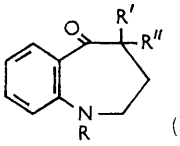
946. *Azabenzocycloheptenones. Part V.* 2,3,4,5-Tetrahydro-5-oxobenz[b]azepines.*

By W. H. Bell, E. D. Hannah, and G. R. Proctor.

Some transformation products of the tetrahydrobenzazepine (I; R = R′ = R″ = H) are described but attempted conversion into the oxygenated derivatives (I; R = R″ = H, R′ = OH) and (I; R = H, R′R″ = O) was unsuccessful. The latter were obtained from the diester (II) by the acyloin reaction.

The amino-ketone (I; R = R′ = R″ = H) can now be obtained in substantial quantities [1] and the present Paper describes some attempts to use it in synthesis of azabenzotropolones.

The methods that were successful [1] for conversion of the ketone (I; R′ = *p*-$C_6H_4Me{\cdot}SO_2$, R′ = R″ = H) to the corresponding diketone (I; R′ = *p*-$C_6H_4Me{\cdot}SO_2$, R′R″ = O) were found to be ineffective: oxidation of the ketone (I; R = R′ = R″ = H) with selenium dioxide gave intractable products; no reaction occurred with ethyl formate; and bromination with two mol. of bromine gave a mixture from which were isolated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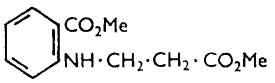
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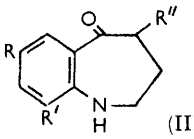
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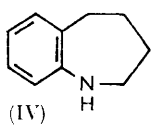
two dibromides, probably (III; R = R″ = Br, R′ = H) and (III; R = H, R′ = R″ = Br), and a tribromide (III; R = R′ = R″ = Br). [Structural assignments were based on elementary analysis, nuclear magnetic resonance (n.m.r.) data, and consideration of the directing influences of the relevant groups.] Hydrolysis of the dibromide (III; R = R″ = Br, R′ = H) yielded, unexpectedly, a debrominated product (III; R = Br, R′ = R″ = H). The further bromination of these compounds is under investigation.

Since one of the difficulties in this work has been [1] the removal of the toluene-*p*-sulphonyl group, the possibility of metal–ammonia cleavage [2] was examined. Both ketones (I; R = *p*-$C_6H_4Me{\cdot}SO_2$, R′ = R″ = H and R′R″ = O) form ethylene ketals,[3a] but these were cleaved by calcium in liquid ammonia [3b] to the base (IV), the structure of which was confirmed by synthesis from the ketone (I; R = R′ = R″ = H) by standard procedures.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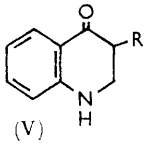
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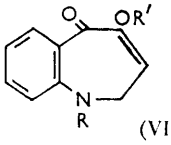
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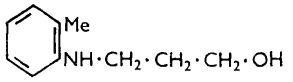
(VII)

As a result, the application of the acyloin reaction to the diester (II) was re-examined. Previous work [4] had established that reaction in the conventional fashion gave the dihydroquinolones (V; R = H and CO_2Me); it now seems that this result may have been due to the effect of sodium salts of phenols present in the xylene, for, when carefully purified toluene was used, the diester (II) was recovered quantitatively. Liquid ammonia as solvent has been recommended,[5] and, initially, gave the keto-ester (V; R = CO_2Me);

* Part IV, Paterson and Proctor, 1962, 3468.

[1] Proctor, *J.*, 1961, 3989.
[2] Birch and Smith, *Quart. Rev.*, 1958, **12**, 17.
[3] (*a*) Sulzbacher, Bergmann, and Pariser, *J. Amer. Chem. Soc.*, 1948, **70**, 2827; (*b*) Johnson, Shulman, Williamson, and Pappo, *J. Org. Chem.*, 1962, **27**, 2017.
[4] Proctor and Thomson, *J.*, 1957, 2312.
[5] Sheehan, Coderre, and Cruickshank, *J. Amer. Chem. Soc.*, 1953, **75**, 6232.

but when the ammonia was purified by distillation through a column packed with potassium hydroxide, thin-layer chromatography [6] revealed several products. The keto-ester (V; R = CO_2Me) was usually present along with polymeric materials and viscous tars which were chromatographed on silica and on neutral deactivated alumina. In this way were isolated poor yields of the acyloin (I; R′ = R″ = H, R′ = OH) and the enol-ether (VI; R = H, R′ = Et) from which a *N*-toluene-*p*-sulphonyl derivative was obtained identical with a compound made [1] from the diketone (I; R = *p*-$C_6H_4Me{\cdot}SO_2$, R′R″ = O) in which the presence of the seven-membered ring has been established. Since it was obvious [1] that the enol-ether had been formed during chromatography, the presence of the diketone (I; R′ = H, R′R″ = O) in the crude reaction product is inferred; [7] it was made more certain when it was found that, while the purified acyloin was resistant to reduction, the crude product (which gave two carbonyl peaks in the infrared spectrum) reacted with lithium aluminium hydride in tetrahydrofuran to give an amino-alcohol. The nuclear magnetic resonance (n.m.r.) spectrum was consistent with structure (VII) and this was confirmed by synthesis from *o*-toluidine and ethyl acrylate [8b] followed by reduction (reaction of o-toluidine with allyl alcohol [8c] did not give the expected product). It was then found that the diketone (I; R′ = *p*-$C_6H_4Me{\cdot}SO_2$, R′R″ = O), after cleavage and reduction, gave the same amino-alcohol. Thus, although the presence of the amino-diketone (I; R′ = H, R′R″ = O) can be accepted with certainty, it could only be isolated as the enol-ether. It has been held that *o*-diketones are intermediates in the acyloin reaction and they are major products in certain cases.

The acyloin (I; R′ = R″ = H, R′ = OH) could not be dehydrogenated by bismuth oxide,[9] and other reagents either had no effect or gave unrecognisable products. The acyloin reacted with triphenylmethyl perchlorate [10,11] in methylene chloride. The product had apparently become *N*-methylated; this was confirmed by examination of the ferro-tungstate [12] and chloroplatinate and by the observation that the amino-ketone (I; R = R′ = R″ = H) could be *N*-methylated in the same medium.

Further investigation of the acyloin reaction showed that when too little liquid ammonia was used there was a need to employ more than the calculated amount [13] of sodium; this was presumably due to the sodium's being incompletely dissolved and when methanol was added cleavage took place giving the amino-alcohol (VII) as the principal product. When bromobenzene was used instead of methanol, some *N*-phenylation of the product occurred.

Huisgen and his co-workers [14] reported that similar aryl alkyl diesters would not undergo the acyloin reaction. The present investigation showed that, while some of the expected ketone was obtained, the complexity of the product made the process unattractive for azatropolone syntheses.

Experimental

2,3,4,5-Tetrahydrobenz[b]*azepin-5-one* (I; R = R′ = R″ = H).[1]—The ketone (I; R = *p*-$C_6H_4Me{\cdot}SO_2$, R′ = R″ = H) (100 g.), acetic acid (500 ml.), concentrated hydrochloric acid (500 ml.), and zinc chloride [15] (85 g.) were refluxed for 14 hr., cooled, diluted with water, and extracted with chloroform [the neutral extract contained starting material (20 g.)]. After filtration, the aqueous layer was treated with ammonia (*d* 0·88) and ice, and extracted with

[6] Stahl, *Arch. Pharm.*, 1959, **65**, 531.
[7] Totton, Freeman, Powell, and Yarboro, *J. Org. Chem.*, 1961, **26**, 343.
[8] (*a*) Pierce and Adams, *J. Amer. Chem. Soc.*, 1923, **45**, 794; (*b*) Johnson, Woroch, and Buell, *ibid.*, 1949, **71**, 1903; (*c*) Hromatka, *Ber.*, 1942, **75**, 379 (*Chem. Abs.*, 1943, **37**, 3462.)
[9] Rigby, *J.*, 1951, 793; Cram and Antar, *J. Amer. Chem. Soc.*, 1958, **80**, 3114.
[10] Dauben, Honnen, and Harmon, *J. Org. Chem.*, 1960, **25**, 1442.
[11] Bonthrone and Reid, *J.*, 1959, 2773.
[12] Brown, *J.*, 1962, 1512.
[13] McElvain, *Org. Reactions*, Vol. IV, p. 260.
[14] Ugi, Huisgen, and Pawellek, *Annalen*, 1961, **641**, 63.
[15] Klamann and Hofbauer, *Annalen*, 1953, **581**, 182.

chloroform. The extract was dried and evaporated, leaving the product (36 g.) which was purified by chromatography, distillation *in vacuo*, and crystallisation from light petroleum (b. p. 60—80°); it was a waxy solid (22 g.), m. p. 69° (Found: C, 74·6; H, 7·0; N, 8·7. Calc. for $C_{10}H_{11}NO$: C, 74·5; H, 6·9; N, 8·7%). The infrared spectrum was identical with that previously reported.[1] The N-*acetate* was obtained with acetic anhydride in pyridine and crystallised from light petroleum in prisms, m. p. 122° (Found: C, 70·65; H, 5·95; N, 6·65. $C_{12}H_{13}NO_2$ requires C, 70·9; H, 6·4; N, 6·9%). The N-*benzoate* [from light petroleum (b. p. 60—80°)] had m. p. 117° (Found: C, 76·7; H, 5·8; N, 4·85. $C_{17}H_{15}NO_2$ requires C, 76·95; H, 5·7; N, 5·3%).

2,3,4,5-*Tetrahydro*-1-*methylbenz*[b]*azepin*-5-*one* (I; R = Me, R′ = R″ = H).[16]—The preceding amino-ketone (0·7 g.), methylene chloride (80 ml.), and triphenylmethyl perchlorate[10] (3·2 g.; washed with ether until free from acetic anhydride) were left at room temperature for 12 days and the mixture was poured into water. The organic layer was extracted with 22% aqueous hydrochloric acid, giving, on basification and recovery, an oil, b. p. 120°/0·15 mm (Found: C, 75·7; H, 7·25; N, 7·5. Calc. for $C_{11}H_{13}NO$: C, 75·4; H, 7·5; N, 8·0%), $\nu_{max.}$ (liquid film) 1890 cm.$^{-1}$ (C=O). There was no infrared absorption ascribed to N–H stretching.

2,3,4,5-*Tetrahydrobenz*[b]*azepin*-5-*ol*.—The amino-ketone (I; R = R′ = R″ = H) (640 mg.), tetrahydrofuran (80 ml.), and lithium aluminium hydride (1·5 g.) were refluxed for 5 hr. After the addition of ice, extraction with chloroform furnished a tar (250 mg.). The N-*benzoyl benzoate* crystallised from light petroleum (b. p. 40—60°) as prisms, m. p. 103° (Found: C, 77·9; H, 5·2; N, 3·6. $C_{24}H_{21}NO_3$ requires C, 77·6; H, 5·7; N, 3·75%).

2,3-*Dihydrobenz*[b]*azepine*.—The above amino-alcohol was heated *in vacuo*, giving the *amine* as an almost colourless oil, b. p. 95—100°/0·4 mm. (Found: C, 82·15; H, 7·15; N, 10·0. $C_{10}H_{11}N$ requires C, 82·7; H, 7·65; N, 9·65%). The *benzoyl derivative*, crystallised from light petroleum (b. p. 60—80°), had m. p. 80° (Found: C, 82·1; H, 5·95; N, 5·4. $C_{17}H_{15}NO$ requires C, 81·9; H, 6·05; N, 5·6%).

2,3,4,5-*Tetrahydrobenz*[b]*azepine*.[17]—(*a*) The above amine (740 mg.) in ether (25 ml.) was added to calcium in liquid ammonia. After removal of ammonia, the product was extracted with methylene chloride and distilled, yielding an almost colourless oil, b. p. 100°/0·5 mm. (Found: C, 80·9; H, 8·75; N, 9·3. Calc. for $C_{10}H_{13}N$: C, 81·6; H, 8·9; N, 9·5%). The *benzoyl derivative*, crystallised from light petroleum (b. p. 60—80°), had m. p. 85—86° (Found: C, 81·2; H, 6·85; N, 6·3. $C_{17}H_{17}NO$ requires C, 81·25; H, 6·8; N, 5·6%).

(*b*) The ketal from the ketone (I; R = *p*-$C_6H_4Me{\cdot}SO_2$, R′ = R″ = H) (2·17 g.) in tetrahydrofuran (25 ml.) was added to calcium in liquid ammonia. Working up as in (*a*) gave an oil (500 mg.) whose infrared spectrum was identical with that of the oil obtained in (*a*). The diketal from the amino-diketone (I; R = *p*-$C_6H_4Me{\cdot}SO_2$, R′R″ = O) behaved similarly.

Ethylene Ketal of 2,3,4,5-*Tetrahydro*-1-*toluene*-p-*sulphonylbenz*[b]*azepin*-5-*one*.—The ketone (3·25 g.), ethylene glycol[3a] (2 ml.), benzene (150 ml.), and toluene-*p*-sulphonic acid (350 mg.) were refluxed together for 4 hr., water being removed as formed by means of a Dean and Stark separator. The benzene was washed with aqueous sodium hydrogen carbonate, then with water, and dried. After removal of the solvent, the *ketal* crystallised from light petroleum (b. p. 60—80°) in needles, m. p. 120° (3·0 g.) (Found: C, 63·9; H, 6·0; N, 3·6; S, 8·6. $C_{19}H_{21}NO_4S$ requires C, 63·5; H, 5·9; N, 3·9; S, 8·9%). The infrared spectrum showed no absorption due to C=O stretching.

Ethylene Ketal of 2,3,4,5-*Tetrahydro*-1-*toluene*-p-*sulphonylbenz*[b]*azepine*-4,5-*dione*.—The diketone (3·05 g.), ethylene glycol (4 ml.), benzene (125 ml.), and toluene-*p*-sulphonic acid (300 mg.) were refluxed for 5 hr. The *ketal* (1·5 g.) crystallised from toluene in needles, m. p. 194° (Found: C, 58·1; H, 6·3; N, 2·9. $C_{21}H_{23}NO_6S{\cdot}H_2O$ requires C, 57·9; H, 5·8; N, 3·2%).

Bromination of 2,3,4,5-*Tetrahydrobenz*[b]*azepin*-5-*one*.—The amino-ketone (I; R = R′ = R″ = H) (5·3 g.) in chloroform (150 ml.) was treated with bromine (3·35 ml.) in chloroform (50 ml.). After 2 days at 20°, the mixture was diluted with water and basified with aqueous sodium hydroxide, and the chloroform extract was washed with water. The product, on recovery, was purified by chromatography on neutral deactivated aluminia. Three compounds were eluted in the following order: (a) The *tribromo*-derivative (III; R = R′ = R″ = Br), a yellow solid (86 mg.), m. p. 104° [from light petroleum (b. p. 60—80°)] (Found: C, 31·5; H, 2·5; N, 3·4; Br, 59·8. $C_{10}H_8Br_3NO$ requires C, 31·0; H, 2·1; N, 3·5; Br, 60·2%). (*b*) The

[16] Astill and Bockelheide, *J. Amer. Chem. Soc.*, 1955, **77**, 4080.
[17] Von Braun and Bartsch, *Ber.*, 1912, **45**, 3382.

dibromo-derivative (III; R = R″ = Br, R′ = H), a yellow solid, m. p. 133° (3·2 g.) (Found: C, 37·45; H, 2·5; N, 4·55; Br, 50·9. $C_{10}H_9Br_2NO$ requires C, 37·6; H, 2·85; N, 4·4; Br, 50·1%); the 3 aromatic protons had coupling constants of 8·5, 2·5, and 1·0 c./sec. (these signals appeared as two doublets and one quartet); (*c*) an orange-yellow powder, m. p. 116° (400 mg.). Satisfactory analyses could not be obtained, but the n.m.r. spectrum suggested formula (III; R = H, R′ = R″ = Br) for this substance.

7-Bromo-2,3,4,5-tetrahydrobenz[b]*azepin-5-one* (III; R = Br, R′ = R″ = H).—The bromo-ketone (III; R = R″ = Br, R′ = H) (2·57 g.), ethanol (100 ml.), and saturated sodium hydrogen carbonate (50 ml.) were refluxed for 3 hr., then diluted with water and extracted with chloroform. The organic layer was washed with water, dried, and evaporated, yielding the crude product which was chromatographed on neutral deactivated alumina and crystallised from light petroleum (b. p. 60—80°). The bromo-ketone (III; R = Br, R′ = R″ = H) formed yellow crystals (500 mg.), m. p. 107° (Found: C, 50·0; H, 4·35; N, 5·85; Br, 33·4. $C_{10}H_{10}BrNO$ requires C, 50·0; H, 4·2; N, 5·85; Br, 33·3%). The n.m.r. spectrum showed 3 aromatic protons (two doublets and a quartet). The red 2,4-*dinitrophenylhydrazone hydrochloride*, crystallised from acetic acid, had m. p. 247° (Found: C, 42·0; H, 3·7; N, 15·1. $C_{16}H_{15}BrClN_5O_4$ requires C, 42·05; H, 3·3; N, 15·3%).

Acyloin Reaction.—Liquid ammonia (1 l.) was distilled through potassium hydroxide pellets into a flask at −70°, fitted with a paddle stirrer and a drying tube packed with potassium hydroxide. After addition of ether (750 ml.), the apparatus was flushed with oxygen-free nitrogen while sodium (6·1 g.) was added in small pieces. The solution turned blue immediately: it was then stirred for 1 hr., after which methyl *N*-(2-methoxycarbonylethyl)-anthranilate (11·9 g.) in ether (750 ml.) was added dropwise in 2 hr. with stirring, the blue colour finally giving way to yellow. After being kept under nitrogen overnight the mixture was treated with ethanol (30 ml.) and, after 0·5 hr., was extracted with 4N-hydrochloric acid (3 × 200 ml.). The extracts were basified with aqueous ammonia (*d* 0·88), and the product (5·4 g.) was extracted with chloroform. After removal of the solvent, purification was effected by chromatography on neutral deactivated alumina or on silica gel. Eluents and product were as follows: (i) benzene, traces of the keto-ester (V; R = CO_2Me), m. p. and mixed m. p. 113°; (ii) chloroform containing 2% of ethanol, an involatile tar considered to be the *enol-ether* (VI; R = H, R′ = Et) (Found: C, 70·9; H, 6·1; N, 7·0. $C_{12}H_{13}NO_2$ requires C, 70·9; H, 6·45; N, 6·9%), $\nu_{max.}$ (liquid film), 3300 (N–H) and 1665 cm.$^{-1}$ (C=O); the n.m.r. spectrum showed a quartet (τ 8·15) and triplet (τ 8·83) associated with the OEt group, together with a doublet (τ 5·55) attributed to the β-olefinic proton; [18] (iii) with chloroform–methanol (10 : 1) a gum which was precipitated from methylene chloride by ether as an amorphous *substance*, m. p. 70° (I; R = R″ = H, R′ = OH) (Found: C, 68·3; H, 5·86; N, 7·5. $C_{10}H_{11}NO_2$ requires C, 67·8; H, 6·25; N, 7·9%), $\nu_{max.}$ (in Nujol) 3300 (NH), 3200—3100 (OH), and 1668 cm.$^{-1}$ (C=O); the position of the hydroxyl proton (τ 5·45) in the n.m.r. spectrum was not shifted on addition of dimethyl sulphoxide.

The *dibenzoate*, obtained from benzoyl chloride in pyridine, was an oil, b. p. 196°/0·1 mm. (Found: C, 75·25; H, 4·5; N, 3·7. $C_{24}H_{19}NO_4$ requires C, 75·0; H, 5·0; N, 3·65%).

In several experiments when bromobenzene was added to the reaction mixture before removal of liquid ammonia, the *hydroxy-ketone* (I; R = Ph, R′ = OH, R″ = H) was isolated as a powder, m. p. 150° (Found: C, 76·2; H, 6·05; N, 6·0. $C_{16}H_{15}NO_2$ requires C, 75·9; H, 5·95; N, 5·55%).

*2,5-Dihydro-4-methoxy-1-toluene-*p*-sulphonylbenz*[b]*azepin-5-one* (VI; R = *p*-$C_6H_4Me\cdot SO_2$, R′ = Me).—(a) The crude product from the acyloin reaction (600 mg.) was treated with toluene-*p*-sulphonyl chloride (1·8 g.) in pyridine (50 ml.). After 2 days at 20°; the mixture was worked up as usual and the neutral product (870 mg.) was chromatographed on neutral active alumina. Elution with chloroform–methanol (24 : 1) gave the *enol-ether* (220 mg.) which crystallised from ether–light petroleum (b. p. 60—80°) as a powder, m. p. 135° (Found: C, 63·0; H, 5·15; S, 8·95. $C_{18}H_{17}NO_4S$ requires C, 62·95; H, 5·0; S, 9·3%).

(*b*) The diketone [1] (I; R = *p*-$C_6H_4Me\cdot SO_2$, R′R″ = O) (220 mg.) was chromatographed on neutral deactivated alumina. Elution with chloroform–methanol (24 : 1) and crystallisation from methylene chloride–light petroleum (b. p. 60—80°) gave the product, m. p. 133—135° undepressed on admixture with the material from (*a*).

[18] Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1962.

2,3,4,5-*Tetrahydro*-4-*hydroxy*-1-*toluene*-p-*sulphonylbenz*[b]*azepin*-5-*one* (I; R = toluene-*p*-sulphonyl, R′ = H, R″ = OH).—Elution of the column reported in (*a*) above with chloroform–methanol (99 : 1) gave, after crystallisation from carbon tetrachloride, the *hydroxy-ketone* (170 mg.), m. p. 150—152° (Found: C, 62·1; H, 5·35; S, 8·9. $C_{17}H_{17}NO_4S$ requires C, 61·6; H, 5·2; S, 9·2%). The material previously reported [1] to have this structure was a mixture.

2,3,4,5-*Tetrahydro*-4-*hydroxy*-1-*methylbenz*[b]*azepin*-5-*one* (I; R = Me, R′ = OH, R″ = H).—The acyloin (I; R = R″ = H, R′ = OH) (400 mg.), triphenylmethyl perchlorate (2 g.), and methylene chloride (85 ml.) were left together in the dark for 24 hr. and poured into water. The organic layer was extracted three times with 6N-hydrochloric acid. The extracts were basified (cooling) with ammonia (*d*, 0·88), and the product (250 mg.) was extracted with chloroform. It was purified by chromatography on alumina and re-extraction with dilute hydrochloric acid, giving an oily *ketone* (Found: C, 68·85; H, 7·25; N, 7·6. $C_{11}H_{13}NO_2$ requires C, 69·1; H, 6·85; N, 7·35%). The *ferrotungstate* [12] was a buff powder, decomp. >300° (Found: C, 17·0; H, 2·2; N, 1·75. $C_{11}H_{13}NO_2,12WO_3,0{\cdot}5Fe_2O_3$ requires C, 17·75; H, 1·75; N, 1·9%). The *hexachloroplatinate* was a fine powder (Found: Pt, 24·52. $C_{22}H_{26}N_2O_4,PtCl_6$ requires Pt, 24·63%).

N-(3′-*Hydroxypropyl*)-o-*toluidine* (VII).—(*a*) The crude acyloin (I; R = R″ = H, R′ = OH) (350 mg.), lithium aluminium hydride (1 g.), aluminium chloride (1 g.), and tetrahydrofuran (45 ml.) were refluxed for 5 hr. After the addition of ice and dilute sodium hydroxide, the basic fraction was isolated and distilled twice, b. p. 110°/0·1 mm. (Found: C, 72·8; H, 8·9; N, 8·7. $C_{10}H_{15}NO$ requires C, 72·7; H, 9·15; N, 8·5%). The n.m.r. spectrum of this *product* (VII) showed 4 aromatic protons (τ 2·8—3·45), 3 methyl protons (singlet, τ 7·9), 2 methylene protons (triplet, τ 6·3), 2 methylene protons (triplet, τ 6·8), 2 methylene protons (quintuplet, τ 8·2), and 2 protons (presumably N–H and O–H) in overlapping singlets (τ 6·65) which were shifted downfield by addition of dimethyl sulphoxide. The N-*benzoyl benzoate* had m. p. 140° (Found: C, 77·25; H, 6·2; N, 3·8. $C_{24}H_{23}NO_3$ requires C, 77·2; H, 6·2; N, 3·75%).

(*b*) The diketone (I; R = *p*-$C_6H_4Me{\cdot}SO_2$, R′R″ = O) (4 g.), lithium aluminium hydride (2·5 g.), and tetrahydrofuran (40 ml.) were refluxed for 6 hr. After being worked up, the product was dissolved in tetrahydrofuran (50 ml.) and added to calcium in liquid ammonia. The basic fraction was refluxed with lithium aluminium hydride (1 g.), mercuric chloride (1 g.), and tetrahydrofuran (40 ml.) for 4·5 hr. The basic product (950 mg.) was distilled *in vacuo* (b. p. 105—110°/0·1 mm.), giving material identical (infrared) with that obtained as in (*a*) and giving an *N*-benzoyl benzoate, m. p. 140° undepressed on admixture with the benzoate obtained as in (*a*).

(*c*) Ethyl β-*o*-toluidinopropionate was prepared by a standard procedure [8b] and had b. p. 190—200°/12 mm. It was reduced by sodium in ethanol [19] in 44% yield to the product obtained as in (*a*) and (*b*).

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[19] Ford and Marvel, *Org. Synth.*, 1930, **10**, 62.