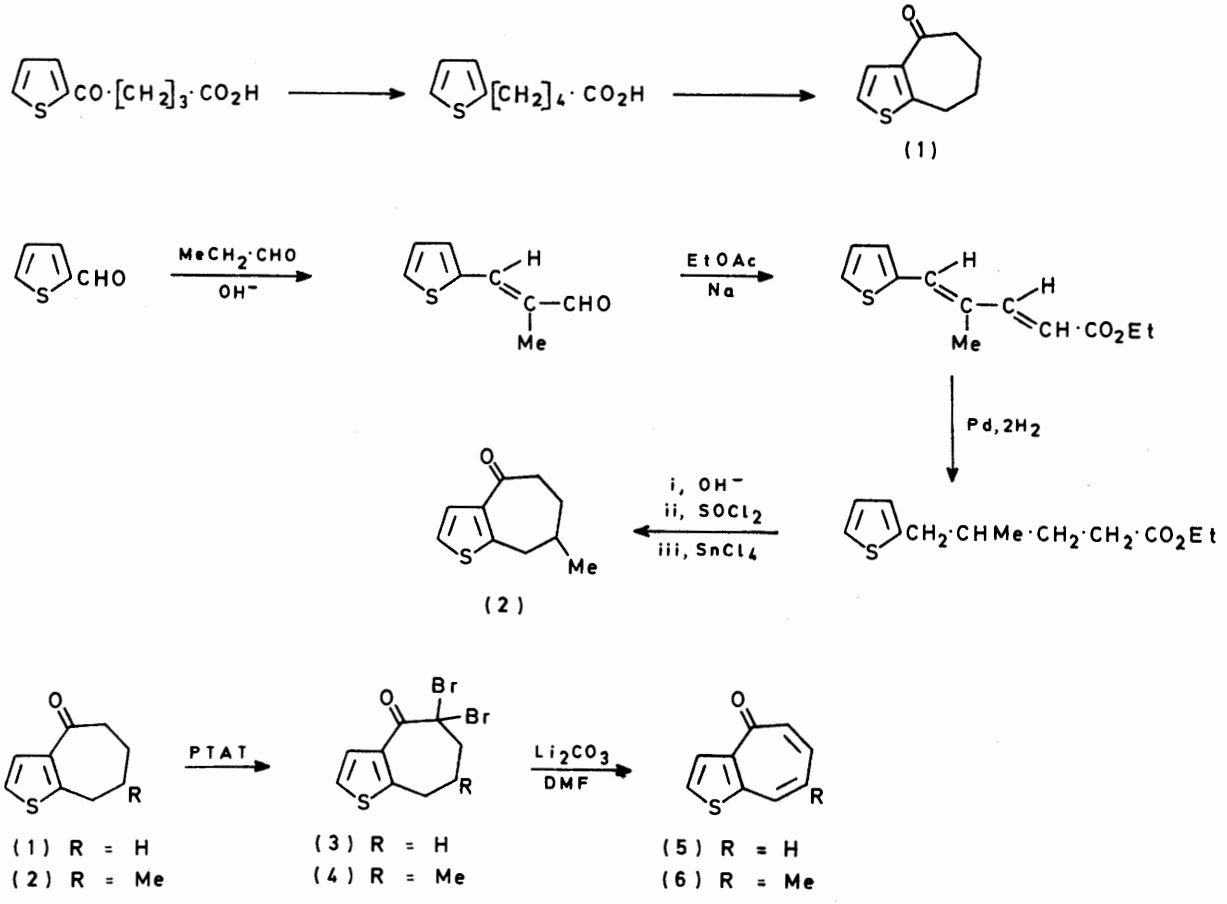
Annelated Tropones. Part 3.[1] Photochemistry of Some Cyclohepta[*b*]-thiophen-4-ones

By **Gurnos Jones** * and **Michael J. Robinson**, Department of Chemistry, University of Keele, Keele, Staffordshire ST5 5BG

On irradiation, methanolic solutions of the cyclohepta[*b*]thiophen-4-ones (5)—(7) give dimers, shown by spectral evidence to be [$_{\pi}4 + _{\pi}2$] dimers, formed by reaction of the 5,6-bond of one thienotropone molecule with the 5,7-diene system of another. The dimers are of the head-to-head type and have a *trans*-ring junction. Irradiation of 2,6-dimethylcyclohepta[*b*]thiophen-4-one (8) leads to an intramolecular electrocyclic disrotatory reaction, giving a tricyclic ketone (14). The syntheses of the parent cycloheptathiophenone (5) and of the 7-methyl derivative (8) are described, and that of 7,8-dihydro-2-methylcyclohepta[*b*]thiophen-4-one (17).

WE have reported a synthesis by which benzocyclohepten-5-ones,[2] cyclohepta[*b*]-furan- and -thiophen-4-ones,[1] and cyclohepta[*b*]pyridin-9-ones [1] can be obtained. With a range of annelated tropones available, we have started to investigate the interaction between the tropone and the fused ring, and its effect on the reactivity of the tropone ring in addition reactions. Our first report concerns the photochemical behaviour of the cyclohepta[*b*]thiophen-4-ones (5)—(8). Of these, compounds (7) and (8) were reported in our previous paper; [1] the parent compound (5) and the methyl derivative (6) were prepared as shown in the Scheme. The tetrahydrothieno-derivatives (1) and (2) were brominated with phenyltrimethylammonium tribromide (PTAT), and the dibromo-ketones (3) and (4) were dehydrobrominated with lithium carbonate in boiling dimethylformamide (DMF).

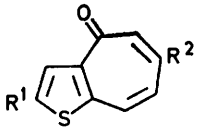


SCHEME

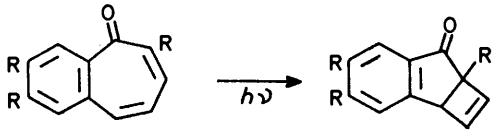
We [2] and others [3,4] have reported that solutions of the benzocyclohepten-5-ones (9) and (10), irradiated with a medium pressure Hanovia lamp, gave tricyclic compounds of type (11). With the parent compound (9) the tricyclic compound was the major product, although

[1] G. Jones, R. K. Jones, and M. J. Robinson, *J.C.S. Perkin I*, 1973, 968 is considered as Part 2.
[2] E. W. Collington and G. Jones, *J. Chem. Soc.* (*C*), 1969, 2656.
[3] E. J. Forbes and J. Griffiths, *J. Chem. Soc.* (*C*), 1966, 2072.
[4] E. J. Forbes, J. Griffiths, and R. A. Ripley, *J. Chem. Soc.* (*C*), 1968, 1149.

traces of a dimer were formed.[2] Irradiation under similar conditions of methanolic solutions of the cycloheptathiophenones (5) and (7) gave in each case only



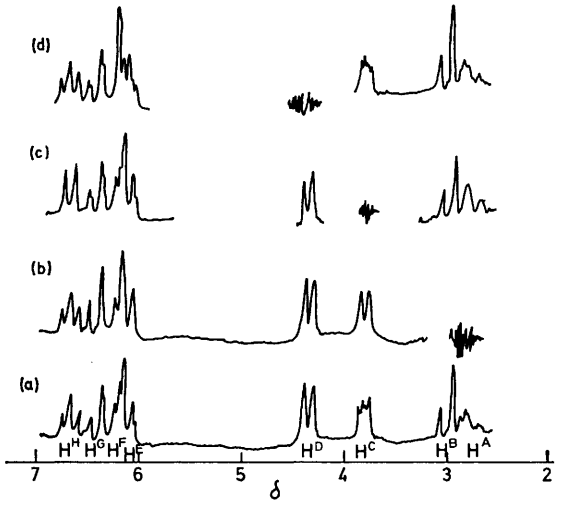
(7) R^1 = Me, R^2 = H
(8) R^1 = R^2 = Me



(9) R = H
(10) R = OMe

(11)

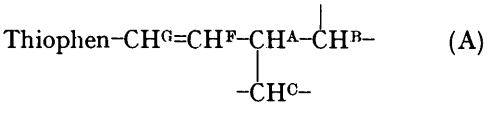
one non-polymeric product. Molecular weight determinations showed that these products were dimers. The spectral data, which led to the structural assignments, were very similar for the two compounds; only that of the dimer from the methyl derivative (7) will be discussed in detail. The tricyclic compound (11) and the



(a) 90 MHz ^{1}H n.m.r. spectrum of the dimer (12); (b) result of irradiation at H^A; (c) result of irradiation at H^C; (d) result of irradiation at H^D

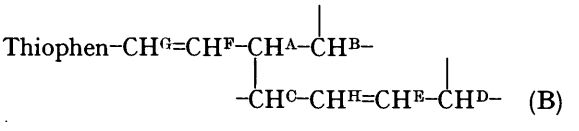
similar thiophen system (14) described later show characteristically high frequency carbonyl absorptions at *ca.* 1 704 cm^{-1}; careful monitoring of the photoreaction solutions containing compound (7) showed at no time any such carbonyl absorption, so that no considerable concentration of tricyclic compound is formed at any stage of the irradiation.

The dimer from compound (7) was not symmetrical, showing in the ^{1}H n.m.r. spectrum (220 MHz) eight well separated one-proton signals, two methyl singlets of similar chemical shift, and one two-proton signal, a complex multiplet. Thus, all [$_\pi$2 + $_\pi$2] dimers of symmetrical structure are eliminated. The i.r. carbonyl absorption, a single broad band at 1 670 cm^{-1}, showed that the dimer had no 7,8-dihydrocyclohepta[*b*]thiophen-4-one fragment [see compound (17) for such a chromophore], and hence no mixed [$_\pi$2 + $_\pi$2] dimer from combination of the 5,6-bond of one tropone molecule and the 7,8-bond of the other was present. The u.v. absorption ($\lambda_{max.}$ 229, 246sh, 266sh, and 325 nm) confirmed that a 5,6-dihydrocycloheptathiophenone was present. A detailed examination of the ^{1}H n.m.r. spectrum, with use of double irradiation and INDOR, indicated that the most probable structure was that of a [$_\pi$4 + $_\pi$2] dimer; the full spectrum and the results of double irradiation are shown in the Figure. The signals for the two protons on the thiophen ring are clearly separated from the other signals and from each other, as singlets at δ 7.1 and 7.27. The other eight proton absorptions fall into two groups, δ 6.15—6.8 (alkene H) and 2.8—4.45 (H attached to *sp*^{3}-hybridized carbons). The signals are designated H^A—H^H (from high to low field). The only simple alkene signal (H^G), a doublet of doublets (*J* 9 and 2 Hz), must be due to a proton next to a thiophen ring, and must be coupled to one of the alkene protons (H^E or H^F, *J* 9 Hz) and to H^A (*J* 2 Hz), probably allylically. The signal for H^A is complex, but represents a key to a large part of the structure. The fact that the H^B signal is a doublet (*J* 12 Hz) must be due to coupling with H^A, since irradiation at this point causes no change in the lower field signals. Irradiation at δ 2.85 causes (i) simplification of the signal for H^C to a doublet (*J* 8 Hz), (ii) simplification of the multiplet at δ 6.2—6.4, which shows that H^A is coupled also to H^F, and (iii) disappearance of the allylic coupling to H^G. We can thus write partial structure (A).



Thiophen–CH^G=CH^F–CH^A(–CH^C–)–CH^B– (A)

An INDOR scan, with irradiation at δ 4.40 (H^D), reveals a quartet at δ 6.25; the same quartet is revealed by an INDOR scan with irradiation at δ 6.75 (H^H). Finally, irradiation at δ 3.85 (H^C) simplifies the signal at δ 2.9 (H^A) and causes the signal at δ 6.75 (H^H) to collapse to a doublet. With this further information the enlarged sequence (B) can be written. As no feasible structure can

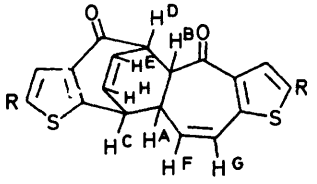


Thiophen–CH^G=CH^F–CH^A(–CH^C–CH^H=CH^E–CH^D–)–CH^B– (B)

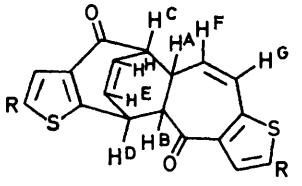
have an *sp*^{3}-hybridized carbon which has only one adjacent methine group, we can complete the sequence by connecting H^B to H^D (*J* zero) to obtain a [$_\pi$4 + $_\pi$2] dimer in which the protons from one tropone ring are H^C, H^D, H^E, and H^H, those of the second ring being H^A, H^B, H^F, and H^G. The possible gross structures are (12) and (13).

The two features which remain to be defined are whether the assembly is head-to-head (12) or head-to-tail (13) and the stereochemistry of the fusion at the 5- and

6-positions. Tropone itself forms a [$_{\pi}4 + {}_{\pi}2$] dimer,[5] as does 2-chlorotropone,[6] and these are head-to-head dimers with a *trans* ring fusion. For a *trans*-fused system J_{AB} should be 8—13 Hz; for the head-to-head (12)



(12) R = Me
(19) R = H



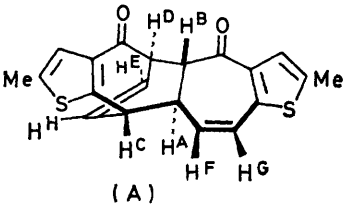
(13) R = Me

arrangement the other angles can be deduced from Dreiding models, with $J_{BD} = 0$ (90°) and $J_{AC} = 2$ (60°); all the data are in good agreement with those observed. This arrangement also allows for an allylic interaction between H^A and H^G, but has H^C and H^F with zero torsion angle and thus uncoupled. Finally, structure (12) agrees with the order of chemical shift of H^A—H^D, H^D being the most deshielded and H^A the least.

The head-to-head structure was confirmed by addition of a europium shift reagent to the dimer from the cycloheptathiophenone (5). Model experiments indicated complex formation with the carbonyl group, causing large shifts in signals for H-3 (thiophen ring, β-position) and H-5. Addition of shift reagent to the dimer would therefore be predicted to cause downfield shifts in the H^B and H^D signals for a head-to-head dimer, and in those of H^C and H^D for a head-to-tail dimer; the former was observed, the H^C signal being unchanged. The stereochemistry of the favoured structure (12) is shown in formula (A).

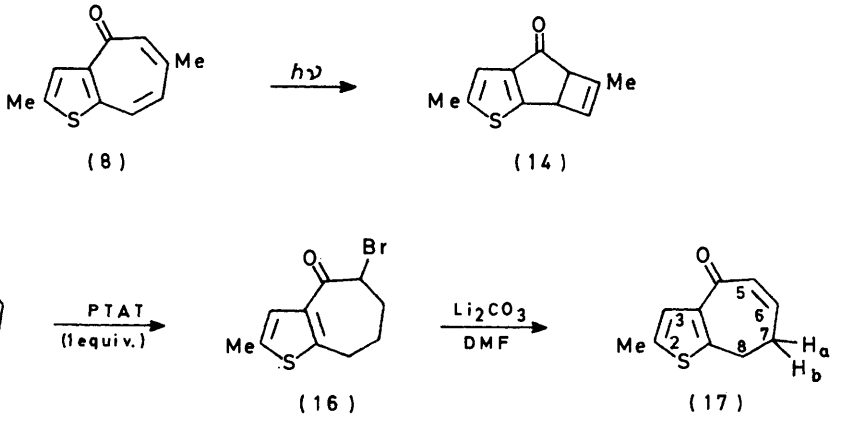
As further evidence for structure (12) we attempted to prepare and dimerise cycloheptathiophenones with substituents on the seven-membered ring. The previously reported[1] 2,6-dimethyl derivative (8), irradiated in methanol, gave no dimer. The major photoproduct had a molecular weight of 190.045 ($C_{11}H_{10}OS$ requires 190.045 3) and was hence an isomer of compound (8). The i.r. spectrum ($\nu_{max.}$ 1 702 cm^{-1}) indicated a tricyclic structure; the ^1H n.m.r. spectrum showed signals at δ 1.82 (3 H, br), 2.45 (3 H, s), 3.8 and 4.05 (each 1 H, br), and 6.1 and 6.65 (each 1 H, s), in excellent agreement with those reported[2] for the tricyclic compound (11). The photoproduct from compound (8) thus results from an electrocyclic reaction, and is compound (14), providing indirect evidence that the 5,6-bond is involved in dimer formation, since a 6-methyl group is seen to suppress dimerisation.

In an attempt to prepare a deuteriocycloheptathiophenone the tetrahydro-derivative (15) was converted into the monobromo-ketone (16) and this was dehydrobrominated with lithium carbonate in boiling dimethylformamide. The i.r. spectrum of the product showed



(A)

peaks at 1 670, 1 640, and 1 610 cm^{-1}, very similar to those of the cycloheptathiophenone (7) and indicative of the chromophore 'thiophen–CO–C=C'. The ^1H n.m.r. spectrum showed signals at δ 2.3 (3 H, s, CH_3), 2.5 (2 H, t), 2.8 (1 H, br) and 3.0 (1 H, t) (7-H_a and -H_b), 6.08 (1 H, d, J 12 Hz, H-5), 6.5 (1 H, m, H-6), and 7.1 (1 H, s, H-3). The alkene proton shifts, in particular, are characteristic of an αβ-unsaturated ketone. All attempts to cause specific deuteriation under basic conditions at position 7 were unsuccessful; the anion, when formed, must be delocalised, since deuterium exchange occurred at several sites to give a mixture of deuteriated cycloheptathiophenones.

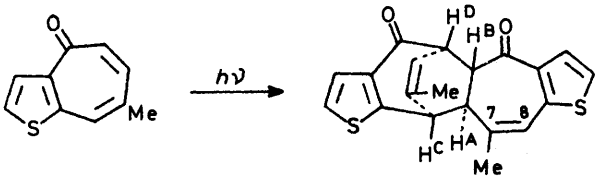


(8) (14) (15) (16) (17)

[5] A. S. Kende, *J. Amer. Chem. Soc.*, 1966, **88**, 5026; A. S. Kende and J. E. Lancaster, *ibid.*, 1967, **89**, 5283.

[6] T. Mukai, H. Tsuruta, A. Takeshita, and H. Watanabe, *Tetrahedron Letters*, 1968, 4065.

Irradiation of a methanolic solution of 7-methylcyclohepta[*b*]thiophen-4-one (6) gave a mixture of products. After much preparative layer chromatography a small amount of a dimer was obtained, in spectral characteristics very similar to those from the tropones (5) and (7). The ^{1}H n.m.r. spectrum, however, was much simplified, and confirmed structure (18), and hence structures (12) and (19) for the previously obtained dimers. In terms of the same lettering as for the dimer (12), in compound (18) the signals for H^A and H^B are



(18)

coincident [δ 3.1 (br s)], that for H^C is a broadened singlet at δ 3.95, and that for H^D a doublet at δ 4.45. Only two alkene proton signals remain, a broadened doublet at δ 5.9 (H^F) and a broadened singlet at δ 6.45 (H^G); H^D and H^F are shown by double irradiation to be coupled, and the H^C signal shown to be broadened by coupling with $H^{A/B}$. The major coupling of H^C in compound (12) was to H^H [replaced in dimer (18) by a methyl group], and this sequence was shown only by the head-to-head structure; H^G is confirmed as one of the original 8-protons giving a doublet in compound (12) but a singlet in compound (18) owing to the presence of the 7-methyl group.

EXPERIMENTAL

All photochemical experiments were done with a Hanovia medium-pressure lamp and a Pyrex filter. Solutions were stirred by a nitrogen stream. Column chromatography was performed with Woelm alumina (activity shown in parentheses); in preparative layer chromatography, 20 × 40 cm plates coated with Merck Kieselgel PF_{254} were used. M.p.s were taken with a Kofler hot-stage apparatus. INDOR and some decoupling experiments were done with a Perkin-Elmer R90 (90 MHz) instrument; other n.m.r. spectra were taken with a P.E.–Hitachi R 24, a JEOL HA-100, or a Varian 220 MHz instrument. Exact mass measurements were made by the P.C.M.U., Harwell.

4-(2-*Thenoyl*)*butanoic Acid*.—Prepared as described by Yur'ev and Elyakov [7] *via* the methyl ester (50% yield), which was hydrolysed (in 85% yield) by methanolic 10% sodium hydroxide, the acid had m.p. 91° (lit.,[7] 91°).

5-(2-*Thienyl*)*pentanoic acid*.—Prepared by Huang Minlon reduction, by the method described by Badger, Rodda, and Sasse [8] for a similar compound, in 60% yield, the acid had b.p. 148—150° at 1 mmHg m.p. 36° (lit., m.p. 36°).

5,6,7,8-*Tetrahydro*-4H-*cyclohepta*[b]*thiophen*-4-*one* (1).—A solution of 5-(2-thienyl)pentanoic acid (26.5 g) and thionyl chloride (10.8 ml) in dry ether (400 ml) was treated with 12 drops of dry pyridine and the cloudy mixture was boiled (2—3 h). Evaporation gave a residue showing $\nu_{max.}$ 1 800 cm^{-1} (acid chloride). The crude residue was dissolved in dry carbon disulphide (100 ml). This solution, and tin(IV) chloride (30 ml) were added simultaneously with stirring during 8 h to ice-cold carbon disulphide (1.5 l) under nitrogen. The mixture was allowed to come to room temperature overnight, then ice-cold 2N-hydrochloric acid was added cautiously. The carbon disulphide solution was separated from the aqueous mixture, dried ($MgSO_4$), and evaporated, leaving almost pure tetrahydrocycloheptathiophenone (1), b.p. 110—112° at 0.3 mmHg (4.03 g). A red solid remained after the separation of the carbon disulphide layer; this was stirred vigorously with 2N-hydrochloric acid and chloroform, and the dark red chloroform solution was separated, dried ($MgSO_4$), and evaporated, giving a waxy solid. Stirring the waxy solid with cold acetone gave a white solid and a solution of the thienotropone (1) in acetone, which after distillation yielded 3.8 g of purified material. In other experiments the two cycloheptathiophenone fractions were combined before distillation, but without perceptible improvement in the yield (33%). The *tetrahydrothienotropone* (1), b.p. 92° at 0.1 mmHg (Found: C, 64.8; H, 5.95. $C_9H_{10}OS$ requires C, 65.05; H, 6.0%) had $\nu_{max.}$ (CCl_4) 1 660 cm^{-1}, δ 1.7—2.2 (4 H, m, H-6 and -7), 2.7 (2 H, t, H-8), 3.1 (2 H, t, H-5), 6.9 (1 H, d, *J* 5 Hz, H-2), and 7.32 (1 H, d, 5 Hz, H-3).

5,5-*Dibromo*-5,6,7,8-*tetrahydro*-4H-*cyclohepta*[b]*thiophen*-4-*one* (3).—Phenyltrimethylammonium tribromide (PTAT) (6.2 g) was added to a stirred solution of the ketone (1) (2.5 g) in dry tetrahydrofuran (100 ml); after 5 min t.l.c. showed the starting material to have gone. More PTAT (6.2 g) was added, and stirring continued (3 h). The solid was filtered off and the solution evaporated. The crude mixture from several experiments (12 g of ketone in all) was chromatographed on alumina (III; 500 g), with petroleum (b.p. 60—80°)–benzene (1 : 1) as eluant (100 ml fractions). Fractions 7—9 were almost pure *dibromo-ketone* (3), m.p. 57—58° (from methanol) (Found: C, 33.4; H, 2.45. $C_9H_8Br_2OS$ requires C, 33.3; H, 2.47%) (yield 80%), δ ($CDCl_3$) 2.2 (2 H, m, H-7), 2.9—3.3 (4 H, two overlapping t, H-5 and -8), 7.05 (1 H, d, *J* 5 Hz, H-2), and 7.26 (1 H, d, *J* 5 Hz, H-3). Later fractions from the column gave some 5-*monobromo-derivative*, m.p. 50—51° [from petroleum (b.p. 40—60°)] (Found: C, 44.1; H, 3.5. C_9H_9BrOS requires C, 44.1; H, 3.7%), δ ($CDCl_3$) 1.5—2.5 (4 H, m), 3.0 (2 H, t, H-8), 4.8 (1 H, t, H-5), 6.9 (1 H, d, *J* 5 Hz, H-2), and 7.25 (1 H, d, *J* 5 Hz, H-3).

4H-*Cyclohepta*[b]*thiophen*-4-*one* (5).—A mixture of the dibromo-ketone (3) (10 g) and lithium carbonate (8.75 g) with dry dimethylformamide (DMF) (250 ml) was stirred and boiled under nitrogen (2.5 h), then filtered and evaporated (water pump, then oil pump). The solid removed in the filtration was washed with chloroform. The residue from evaporation of the filtrate was shaken with aqueous sodium hydrogen carbonate and chloroform, and the combined chloroform extracts and washings were dried (Na_2SO_4) and evaporated. Two such experiments (20 g of dibromo-ketone) gave 8.7 g of crude cycloheptathiophenone. Distillation gave a fraction of b.p. 112—116 at 0.07 mmHg (5.9 g, 60%), still containing a small amount of impurity. P.l.c. (ethyl acetate–toluene 1 : 1) gave pure *cyclohepta*[b]*thiophen*-4-*one* (5), m.p. 36—39° [from petroleum (b.p. 40—60°)] (Found: C, 67.0; H, 3.8. C_9H_8OS requires C, 66.65; H, 3.7%), $\lambda_{max.}$ (95% EtOH) 242, 323, 345, and 356 nm, δ 6.4—7.0 (3 H, m), 7.32 (1 H, d, *J* 11 Hz, H-8), 7.47 (1 H, d, *J* 5 Hz), and 7.77 (1 H, d, *J* 5 Hz).

[7] Yu. K. Yur'ev and G. B. Elyakov, *Doklady Akad. Nauk S.S.S.R.*, 1952, **86**, 337 (*Chem. Abs.*, 1953, **47**, 8725).

[8] G. M. Badger, H. J. Rodda, and W. H. F. Sasse, *J. Chem. Soc.*, 1954, 4162.

(E)-2-*Methyl*-3-(2-*thienyl*)*prop*-2-*enal*.—A solution of thiophen-2-carbaldehyde (11 g) and sodium hydroxide (2.5 g) in water (30 ml) and ethanol (15 ml) was cooled to 0 °C, under nitrogen, and a solution of propionaldehyde (25 g) in water (40 ml) was added dropwise with vigorous stirring (3—4 h). The solution was neutralised with ice-cold acetic acid and the product extracted with ether. The extract was dried (Na_2SO_4) and distilled; the *thienylpropenal* (10.2 g, 54%) had b.p. 140—149° at 17 mmHg, m.p. 27—30° (Found: C, 62.8; H, 5.6. C_8H_8OS requires C, 63.15; H, 5.3%), $\nu_{max.}$ (film) 1 665 and 1 610 cm^{-1}, $\lambda_{max.}$ (95% EtOH) 320 nm (log ε 4.29), δ ($CDCl_3$) 2.0 (3 H, s), 7.1 (1 H, t, H-3 of thiophen), 7.3br (2 H, *H*C:CMe and thiophen H), 7.52 (1 H, d, *J* 4 Hz, thiophen H), and 9.4 (1 H, s, CHO) [addition of Eu(fod)$_3$ shifted the CH_3 and :CH signals downfield]. The *oxime* had m.p. 130—131° (from aqueous ethanol) (Found: C, 57.4; H, 5.4; N, 8.6. C_8H_9NOS requires C, 57.5; H, 5.45; N, 8.4%).

Ethyl 4-*Methyl*-5-(2-*thienyl*)*penta*-2,4-*dienoate*.—To a stirred mixture (nitrogen atmosphere) at 0 °C of sodium wire (9.66 g) and dry, distilled ethyl acetate (200 ml) was added, dropwise, a solution of the thienylpropenal (61 g) in ethyl acetate (100 ml). After the addition, the mixture was allowed to come to room temperature and stirred (36 h). Ice-cold dilute acetic acid was added and the ethyl acetate layer removed. The aqueous layer was extracted with methylene chloride, and the combined organic extracts were shaken with saturated sodium hydrogen carbonate solution, then water, dried ($MgSO_4$) and evaporated to leave the crude ester. Distillation under nitrogen gave the *ethyl thienylpentadienoate*, b.p. 135—145° at 0.5 mmHg, m.p. 56—60° (60 g, 67%) (Found: C, 64.9; H, 6.4. $C_{12}H_{14}O_2S$ requires C, 64.85; H, 6.3%), $\nu_{max.}$ (film) 1 595, 1 610, and 1 700 cm^{-1}, $\lambda_{max.}$ (95% EtOH) 338 nm (log ε 4.47), δ ($CDCl_3$) 1.28 (3 H, t, *J* 7 Hz, CH_3·CH_2·O), 2.05 (3 H, s), 4.15 (2 H, q, *J* 7 Hz, CH_3·CH_2·O), 5.85 (1 H, d, *J* 15 Hz, CH:C*H*·CO_2Et), and 6.8—7.5 (5 H, m).

Ethyl 4-*Methyl*-5-(2-*thienyl*)*pentanoate*.—A solution of the ethyl thienylpentadienoate (33 g) in 95% ethanol (600 ml) containing 10% palladium–charcoal (1.5 g) was hydrogenated at atmospheric temperature and pressure. Uptake slowed considerably when about 0.4 mol. equiv. had been absorbed, and further batches of catalyst (3 × 1.5 g) were added before uptake of 2 mol. equiv. was complete. Filtration, evaporation, and distillation gave the *ethyl thienylpentanoate*, b.p. 110—115° at 0.3 mmHg (25.5 g, 75%) (Found: C, 64.0; H, 8.0. $C_{12}H_{16}O_2S$ requires C, 63.7; H, 7.95%), $\nu_{max.}$ (film) 1 730 cm^{-1}, $\lambda_{max.}$ (95% EtOH) 235 nm (log ε 3.92), δ ($CDCl_3$) 1.0 (3 H, d, C*H*$_3$·CH), 1.3 (3 H, t, C*H*$_3$·CH_2·O), 1.5—2.2 (3 H, m), 2.35 (2 H, d, C*H*$_2$·CH), 2.5—3.0 (2 H, m), 4.15 (2 H, q, CH_3·C*H*$_2$·O), and 6.7—7.2 (3 H, m, thiophen H). Hydrolysis of the ester (25 g) by boiling aqueous alcoholic sodium hydroxide (100 ml; 10% NaOH, 1 : 3 H_2O–EtOH) (3 h) was followed by dilution and extraction with ether (giving 4.7 g of unchanged ester). Acidification of the aqueous layer and further extraction with ether gave, after drying ($MgSO_4$) and evaporation, the free acid (16 g, 82%), $\nu_{max.}$ 2 800—2 500m and 1 700s cm^{-1}, δ ($CDCl_3$) 1.0 (3 H, d, *J* 6 Hz, CH_3·CH), 1.4—2.1 (3 H, m), 2.35 (2 H, d, C*H*$_2$·CH), 2.5—3.0 (2 H, m), and 6.7—7.2 (3 H, m, thiophen H).

5,6,7,8-*Tetrahydro*-7-*methyl*-4H-*cyclohepta*[b]*thiophen*-4-*one* (2).—A solution of distilled thienylpentanoic acid (26.5 g) and thionyl chloride (10.8 ml) in dry ether (350 ml) was treated with 12 drops of dry pyridine and boiled for 2 h. Evaporation gave an oil, $\nu_{max.}$ 1 795 cm^{-1}, which was dissolved in carbon disulphide (100 ml) and added, with tin(IV) chloride (30 ml), also in carbon disulphide (50 ml), to ice-cold carbon disulphide (1.5 l) over 8 h. Work-up as described for compound (1) gave, from the combined carbon disulphide and acetone extracts, 17 g of crude cyclic ketone. Distillation gave the 7-*methyltetrahydrocycloheptathiophenone* (2), b.p. 90—94° at 0.4 mmHg (15.5 g, 66%) (Found: C, 66.45; H, 6.65. $C_{10}H_{12}OS$ requires C, 66.65; H, 6.65%), $\nu_{max.}$ (film) 1 660 cm^{-1}, δ ($CDCl_3$) 1.1 (3 H, d, *J* 6 Hz), 1.3—3.5 (7 H, complex m), 7.03 (1 H, d, *J* 5 Hz, H-2), and 7.45 (1 H, d, *J* 5 Hz, H-3).

5,5-*Dibromo*-5,6,7,8-*tetrahydro*-7-*methyl*-4H-*cyclohepta*[b]-*thiophen*-4-*one* (4).—The cyclic ketone (2) [6 × 2 g, each portion in THF (100 ml)] was treated with PTAT (6.7 g each) over 10 min. T.l.c. showed one major product. The solutions were filtered and evaporated, and the residue treated with cold sodium hydrogen carbonate solution and chloroform. The dried chloroform extracts were evaporated and the residue chromatographed on alumina (500 g; IV) in petroleum (b.p. 40—60°). The *dibromo-ketone* (4) (9.5 g, 45%) crystallized from methanol; m.p 93—95° (Found: C, 35.75; H, 3.05. $C_{10}H_{10}Br_2OS$ requires C, 35.5; H, 3.0%), $\nu_{max.}$ (Nujol) 1 670 cm^{-1}, δ ($CDCl_3$) 1.15 (3 H, d, *J* 6 Hz, C*H*$_3$·CH), 2.3—3.4 (5 H, m), 7.0 (1 H, d, *J* 5 Hz, H-2), and 7.3 (1 H, d, *J* 5 Hz, H-3).

7-*Methyl*-4H-*cyclohepta*[b]*thiophen*-4-*one* (6).—Solutions of the dibromo ketone (4) (5 and 4.5 g, each in 250 ml of dry DMF) were boiled with lithium carbonate (2.5 g in each) under nitrogen (3.5 h). Evaporation of the combined solutions gave a solid, which was shaken with aqueous sodium hydrogen carbonate and chloroform. The chloroform extracts gave a solid on evaporation. The 7-*methylcycloheptathiophenone* (6) had m.p. 98—99° (from cyclohexane) (3.5 g, 70%) (Found: C, 68.1; H, 4.6. $C_{10}H_8OS$ requires C, 68.2; H, 4.55%) $\nu_{max.}$ (Nujol) 1 580 and 1 630 cm^{-1}, $\lambda_{max.}$ (95% EtOH) 237, 330, and 352sh nm (log ε 4.40, 4.05, —), δ ($CDCl_3$) 2.4 (3 H, s), 7.0 (2 H, s), 3.35br (1 H, s, H-8), 3.5 (1 H, d, *J* 5 Hz, H-2), and 7.9 (1 H, d, *J* 5 Hz, H-3) [on addition of a small amount of Pr(fod)$_3$ the spectrum became first-order; a large upfield shift was shown by the signals for H-3 and H-5 and $J_{5,6}$ was thus revealed as 12 Hz].

General Procedure for Photochemical Reactions involving Cycloheptathiophenones.—A solution of the cycloheptathiophenone (2 g) in methanol (1 l) was irradiated as described earlier. Samples were taken and evaporated at intervals for t.l.c. and n.m.r. examination. Irradiation was stopped when the dimer concentration remained constant. Some unchanged cycloheptathiophenone was always present. Evaporation gave a residue, best separated by p.l.c.

4a,5,10,10a-*Tetrahydro*-5,10-*ethenoheptaleno*[2,3-b:8,7-b′]-*dithiophen*-4,6-*dione* (19). Separated by p.l.c. (ethyl acetate–toluene, 1 : 1), the fastest moving band was eluted with methanol. The *dimer* of (5) (382 mg, 19%) had m.p. 198—201° (from carbon tetrachloride) (Found: C, 65.9; H, 3.55. $C_{18}H_{12}O_2S_2$ requires C, 66.65; H, 3.7%), $\nu_{max.}$ 1 670 cm^{-1}, δ ($CDCl_3$) 2.9 (1 H, m), 3.1 (1 H, d, *J* 12 Hz), 4.0 (1 H, d of d, *J* 8 and 4 Hz), 4.5 (1 H, d, *J* 8 Hz), 6.2—6.5 (2 H, m), 6.65 (1 H, d of d, *J* 8 and 1 Hz), 6.8 (1 H, d of d, *J* 8 and 8 Hz), 7.09 (1 H, d, *J* 5 Hz), and 7.21 (1 H, d, *J* 5 Hz), *m/e* 324 (M^+), and 162 (100%) [double irradiation showed a coupling sequence similar to that described in the Discussion section for the dimer (12)].

4a,5,10,10a-*Tetrahydro*-2,8-*dimethyl*-5,10-*ethenoheptaleno*-[2,3-b:8,7-b′]*dithiophen*-4,6-*dione* (12). Isolated by p.l.c.

(benzene–chloroform, 1 : 1; 3 elutions) from the cycloheptathiophenone (7) (1 g), the *dimer* (12) (138 mg, 13.8%) had m.p. 195—196° [from petroleum (b.p. 40—60°)] (Found: C, 67.9; H, 5.1. $C_{20}H_{16}O_2S_2$ requires C, 68.2; H, 4.55%), $\nu_{max.}$ ($CHCl_3$) 1 670 cm^{-1}, $\lambda_{max.}$ (95% EtOH) 229, 246sh, 266sh, and 325 nm (log ε 4.40, —, —, and 3.63), for n.m.r. spectrum see Figure; *m/e* 352 (M^+) and 176.

4a,5,10,10a-*Tetrahydro*-11,14-*dimethyl*-5,10-*ethenoheptaleno*[2,3-b:8,7-b']*dithiophen*-4,6-*dione* (18). Isolated by p.l.c. [prelimanary separation with ethyl acetate–toluene (1 : 1), then chloroform–toluene (1 : 3)], only *ca.* 100 mg (5%) of crude *dimer* of (6) was obtained, m.p. 204—206° (from carbon tetrachloride) [Found: C, 66.7; H, 4.5. $(C_{20}H_{16}O_2S_2)_2,CH_3OH$ requires C, 66.9; H, 4.9%], $\nu_{max.}$ (CCl_4) 1 675 cm^{-1}, $\lambda_{max.}$ (95% EtOH) 230, 263sh, and 330 nm (log ε 4.32, 3.91, and 3.61), δ ($CDCl_3$) 1.9 (3 H, d, 1 Hz), 2.08br (3 H, s), 3.15br (2 H, s), 3.92br (1 H, s), 4.45 (1 H, d, *J* 7 Hz), 5.85br (1 H, d, *J* 7 Hz), 6.45br (1 H, s), 6.9—7.1 (2 H, overlapping d, each *J* 5 Hz), 7.4 (1 H, d, *J* 5 Hz), and 7.55 (1 H, d, *J* 5 Hz), *m/e* 352 (M^+) and 176 (100%).

4,9-*Dimethyl*-10-*thiatricyclo*[5.3.0.$0^{2,5}$]*deca*-1(7),3,8-*trien*-6-*one* (14). The cycloheptathiophenone (8) (2 g) was irradiated in methanol, and the products separated by p.l.c. (chloroform–benzene, 1 : 1; two elutions). The slowest running band gave starting material (0.53 g). The fastest running band gave, on elution, the *tricyclic compound* (14) as an oil, b.p. 110° at 0.05 mmHg (bulb tube distillation) (Found: M^+, 190.045 0. $C_{11}H_{10}OS$ requires *M*, 190.045 3), $\nu_{max.}$ 1 702 cm^{-1}; for n.m.r. data see Discussion section.

5-*Bromo*-5,6,7,8-*tetrahydro*-2-*methyl*-4H-*cyclohepta*[b]*thiophen*-4-*one* (16).—Solutions of the 2-methyltetrahydrocycloheptathiophenone (10 × 1.8 g, each in 40 ml of tetrahydrofuran) were treated with PTAT (3.9 g each). Work-up as before gave a crude product, which was chromatographed on alumina (IV; 500 g) in petroleum (b.p. 40—60°). The *monobromo-ketone* (16) had m.p. 41—42° (from petroleum) (14.9 g, 56%) (Found: C, 46.2; H, 4.25. $C_{10}H_{11}BrOS$ requires C, 46.3; H, 4.25%), δ ($CDCl_3$) 1.5—2.5 (7 H, m covering s), 3.0 (2 H, t, 8-H_2), 4.65 (1 H, t, CHBr), and 6.88 (1 H, s).

7,8-*Dihydro*-2-*methyl*-4H-*cyclohepta*[b]*thiophen*-4-*one* (17). —A solution of the monobromo-ketone (16) (14 g) in dry DMF (400 ml) was boiled under nitrogen with lithium carbonate (14 g; 2.5 h). The mixture was filtered hot, the solid washed with chloroform, and the mixture evaporated. The crude residue was chromatographed on alumina (400 g; IV), eluting with petroleum (b.p. 40—60°) containing increasing percentages of benzene; 50 : 50 benzene–petroleum eluted the *dihydrocycloheptathiophenone* (17), b.p. 100° at 0.01 mmHg (9.5 g, 95%) (Found: C, 67.4; H, 5.75. $C_{10}H_{10}OS$ requires C, 67.4; H, 5.6%), $\nu_{max.}$ (film) 1 670, 1 640, and 1 610 cm^{-1}, $\lambda_{max.}$ (45% EtOH) 237, 272, and 325 nm (log ε 4.63, 3.89, and 3.60); for n.m.r. data see Discussion section.

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