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[4,5-c] FUROTROPONE

A NEW HETEROCYCLIC SYSTEM

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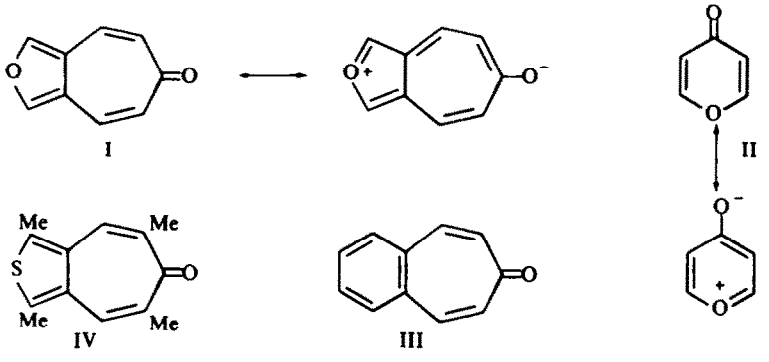
Abstract—[4,5-c] Furotropone has been prepared by the condensation of 3,4-furandicarboxaldehyde and acetone. It readily forms carbonyl derivatives and incorporates deuterium in a specific manner when dissolved in concentrated perdeuterosulphuric acid. A comparison of its properties with those of tropone and 4,5-benzotropone shows that its aromatic character is far less than that of the former and is comparable to that of the latter. A reappraisal of the properties of 4,5-benztropone shows that it has much less aromatic character than the evidence in the literature suggests.

A COMPARISON of the bicyclic structure I in both its non-polar and dipolar forms with γ-pyrone (II) suggests that as a 10-π electron system, analogous to azulene, it might have aromatic character. It should thus be comparable in its properties at least to the analogous 4,5-benztropone (III), and if the delocalization of the π-electrons was extensive enough then its properties might be comparable to those of tropone itself. Only one similar structure has been reported,[1] that of the thiophene analogue (IV), but here the heavy substitution precludes a simple comparison of many of its properties with those of other systems. Accordingly we have synthesized the bicyclic compound (I) and have compared its properties with those of tropone and 4,5-benztropone (III). By analogy with the nomenclature used in naming the benztropone (III) we designate the new heterocyclic I, [4,5-c] furotropone.



Preparation of [4,5-c] *furotropone.* This compound has been prepared from the intermediate 3,4-furandicarboxaldehyde.* The Diels–Alder adduct of furan and acetylene dicarboxylic ester was reduced catalytically to give dimethyl 3,6-oxy-3,4,5,6-tetrahydrophthalate (V; R = Me). Distillation of the adduct (V) under the conditions

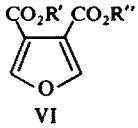
* When we commenced our work this compound was unknown. Our method differs from that reported[2] and gives much higher yields.

(ca. 145°/14 mm) employed by Alder and Rickert[3] resulted in only a small amount of decomposition to 3,4-dicarbomethoxyfuran (VI; R′ = R″ = Me). A quantitative yield of the ester (VI; R′ = R″ = Me) was however obtained by heating the ester (V) under nitrogen at 200° at atmospheric pressure. We found also that the acid (V; R = H) smoothly lost ethylene when heated in quinoline at 190° and gave a high yield of the acid (VI; R′ = R″ = H). Methylation of this acid was completed only by using a large excess of diazomethane and leaving the reaction mixture overnight. Using shorter reaction times gave the half ester (VI; R′ = H; R″ = Me).

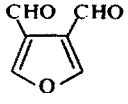
An attempt to convert the ester (VI; R′ = R″ = Me) into the required aldehyde (VII) by the McFadyen–Stevens reaction failed because we could not make the bis-tosylhydrazide of the ester. That the furan nucleus is stable under the conditions[4] of the decomposition was demonstrated when a good yield of furfural was obtained from furan-2-tosylhydrazide. The dialdehyde was however obtained from the alcohol (VIII) which was obtained be reducing the ester (VI; R′ = R″ = Me) with lithium aluminium hydride. The alcohol, which is unstable to acid, was oxidised by lead tetra-acetate in pyridine,[5] a reagent which smoothly oxidises furfuryl alcohol to furfural. Even with modified reaction conditions best yields of the aldehyde (VII) were however no higher than 32%, and it was always accompanied by the half aldehyde (IX). Although steric hindrance is a factor involved in the low yields it seemed likely that the proximity of the groups involved was more important. The situation was exploited by oxidising the alcohol (VIII) with manganese dioxide. The half aldehyde (IX) was obtained in high yield uncontaminated by the dialdehyde (VII). Application of our modified lead tetra-acetate/pyridine procedure to the half-aldehyde (IX) gave a high yield of the desired aldehyde (VII). The use of nickel peroxide was less successful.[6]

Condensation of 3,4-furandicarboxaldehyde with diethyl acetonedicarboxylate, using the conditions employed for the analogous reaction with *o*-phthalaldehyde,[7] gave a poor yield of the ester (X; R = CO_2Et). Using a mixture of piperidene and acetic acid and removal of the water produced during the reaction raised the yields

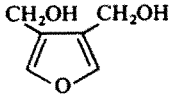
V



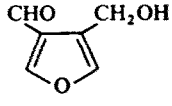
VI



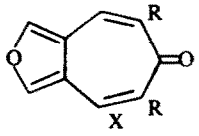
VII



VIII



IX



X

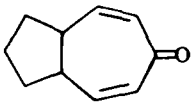
to over 70%. The structure of the ester was assigned on the basis of its elemental analysis and spectral properties. In particular its NMR spectrum showed the presence of only four protons in the aromatic region when integrated against the ten aliphatic protons of the ester groups.

Hydrolysis of the ester (X; R = CO_2Et) with 20% sulphuric acid gave a mixture of mono- and di-carboxylic acids. Decarboxylation of the mixture of acids using 0·5% hydrochloric acid[8] gave a poor yield of the desired compound (I). Other standard methods were no more successful. The poor overall yield of the furotropone

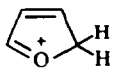
from the dialdehyde (VII) encouraged us to attempt a condensation with acetone. Using diethylamine as catalyst under a variety of conditions failed to yield any troponoid material. However using aqueous ethanolic sodium hydroxide at room temperature with a short reaction time gave a 35% yield of the furotropone; this in spite of the reported[2] sensitivity of the dialdehyde to alkali.* This is believed to be the only example of a condensation of a dialdehyde with acetone to give a 7-membered ring. Under either the conditions reported[9] or those described above *o*-phthalaldehyde gives a good yield of 2-acetylinden-2-one when condensed with acetone. No troponoid material could be detected. The contrast between the two reactions is notable and must derive from the small difference in the geometrical disposition of the functional groups in the two aldehydes. Our preparation of 4,5-benztropone, which we required for purposes of comparison, followed the described method.[7,8] The yield of the product of the condensation of *o*-phthalaldehyde and diethyl acetonedicarboxylate was much improved by using piperidine-acetic acid as the catalyst in benzene.

[4,5-c] Furotropone was obtained as colourless needles, m.p. 140°. It is a thermally stable compound which can be kept for some months when pure. Its structure has been assigned on the basis of its elemental analysis, mass spectrum and spectral properties. Those properties, physical and chemical, which relate to its aromatic character are described in the sequel and are compared to those of tropone and the closely analogous 4,5-benztropone (III).

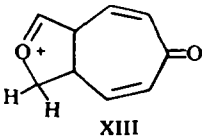
IR spectra. [4,5-c] Furotropone shows strong absorption at 1632 and 1599 cm^{-1}, which compares with 1649, 1633 and 1582 cm^{-1} for tropone and 1638, 1630 and 1590 cm^{-1} for 4,5-benztropone (in methylene chloride). Goetz *et al.*[10] have shown that for a number of tropones it is only the lowest frequency band which is solvent dependent and conclude that, on the basis of earlier work, this band is due to the CO stretching mode. We find that furotropone and benztropone behave similarly and in cyclohexane display bands at 1632 and 1608, and 1640, 1635 and 1607 cm^{-1} respectively. Since it has been shown that for geometrically similarly disposed CO groups there is a good correlation between the frequency and the calculated bond order,[11] we may infer that delocalization of electrons increases (bond order of CO decreases) as we go from tropone (1582), to benztropone (1590) to furotropone (1599 cm^{-1}), i.e. furotropone is less aromatic than either of the others. By this criterion furotropone has more delocalization than a cross-conjugated cycloheptadienone for all its bands appear at lower frequencies than the carbonyl band of the dienone (XI).[12]



XI



XII



XIII

UV spectra. The UV spectrum of [4,5-c] furotropone in ethanol is similar to that of 4,5-benztropone but its maxima are shifted about 25 mμ towards the blue. It would seem that there is greater delocalization in the latter. A comparison of these spectra

* The sensitivity of 3,4-furandicarboxaldehyde to alkali, which is not shared by *o*-phthalaldehyde, involves nucleophilic attack of the furan ring.

with those obtained in strongly acidic media shows that the spectrum of benztropone changes less than that of furotropone. That of tropone itself is changed only slightly under similar conditions. Since the spectra of simple carbonyl compounds much altered on protonation, we may tentatively conclude that tropone is the most aromatic of the three.

NMR spectra. Of all physical measurements which have been used to gauge aromaticity, NMR has received widest, though not universal, acceptance. By this criterion [4,5-c] furotropone is not very aromatic. It shows a singlet at τ 1·94 for the protons on the furan ring and doublets at τ 2·63 and 3·48 (J = 12 c/s) for those on the tropone ring. This assignment derives from the spectrum of [4,5-c] [2,7-^{2}H] furotropone (X; R = D) (obtained from 3,4-furandicarboxaldehyde and deuteroacetone) which shows singlets at τ 1·94 and 2·63. The protons on the tropone ring of 4,5-benztropone show at τ 2·73 and 3·35 (J = 12 c/s) indicating that charge alternation is a feature of the two tropones, and that their delocalization of electrons is comparable. This delocalization is much less than in tropone, which shows a broadened singlet at τ 3·05. The olefinic protons of the geometrically similar dienone (XI) show at τ 3·79 and 4·13 (J = 12·5 c/s)[12] indicating that the two bicyclic tropones can sustain a ring current, but much less so than tropone.

Chemical reactivity. The small degree of aromaticity present in the [4,5-c] furotropone system is evidenced by the case with which it forms an oxime and dinitrophenylhydrazone. Despite a report to the contrary[8] we find that 4,5-benztropone also forms an oxime and dinitrophenylhydrazone under standard conditions. Tropone itself does form an oxime but only as a minor product in competition with the formation of 2-aminotropone.[13] As would be expected from the above results the double bonds in both bicyclic tropones are easily reduced. The properties of the furan ring are however modified for [4,5-c] furotropone does not form a Diels–Alder adduct even with tetracyanoethylene.

A solution of the furotropone in concentrated sulphuric gave an NMR spectrum (Experimental) which indicated that protonation was occurring on the carbonyl oxygen. In perdeutero-concentrated sulphuric acid however the signal due to the furan-ring protons slowly disappeared. The isolated material showed only doublets at τ 2·63 and 3·48 (J = 12 c/s) as in the parent compound, showing that only the protons on the furan ring had exchanged with deuterium. Recently the furonium ion (XII) has been detected in a solution of furan itself in concentrated sulphuric acid.[14] Our failure to detect a similar species (XIII) is probably due to the low concentration present, since as we have shown the bulk of the furotropone is protonated on the carbonyl oxygen. Deuterium exchange must then proceed as an electrophilic substitution on the low concentration of the unprotonated form. The ability of the furan moiety to behave as such shows that its conjugation with the dienone moiety is easily interrupted.

Thus physical and chemical properties indicate that while [4,5-c] furotropone and 4,5-benztropone are comparable in themselves thay have appreciably less aromatic character than tropone. Although both will sustain a small ring current in the tropone ring neither can be seriously considered as a 10-π electron aromatic system.

EXPERIMENTAL

IR spectra were recorded on a Perkin–Elmer 125 or 257 spectrophotometer. UV spectra were recorded on a Unicam SP 800. NMR were recorded at 60 Mc/s using tetramethylsilane as an internal standard. M.ps are uncorrected.

Dimethyl 3,6-*oxy*-3,4,5,6-*tetrahydrophthalate*

Furan (14·0 g) and dimethyl acetylenedicarboxylate (28·0 g) were heated together at 100° for 17 hr in a sealed tube. A soln of the adduct in EtOAc was shaken under H_2 with 5% Pd–$CaCO_3$ (450 mg) at atm press until uptake was complete. Distillation of the filtered soln afforded dimethyl 3,6-oxy-3,4,5,6-tetrahydrophthalate (29·6 g, 70%) b.p. 91–94°/0·2 mm. Recrystallization from light petroleum afforded colourless needles, m.p. 50°; ν_{max} (CH_2Cl_2) 1739, 1718 and 1630 cm^{-1}.

The di-acid was obtained in quantitative yield by boiling the ester with 12% NaOH aq for 6 hr. Recrystallization from EtOAc afforded needles, m.p. 167°.

Dimethyl 3,4-*Furandicarboxylate*

Dimethyl 3,6-oxy-3,4,5,6-tetrahydrophthalate (21·0 g) was stirred under N_2 at 195–200° for 2 hr when the evolution of ethylene had ceased. Chromatography of the residue in benzene–ether on silica gel afforded dimethyl 3,4-furandicarboxylate (18 g, 98%). Recrystallization from benzene–light petroleum gave colourless needles, m.p. 46°; ν_{max} (CH_2Cl_2) 1750 (broad) and 1540 cm^{-1}; λ_{max} (EtOH) 238 mμ (log ε 3·59); NMR* (CH_3CN) τ 2·26 (2H. s) and 6·49 (6H, s).

3,4-*Furandicarboxylic acid*

A soln of 3,6-oxy-3,4,5,6-tetrahydrophthalic acid (8·48 g) in quinoline (30 ml) was heated to 180–190° until the evolution of ethylene had ceased (ca. 3 hr). The cooled soln was treated with 50% HCl (170 ml) and then continuously extracted with ether for 16 hr. 3,4-Furandicarboxylic acid (6·3 g 88%) was thereby obtained as a solid, m.p. 204–210°, raised to 212° by recrystallization from EtOAc.

Methylation of 3,4-*furandicarboxylic acid*

A soln of the acid (3·12 g) in ether (150 ml) and MeOH (12 ml) at 0° was added to a chilled soln of diazomethane (ca. 2 g) in ether (50 ml) over 1 hr. After a further 3 hr at 0° the soln was washed with sat $NaHCO_3$ aq (2 × 30 ml), water and dried. Distillation of ether and of the residue afforded dimethyl 3,4-furandicarboxylate (840 mg, 23%), b.p. 102°/1·6 mm. Recrystallization from cyclohexane afforded colourless rhombs, m.p. 45°.

Acidification of the $NaHCO_3$-extracts and continuous extraction with ether gave 3-*carbomethoxy*-4-*furancarboxylic acid* (1·4 g, 41%) as colourless crystals, m.p. 133–135°, raised to 137° by recrystallization from water. (Found: C, 49·1; H, 3·7. $C_7H_6O_5$ requires: C, 49·4; H, 3·6%); ν_{max} (CH_2Cl_2) 1738, 1690, 1670, 1565 and 1531 cm^{-1}; λ_{max} (EtOH) 240 mμ (log ε 3·47).

By the use of a larger excess of diazomethane and by allowing the soln to stand for 10 hr, the di-ester was obtained in quantitative yield.

2-*Furohydrazide*

A soln of methyl 2-furoate (5·15 g) and hydrazine hydrate (2·48 g) in water (2·5 ml) and EtOH (5 ml) was heated under reflux for 2 hr. Work-up in the usual manner and recrystallization from benzene afforded colourless rhombs, m.p. 78° (Lit.[15] m.p. 80°); ν_{max} (CH_2Cl_2) 3430, 3330, 1661, 1620 and 1587 cm^{-1}. Its *tosylate* prepared in the usual manner in pyridine, crystallized from EtOH in colourless rhombs, m.p. 218–219°. (Found: C, 51·1; H, 4·3; N, 10·2; S, 11·3. $C_{12}H_{12}N_2O_4S$ requires: C, 51·4; H, 4·3; N, 10·0; S, 11·4%); ν_{max} (CH_2Cl_2) 3384, 3250, 1676 and 1584 cm^{-1}.

Furfural. To a stirred soln of 2-furohydrazide tosylate (1·0 g) in dry ethylene glycol (10 ml) at 160° was added anhyd Na_2CO_3 (1·9 g). After 75 sec at this temp water (100 ml) was added. Extraction with ether and distillation afforded furfural (210 mg, 60%) shown to be pure by TLC and IR.

3,4-*Di*(*hydroxymethyl*)*furan*

A soln of dimethyl 3,4-furandicarboxylate (30·9 g) in dry ether (100 ml) was added dropwise over 1 hr to a suspension of LAH (17 g) in dry ether (400 ml). After the mixture had been heated under reflux for

* s = singlet; qu = quartet; tr = triplet; d = doublet.

6 hr it was cooled and treated cautiously with 5% NaOH (1 l). The ether layer was separated, washed with water, dried and evaporated. Distillation of the residue afforded 3,4-*di(hydroxymethyl)furan* (16·6 g, 76%) as a colourless liquid b.p. 101–103°/0·08 mm, n_D^{20} 1·5120. (Found: C, 56·3; H, 6·1. $C_6H_8O_3$ requires: C, 56·2; H, 6·3%); ν_{max} (film) 3450 (broad), 2980, 2930, 1553 and 1008 (broad) cm^{-1}; NMR τ 2·71 (2H, s), 5·54 (4H, s) and 5·72 (2H, broad s removed by D_2O).

Oxidation of 3,4-*di(hydroxymethyl)furan*

(a) *With lead tetra-acetate.* To a stirred soln of the di-alcohol (500 mg) in anhyd pyridine (80 ml) at room temp was added lead tetra-acetate (3·46 g) over 3 hr. After stirring for a further 5 hr, the soln was acidified, filtered and extracted with CH_2Cl_2 (4 × 125 ml). The combined extracts were washed with dil acid, dil alkali and water and dried. Evaporation of the solvent and chromatography of the residue in benzene on alumina afforded 3,4-furandicarboxaldehyde (160 mg, 32%). Recrystallization from cyclohexane afforded colourless needles, m.p. 78°. (Found: C, 58·4; H, 3·5. Calc. for $C_6H_4O_3$ C, 58·1; H, 3·3%); ν_{max} (CH_2Cl_2) 1694, 1688, 1560 and 1536 cm^{-1}; λ_{max} (EtOH) 213, 261 mμ (log ε 3·83 and 3·59); NMR τ 0·69 (2H, s) and 2·58 (2H, s).

The *oxime*, prepared in the usual manner, crystallized (after sublimation) from aqueous EtOH in needles, m.p. 210–211° (dec). (Found: C, 46·8; H, 4·3; N, 18·1. $C_6H_6N_2O_3$ requires: C, 46·8; H, 3·9; N, 18·2%); ν_{max} (Nujol) 1645, 1515 and 1070 cm^{-1}.

Further elution with benzene–$CHCl_3$ yielded 3-*hydroxymethyl-4-furancarboxaldehyde* (75 mg, 15%), m.p. 27–31°. Recrystallization from ether–light petroleum afforded colourless plates, m.p. 32° (Found: C, 57·2; H, 4·6. $C_6H_6O_3$ requires: C, 57·1; H, 4·8%); ν_{max} (CH_2Cl_2) 3600, 3470 (broad), 1671, 1533 and 1013 cm^{-1}; λ_{max} (EtOH) 220 and 257 mμ (log ε 3·33 and 3·68; NMR τ 0·15 ('H), 1094 (1H), 3·60 (1H), 5·40 (2H) and 6·45 (1H broad)—all singlets.

(b) *With manganese dioxide.* A suspension of MnO_2 (45 g) in a soln of the di-alcohol (5·0 g) in CH_2Cl_2 (100 ml) was agitated for 4 hr. The MnO_2 was then filtered off and washed with hot CH_2Cl_2 (300 ml). Evaporation of the combined filtrate and washings, and recrystallization of the residue from ether–light petroleum afforded 3-hydroxymethyl-4-furancarboxaldehyde (4·4 g, 80%) in colourless plates, m.p. 31–32°.

Oxidation of 3-*hydroxymethylfuran-4-carboxaldehyde*

(a) *With nickel peroxide.* A soln of the half-aldehyde (300 mg) in ether (5 ml) was shaken with nickel peroxide (1·3 g, 1·1 moles[6]) at room temp for 6 hr. Removal of the solid and evaporation of the solvent left a gum which was chromatographed on alumina. Elution with benzene afforded 3,4-furandicarboxaldehyde (39 mg, 13%) and starting material (124 mg, 41%).

(b) *With lead tetra-acetate.* To a stirred soln of 3-hydroxymethyl-4-furancarboxaldehyde (3·45 g) in dry pyridine (120 ml) at room temp was added lead tetra-acetate (12·1 g) over 1 hr. After a further 2·5 hr the soln was poured into cold dil HCl. Filtration and continuous extraction of the filtrate with ether afforded after the usual work-up a residue (2·85 g) which was chromatographed on alumina in benzene. Elution with benzene gave 3,4-furandicarboxaldehyde (1·79 g, 52%) as colourless needles, m.p. 78°, from cyclohexane. Elution with benzene–$CHCl_3$ afforded starting material (0·76 g, 22%).

2,7-*Dicarbethoxy*-[4.5-c] *furotropone* (X; R = CO_2Et)

A soln of 3,4-furandicarboxaldehyde (1·5 g), diethyl acetonedicarboxylate (2·41 g) and piperidine (1 drop) in benzene (10 ml) was boiled under reflux for 2 hr, water being removed by a Dean–Stark attachment. The cooled soln was chromatographed on neutral alumina. Elution with benzene and recrystallization (charcoal) of the residue there from benzene–light petroleum afforded 2,7-*dicarbethoxy*-[4.5-c] *furotropone* (2·6 g, 74%) as colourless rhombs, m.p. 122°. (Found: C, 62·2; H, 5·1. $C_{15}H_{14}O_6$ requires: C, 62·1; H, 4·9%); ν_{max} (CH_2Cl_2) 1718–1723, 1614 cm^{-1}; λ_{max} (EtOH) 219, 260 mμ (log ε 4·14 and 4·49); NMR τ 1·93 (2H, s), 2·12 (2H, s), 5·7 (4H, qu) and 8·66 (6H, tr, J = 7 c/s).

2,7-*Dicarboxy*-[4.5-c] *furotropone* (X; R = CO_2H)

A soln of 2,7-dicarbethoxy-[4.5-c] furotropone (800 mg) in 20% H_2SO_4 (16 ml) was heated at 100° under N_2 for 6 hr. The cooled soln was filtered, and the ppt (0·62 g) was dissolved in $NaHCO_3$ aq (10 ml). The resultant soln was brought to pH 7 and heated with charcoal. Acidification of the filtered soln gave a yellow crystalline ppt (590 mg). Recrystallization from MeOH afforded 2,7-*dicarboxy*-[4.5-c] *furotropone* as pale-yellow needles, m.p. 220–222° (d). (Found: C, 46·3; H, 3·2. $C_{11}H_6O_6$ requires: C, 56·4; H, 2·6%); ν_{max} (CH_2Cl_2) 1602, 885 cm^{-1}; *m/e* 234.

[4,5-c] *Furotropone*

(a) A soln of the di-acid obtained above (400 mg) in 0·5N HCl (3·6 ml) was heated in a sealed tube at 175–180° for 3 hr. The cooled soln was extracted with ether (4 × 30 ml) and the combined extracts washed with Na_2CO_3aq and water and dried. Removal of the solvent and recrystallization of the residue from light petroleum afforded [4.5-c] *furotropone* (37 mg, 7%) as colourless needles, m.p. 140°. (Found: C, 73·9; H, 4·0. $C_9H_6O_2$ requires: C, 74·0; H, 4·1%); ν_{max} (CH_2Cl_2) 1632, 1599 and 1525 cm^{-1}; λ_{max} (EtOH) 211, 216, 250, 255 (sh), 292 and 301 mμ (log ε 4·08, 4·05, 4·57, 4·55, 3·67 and 3·67); NMR τ 1·94 (2H, s), 2·63 (2H, d) and 3·48 (2H, d J = 12 c/s); m/e = 146.

(b) A soln of 3,4-furancarboxaldehyde (656 mg) and acetone (307 mg) in EtOH (10 ml) was added slowly to 10% NaOH (9 ml) over 5 min. After a further 5 min, the soln was poured into water (40 ml). Extraction with CH_2Cl_2 (4 × 40 ml) and evaporation of the dried extracts left a residue which was chromatographed in benzene–$CHCl_3$ on silica gel. Elution with the same solvent afforded [4,5-c] furotropone (296 mg, 38%), obtained as colourless needles, m.p. 140°, from cyclohexane.

The *oxime* was prepared by heating the tropone (120 mg), hydroxylamine hydrochloride (100 mg), and pyridine (0·6 ml) in EtOH (1 ml) under reflux for 1 hr. Addition of water (10 ml) and recrystallization of the ppt from aqueous EtOH afforded the *oxime* as colourless needles (93 mg), m.p. 151–152°. (Found: C, 66·8; H, 4·4; N, 8·8. $C_9H_7NO_2$ requires: C, 67·1; H, 4·4; N, 8·7%); ν_{max} (CH_3Cl_2) 3558, 1636, 1520, 1055 and 950 cm^{-1}; λ_{max}(EtOH) 252, 264, 291 mμ (log ε 4·47, 4·33 and 3·98); mol wt (mass spec.) 161.

The *dinitrophenylhydrazone* was prepared by allowing a soln of the tropone in Brady's reagent to stand for 7 days. Recrystallization of the ppt from AcOH afforded the *dinitrophenylhydrazone* in maroon crystals (111 mg), m.p. 300° (Found: C, 54·9; H, 3·3; N, 16·9. $C_{15}H_{10}N_4O_5$ requires: C, 55·2; H, 3·1; N, 17·2%); ν_{max} (CH_2Cl_2) 1611 and 1590 cm^{-1}.

Protonation and deuteration of [4,5-c] *furotropone*

A soln of the tropone in 7·5 M H_2SO_4 gave an orange soln which showed λ_{max} 240, 248, 270, 278, 323, 338 and 458 mμ (log ε 3·85, 3·89, 4·38, 3·70, 3·65 and 3·05).

A soln of the tropone (70 mg) in conc H_2SO_4 (0·5 ml) gave NMR signals at τ 0·40 (2H, s), 0·55 (2H, d) and 1·95 (2H, d J = 12 c/s). Dilution with water (20 ml) and extraction with CH_2Cl_2 afforded the tropone (60 mg), m.p. 138–139°.

[4,5-c] Furotropone (73 mg) was dissolved in conc perdeuterosulphuric acid (0·5 ml). Dilution with D_2O and work-up as described above gave after 1 hr [8-^{2}H] *furotropone*. NMR τ 1·94 (1H, s), 2·63 (2H, d) and 3·48 (2H, d J = 12 c/s). Work-up after 3 hr gave [8.10-^{2}H] *furotropone*. NMR τ 2·82 (2H, d) and 3·61 (2H, d J = 12 c/s).

[4,5-c] [2.7-^{2}H] *Furotropone*

3,4-Furandicarboxaldehyde (100 mg) and perdeuterioacetone (40 mg) were dissolved in a soln of Na (230 mg) in D_2O (5 ml). After 20 min the reaction mixture was extracted with CH_2Cl_2 (2 × 10 ml). Evaporation of the dried extracts and chromatography of the residue in benzene on silica afforded [2,7-^{2}H] furotropone (40 mg, 33%). Recrystallization from cyclohexane gave colourless needles, m.p. 140°, undepressed on admixture with undeuterated material; ν_{max} (CH_2Cl_2) 1615, 1590, 1524 cm^{-1}; NMR τ 1·94 (2H, s) and 2·63 (2H, s).

2,7-*Dicarbethoxy*-4,5-*benztropone*

A soln of *o*-phthalaldehyde (1·5 g), diethyl acetonedicarboxylate (2·25 g) and piperidine–acetic acid catalyst (5 drops) in benzene (20 ml) was heated under reflux for 3 hr. Water was removed during the reaction by a Dean–Stark attachment. The solvent was then removed and the residue chromatographed in benzene-light petroleum on alumina to give a solid (2·6 g). Recrystallization from light petroleum gave 2,7-dicarbethoxy-4,5-benztropone (2·19 g, 65%) as colourless rhombs, m.p. 95°; ν_{max} (CH_2Cl_2) 1725, 2625, 1550 cm^{-1}; NMR τ 2·28 (2H, s) 2·67 (4H, d J = 3 c/s) 5·80 (4H, qu) and 8·67 (6H, tr).

4,5-*Benztropone*

The above ester was hydrolysed and partially decarboxylated by the method of Thiele and Schneider.[7] The mixture of mono- and di-carboxylic acids obtained was decarboxylated by the method of Thiele and Weitz.[8] 4,5-Benztropone was thereby obtained as pale-yellow plates (from benzene–light petroleum) m.p. 66° (Lit. m.p. 65–66°)[8] ν_{max} (CH_2Cl_2) 1630, 1590 cm^{-1}; NMR τ 2·53 (4H, s) and d's at 2·73 and 3·35 (each 2H J = 12 c/s).

The *oxime* was prepared in high yield by heating a mixture of the tropone (65 mg), hydroxylamine hydrochloride (50 mg) in pyridine (0·3 ml) and EtOH (0·5 ml) under reflux for 1·5 hr. Work-up in the usual manner and recrystallization of the product from aqueous EtOH afforded the *oxime* as yellow needles, m.p. 174° (Found: C, 76·9; H, 5·3; N, 7·9. $C_{11}H_9NO$ requires: C, 77·2; H, 5·3; N, 8·2%); ν_{max} (CH_2Cl_2) 3560, 1640, 1620 and 1557 cm^{-1}; λ_{max} (EtOH) 275, 286, 318, 332 and 348 mμ (log ε 4·58, 4·41, 3·56, 3·64 and 3·52), mol wt (mass spec) 171.

The *dinitrophenylhydrazone* was prepared with Brady's reagent. The ppt (94%) was collected after 30 hr and recrystallized from EtOH to give red crystals, m.p. 260°. (Found: C, 60·6; H, 3·8; N, 16·8. $C_{17}H_{12}N_4O_4$ requires: C, 60·7; H, 3·6; N, 16·7%).

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