I; R = H).

The synthetical route [1] to the ketone (II; R = toluene-*p*-sulphonyl, R′ = R″ = H) has been much improved. Three routes to the α-diketone (V; R = toluene-*p*-sulphonyl) have been developed: they are, first selenium dioxide oxidation, secondly ozonolysis [3] of the α-hydroxymethylene-ketone (II; R′, R″ = CH·OH, R = toluene-*p*-sulphonyl) and thirdly,[4] the mild hydrolysis of the α-dibromo-ketone (II; R = toluene-*p*-sulphonyl, R′ = R″ = Br). The second method we found gave the most refined product, but for general utility, the third method is preferred.

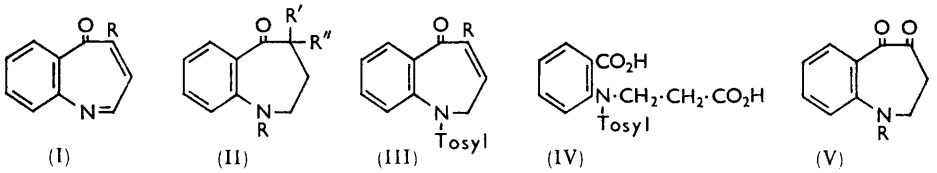
Treatment of either the ketone (II; R = toluene-*p*-sulphonyl, R′, R″ = CH·OH) with excess ozone or the diketone (V; R = toluene-*p*-sulphonyl) with alkaline hydrogen

* Part II, *J.*, 1957, 2312.

[1] Proctor and Thomson, *J.*, 1957, 2312.
[2] Proctor, *Chem. and Ind.*, 1960, 408.
[3] Caunt, Crow, and Haworth, *J.*, 1951, 1316.
[4] Cf. Wittig and Vidal, *Ber.*, 1948, **81**, 370.

peroxide yielded the known diacid (IV): this confirmed the structures of these heterocyclic intermediates.

It was found that the N–S bond in the molecule (V; R = toluene-*p*-sulphonyl) was resistant to cleavage. Boiling with concentrated hydrochloric acid and glacial acetic acid,[5,6] or treatment with hydrogen bromide and acetic acid in the presence of phenol [7]



was without appreciable effect. Treatment with polyphosphoric acid led to resinification without loss of sulphur, while reaction with calcium in liquid ammonia gave a poor yield of an amino-monoketone. It appears that the amino-diketone (V; R = H) is not available by this route.

A more subtle approach was to force the molecule (V; R = toluene-*p*-sulphonyl) into the enol configuration (III; R = OAc) and bring about the extrusion of the toluene-*p*-sulphonyl group by base-catalysed elimination,[9] a method we have successfully employed for the conversion of the vinylogous ketone (VIII) into the azatropone [2] (IX). The enol acetate (III; R = OAc) was, however, partly deacetylated and partly converted into a sulphur-containing acid which we were unable to purify.

The failure to extrude the toluene-*p*-sulphonyl group may be due to participation of the *O*-acetyl group as an electron-source, inhibiting the formation of the anion (VI) which is a necessary intermediate in the elimination.

By analogy with the tropolones,[10] bromination of (V; R = toluene-*p*-sulphonyl) followed by dehydrobromination ought to give an intermediate (VII) in the same state of oxidation as the desired azatropolone, from which the latter should be obtained by acid treatment. Unexpectedly, however, treatment of the α-diketone (V; R = toluene-*p*-sulphonyl) with two moles of bromine in glacial acetic acid yielded the dibromide (II; R = toluene-*p*-sulphonyl, R′ = R″ = Br). Bromination in chloroform gave a mixture containing much starting material.

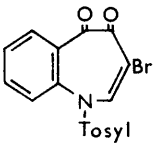
Also related to the dibenzo-compound (VIII) is the ketone (III; R = H) which might be expected to permit elimination of the toluene-*p*-sulphonyl group. A synthesis was attempted in the following way. The ketone (II; R = toluene-*p*-sulphonyl, R′ = R″ = H) easily gave mono- (II; R = toluene-*p*-sulphonyl, R′ = H, R″ = Br) and di-bromo-compounds (II; R = toluene-*p*-sulphonyl, R′ = R″ = Br). The latter had been oriented by conversion into the dione (V; R = toluene-*p*-sulphonyl).

Neither of the bromo-compounds could be dehydrobrominated with triethylamine or collidine to the corresponding αβ-unsaturated ketones. When mild conditions were employed, most of the starting materials were recovered but on more vigorous treatment, the molecules were partially debrominated. In a similar case, Rees [11] found hydrated sodium acetate to be an effective dehydrobrominating agent: we found it to have no effect, and, on the other hand, the use of lithium chloride in dimethylformamide [12] gave no recognisable products from (II; R = toluene-*p*-sulphonyl, R′ = R″ = Br).

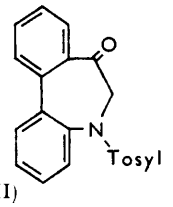
[5] Clemo and Perkin, *J.*, 1924, **125**, 1608.
[6] Johnson, Woroch, and Buell, *J. Amer. Chem. Soc.*, 1949, **71**, 1901.
[7] Weisblat, Magerlein, and Myers, *J. Amer. Chem. Soc.*, 1953, **75**, 3630.
[8] (*a*) Sondheimer, Mancera, Rosenkranz, and Djerassi, *J. Amer. Chem. Soc.*, 1953, **75**, 1282; (*b*) Barton, McGhie, Pradhan, and Knight, *J.*, 1955, 876.
[9] (*a*) Holmes and Ingold, *J.*, 1926, 1305; (*b*) Fenton and Ingold, *J.*, 1928, 3295.
[10] Cook, Gibb, Raphael, and Somerville, *J.*, 1952, 606.
[11] Rees, *J.*, 1959, 3111.
[12] Mazur and Sondheimer, *J. Amer. Chem. Soc.*, 1958, **80**, 5229.

An alternative route to the ketone (III; R = H), based on the dehydration of the hydroxy-ketone (II; R = toluene-*p*-sulphonyl, R′ = OH, R″ = H) with phosphorus pentoxide in toluene at the b. p., caused rupture of the molecule: traces of basic materials were all that could be found.

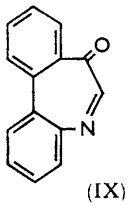
(VI)



(VII)



(VIII)



(IX)

These results suggest that the toluene-*p*-sulphonyl group should be removed from (II; R = toluene-*p*-sulphonyl, R′ = R″ = H) as a preliminary to further dehydrogenation. Although, by comparison with closely related six-membered ring compounds,[5,6] the ketone (II; R = toluene-*p*-sulphonyl, R′ = R″ = H) is rather resistant to cleavage by acids, the amino-ketone (II; R = R′ = R″ = H) has been obtained as an oil which could be distilled *in vacuo* without appreciable decomposition. It forms a 2,4-dinitrophenylhydrazone [cf. 13,14] and a picrate.

The possibility of converting the amino-ketone (II; R = R′ = R″ = H) into the azatropolone (I; R = OH) and the azatropone (I; R = H) is now being examined.

Experimental

Ethyl γ-N-(o-*Methoxycarbonylphenyl*)*toluene*-p-*sulphonamidobutyrate*.—Methyl *N*-toluene-*p*-sulphonylanthranilate (302 g.), anhydrous sodium carbonate (300 g.), and decalin (1·5 l.) were refluxed and stirred while ethyl γ-bromobutyrate (234 g.) was added during 1·5 hr. After a further 4 hr., the mixture was cooled, diluted with chloroform, and filtered, and the residue washed well with chloroform. Evaporation of the solvents gave an oil (400 g.) which was crystallised from ethanol giving 197 g. of product, m. p. 98—100° (yield 47%). The second crop (52 g.) had m. p. 80°, and the liquor gave an oil (146 g.) which was recycled.

2,3,4,5-*Tetrahydro*-5-*oxo*-1-*toluene*-p-*sulphonylbenz*[b]*azepine* (II; R = *toluene*-p-*sulphonyl*, R′ = R″ = H).—Potassium (10 g.) was dissolved in t-butyl alcohol (excess); after the latter was distilled off, toluene (1 l.) was added and the mixture distilled to constant boiling point. To this refluxing, stirred solution under dry nitrogen (oxygen-free) was added the above ester (50 g.) in dry toluene (500 ml.) slowly during 2 hr. with steady distillation of solvent. After the boiling point had again reached 110° (*ca.* 1 hr.), the mixture was cooled and diluted with water and dilute hydrochloric acid, and the aqueous layer separated and washed with chloroform. The combined organic layers were evaporated leaving the *keto-ester* (II; R = toluene-*p*-sulphonyl, R′ = CO_2Et, R″ = H) which crystallised from light petroleum (b. p. 80—100°) in needles, m. p. 120° (Found: C, 61·0; H, 5·2; N, 3·4. $C_{19}H_{19}NO_5S$ requires C, 61·1; H, 5·1; N, 3·75%); $\nu_{max.}$ 1645 cm.$^{-1}$ (in Nujol).

The 2,4-dinitrophenylhydrazone of the keto-ester was obtained from methanol–acetic acid as an orange solid, m. p. 208° (Found: C, 54·7; H, 4·5. $C_{25}H_{23}N_5O_8S$ requires C, 54·3; H, 4·2%); $\nu_{max.}$ 1735, 1620, and 1590 (in Nujol).

The keto-ester (42·5 g.) was refluxed with ethanol (100 ml.), glacial acetic acid (300 ml.), concentrated hydrochloric acid (50 ml.), and water (50 ml.) for 8 hr. The mixture was cooled, diluted with water, and extracted with chloroform, and the extract evaporated *in vacuo* leaving a residue which was purified by chromatography on alumina and by crystallisation from methanol. The product had m. p. 126° [1] (yield 71%).

2,3,4,5-*Tetrahydro*-4-*hydroxymethylene*-5-*oxo*-1-*toluene*-p-*sulphonylbenz*[b]*azepine* (II; R = *toluene*-p-*sulphonyl*, R′, R″, = CH·OH).—A solution of the above ketone (9·7 g.), ethyl formate (10 ml.), and dry toluene (150 ml.) was cooled to 0° and added to a suspension of

[13] Astill and Boekelheide, *J. Amer. Chem. Soc.*, 1955, **77**, 4080.
[14] Braunholtz and Mann, *J.*, 1957, 4174; 1958, 3377.

sodium ethoxide (from 6 g. of sodium) in toluene (80 ml.) at 0°. After 24 hr. at 20°, the mixture was diluted with water, and the toluene layer washed with cold sodium hydroxide (10% aqueous). The combined alkaline washings were acidified with ice-cooling and extracted with chloroform (3 × 50 ml.), which was dried and evaporated to leave a residue (9·6 g.). This crystallised from light petroleum (b. p. 100—120°) giving crystals, m. p. 126° (8·7 g.) (Found: C, 63·4; H, 5·1; N, 3·9; S, 9·9. $C_{18}H_{17}NOS$ requires C, 62·95; H, 5·0; N, 4·1; S, 9·35%); $\nu_{max.}$ 1645 and 1595 cm.$^{-1}$ (in Nujol). The 2,4-*dinitrophenylhydrazone* was obtained from methanol–glacial acetic acid as crimson needles, m. p. 207° (Found: C, 54·8; H, 4·3; N, 13·4; S, 6·9. $C_{24}H_{21}N_5O_7S$ requires C, 55·05; H, 4·1; N, 13·4; S, 6·1%).

The *methyl ether* was obtained with refluxing methanol containing traces of mineral acid. It had m. p. 197° (Found: C, 64·1; H, 5·5; N, 3·8; S, 9·2. $C_{19}H_{19}NO_4S$ requires C, 63·85; H, 5·4; N, 4·0; S, 9·0%); $\nu_{max.}$ (in Nujol) 1670, 1605, and 1590 cm.$^{-1}$.

4-*Bromo*-2,3,4,5-*tetrahydro*-5-*oxo*-1-*toluene*-p-*sulphonylbenz*[b]*azepine* (II; R = *toluene*-p-*sulphonyl*, R′ = Br, R″ = H).—The monoketone (II; R = toluene-*p*-sulphonyl, R′ = R″ = H) (6·6 g.) in chloroform (100 ml.) was treated with bromine (1 ml.). After 1 hr. at 20° the solvent was removed under reduced pressure; the product crystallised from methanol in needles (7 g.), m. p. 132° (Found: C, 51·7; H, 4·4; Br, 19·8; N, 3·55. $C_{17}H_{16}BrNO_3S$ requires C, 51·75; H, 4·1; Br, 20·2; N, 3·55%); $\nu_{max.}$ 1695 cm.$^{-1}$ (in Nujol) (>C=O). The 2,4-dinitrophenylhydrazone, m. p. 236°, was identical with that obtained from the monoketone (II; R = toluene-*p*-sulphonyl, R′ = R″ = H).

4,4-*Dibromo*-2,3,4,5-*tetrahydro*-5-*oxo*-1-*toluene*-p-*sulphonylbenz*[b]*azepine* (II; R = *toluene*-p-*sulphonyl*, R′ = R″ = Br).—The monoketone (II; R = toluene-*p*-sulphonyl, R′ = R′ = H (4·8 g.) in chloroform (100 ml.) was treated with bromine (1·47 ml.) as in the previous example. The product was obtained from ethanol as needles (5·6 g.), m. p. 173° (Found: C, 42·9; H, 3·3; Br, 33·1; N, 2·9. $C_{17}H_{15}Br_2NO_3S$ requires C, 43·1; H, 3·2; Br, 33·8; N, 2·95%); $\nu_{max.}$ 1715 cm.$^{-1}$ (in Nujol) (>C=O). The product failed to form a 2,4-dinitrophenylhydrazone.

2,3,4,5-*Tetrahydro*-5-*oxobenz*[b]*azepine* (II; R = R′ = R″ = H).—(*a*) The ketone (II; R = toluene-*p*-sulphonyl, R′ = R″ = H) (4·92 g.), concentrated hydrochloric acid (200 ml.), and glacial acetic acid (200 ml.) were refluxed 8 hr., cooled, and extracted with chloroform.* After separation, the aqueous layer was treated with ammonia (*d* 0·88) and ice, and extracted with chloroform. The extract was dried and evaporated leaving the *product* (0·72 g.) which distilled as a clear yellow oil (600 mg.), b. p. 135—140°/0·1 mm.; $\nu_{max.}$ 3340, 1665, and 1600 cm.$^{-1}$ (liquid film) (Found: C, 73·5; H, 6·8; N, 8·8. $C_{10}H_{11}NO$ requires C, 74·5; H, 6·9; N, 8·7%).

The 2,4-*dinitrophenylhydrazone* was a dark violet solid, m. p. 248° (Found: C, 56·15; H, 4·5; N, 20·3. $C_{16}H_{15}N_5O_4$ requires C, 56·3; H, 4·4; N, 20·5%); the *picrate* was obtained from ethanol as a yellow product, m. p. 228° (Found: N, 13·0. $C_{18}H_{20}N_4O_4$ requires N, 12·85%).

(*b*) The ketone (0·64 g.) was heated with polyphosphoric acid (10 g.) on the steam bath for 3 hr. After dilution with water and extraction with chloroform, the aqueous layer was basified with ammonia (*d* 0·88) and extracted with chloroform, and the extract dried and evaporated leaving the crude amino-ketone (148 mg.). Distillation *in vacuo* gave the pure product (100 mg.) as before.

(*c*) The ketone (1·17 g.) in tetrahydrofuran (15 ml.) was added to a suspension of calcium (2 g.) in liquid ammonia (100 ml.), and the mixture agitated for 10 min. An excess of dry bromobenzene was then added and the ammonia allowed to evaporate in a stream of nitrogen. The basic fraction (100 mg.) was isolated as before.

2,3,4,5-*Tetrahydro*-4,5-*dioxo*-1-*toluene*-p-*sulphonylbenz*[b]*azepine* (V; R = *toluene*-p-*sulphonyl*).—(*a*) The hydroxymethylene ketone (II; R = toluene-*p*-sulphonyl, R′, R″ = CH·OH) (5·6 g.) in dry ethyl acetate (150 ml.) was treated with 72·5% † of the calculated amount of ozone at −70°. The mixture was hydrogenated at 20° in presence of pre-reduced palladium hydroxide on barium carbonte (2%). After filtration, the ethyl acetate solution was washed with cold aqueous sodium hydroxide (10%) followed by dilute hydrochloric acid and was dried and evaporated, leaving the product (2·43 g.) which crystallised from light petroleum (b. p. 100—120°) as a pale yellow solid, m. p. 148° (Found: C, 61·65; H, 5·0; N, 4·25. $C_{17}H_{15}NO_4S$ requires C, 62·0; H, 4·6; N, 4·25%); $\nu_{max.}$ (in Nujol) 1710, 1680, and 1580 cm.$^{-1}$.

The 2,4-*dinitrophenylhydrazone* was obtained from nitrobenzene as an orange product, m. p.

* The neutral extract contained starting material (2·89 g.).

† Use of too much ozone leads to the formation of *N*-toluene-*p*-sulphonyl-*N*-2′-carboxyethylanthranilic acid (IV), m. p. and mixed m. p. 189°.[1]

252° (Found: C, 54·55; H, 4·35; N, 13·9. $C_{23}H_{19}N_5O_7S$ requires C, 54·2; H, 3·75; N, 13·75%).

The *quinoxaline* derivative was made from the diketone with *o*-phenylenediamine in ethanol: by crystallisation from methanol or sublimation *in vacuo* the yellow product, m. p. 198°, was obtained (Found: C, 68·5; H, 5·1; N, 10·6; S, 7·5. $C_{23}H_{19}N_3O_2S$ requires C, 68·8; H, 4·75; N, 10·5; S, 8·0%).

When the diketone was chromatographed on active alumina, elution with chloroform (containing 1% of ethanol) gave in poor yield a yellow product, m. p. 142°, which was judged to be the *ethyl ether* of the enol ketone (Found: C, 63·8; H, 5·3; N, 4·3; S, 8·95. $C_{19}H_{19}NO_4S$ requires C, 63·85; H, 5·35; N, 3·9; S, 8·95%); $\nu_{max.}$ (in Nujol) 1695, 1642, and 1605 cm.$^{-1}$. The *oxime* was obtained from aqueous methanol as a fine powder, m. p. 136° (Found: N, 7·2. $C_{19}H_{20}N_2O_4S$ requires N, 7·5%).

(*b*) To the monoketone (II; R = toluene-*p*-sulphonyl, R′ = Br, R″ = H) (5·4 g.) dissolved in glacial acetic acid (100 ml.) was added selenium dioxide (1·95 g.) dissolved in water (10 ml.). The mixture was refluxed for 2½ hr., cooled, filtered, stirred with mercury,[18] diluted with water, and extracted with chloroform. The latter was shaken successively with dilute sodium hydroxide, dilute hydrochloric acid, and water, dried, and evaporated, leaving a residue (4·7 g.) from which the product was obtained by crystallisation from light petroleum (b. p. 100—120°).

(*c*) The α-dibromo-ketone (II; R = toluene-*p*-sulphonyl, R′ = R″ = Br) (1·38 g.), potassium hydrogen carbonate (3·5 g.), and water (50 ml.) were vigorously refluxed for 4 hr., cooled, and extracted with chloroform. The extract was washed with dilute hydrochloric acid and with water, dried, and evaporated leaving a glass (0·93 g.) from which the diketone was obtained by crystallisation from light petroleum (b. p. 100—120°).

Action of Dilute Alkali on the o-*Diketone* (V; R = *toluene*-p-*sulphonyl*).—The dione (380 mg.) in methanol (25 ml.) was treated with dilute sodium hydroxide (10%; 1 ml.). After 1 hr. the mixture was diluted with water, acidified with dilute hydrochloric acid, and extracted with chloroform. The extract, on evaporation, yielded the unchanged dione (350 mg.), having an infrared spectrum identical with that of the pure dione.

Action of Calcium and Liquid Ammonia on the Diketone (V; R = *toluene*-p-*sulphonyl*).—The diketone (V; R = toluene-*p*-sulphonyl) (1·8 g.) in dry toluene (60 ml.) was added rapidly with mechanical stirring to a suspension of calcium (4 g.) in liquid ammonia (150 ml.). After 3 min., dry bromobenzene (8 g.) in toluene (50 ml.) was added slowly and stirring continued for 2 hr. The mixture was acidified and the aqueous layer separated and treated with ice and ammonia (*d* 0·88) until alkaline: it was then extracted with chloroform which extract was subsequently dried and evaporated, leaving the product (0·25 g.). The latter was distilled at 0·1 mm. yielding a brown oil (80 mg.); $\nu_{max.}$ 3400, 1665, and 1600 cm.$^{-1}$. The infrared spectrum, although similar to that of the amino-ketone (II; R = R′ = R″ = H) lacks the detail of the latter.

The Reaction between the Diketone (V; R = *toluene*-p-*sulphonyl*) *and Isopropenyl Acetate.*—The dione (1·39 g.), isopropenyl acetate (90 ml.),[19] and concentrated sulphuric acid (4 drops) were refluxed vigorously for 2 hr., while the volatile products were collected through a short vertical condenser. The mixture was cooled and treated with benzene and water; the benzene layer was removed, dried, and evaporated, leaving the product (1·26 g.). The quality of the latter could not be much improved by crystallisation from aqueous methanol or by chromatography on alumina, but it showed $\nu_{max.}$ 1752(s) (in Nujol). When this " enol acetate " (III; R = Ac) was treated with potasium t-butoxide in toluene at room temperature, it was recovered in 65% yield, the remainder (20%) being a sulphur-containing acid which could not be purified.

Action of Polyphosphoric Acid on the Diketone (V; R = *toluene*-p-*sulphonyl*).—The diketone (2 g.) was treated with polyphosphoric acid (excess) at 165—170° for 80 min., the black insoluble residue contained sulphur but could not be purified.

At lower temperatures similar insoluble materials were obtained accompanied by traces of the starting material identified by the infrared spectrum.

Action of Bromine on the Diketone (V; R = *toluene*-p-*sulphonyl*).—The diketone (0·21 g.), glacial acetic acid (25 ml.), and bromine (0·22 g.) were left at 20° for 4 days and then poured into water (100 ml.) and chloroform (30 ml.); after being shaken, the chloroform was removed,

[15] Nozoe, Seto, Matsumara, and Terasawa, *Chem. and Ind.*, 1954, 1356.
[16] Rosenkranz, Kaufmann, Pataki, and Djerassi, *J. Amer. Chem. Soc.*, 1950, **72**, 1046.
[17] Birch and Smith, *Quart. Rev.*, 1958, **12**, 17.
[18] Jacques, Ourisson, and Sandris, *Bull. Soc. chim. France*, 1955, 1293.
[19] Irvine, Henry, and Spring, *J.*, 1955, 1319.

washed with water, dried, and evaporated, leaving the product (0·3 g.) which crystallised from aqueous methanol in needles, m. p. 166° undepressed on admixture with the dibromo-ketone (II; R = toluene-*p*-sulphonyl, R′ = R″ = Br).

Action of 2,4-*Dinitrophenylhydrazine on the Bromo-ketone* (II; R = *toluene*-p-*sulphonyl*, R′ = Br, R = H).—Treatment of the bromo-ketone with an alcoholic solution of 2,4-dinitrophenylhydrazine containing concentrated hydrochloric acid (*ca.* 2%) gave an orange precipitate, which crystallised from glacial acetic acid in prisms, m. p. 236° undepressed on admixture with the 2,4-dinitrophenylhydrazone of the ketone (II; R = toluene-*p*-sulphonyl, R′ = R″ = H).

Action of Triethylamine on the Bromo-ketone (II; R = *toluene*-p-*sulphonyl*, R′ = Br, R″ = H).—The bromo-ketone (3·34 g.), dry carbon tetrachloride (115 ml.), and triethylamine (25 ml.) were refluxed for 7 hr. and then evaporated under reduced pressure. The residue was shaken with dilute hydrochloric acid and benzene; after being dried (Na_2SO_4) the latter was chromatographed on alumina and the eluted material crystallised from methanol, yielding crystals (1·6 g.), m. p. 129—130° undepressed by admixture with the starting material. Elution of the column with polar solvents gave a fine granular dark product (1·1 g.) having an infrared spectrum identical with that of the starting material.

Action of Collidine on the Bromo-ketone (II; R = *toluene*-p-*sulphonyl*, R′ = Br, R″ = H).—The bromo-ketone (3·0 g.) was refluxed for 24 hr. with collidine (40 ml.). The mixture was cooled and treated with excess of dilute hydrochloric acid and chloroform; the latter extract was washed with water, dried, and evaporated. The residual oil was chromatographed on alumina and gave the monoketone (II; R = toluene-*p*-sulphonyl, R′ = R″ = H) (0·8 g.), m. p. and mixed m. p. 124°. After treatment with collidine [20] for 28 hr. at 100° and similar working up, the bromo-ketone was recovered in 75% yield.

Action of Triethylamine on the Dibromo-ketone (II; R = *toluene*-p-*sulphonyl*, R′ = R″ = Br).—The dibromo-ketone (2·84 g.) was refluxed for 7 hr. with triethylamine (15 ml.) and dry carbon tetrachloride (150 ml.) and worked up as in the previous section. Crystallisation of the product from ethanol gave starting material (800 mg.), m. p. and mixed m. p. 165°, and monobromo-ketone (II; R = toluene-*p*-sulphonyl, R′ = Br, R″ = H) (510 mg.), m. p. and mixed m. p. 129°.

2,3,4,5-*Tetrahydro*-4-*hydroxy*-5-*oxo*-1-*toluene*-p-*sulphonylbenz*[b]*azepine* (II; R = *toluene*-p-*sulphonyl*, R′ = OH, R″ = H).—The bromo-ketone (II; R = toluene-*p*-sulphonyl, R′ = Br, R″ = H) (1·78 g.) was refluxed with ethanol (60 ml.) and aqueous sodium carbonate (10%; 20 ml.) for 1 hr., and the mixture cooled, diluted with water, and extracted with chloroform. The extract was dried and evaporated leaving the product as a tar (1·45 g.). After chromatography on silica gel and crystallisation from light petroleum (b. p. 100—120°), this was obtained as a fine powder, m. p. 196°, but satisfactory analyses could not be obtained. The 2,4-*dinitrophenylhydrazone*, which crystallised from glacial acetic acid, had m. p. 231° (Found: C, 54·2; H, 4·3; N, 13·6. $C_{23}H_{21}N_5O_7S$ requires C, 54·0; H, 4·15; N, 13·7%).

Treatment of the Hydroxy-ketone (II; R = *toluene*-p-*sulphonyl*, R′ = OH, R″ = H) *with Phosphorus Pentoxide*.—The hydroxy-ketone (120 mg.), phosphorus pentoxide (1 g.), and dry toluene (40 ml.) were refluxed for 6 hr., the mixture cooled and diluted with water, and the organic layer washed with water and chromatographed on alumina to yield a crystalline product (10 mg.), m. p. 152°, from light petroleum (b. p. 60—80°). This product had no infrared carbonyl absorption. Basification of the acid washings and solvent extraction yielded a yellow basic ketone (10 mg.).

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[20] Buchanan and Lockhart, *J.*, 1959, 3586.