

Thermal Rearrangements of Tropolone Ethers.† Part 4¹

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The Claisen rearrangements of prop-2-ynyl ethers of 3-chloro- and 3-phenyl-tropolone are described. Products arising from an apparent [3,7] sigmatropic shift predominate in the thermolysis of 3-chloro-2-(prop-2-ynoxy)-tropolone, but the corresponding 3-phenyltropolone ether rearranges largely *via* the normal [3,3] shift. The occurrence of a novel [1,9] sigmatropic inter-oxygen alkyl migration in thermolyses of benzyl and cyclopropyl methyl ethers of tropolones is described, together with silatropic shifts in tropolone trimethylsilyl ethers.

In a previous paper¹ we reported that Claisen rearrangement of certain 3-substituted tropolone allyl and prop-2-ynyl ethers gave products apparently formed by a novel [3,7] sigmatropic shift. For example, thermolysis of the ether (2a) at about 180 °C gave exclusively the furotropone (5a), arising from the dienedione (3a) formed by migration with inversion of the prop-2-ynyl group to the 7-position. The same furotropone (5a) was obtained from the isomeric ether (1a) by way of a normal Claisen [3,3] sigmatropic shift. In contrast, both pairs of prop-2-ynyl ethers of 3-methyl- and 3-n-propyl-tropolone rearranged almost entirely *via* [3,3] sigmatropic shifts, (1b) and (2b) being converted mainly into (5b) and (6b), respectively. In these cases 'cross' products (5b) resulting from (2b) by apparent [3,7] shift were isolated in only minor amounts. We now describe further examples which confirm the influence of ring substituents in determining the course of these rearrangements.

In this series rearrangement of prop-2-ynyl ethers generally leads to stable products resulting from rapid, irreversible intramolecular cyclisation of the intermediate 7-allynyl-3,5-diene-1,2-diones (3) or (4).^{1,2} Fewer products and mechanistic ambiguities are encountered in isomerisations of prop-2-ynyl ethers than in those of the allyl analogues,³ so that studies on the former have been preferred.

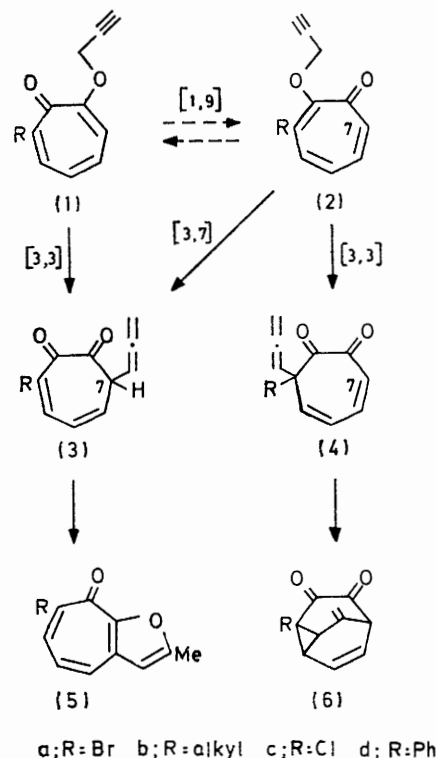
Propynylation of 3-chlorotropolone gave the expected mixture of ethers (1c) and (2c) in only moderate yield; they were readily separated by crystallisation and distinguished structurally on the basis of their u.v. and n.m.r. spectra.¹ The corresponding ethers (1d) and (2d) of 3-phenyltropolone were obtained similarly and separated chromatographically, but the complexity of the low-field region in their n.m.r. spectra precluded structural differentiation by this means. However the presumption, based on experience with all the other ethers of 3-substituted tropolones so far encountered, that the isomer formed in minor amount has the more hindered ether function as in (2), was borne out by the course of their rearrangements.

Isomerisations of the 3-phenyl- and 3-chloro-tropolone prop-2-ynyl ethers in refluxing *p*-cymene (176 °C) were complete in 2 h. Rearrangement products (5) and (6) were readily identified by comparison of spectral data

† This series was formerly entitled 'Claisen Rearrangements of Tropolone Ethers'.

¹ Part 3, R. M. Harrison, J. D. Hobson, and A. W. Midgley, *J.C.S. Perkin I*, 1973, 1960.

with those of the various analogues already characterised;¹ yields arising from the two competing reaction



pathways involved in the isomerisations of the more hindered ethers (2) are compared in the Table.

Thermolysis^a products of 3-substituted 2-(prop-2-ynoxy)tropolones

| Ether (2) | Products (%) ^b of | | | |
|-------------------|------------------------------|----|-----------------------------|----|
| | [3,3] shift | | [3,7] shift | |
| (2a) | (5b) (R = Me) | 81 | (5a) (R = Me) | 67 |
| (2b) | (5b) (R = Pr ⁿ) | 69 | (5b) (R = Pr ⁿ) | 9 |
| (2c) | (6d) | 53 | (5c) | 65 |
| (2d) ^c | | | (5d) | 14 |

^a Ca. 10% solutions in *p*-cymene refluxed for 2 h, except (2d).

^b Material isolated. ^c Refluxing *n*-decane for 4½ h.

The behaviour of the 3-chloro-ether (2c) closely parallels that of the 3-bromo-compound (2a) in that the

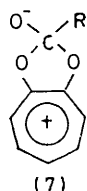
² A. Pryde, J. Zsindely, and H. Schmid, *Helv. Chim. Acta*, 1974, 57, 1598.

³ M. M. Al Holly, R. M. Harrison, and J. D. Hobson, *J. Chem. Soc. (C)*, 1971, 3084; R. M. Harrison and J. D. Hobson, *J.C.S. Perkin I*, 1973, 1958.

corresponding furotropone (5c), formed by way of a [3,7] shift, was the sole isolable product. The 3-phenyl compound (2d) on the other hand gave predominantly the tricyclic α -diketone (6d) *via* a normal [3,3] shift, though accompanied by a lesser amount of the cross product (5d). The latter was also produced directly from the isomeric ether (1d) in high yield as the only thermolysis product. In all the pairs of ethers studied the apparent [3,7] shift occurred to an observable extent only in the case of the more sterically compressed ethers (2), and not in the isomers (1) with an unsubstituted site next to the ether function. Moreover, from the limited data so far available, substantial cross product formation appears to be favoured by inductively electron-withdrawing substituents.

Of the various reaction pathways previously considered¹ for this rearrangement mode, some evidence in favour of a direct [3,7] shift was obtained from kinetic studies on the bromo-ethers (1a) and (2a), but the possibility of concurrent inter-oxygen transfer of a prop-2-ynyl or allyl group, *e.g.* (1) \rightleftharpoons (2), was not excluded. Unfortunately, it was not possible to obtain reliable quantitative data by using the 3-chloro-analogues, since clear first-order kinetics were not observed. However, careful monitoring by g.l.c. at frequent time intervals again failed to reveal any trace of the other isomer in solutions of either pure (1c) or pure (2c) undergoing thermolysis.

To the best of our knowledge examples of inter-oxygen alkyl transfer have not been reported in connection with tropolone ethers, although the suprafacial process, with retention of configuration at the migrating carbon, would be a symmetry-allowed [1,9] sigmatropic shift. The familiar intramolecular prototropy characteristic of monomeric tropolones^{4,5} can be regarded as the prototype for this general process, but the rapid, reversible, inter-oxygen acyl transfers revealed by recent n.m.r. studies of *O*-acyltropolones are in a different category, being distinguished by the probable intervention of an intermediate zwitterion (7).⁶



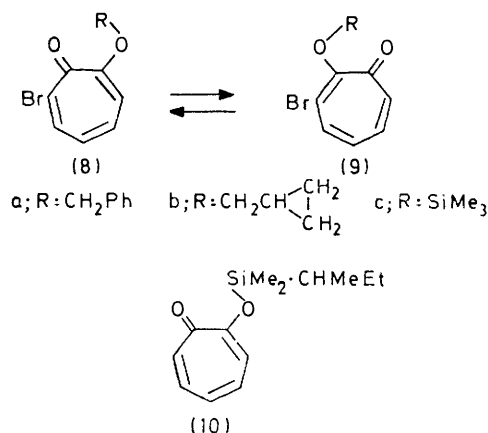
Exploratory pyrolyses of 4-methyltropolone methyl ethers under nitrogen, combined with g.l.c. analysis, provided no evidence that either ether was significantly transformed into its isomer at temperatures up to 350 °C, above which thermal decomposition became rapid. Tropolone benzyl or cyclopropylmethyl ethers seemed likely to be of more interest, being more akin to the allyl and prop-2-ynyl groups in relation to the stabilis-

⁴ D. J. Bertelli, T. G. Andrews, and P. O. Crews, *J. Amer. Chem. Soc.*, 1969, **91**, 5286.

⁵ L. Weiler, *Canad. J. Chem.*, 1972, **50**, 1975.

ation of any charge developed in the transition state,⁷ though unable to undergo Claisen-type [3,3] shift.

The benzyl ethers (8a) and (9a) of 3-bromotropolone were readily separated and distinguished in the usual way through their u.v. and n.m.r. spectra. Examination of solutions of each in refluxing *p*-cymene (176 °C), periodically by g.l.c., showed clear evidence of interconversion. After 24 h both solutions had equilibrated to a mixture containing (8a) and (9a) in the ratio 5 : 1, respectively. Further heating caused no alteration of this ratio but only slow decomposition of the ethers. Confirmation that the interconversion was truly intramolecular rather than a radical cleavage-recombination



was obtained by carrying out the rearrangement in the presence of a radical trap. Thermolysis of each ether [(8a) and (9a)] in *p*-cymene containing a 10-molar excess of 2,6-dimethylphenol gave the same equilibrium mixture, but on prolonged heating a gradual decrease in concentration of the ethers was observed accompanied by the formation of tar and several new products, the most abundant of which was identified as 4-benzyl-2,6-dimethylphenol.

Repetition of these thermolyses with 2,6-di-*t*-butylphenol as the radical trap resulted in greatly reduced tar formation and only one product other than the two ethers, again identified as the 4-benzyl derivative of the phenol. The yield of this compound after 24 h, the time required for complete equilibration of the two ethers, was only 6%, from which it is concluded that homolysis to benzyl radicals is slow relative to interoxygen migration.

Interconversion of the isomeric cyclopropylmethyl ethers (8b) and (9b) of 3-bromotropolone was also observed under similar conditions, although this proceeded less readily and was accompanied by the formation of tar and other unknown products.

These results thus confirm the existence of a reaction pathway allowing inter-oxygen migration of certain

⁶ S. Masamune, A. V. Kemp-Jones, J. Green, D. L. Rabinstein, M. Yasunami, K. Tabase, and T. Nozoe, *J.C.S. Chem. Comm.*, 1973, 283; V. J. Minken, L. P. Olekhovich, Yu. A. Zhdanov, Z. N. Budarina, and V. P. Metlushenko, *Tetrahedron Letters*, 1974, 563.

⁷ C. G. Krespan, *Tetrahedron*, 1967, **23**, 4243.

alkyl residues, having an activation energy comparable with the Claisen rearrangement of allyl and prop-2-ynyl ethers. However, our failure to observe directly such interconversions in the case of (2a) and (2c) leads us to prefer the direct [3,7] shift to rationalise the comparatively rapid and exclusive conversion of these ethers into the 'cross' products (5).

Finally, the work of Pinnavaia and his co-workers⁸ on the rapid inter-oxygen exchange occurring in β -diketone enol trimethylsilyl ethers prompted some preliminary exploration of the corresponding tropolone ethers. With chloro(trimethyl)silane and pyridine in hexane, tropolone gave an oily, extremely moisture-sensitive trimethylsilyl ether. The ¹H n.m.r. spectrum of a solution in hexadeuteriobenzene was matched with a computer-generated spectrum to obtain accurate values of chemical shifts and coupling constants. Comparison with the data reported by Bertelli *et al.*⁴ for tropolone itself revealed a close match of the ring proton coupling constants, indicating the presence of an analogous dynamic equilibrium. In the case of 3-bromotropolone a single crystalline trimethylsilyl ether was obtained, which, in C₆D₆ solution gave ring proton n.m.r. signals sufficiently differentiated to allow approximate first-order analysis. Again, the spectrum showed a close similarity to that of the free tropolone in the same solvent, the near identity of coupling constants suggesting a similar population distribution of the tautomers (8c) and (9c).⁹ The remarkably low energy barrier between these was evident from the lack of significant changes in the n.m.r. spectra given by solutions of either trimethylsilyl ether in [²H₈]toluene measured at temperatures down to -95 °C. Subsequent to our observations,¹⁰ Reich and Murcia have reported¹¹ low temperature ¹H and ¹³C n.m.r. measurements on the degenerate silatropic equilibrium shown by (10), demonstrating that the inter-conversion proceeds with retention of configuration at silicon, and involves an estimated activation energy of only *ca.* 8 kcal mol⁻¹. This low value, ascribable to the propensity of silicon to become pentaco-ordinate,¹² is clearly markedly different from that involved in the inter-oxygen migration of saturated carbon residues, although examples of the latter may yet be found which will allow the equilibrium to be studied by variable temperature n.m.r. techniques.

EXPERIMENTAL

Analytical g.l.c. separations were carried out on Pye 104 instruments with 3 m × 4 mm glass columns packed with 5% fluorosilicone oil (QF-1) on B.D.H. silanised Supasorb. 100 MHz N.m.r. spectra were recorded on Perkin-Elmer R14 and Varian XL-100 instruments with tetramethylsilane as internal reference.

3-Chlorotropolone Prop-2-ynyl Ethers.—3-Chlorotropol-

⁸ T. J. Pinnavaia, W. T. Collins, and J. J. Howe, *J. Amer. Chem. Soc.*, 1970, **92**, 4544.

⁹ Cf. H. Sugiyama, S. Ito, and T. Nozoe, *Tetrahedron Letters*, 1965, 179; H. Sugiyama, *Sci. Reports Tôhoku Univ., Ser. A*, 1968, **20**(1), 34.

¹⁰ R. M. Harrison, Ph.D. Thesis, University of Birmingham, 1972.

one ¹³ sodium salt, dried (P₂O₅) *in vacuo* for 2 days, was stirred with anhydrous potassium carbonate (4 g) and prop-2-ynyl bromide (2.45 cm³) in dry dimethylformamide (50 cm³) at 50–60 °C for 28 h. The cooled mixture was poured into water (150 cm³) and ether (30 cm³) and the crystals (0.58 g) which separated were collected, washed with water and ether, dried, and recrystallised from ethyl acetate–light petroleum (b.p. 60–80 °C), giving 2-chloro-7-(prop-2-ynyloxy)tropolone (1c) (0.48 g), m.p. 130–132°. Sublimation at 90–100 °C (bath) and 0.02 mmHg afforded a sample, m.p. 134–135° (Found: C, 61.7; H, 3.6; Cl, 17.9. C₁₀H₇ClO₂ requires C, 61.7; H, 3.6; Cl, 18.2%); ν_{\max} (hexachlorobutadiene) 3 197, 2 925, and 2 130 cm⁻¹; ν_{\max} (Nujol) 1 610, 1 585, 1 280, 1 245, 1 200, 970, and 755 cm⁻¹; λ_{\max} (EtOH) 252, 256, 325, 355, and 371sh nm (ϵ 28 900, 29 600, 7 900, 7 000, and 5 100); τ (CDCl₃) 2.01br (1 H, d, *J* 9.7 Hz, 3-H), 2.61–3.17 (3 H, m, ring protons), 5.01 (2 H, d, *J* 2.3 Hz, ·OCH₂·), and 7.39 (1 H, t, *J* 2.3 Hz, CH); *m/e* 196/194 (*M*⁺), 167/165, 141, 140, 139, 105, 103, 99, 77, 72, and 63.

More of this product (0.56 g, total yield 33%) was obtained from the combined ethereal extracts of the aqueous phase. Evaporation of the residual ethereal mother liquors, followed by extraction of the residue with hot hexane and concentration gave crystals (0.54 g, 19%) of the isomeric 3-chloro-2-(prop-2-ynyloxy)tropolone (2c), m.p. 96–98° (Found: C, 61.4; H, 3.9; Cl, 18.0%), ν_{\max} (hexachlorobutadiene) 3 215, 2 925, and 2 122 cm⁻¹; ν_{\max} (Nujol) 1 625, 1 570, 1 268, 1 175, 798, and 725 cm⁻¹; λ_{\max} (EtOH) 247 and 320br nm (ϵ 25 400 and 7 100); τ (C₆D₆) 3.16 (1 H, d, *J* 11.5 Hz), 3.31 (1 H, d, *J* 11.5 Hz), 3.79br (1 H, q, *J* 8.1 and 1.18 Hz), 4.18br (1 H, q, *J* 8.1 and 11.6 Hz), 5.51 (2 H, d, *J* 2.4 Hz, ·OCH₂·), and 7.97 (1 H, t, *J* 2.4 Hz, CH); *m/e* 196/194 (*M*⁺), 167/165, 142, 141, 140, 139, 131, 112, 103, 99, 77, 73, and 64.

3-Phenyltropolone Prop-2-ynyl Ethers.—The mixture resulting from stirring 3-phenyltropolone¹⁴ (1.53 g) with anhydrous potassium carbonate (5 g) and prop-2-ynyl bromide (1.2 cm³) in dimethylformamide (50 cm³) at room temperature for 24 h was poured into water. The precipitated crystalline solid (1.1 g) was collected, washed with water and ether, and recrystallised from ethyl acetate–light petroleum (b.p. 60–80 °C). Sublimation at 110 °C (bath) and 0.01 mmHg afforded pale yellow crystals of 2-phenyl-7-(prop-2-ynyloxy)tropolone (1d) (0.75 g, 41%), m.p. 152–153° (Found: C, 81.0; H, 5.1. C₁₆H₁₂O₃ requires C, 81.3; H, 5.1%); ν_{\max} (Nujol) 3 180, 3 160, 2 110, 1 580, and 1 560 cm⁻¹; λ_{\max} (EtOH) 236 and 340br nm (ϵ 20 950 and 10 500); τ (C₆D₆) 2.46–2.74 (6 H, m) and 2.94–3.15 (3 H, m, tropolone ring protons), 5.14 (2 H, d, 2.3 Hz, ·OCH₂·), and 7.49 (1 H, t, *J* 2.3 Hz, :CH); *m/e* 235 (*M*⁺), 197, 183, 182, 141, 115, 57, and 51.

An oil (0.55 g) containing the isomeric ether was isolated from the aqueous mother liquors with ether and purified by chromatography on silica. 1:1 Ether–light petroleum (b.p. 40–60 °C) eluted 3-phenyl-2-(prop-2-ynyloxy)tropolone (2d) (257 mg, 14%); distillation at 100 °C (bath) and 0.001 mmHg gave the ether as a yellow oil (Found: C, 81.6; H, 5.2%), ν_{\max} (film) 3 190, 2 930, 2 120, 1 575, 1 265, 1 160, 1 010, 765, and 705 cm⁻¹; λ_{\max} (EtOH) 222, 274, and 324 nm

¹¹ H. J. Reich and D. A. Murcia, *J. Amer. Chem. Soc.*, 1973, **95**.

¹² L. H. Sommer, 'Stereochemistry, Mechanism, and Silicon,' McGraw-Hill, New York, 1965.

¹³ E. Sebe, S. Matsumoto, and S. Kasuga, *J. Chinese Chem. Soc. (Taiwan)*, 1961, Ser. II, **8**, 193 (*Chem. Abstr.*, 1963, **59**, 2702).

¹⁴ W. von E. Doering and J. R. Mayer, *J. Amer. Chem. Soc.*, 1953, **75**, 2387; T. Nozoe, T. Mukai, and J. Minegishi, *Proc. Japan Acad.*, 1952, **28**, 2387.

(ϵ 16 000, 11 950, and 7 250); τ (C_6D_6) 2.68—2.96 (6 H, m) and 3.28—3.92 (3 H, m) (ring protons), 4.92 (2 H, d, J 2.3 Hz, OCH_2), and 8.09 (1 H, t, 2.3 Hz, :CH); m/e 235 (M^+), 197, 181, 169, 141, 115, 89, and 51.

Claisen Rearrangements.—(a) *Of 3-chlorotropolone prop-2-ynyl ethers.* Solutions of the ethers in *p*-cymene were refluxed under nitrogen for 2 h and the products were isolated by removal of the solvent *in vacuo* and extraction of the residue with boiling light petroleum (b.p. 60—80 °C). From 2-chloro-7-(prop-2-ynyloxy)tropone (1c) (0.38 g) was obtained 7-chloro-2-methylcyclohepta[b]furan-8-one (5c) (0.29 g, 76%), purified by recrystallisation from light petroleum (b.p. 80—100 °C) and sublimation at 90 °C (bath) and 0.01 mmHg to give crystals, m.p. 123—124° (Found: C, 62.0; H, 3.9; Cl, 17.9. $C_{10}H_7ClO_2$ requires C, 61.7; H, 3.6; Cl, 18.2%), $\nu_{\max.}$ (hexachlorobutadiene) 3 100, 3 025, 2 960, and 2 920 cm^{-1} ; $\nu_{\max.}$ (Nujol) 1 620, 1 585, 1 250, 1 160, 955, 872, and 800 cm^{-1} ; $\lambda_{\max.}$ (EtOH) 233, 239, 274, 305sh, 317sh, 332, 347, and 368 nm (ϵ 15 100, 12 300, 32 650, 6 100, 5 500, 4 000, 4 350, and 3 200); τ (C_6D_6) 2.59br (1 H, d, J 10 Hz, 6-H), 3.30br (1 H, d, J 11 Hz, 3-H), 3.91br (1 H, q, J 10 and 11 Hz, 4-H), 4.25 (1 H, d, J 0.9 Hz, 2-H), and 8.13 (3 H, d, J 0.9 Hz, 2-Me); m/e 196 and 194 (M^+), 168 and 166 [($M - CO$)⁺], 167 and 165, 159, 131, 103, 78, and 51.

T.l.c. of the combined mother liquors revealed the presence of a second product, which was isolated by chromatography on silica. Ether (15%)—light petroleum (b.p. 40—60 °C) eluted a yellow oil (7 mg), $\nu_{\max.}$ (film) 3 070, 2 980, 2 930, 1 750, 1 710, 1 650, 1 150, 900, 830, and 715; $\lambda_{\max.}$ (cyclohexane) 260 and 425 nm; m/e 196 and 194 (M^+), 168, 166, 158, 156, 141, 139, 125, 119, 103, 91, 84, 77, and 51, to which structure (6c) is tentatively assigned.

Rearrangement of 3-chloro-2-(prop-2-ynyloxy)tropone (2c) (0.20 g) gave a partially crystalline gum from which 7-chloro-2-methylcyclohepta[b]furan-8-one (5c) (0.13 g, 65%) was isolated by extraction with boiling light petroleum (b.p. 60—80 °C); recrystallisation from the same solvent gave crystals, m.p. 121—122°, identical with the material obtained as described above. T.l.c. of the oily material (23 mg) obtained from the mother liquors showed the presence of at least six products which were not further investigated.

Quantitative studies of the rates of isomerisation of the chloro-ethers (1c) and (2c) were carried out as previously described.¹

(b) *Of 3-phenyltropolone prop-2-ynyl ethers.* A solution of 2-phenyl-7-(prop-2-ynyloxy)tropone (1d) (260 mg) in *p*-cymene (30 cm^3) was refluxed under nitrogen for 2 h. Removal of the solvent *in vacuo* and extraction of the residue with boiling light petroleum (b.p. 60—80 °C), followed by concentration and cooling of the extract resulted in separation of 2-methyl-7-phenylcyclohepta[b]furan-8-one (5d) (203 mg, 78%). A further recrystallisation from light petroleum gave pale yellow crystals, m.p. 114—116° (Found: C, 81.2; H, 5.4. $C_{16}H_{12}O_2$ requires C, 81.3; H, 5.1%), $\nu_{\max.}$ (Nujol) 3 060, 1 620, 1 565, 1 250, 1 155, 957, 822, 759, and 700 cm^{-1} ; $\lambda_{\max.}$ (EtOH) 277 and 329 nm (ϵ 30 400 and 7 750); τ (C_6D_6) 2.38—2.70 (7 H, m) and 2.99br (1 H, q, J 9.1 and 10.7 Hz, 2 \times Me); m/e 235 (M^+), 206, 205, 177, 165, 118, 117, 103, 89, and 76.

The isomeric ether 3-phenyl-2-(prop-2-ynyloxy)tropone (2d) (142 mg) in *n*-decane (20 cm^3) was refluxed under nitrogen for 4½ h. The cooled solution was filtered and the residue obtained by evaporation of the solvent *in vacuo* was taken up in ether and chromatographed on silica. Ether—light petroleum (b.p. 40—60 °C) (1 : 2) eluted 9-methylene-

2-phenyltricyclo[3.2.2.0^{2,8}]non-6-ene-3,4-dione (6d) (75 mg, 53%), obtained after distillation at 100 °C (bath) and 0.001 mmHg as a yellow oil (Found: C, 81.6; H, 5.5%), $\nu_{\max.}$ (film) 3 060, 2 980, 1 730, 1 700, 1 645, 1 440, 1 110, 900, 835, 770, 750, and 700 cm^{-1} ; $\lambda_{\max.}$ (cyclohexane) 222, 254, 268sh, 275, and 427 nm (ϵ 9 600, 2 000, 1 750, 1 600, and 80); τ ($CDCl_3$) 2.65 (5 H, s, Ph), 3.46br (1 H, q, J 5.2 and 8.6 Hz) and 4.20br (1 H, q, J 7.2 and 8.6 Hz) (ethylenic protons), 4.69 and 4.80 (2 \times 1 H, 2 \times 2, :CH_2), 5.82 (1 H, q, J 1.8 and 7.1 Hz, -CH-CO), and 7.15 (2 H, m, cyclopropane protons); m/e 235 (M^+), 207, 179, 165, 91, 76, and 63. Further elution with ether—light petroleum gave starting material (11 mg) and 2-methyl-7-phenylcyclohepta[b]furan-8-one (5d) (20 mg), both identified by t.l.c. and g.l.c.

3-Bromotropolone Benzyl Ethers.—3-Bromotropolone sodium salt (4 g), anhydrous potassium carbonate (5 g), and benzyl bromide (4.28 cm^3) in dimethylformamide (50 cm^3) were stirred for 36 h at 50—60 °C. After cooling and dilution with water (200 cm^3) isolation with ether gave an oily yellow solid; repeated extractions with hot light petroleum (b.p. 60—80 °C) gave 2-benzyloxy-7-bromotropone (8a) (2.0 g) as needles, m.p. 96—97° (Found: C, 57.7; H, 4.0; Br, 27.7. $C_{14}H_{12}BrO_2$ requires C, 57.8; H, 3.8; Br, 27.5%); $\nu_{\max.}$ (Nujol) 1 612, 1 587, 1 287, 1 247, 986, and 732 cm^{-1} ; $\lambda_{\max.}$ (EtOH) 256, 328, 345, 361, and 371sh nm (ϵ 29 400, 9 600, 7 800, 8 700, and 6 000); τ (C_6D_6) 2.6—3.0 (5 H, m, Ph), 3.7—4.3 (3 H, m, tropone ring), and 5.34 (2 H, s, -OCH_2); m/e 292/290 (M^+), 202/200 [($M - PhCH_2$)⁺], 174, 172, 91, and 65. The combined mother liquors were evaporated, giving an oil (1.93 g) which was taken up in ether and chromatographed on silica. Elution with 1 : 1 ether—light petroleum gave a mixture of benzyl alcohol and the isomeric ether; removal of the former by distillation at 60 °C (bath) and 13 mmHg followed by distillation at 100 °C (bath) and 0.03 mmHg gave 2-benzyloxy-3-bromotropone (9a) as an oil (0.6 g, 11%) which slowly crystallised at 0 °C. Recrystallisation from light petroleum (b.p. 40—60 °C) gave needles, m.p. 43—44° (Found: C, 58.0; H, 4.0%), $\nu_{\max.}$ (film) 3 062, 3 030, 2 953, 1 627, 1 591, 1 461, 1 230, 1 179, 994, and 703 cm^{-1} ; $\lambda_{\max.}$ (EtOH) 253 and 322br nm (ϵ 19 000 and 6 600); τ (C_6D_6) 2.45—2.95 (5 H, m, Ph), 3.10br (1 H, d, J 11.7 Hz), 3.22br (1 H, d, J 12.6 Hz), 3.83br (1 H, q, J 12.5 and 8.3 Hz), and 4.30br (1 H, q, J 11.7 and 8.3 Hz) (tropone ring protons), and 4.61 (2 H, s, -OCH_2); m/e 292/290 (M^+), 211, 202, 200, 186, 184, 174, 172, 105, 91, 77, and 65.

Thermolysis of 3-Bromotropolone Benzyl Ethers.—Samples of each ether (*ca.* 4 mg) in *p*-cymene (0.1 cm^3) were sealed under nitrogen in glass ampoules which were maintained at 176 °C for various times up to 6.5 days. Ampoules were opened periodically, and the contents were dissolved in ethyl acetate and analysed by direct injection of samples on to the column packing of a 1 m \times 4 mm column of 5% QF-1 on silanised Supasorb at 175 °C (nitrogen carrier flow rate 80 cm^3 min^{-1}). Injection of standard mixtures showed that ratios of peak areas gave a poor direct measure of relative concentrations, which were therefore determined by comparison with a peak area ratio/concentration ratio calibration graph (injection of the pure benzyl ethers showed that isomerisation on the column occurred to the extent of less than 5%). From pure (8a), the ratio (8a) : (9a) reached 15 : 1 after 6 h and 5 : 1 after 24 h; from pure (9a), concentration ratios of 1.5 : 1, 3.5 : 1, and 5 : 1, were observed after 8, 18, and 24 h, respectively. Solutions heated for longer times showed no alteration in the final ratio but increasing decomposition of the ethers accompanied by the appearance

of various unidentified new peaks in the g.l.c. trace; no 3-bromotropolone was detected.

The isomerisation of 2-benzyl-3-bromotropone (9a) (40 mg) in *p*-cymene (1 ml) at 176 °C was also carried out preparatively; the product obtained after heating for 24 h gave crystals, m.p. 94–96° (15 mg) identical with 2-benzyl-3-bromotropone (8a).

Radical Trapping Experiments.—Solutions of 2-benzyl-3-bromotropone (9a) (3.5 mg) and 2,6-dimethylphenol (15 mg) in *p*-cymene (0.1 cm³) were sealed under nitrogen in glass ampoules and immersed in a bath maintained at 176 °C. Samples were removed and quenched at 3 h intervals during the first 15 h, and thereafter at 12 h intervals for 4 days. G.l.c. revealed the formation of the equilibrium mixture after 24 h, and the development of several new peaks was accompanied by reduction in the concentration of the ethers during subsequent heating; the major new peak was shown by its retention times on QF-1, silicone gum E30, and Carbowax 20M to be 4-benzyl-2,6-dimethylphenol.

Repetition of the above experiment with 2,6-di-*t*-butylphenol resulted in the observation of only a single major product in addition to the two ethers, shown by comparison of its retention times on three different columns to be 4-benzyl-2,6-di-*t*-butylphenol. From the ether (9a) the cross product was formed to the extent of 6% after 24 h, increasing to ca. 70% after 6 days, the ratio of the ethers remaining approximately constant at 5 : 1 in favour of (8a). Analogous results were obtained by using the phenolic radical traps in thermolyses of the ether (8a) as starting material.

3-Bromotropolone Cyclopropylmethyl Ethers.—A mixture of 3-bromotropolone (2.64 g), anhydrous potassium carbonate (4 g), and bromomethylcyclopropane (3.58 g) in dry dimethylformamide (50 cm³) was stirred at 50–60 °C for 42 h. Addition of water and isolation with ether gave a red oil which was extracted with boiling light petroleum (b.p. 60–80 °C); the concentrated extract slowly deposited a solid which was recrystallised twice from the same solvent to give 2-bromo-7-cyclopropylmethoxytropone (8b) (460 mg) as yellow needles, m.p. 81–82° (Found: C, 51.8; H, 4.3. C₁₁H₁₁BrO₂ requires C, 51.8; H, 4.3%), τ (C₆D₆) 2.27br (1 H, d, *J* 9.4 Hz) and 4.14–3.45 (3 H, m) (ring protons), 6.54 (2 H, d, *J* 6.6 Hz, OCH₂), and 8.94–9.13 (1 H, m) and 9.63–9.85 (4 H, m) (cyclopropane protons). The combined mother liquors were concentrated and chromatographed on alumina; elution with ether–light petroleum (b.p. 40–60 °C) gave a yellow oil shown by t.l.c. to be free of the above compound; distillation at 100 °C (bath) and 0.02

mmHg 3-bromo-2-cyclopropylmethoxytropone (9b) (Found: C, 51.7; H, 4.2%), *m/e* 254 and 256 (*M*⁺), τ (C₆D₆) 2.97br (1 H, d, *J* 11.5 Hz), 3.15br (1 H, d, *J* 12.0 Hz), 3.74br (1 H, q, *J* 12.0 and 8.4 Hz), and 4.22br (1 H, q, *J* 11.5 and 8.4 Hz) (ring protons), 5.81 (2 H, d, *J* 6.8 Hz, OCH₂), 8.73–9.00 (1 H, m, cyclopropane CH), and 9.65–9.83 (4 H, m, cyclopropane CH₂).

After heating either ether in refluxing *p*-cymene for 24 h, g.l.c. analysis showed evidence of interconversion, but also concurrent formation of other unknown products.

Tropolone Trimethylsilyl Ether.—Tropolone (2 g), chloro-(trimethyl)silane (6.3 cm³), and pyridine (4 cm³) in hexane (12 cm³) were stirred for 3 h and then refluxed for 15 h. The solution was filtered in a nitrogen-filled dry box and the residue washed with fresh solvent. Evaporation of the filtrate *in vacuo* and distillation of the residual oil at 50 °C (bath) and 0.03 mmHg gave 2-trimethylsilyloxytropone (2.5 g, 79%) as an oil (Found: C, 61.6; H, 7.6. C₁₀H₁₄O₂Si requires C, 61.8; H, 7.3%), ν_{\max} (film) 3 015 (CH), 2 950, 2 900, 1 620 (C:C), 1 592 (C:O), 1 302, 1 060, 970, 853, 770, and 712 cm⁻¹; n.m.r. data (derived by using the LAOCOON-III program with iterative refinement; chemical shifts in p.p.m. downfield from the OSiMe₃ singlet, in C₆D₆): 6.48 (3-H), 6.13 (4-H), 5.88 (5-H), 6.13 (6-H), and 6.48 (7-H); *J*_{3,4} 11.0, *J*_{3,5} 0.8, *J*_{3,6} 0.4, *J*_{3,7} –0.3; *J*_{4,5} 9.6, *J*_{4,6} 1.1, *J*_{4,7} 0.4, *J*_{5,6} 9.6, *J*_{5,7} 0.8, *J*_{6,7} 11.0 Hz.

3-Bromotropolone Trimethylsilyl Ether.—A solution of chloro-(trimethyl)silane (1.28 cm³) in anhydrous hexane (5 cm³) was added in small portions during ½ h to a stirred solution of 3-bromotropolone (2 g) in pyridine (0.8 cm³) and hexane (12 cm³). The mixture was stirred for 20 h and then refluxed for 6 h, atmospheric moisture being rigorously excluded. Filtration and evaporation *in vacuo* gave 3-bromo-2-trimethylsilyloxytropone [(8c) \rightleftharpoons (9c)] (1.16 g); recrystallisation from *n*-pentane gave pale tan crystals, m.p. 64–66° (Found: C, 44.2; H, 4.6. C₁₀H₁₃BrO₂Si requires C, 44.0; H, 4.8%); ν_{\max} (Nujol) 1 603 (C:C), 1 584 (C:O), 1 303, 1 250, 1 084, 853, and 750 cm⁻¹; τ (C₆D₆) 2.55br (1 H, d, *J* 10.2, 4-H), 3.27br (1 H, d, *J* 10.4 Hz, 7-H), 3.71br (1 H, d × d, *J* 10.4 and 10.0 Hz, 6-H), 4.19br (1 H, d × d, *J* 10.2 and 10.0 Hz, 5-H), and 9.56 (9 H, s, SiMe₃); *m/e* 274/272 (*M*⁺), 259/257 [(*M* – CH₃)⁺], and 73. The compound was hydrolysed rapidly in moist air. The 60 MHz n.m.r. spectrum of the trimethylsilyl ether in [²H₅]toluene showed no significant changes at temperatures down to –95 °C.

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