Tropolones. Part VII. Orientation in Tropolone.*

By J. W. Cook, J. D. Loudon, and D. K. V. Steel.

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α- and γ-Nitrotropolones and α-bromo-γ-nitrotropolone are prepared and oriented. α- and γ-Aminotropolone and their diazo-reactions are described. α- and γ-Carboxytropolone are prepared, the latter through dehydrogenation of a condensation product of pimelic and oxalic esters. In bromotropolones the replacement of bromine by the *p*-tolylthio-residue is examined.

With the establishment of electrophilic substitution in tropolone there is associated the problem of orienting the substitution products. Dewar's prediction on theoretical grounds (*Nature*, 1950, **166**, 790) that γ-substitution would predominate does not provide a complete solution and the practical approach, based on isomerisation of substituted tropolones to derivatives of benzoic acid, sometimes meets with difficulty (cf. Cook and Loudon, *Quart. Reviews*, 1951, **5**, 99). Nitro- and amino-derivatives of tropolone, as of benzene, thus become important as key-compounds for orientation. This is already recognised in substitution studies by Haworth and Hobson on β-methyltropolone (*J.*, 1951, 561) and by Nozoe and his school on hinokitiol [*Proc. Jap. Acad.*, 1950, **26**, (9), 30; 38; 45: 1950, **26**, (10), 25], on methyltropolones [*ibid.*, 1951, **27**, (8), 410; *Sci. Rep. Tôhoku*, 1952, **35**, (4), 242], and on tropolone itself [*Proc. Jap. Acad.*, 1951, **27**, (4), 190; 1951, **27**, (5), 231; *J. Amer. Chem. Soc.*, 1951, **73**, 1895]. Our own study of nitration in tropolone, of which a preliminary account has already appeared (Cook, Loudon, and Steel, *Chem. and Ind.*, 1951, 669), is summarised below together with the results of further search for significant reference compounds.

Nitration of tropolone yielded γ-nitrotropolone and a small quantity of α-nitrotropolone. These products were identified by isomerisation, *via* their methyl ethers, to *p*- and *o*-nitrobenzoic acid respectively. Their reduction afforded corresponding aminotropolones of which the γ-isomer is very conveniently also prepared by reduction of γ-*p*-tolylazotropolone. This azo-compound is thereby identified and is the sole product, isolated in high yield, of coupling of tropolone with diazotised *p*-toluidine at pH 6·9. Standard procedures applied to diazotised γ-aminotropolone led to γ-bromo-, γ-cyano-, and γ-hydroxy-tropolone. The amine also underwent Skraup's reaction, affording pyrido(3 : 2-βγ)tropolone (Cook, Loudon, and Steel, *Chem. and Ind.*, 1952, 562). α-Aminotropolone, available in relatively small quantity, is less suited to diazo-reactions since by the action of nitrous acid it is converted, in part at least, into salicylic acid, a type of change which was first observed by Nozoe, Kitahara, and Doi for α-aminohinokitiol (*J. Amer. Chem. Soc.*, 1951, **73**, 1895).

Nitration of α-bromotropolone yielded α-bromo-γ-nitrotropolone (m. p. 138—139°) which was oriented by rearrangement, through its methyl ether, to 2-bromo-4-nitrobenzoic acid. This nitration product differs considerably in m. p. from either of the two bromonitrotropolones (m. p.s 112° and 120°) described, but not rigidly oriented, by Nozoe *et al.* (*Proc. Jap. Acad.*, 1951, **27**, 190, 231).

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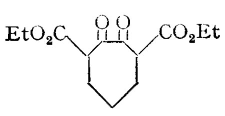
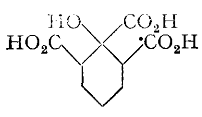
* Part VI, *J.*, 1952, 4416.

Hydrolysis of γ-cyanotropolone afforded γ-carboxytropolone, and this acid served to orient γ-formyltropolone, through the latter's oxidation product, as described in Part VI. The acid was unchanged by sublimation or when heated in pyridine, but was decarboxylated in boiling aniline, tropolone being isolated. It reacted with ethereal diazomethane, forming a methyl ester methyl ether. Hydrogenation of γ-cyanotropolone yielded γ-aminomethyltropolone which was isolated as the picrate.

α-Carboxytropolone which was prepared in Part V (*J.*, 1952, 2350), *via* the nitrile, from α-bromotropolone has now been obtained by a method involving synthesis of the tropolone ring. Naumov and Perminova (*Acta Univ. Asiae Mediae*, 1937, [vi], No. 28; briefly abstracted in *Brit. Abs.*, 1940, *A*, II, 48, but otherwise ignored) claim to have prepared 1 : 4-diethoxycarbonyl*cyclo*heptane-2 : 3-dione (I) by condensing pimelic and oxalic esters. Their compound was characterised through reaction products with phenylhydrazine ("phenylhydrazone," m. p. 189—190°) and *o*-phenylenediamine (condensate, m. p. 142°). We obtained by the same route a compound which appears to be identical with this dione and, although its derivatives differ somewhat from those described in the abstract, structure (I) is completely confirmed by its further reactions. For instance, hydrolysis by acid afforded *cyclo*heptane-1 : 2-dione. Alkaline hydrolysis, on the other hand, proceeded with rearrangement to 2-hydroxy*cyclo*hexane-1 : 2 : 3-tricarboxylic acid (II) which was degraded to 2-oxo*cyclo*hexane-1 : 3-dicarboxylic acid (III) and thence to *cyclo*hexanone. When (I) was heated with bromine (2·5 mols.) in acetic acid αα′-dibromotropolone was obtained—probably through bromination–dehydrobromination of *cyclo*heptane-1 : 2-dione formed in the acidic medium. Attempts to dehydrogenate (I) with palladium–charcoal in trichlorobenzene or with chloranil in xylene were unsuccessful, but by the action of iodine in boiling nitrobenzene (cf. Treibs, *Annalen*, 1952, **576**, 110) a product was obtained from which α-carboxytropolone was isolated, albeit in small yield.



(I)



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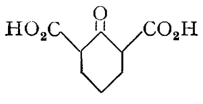

(III)

Unlike most nucleophilic reagents the salts of thiophenols *exhaustively* replace halogen in *o*-/*p*-polyhalogenonitrobenzenes (Loudon, *J.*, 1940, 1525). In Part V (*loc. cit.*) it was shown that *p*-thiocresol reacts with α-bromotropolone in presence of bases to form α-*p*-tolylthiotropolone. This reagent was therefore tested for its capacity to orient, by replacement, potential anions which are substituents in the tropolone nucleus. Its value, however, appears to be limited. For instance, αα′γ-tribromotropolone by reaction with an excess of *p*-thiocresol in pyridine afforded γ-bromo-αα′-di-*p*-tolylthiotropolone in excellent yield. Nozoe, Satô, and Matsui [*Proc. Jap. Acad.*, 1952, **28**, (8), 407], who examined the same reaction under rather different conditions, report the simultaneous formation of an isomer which we have not encountered. Our product was identified by its alternative preparation from αα′-dibromotropolone and *p*-thiocresol, followed by bromination of the resultant αα′-di-*p*-tolylthiotropolone. Despite the resistance to replacement thus shown by the γ-bromo-substituent, γ-bromo-αα′-di-*p*-tolylthiotropolone yielded αα′γ-tri-*p*-tolylthiotropolone when heated at 150° in ethanol with the sodium salt of *p*-thiocresol. On the other hand, γ-nitrotropolone was largely recovered from all attempts to replace the nitro- by the *p*-tolylthio-group. This result, and the contrast it provides to the mobility of the nitro-group in *p*-dinitrobenzene, is readily explicable by resonance-stabilisation in the nitrotropolone anion which is present in the basic medium used. Moreover, although isomerisation was not observed with the tropolones examined, the alkalinity of the reagent caused rearrangement to 2 : 3 : 5-trichlorobenzoic acid when 2 : 3 : 5 : 7-tetrachloro*cyclo*heptatrienone was heated with *p*-thiocresol and sodium hydroxide in ethanol. Under similar conditions the toluene-*p*-sulphonate of tropolone afforded 2-*p*-tolylthio*cyclo*heptatrienone (cf. Part V, *loc. cit.*).

Repeated attempts failed to effect *C*-acylation of tropolone or of its methyl ether by the use of perchloric acid in acetic anhydride (Burton and Praill, *J.*, 1950, 2034, and later papers) or trifluoroacetic anhydride in acetic acid (Bourne, Stacey, Tatlow, and Tedder, *J.*, 1951, 718). From these experiments tropolone was invariably recovered, after hydrolysis where necessary.

EXPERIMENTAL

α- and γ-Nitrotropolone.—(i) A mixture of nitric (0·32 c.c.; *d* 1·42) and acetic (2·9 c.c.) acids was gradually added from a micro-burette to a solution of tropolone (0·6 g.) in acetic acid (10 c.c.). The temperature of the mixture rose to 27° after addition of the first few drops and was kept just below this during subsequent additions. After 12 hr. at room temperature γ-nitrotropolone was filtered off and formed yellow needles (0·16 g.), m. p. 194° (sealed tube), from benzene (Found: C, 50·1; H, 3·0; N, 8·3. Calc. for $C_7H_5O_4N$: C, 50·3; H, 3·0; N, 8·4%). The reaction mother-liquor was diluted with water and continuously extracted with benzene. The recovered solid was fractionally crystallised from benzene, affording first some γ-nitrotropolone (0·16 g.) and then *α-nitrotropolone* (0·08 g.) as yellow prisms, m. p. 153° (from benzene) (Found: C, 50·5; H, 3·2; N, 8·5%). Both isomers give a green colour with ferric chloride in ethanol.

(ii) A similar mixture of products, but in smaller yield, was obtained by mixing solutions of tropolone (0·05 g.) and potassium nitrate (0·048 g.) in concentrated sulphuric acid (1 c.c. each) and, after it had been kept for 12 hr. at room temperature, pouring the orange solution into ice-water.

(iii) A small yield of γ-nitrotropolone was obtained by heating a solution of tropolone (0·1 g.) in water (1·5 c.c.) and nitric acid (0·06 c.c.; *d* 1·42) at 95°, followed by extraction with benzene.

(iv) Nitrogen tetroxide (0·5 g.) in light petroleum (b. p. 60—80°) (5 c.c.) was added with stirring at 10—15° to a solution of tropolone (0·5 g.) in the same solvent (200 c.c.). Stirring was continued for 3 hr., the solvent was decanted, and the residue washed with fresh solvent and then with water. The resultant solid (0·36 g.) afforded mainly γ-nitrotropolone (0·3 g.) and a trace of the α-isomer.

Orientation of α- and γ-Nitrotropolone.—(i) *γ-Nitrotropolone methyl ether* was obtained as bright yellow needles, m. p. 224° (sealed tube) [Nozoe *et al.*, *Proc. Jap. Acad.*, 1951, **27**, (5), 231, give m. p. 232°], from benzene (Found: C, 52·8; H, 3·8; N, 7·9. $C_8H_7O_4N$ requires C, 53·0; H, 3·9; N, 7·7%), when solutions of diazomethane in ether and γ-nitrotropolone (0·1 g.) in methanol (10 c.c.) were mixed and, after 12 hr., evaporated. This methyl ether (0·03 g.) was heated under reflux for 3 hr. with sodium methoxide (from 0·02 g. of sodium) in methanol (5 c.c.). 6N-Sodium hydroxide (2 c.c.) was added and, while the methanol was allowed to evaporate, the whole was heated for 1 hr. at 100°. Acidification and recovery from ether afforded *p*-nitrobenzoic acid, m. p. and mixed m. p. 238—239°.

(ii) *α-Nitrotropolone methyl ether*, prepared from α-nitrotropolone and treated as described for its isomer, formed pale yellow crystals, (micro-)m. p. 127°, from ether (Found: C, 53·0; H, 4·1; N, 8·1%) and afforded *o*-nitrobenzoic acid, m. p. and mixed m. p. 136—140°.

α-Bromo-γ-nitrotropolone.—α-Bromotropolone was nitrated at 15—17° by method (i) described under nitration of tropolone. *α-Bromo-γ-nitrotropolone* so produced had m. p. 138—139° [from benzene–light petroleum (b. p. 60—80°)] (Found: C, 34·3; H, 1·8; N, 5·9. $C_7H_4O_4NBr$ requires C, 34·2; H, 1·6; N, 5·7%). With diazomethane it afforded a methyl ether (m. p. 196° in sealed tube, but not analytically pure) which, by successive treatment with sodium methoxide in boiling methanol and hydrolysis, yielded 2-bromo-4-nitrobenzoic acid, m. p. and mixed m. p. 159—162°.

*γ-*p*-Tolylazotropolone.*—Coupling was best effected in a 0·25M-phosphate buffer with pH *ca.* 6·9 (Hitchcock and Taylor, *J. Amer. Chem. Soc.*, 1937, **59**, 1812). Tropolone (0·5 g.) in the buffer solution (60 c.c.) was coupled with 0·1M-toluene-*p*-diazonium chloride in 0·06N-hydrochloric acid. The precipitated γ-*p*-tolylazotropolone (0·9 g.) formed orange crystals, m. p. 201°, from acetone (Found: C, 70·1; H, 5·2; N, 11·8. Calc. for $C_{14}H_{12}O_2N_2$: C, 69·95; H, 5·0; N, 11·7%). The compound of m. p. 190—193° described in Part I (Cook, Gibb, Raphael, and Somerville, *J.*, 1951, 503) was apparently impure.

γ-Aminotropolone.—A 10% solution of sodium dithionite (10 c.c.) was added to γ-nitrotropolone (0·1 g.) in warm water (10 c.c.)—or to γ-*p*-tolylazotropolone (0·36 g.) in acetone (20 c.c.) and water (10 c.c.). The resultant pale yellow solution was neutralised with ammonia, made faintly acid with acetic acid, and exhaustively extracted with ethyl methyl ketone. *γ-Aminotropolone*, recovered from the extract, crystallised as yellow scales, m. p. 173—175°, from xylene (Found: C, 61·4; H, 5·4; N, 10·5. $C_7H_7O_2N$ requires C, 61·3; H, 5·2; N, 10·2%).

α-*Aminotropolone*, (micro-)m. p. 86° [from light petroleum (b. p. 60—80°)], was obtained by reduction of α-nitrotropolone as described for its isomer (Found : C, 61·5; H, 5·2%). The orange solution obtained by diazotisation in dilute sulphuric acid became red when heated for 30 min. at 100°. Extraction and recovery in ether (charcoal) followed by fractional crystallisation from light petroleum (b. p. 60—80°) afforded (*a*) a more insoluble crystalline substance of (micro-)m. p. 190°, which gave a red-brown colour with ferric chloride in ethanol, but was insufficient in quantity for further characterisation, and (*b*) salicylic acid, (micro-)m. p. 152—155° undepressed by admixture with an authentic sample.

γ-*Hydroxytropolone*.—γ-Aminotropolone (0·13 g.) in 0·36N-sulphuric acid (8 c.c.) was diazotised at 0° with 7% aqueous sodium nitrite (1 c.c.), and the solution was heated under reflux for 2 hr. γ-Hydroxytropolone was recovered in ether and, after sublimation at 150°/1 mm., formed pale yellow crystals, m. p. (decomp.) 244°, from methanol–benzene (Found : C, 61·1; H, 4·7. Calc. for $C_7H_6O_3$: C, 60·9; H, 4·4%). It gave a deep blue colour with ferric chloride in ethanol. Nozoe *et al.* give m. p. (decomp.) 251° for the same compound when prepared in this way [*Proc. Jap. Acad.*, 1951, **27**, (8), 426], and m. p. (decomp.) 245° when obtained by the action of potassium persulphate on potassium tropolone [*ibid.*, 1952, **28**, (9), 488].

γ-*Bromotropolone*.—A solution of diazotised γ-aminotropolone, prepared as just described, was added to aqueous cuprous bromide and, after 1 hr. at room temperature, the whole was heated for 1 hr. at 100°. γ-Bromotropolone was obtained by sublimation at 240—260°/1 mm. of the precipitated copper complex and was identified by mixed (micro-)m. p. 186—188° with an authentic specimen (Part III, Cook, Gibb, and Raphael, *J.*, 1951, 2244).

γ-*Cyanotropolone*.—γ-Aminotropolone (0·32 g.) in 0·72N-sulphuric acid (10 c.c.) at 0° was diazotised with 2% aqueous sodium nitrite (8 c.c.). The cold diazo-solution was stirred into a solution of potassium nickelocyanide and sodium carbonate (cf. Storrie, *J.*, 1937, 1746) and after 12 hr. the mixture was filtered and the filtrate acidified. The resultant precipitate was sublimed up to 200°/0·2 mm. and the sublimate was combined with a small quantity of material recovered in chloroform from the acidified filtrate. γ-*Cyanotropolone* formed yellow needles (0·15 g.), m. p. 236°, from water (Found : C, 65·5; H, 3·4; N, 9·7. $C_8H_5O_2N$ requires C, 65·3; H, 3·4; N, 9·5%). It gave a green-brown colour with ferric chloride in ethanol. When γ-cyanotropolone was treated in alkaline solution with 3% hydrogen peroxide and, after 12 hr., the solution was acidified, an oxidation *product* was obtained as yellow prisms, m. p. (decomp.) 269° (Found : C, 38·1; H, 3·1; N, 8·9. $C_5H_5O_5N$ requires C, 37·8; H, 3·2; N, 8·8%), but was not further investigated.

γ-*Carboxytropolone*, as yellow needles, m. p. (decomp.) 288°, from acetic acid, was obtained when γ-cyanotropolone was heated with (i) 50% potassium hydroxide for 25 min. (the solution was then acidified), or (ii) concentrated hydrochloric acid for 1 hr. (Found : C, 57·7; H, 3·7. $C_8H_6O_4$ requires C, 57·8; H, 3·6%). It gave a green-brown colour with ferric chloride in ethanol and was decarboxylated when heated with boiling aniline for 1 hr. Tropolone was recovered in ether from the acidified aniline solution and, after sublimation, was identified by mixed m. p. 48—49°. With ethereal diazomethane γ-carboxytropolone afforded the *methyl ester methyl ether* as colourless needles, (micro-)m. p. 184° [from benzene–light petroleum (b. p. 60—80°)] (Found : C, 62·1; H, 5·1. $C_{10}H_{10}O_4$ requires C, 61·9; H, 5·2%).

γ-*Aminomethyltropolone*.—γ-Cyanotropolone (0·05 g.) in ethanol (20 c.c.) containing one molar proportion of hydrogen chloride was hydrogenated (3 hr. for completion) in presence of palladised charcoal (0·025 g.). The brown gum, which was obtained on filtration and evaporation, afforded the *picrate* as brown needles, m. p. (decomp.) 208°, from water (Found : C, 44·3; H, 3·55. $C_{14}H_{12}O_9N_4$ requires C, 44·2; H, 3·2%).

1 : 4-*Diethoxycarbonyl*cyclo*heptane*-2 : 3-*dione* (I).—To a cooled suspension of sodium ethoxide (from 2·18 g. of atomised sodium and 4·4 g. of ethanol) in ether (40 c.c.) ethyl oxalate (7 g.) and then ethyl pimelate (10·3 g.) were slowly added. The resultant solution was heated under reflux for 1 hr., the ether was removed, and the residue heated under distillation conditions at 120—125° for 3 hr. The cooled mass was dissolved in water, and the solution acidified and exhausted with ether. After being washed with aqueous sodium carbonate the ethereal solution was shaken with 8N-sodium hydroxide, and the precipitated yellow salt was collected. Acidification of this salt and recovery in ether gave (I) as colourless prisms, m. p. 70° (from ethanol) (Found : C, 57·7; H, 6·3. Calc. for $C_{13}H_{18}O_6$: C, 57·8; H, 6·6%). It reacted with phenylhydrazine in boiling ethanol to form a *dipyrazolone* which separated as colourless crystals, m. p. (decomp.) 309—311° (Found : C, 70·4; H, 5·1. $C_{21}H_{18}O_2N_4$ requires C, 70·4; H, 5·1%); these crystals when recrystallised from hot acetic acid became purple, without

significant change in m. p. or analytical figures. By heating molar proportions of (I) and *o*-phenylenediamine in ethanol for 1 hr., followed by fractional precipitation through cautious addition of water, two *diazines* were obtained as colourless needles, the less soluble having m. p. 143° (from ethanol) (Found : C, 66·3; H, 6·35; N, 8·1. $C_{19}H_{22}O_4N_2$ requires C, 66·7; H, 6·4; N, 8·2%), and the more soluble, m. p. 84° (from ethanol) (Found : C, 66·7; H, 6·3; N, 8·7%).

The dione (I) resisted hydrolysis by aqueous mineral acid. It was heated under reflux for 2 hr. in a mixture of 25% sulphuric acid and an equal volume of acetic acid. Thereafter the addition of a solution of 2 : 4-dinitrophenylhydrazine in ethanol caused precipitation of a solid which was separated by chromatography (benzene–alumina) into unidentified yellow needles (first eluate), m. p. 142—144° (from ethanol) (Found : C, 51·3; H, 4·8; N, 17·3%), and red needles (later eluates), m. p. 198—200° (from benzene). The latter substance was identified by mixed m. p. as the bis-2 : 4-dinitrophenylhydrazone of *cyclo*heptane-1 : 2-dione containing benzene of crystallisation (Part VI, *loc. cit.*) (Found : C, 53·6; H, 5·0; N, 20·1. Calc. for $C_{19}H_{18}O_8N_8,C_6H_6$: C, 53·2; H, 4·3; N, 19·85%).

2-*Hydroxy*cyclo*hexane*-1 : 2 : 3-*tricarboxylic Acid* (II).—The dione (I) (0·1 g.) was heated under reflux with 6N-sodium hydroxide (5 c.c.) for 15 min. during which the precipitated yellow salt became colourless. Acidification and recovery in ether afforded a gum which slowly solidified, forming 2-*hydroxy*cyclo*hexane*-1 : 2 : 3-*tricarboxylic acid* as colourless needles, m. p. (decomp.) 215—216° (sealed tube) from ethyl acetate (Found : C, 46·0; H, 4·8; equiv., 79·7. $C_9H_{12}O_7$ requires C, 46·55; H, 5·2%; equiv., 77·3).

2-*Oxo*cyclo*hexane*-1 : 3-*dicarboxylic Acid* (III).—Compound (II) dissolved with effervescence in cold concentrated sulphuric acid. After 12 hr. the solution was poured into ice, affording the 1 : 3-*dicarboxylic acid* as needles (from water) which melted with decomposition over a range from *ca.* 120° to 140° (Found : C, 51·8; H, 5·6. $C_8H_{10}O_5$ requires C, 51·6; H, 5·4%). [The diethyl ester of this acid is described by Guha and Seshadriengar (*Ber.*, 1936, **69**, 1207).] When warmed with Brady's reagent the acid gave *cyclo*hexanone 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 156—158°.

αα′-Dibromotropolone.—A solution of (I) (1·4 g.) in acetic acid (20 c.c.) containing bromine (2 g.) was heated under reflux for 5 hr. The residue obtained by evaporation *in vacuo* was dissolved in ether, and the solution shaken with strong aqueous sodium hydroxide. The resultant yellow precipitate when dissolved in water and acidified afforded αα′-dibromotropolone as colourless needles (0·4 g.), m. p. and mixed m. p. 156° (from methanol) (Part III, *loc. cit.*).

α-Carboxytropolone.—A solution of (I) (1 g.) in nitrobenzene (5 c.c.) containing a small crystal of iodine was heated under reflux for 30 min. Sufficient 6N-sodium hydroxide was added to the cooled solution to maintain slight alkalinity, and the nitrobenzene was removed in steam. The residual liquor was acidified and extracted first with ether and then with ethyl methyl ketone. The brown mass recovered from the ethereal extract was sublimed up to 160°/20 mm., affording a carboxylic acid as needles (0·5 g.), m. p. 128—130° [from benzene–light petroleum (b. p. 60—80°)] (Found : C, 54·0; H, 6·6%; equiv., 285. $C_{13}H_{20}O_7$ requires C, 54·15; H, 7·0%; equiv., 288). This acid, which did not produce colour with ferric chloride in ethanol, dissolved with effervescence in aqueous sodium hydrogen carbonate and in warm concentrated sulphuric acid. It is regarded as *diethyl* 2-*carboxy*-2-*hydroxy*cyclo*hexane*-1 : 3-*dicarboxylate*, probably formed from unchanged (I) during working up. From the ethyl methyl ketone extract a yellow mass was recovered and sublimed at 100—120°/2 mm., affording α-carboxytropolone (0·01 g.), m. p. and mixed m. p. 202° (decomp.), with the sample described in Part V (Found : C, 57·65; H, 4·0. Calc. for $C_8H_6O_4$: C, 57·8; H, 3·6%) : it gave a green-brown colour with ferric chloride in ethanol.

*γ-Bromo-αα′-di-*p*-tolylthiotropolone.*—(i) αα′γ-Tribromotropolone (0·2 g.) and *p*-thiocresol (0·21 g.) were heated under reflux with pyridine (5 c.c.) for 1 hr., both in presence and in absence of sodium hydroxide (0·067 g.). In each case the precipitate obtained on acidification afforded γ-bromo-αα′-di-*p*-tolylthiotropolone as yellow prisms, m. p. 216°, from acetic acid (Found : C, 56·2; H, 3·9. Calc. for $C_{21}H_{17}O_2BrS_2$: C, 56·6; H, 3·85%). (ii) The same compound, m. p. and mixed m. p. 214—216°, was obtained when αα′-di-*p*-tolylthiotropolone (0·05 g.) [Nozoe *et al.*, *Proc. Jap. Acad.*, 1952, **28**, (8), 410] was heated with bromine (0·025 g.) in acetic acid (2 c.c.) for 1 hr.

*αα′γ-Tri-*p*-tolylthiotropolone*, m. p. 182° (from acetic acid), was obtained when γ-bromo-αα′-di-*p*-tolylthiotropolone (0·26 g.), *p*-thiocresol (0·06 g.), and sodium hydroxide (0·026 g.) were heated in ethanol (5 c.c.) at 150° for 12 hr. and the whole was added to dilute sulphuric acid (Found : C, 69·1; H, 5·0. $C_{28}H_{24}O_2S_3$ requires C, 68·8; H, 4·95%). It gave an orange-brown colour with ferric chloride in ethanol.

2-p-*Tolylthio*cyclo*heptatrienone,* m. p. and mixed m. p. 147—148° [from benzene–light petroleum (b. p. 60—80°)], was obtained when tropolone toluene-*p*-sulphonate (0·09 g.) (Doering and Hiskey, *J. Amer. Chem. Soc.*, 1952, **74**, 5688), *p*-thiocresol (0·04 g.), and sodium hydroxide (0·013 g.) were heated in ethanol for 1 hr. and the solution was then concentrated and poured into water.

Under similar conditions 2 : 3 : 5 : 7-tetrachloro*cyclo*heptatrienone (Doering and Knox, *ibid.*, p. 5683) afforded 2 : 3 : 5-trichlorobenzoic acid which was recovered in ether from the acidified concentrates and had m. p. and mixed m. p. 166°.

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