Claisen Rearrangement of Tropolone Ethers. Part III.[1]

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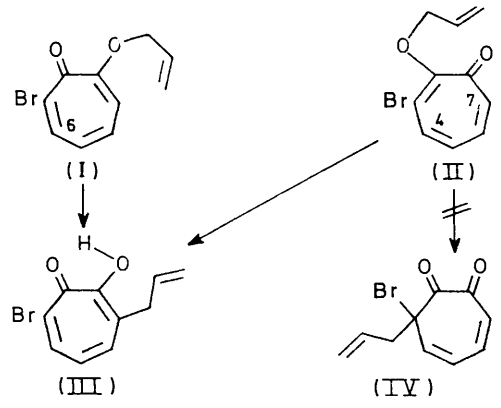
Pairs of allyl and prop-2-ynyl ethers derived from three 3-substituted tropolones have been prepared and structurally distinguished, and their thermal isomerisation products have been identified. Rearrangements of the 7-substituted tropolone ethers generally proceed *via* conventional [3,3] sigmatropic migration, but the 3-substituted isomers afford products resulting from both [3,3] and apparent [3,7] sigmatropic shifts, the proportion of each depending on the nature of the substituent. Kinetic evidence suggesting the operation of a direct [3,7] sigmatropic transfer has been obtained in the case of 3-bromo-2-(prop-2-ynyloxy)tropone.

In an early study of the Claisen rearrangement of tropolone allyl ethers it was reported that both ethers (I) and (II) of 3-bromotropolone rearranged thermally to 3-allyl-7-bromotropolone (III).[2] However, no evidence was provided enabling the ethers to be distinguished, and since one was obtained only as an oil, with no indication as to its purity or homogeneity, the conversion of (II) into (III), rather than into the expected[3] dienedione (IV) or the 5-allyl derivative, seemed to require confirmation; we report here work on this and related rearrangements.

The ethers (I) and (II) were obtained by reaction of silver tropolonate with allyl bromide in acetonitrile, and were separated by crystallisation and column chromatography. As reported,[2] one isomer was an oil, though now demonstrably free from its crystalline congener (spectroscopic and t.l.c. examination). Previously observed[4] differences between the u.v. spectra of 2- and 3-halogenotropones were also evident in the spectra of the two bromo-ethers; maxima at 360 and 374 nm, present only in the spectrum of the crystalline isomer,

[1] Part II, R. M. Harrison and J. D. Hobson, preceding paper.
[2] E. Sebe and S. Matsumoto, *Proc. Japan Acad.*, 1953, **29**, 207.
[3] M. M. Al Holly, R. M. Harrison, and J. D. Hobson, *J. Chem. Soc.* (*C*), 1971, 3084.
[4] J. R. Malpass, Ph.D. Thesis, University of Birmingham, 1967.

showed it to be a 2-bromotropone, *i.e.* (I). This assignment concurred with the n.m.r. data, in particular the presence of a low-field doublet (J 8·7 Hz) centred at τ 1·96 (CCl_4) or 2·44 (C_6D_6) characterising the strongly deshielded 6-proton. On the other hand, the signal appearing at lowest field in the spectrum of the oily isomer was also a doublet centred at τ 2·60 (CCl_4) or 3·11 (C_6D_6) but with the larger splitting (J 12·0 Hz) characteristic of vicinal coupling across a double bond, and therefore attributable to the 4- or 7-proton of (II).[5]



Rearrangement of (I) in refluxing n-nonane (150°) was complete in 4 h giving the normal Claisen product (III) in over 80% yield; this product was thermally stable, being totally recovered after further prolonged refluxing in *p*-cymene. In agreement with the earlier work [2] similar treatment of the isomeric ether (II) also gave (III), though in substantially lower yield (36%) and accompanied by some tar; no trace of the cycloheptadienedione (IV) was detected.

Substantially the same behaviour was displayed by the corresponding prop-2-ynyl ethers (Va) and (VIa), which were obtained by reaction of 3-bromotropolone with prop-2-ynyl bromide in dimethylformamide in the presence of potassium carbonate,* and again readily distinguished structurally on the basis of u.v. and n.m.r. data. In n-nonane at 150° rearrangement of (Va) was relatively slow, and for preparative use refluxing *p*-cymene (176°) was preferred. A single product was obtained in 83% yield having the spectral properties expected for a furotropone (XIa); hydrogenolytic debromination converted it into the known [6] parent compound (XI; R = H) obtained by acid-catalysed cyclisation of 3-acetonyltropolone.

The isomeric ether (VIa) afforded the same furotropone (XIa) in 67% yield under similar conditions. Some tar was formed but no α-diketonic material, *e.g.* (XIIIa), expected to result from (XIIa) *via* intramolecular cycloaddition,[3] was isolated. Exclusive migration towards the unsubstituted '*ortho*' position thus appears to be characteristic of both pairs of allyl and prop-2-ynyl ethers derived from 3-bromotropolone.

In view of the thermal lability of 2-allenylphenol the isomerisation of the intermediate allenyltropolone (VIII) was only to be expected, but the formation of a furo-derivative (XI) is not paralleled in the case of the benzenoid analogue, which cyclises instead to 2*H*-chromen.[7,8] It has been shown [8] that this transformation requires a prior [1,5] sigmatropic shift of a hydrogen atom from the phenolic hydroxy-group to the *sp* carbon atom of the allenyl group, followed by valence isomerisation of the resulting diene. In the present case the analogous sequence (VIII) ⟶ (IX) is disfavoured by the existence of strong intramolecular H-bonding in the tropolone system, and the tautomeric nature of (VIII) provides an alternative electrocyclic pathway leading directly to the furan (XI).

To examine the influence of the 3-substituent on the course of these rearrangements, pairs of ethers derived from two 3-alkyltropolones were prepared and separated. The 3-methyl derivative was obtained in poor yield by reduction of 3-bromo-7-morpholinomethyltropolone (obtained together with some 3,5-disubstituted compound by reaction of 3-bromotropolone with formaldehyde and morpholine) or by amination [9] of 2-methyltropone [10] followed by alkaline hydrolysis. 3-n-Propyltropolone was readily accessible in 67% overall yield from tropolone *via* Claisen rearrangement of tropolone allyl ether followed by catalytic reduction of the resulting 3-allyltropolone.

For experimental convenience, studies on derivatives of these two alkyltropolones were carried out with the more easily separable prop-2-ynyl, rather than the allyl ethers. Clean separations were achieved chromatographically, the more sterically hindered ethers (VI) being produced in only minor amounts (<10%) in each case. Structural assignments were clearly apparent from n.m.r. spectra measured for solutions in C_6D_6; only the less abundant ethers (VIb and c) showed ring proton signals which were clearly resolved, the ones at lowest field in both spectra being doublets (J 12·0 Hz). The magnitude of the splitting indicated vicinal coupling to one proton through a double bond,[5] which can only apply to the 4- or 7-protons in structure (VI). In addition, the methyl signal in the spectrum of (Vb) showed broadening due to allylic coupling; that of its isomer did not.

Isomerisations of the 7-alkyl ethers (Vb and c) proceeded smoothly in refluxing *p*-cymene to give the

* 2-Bromo-7-dimethylaminotropone was obtained as a minor by-product in this reaction, presumably as a consequence of some hydrolysis of the solvent.

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

[6] K. Takase, *Bull. Chem. Soc. Japan*, 1965, **38**, 301.

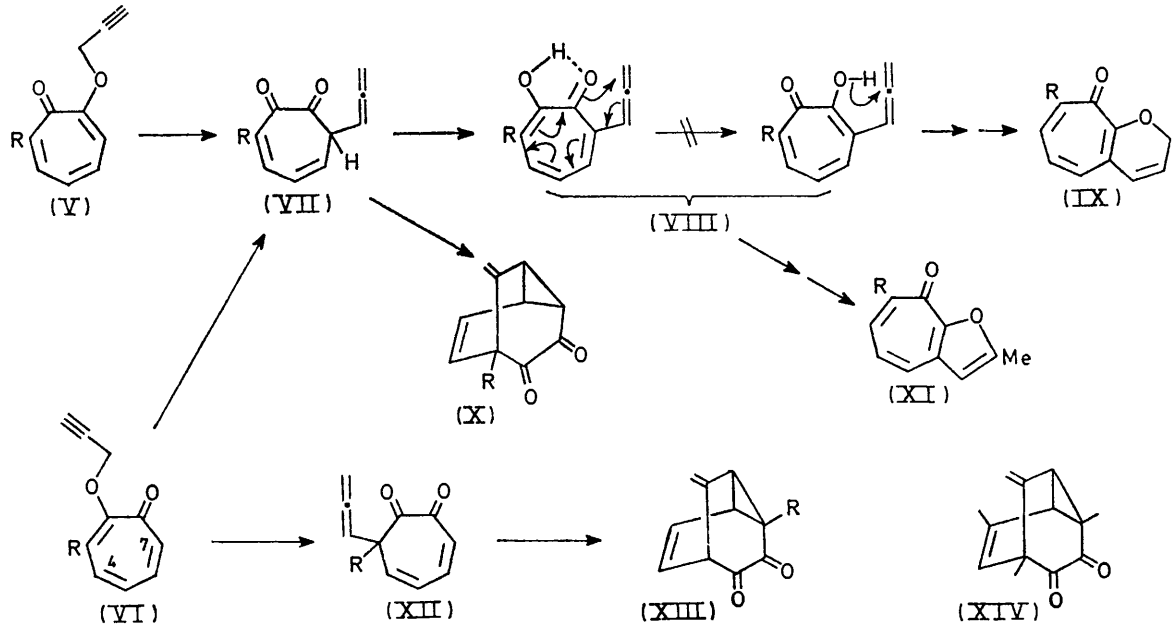
[7] I. Iwai and J. Ide, *Chem. and Pharm. Bull. (Japan)*, 1962, **10**, 926; 1963, **11**, 1042.

[8] J. Zsindely and H. Schmid, *Helv. Chim. Acta*, 1968, **51**, 1510; H. Heimgartner, J. Zsindely, H.-J. Hansen, and H. Schmid, *ibid.*, 1970, **53**, 1212; M. Harfenist and E. Thom, *J. Org. Chem.*, 1972, **37**, 841.

[9] S. Seto, *Sci. Reports Tohoku Univ. (I)*, 1953, **37**, 367; E. Zbiral, J. Jaz, and F. Wessely, *Monatsh.*, 1961, **92**, 1155.

[10] W. T. Brady and J. P. Hieble, *Tetrahedron Letters*, 1970, 3205.

furotropones (XIb and c) in yields of over 80%: the former compound had m.p. and spectral data in good accord with those cited [6] for material obtained by acid-catalysed cyclisation of 3-acetonyl-7-methyltropolone. From the rearrangement of (Vb) traces of an α-diketone (Xb) were also isolated; the amount obtained was insufficient for full characterisation but its light absorption and mass spectra were closely related to those of the hindered ethers (II) and (VIa) of 3-bromotropolone, and to a much smaller extent from the 3-alkyl analogues (VIb and c), could conceivably result from (i) three successive [3,3] sigmatropic shifts, (ii) a direct [3,7] sigmatropic migration involving the bridged transition state (XV), or (iii), prior conversion into the isomeric ether (I) or (V), presumably *via* a suprafacial [1,9] sigmatropic transfer of the allyl or propynyl group



a; R = Br b; R = Me c; R = Pr^n

previously encountered [3] trimethyl analogue (XIV), and also those of the isomeric, but different, compound (XIIIb) obtained from the other ether (VIb). It appears therefore that intramolecular [4 + 2] cycloaddition is competitive with tautomerisation in the allenylcycloheptadienedione (VII) only when an alkyl substituent is present.*

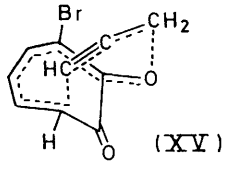
Rearrangements of the less abundant ethers (VIb and c) were also distinguished from that of the bromo-analogue (VIa) in that only traces of the cross-products (XIb and c) were formed, straightforward '*ortho*'-Claisen rearrangement instead leading to the tricyclic α-diketones (XIIIb and c) in over 80% yield. The structures of these products, in particular the location of the alkyl substituent on the cyclopropane ring, were evident from a consideration of their n.m.r. spectra in comparison with that of (XIV). Like the latter,[3] (XIIIb) also underwent acid-catalysed cleavage to a bicyclic enolic α-diketone.

The formation of the cross-products from the sterically

* In n-nonane at 150° tropolone prop-2-ynyl ether itself gave only the furotropone (XI; R = H), base-catalysed hydrolysis of which afforded 3-acetonyltropolone. Both these compounds have been obtained previously by another route, though the u.v. data quoted [6] differ substantially from ours.

between the oxygen atoms, with retention of configuration at the migrating carbon atom.

The first possibility seems remote, especially in reactions involving prop-2-ynyl ethers, in view of the known reluctance of aryl propynyl ethers to undergo a



para-migration,[8] and the possibilities for tautomerisation or intramolecular cycloaddition during such a traverse of the ring. Moreover, in the case of tropolone allyl ethers, a second migration to the 5-position appears to occur only when substantial steric compression is present in the initial '*ortho*'-product.[1]

Pathway (ii) requires a transition state (XV) containing a seven-membered ring, but models reveal no particular prohibition to such a suprafacial migration, which is symmetry-allowed. Circumstantial evidence favouring pathway (iii) has resulted from work in this

laboratory[11] demonstrating the existence of thermal interconversions in other pairs of tropolone ethers (*e.g.* benzyl and cyclopropylmethyl ethers) which occur *via* intramolecular [1,9] sigmatropic migrations. These two mechanisms have identical end results, and since no decision between them based on product analysis appeared to be accessible, attention was turned to kinetic analysis.

Preliminary examination of the thermolyses of the prop-2-ynyl ethers (Va) and (VIa) in *p*-cymene at 176°, using the sealed ampoule technique and g.l.c. to monitor disappearance of the substrate, gave acceptably linear first-order plots from which approximate rate constants of $11{\cdot}1 \times 10^{-2}$ and $8{\cdot}1 \times 10^{-2}$ min^{-1}, respectively, were derived. If it is assumed that mechanism (iii) only is involved, *i.e.* that (VIa) is isomerised to products *via* (Va) in two consecutive rate-controlling steps governed by these rate constants, it can be calculated[12] that the concentration of (Va) should reach a maximum of 30% of the initial concentration of (VIa) after about 10 min.* Careful examination of the reaction mixtures obtained by heating pure (VIa) for this time did not reveal the presence of (Va) in significant quantities, and we therefore tentatively conclude that a substantial proportion of the eventual product (XIa) must be formed from the ether (VIa) *via* a direct [3,7] sigmatropic shift (XV), and not by way of the isomeric ether (Va).

EXPERIMENTAL

Unless otherwise specified u.v. spectra of solutions in cyclohexane were obtained using a Unicam SP 800 spectrophotometer, and i.r. spectra were recorded with Unicam SP 200G and Perkin-Elmer 257 instruments. A Perkin-Elmer R14 spectrometer was used to obtain 100 MHz n.m.r. spectra of solutions in deuteriochloroform with tetramethylsilane as internal reference. Mass spectra were recorded on an A.E.I. MS-9 instrument (direct insertion; ionising energy 70 eV). Analytical and preparative g.l.c. was carried out on Pye 104 and 105 instruments, both equipped with flame ionisation detector. Column packings used were Phase Separations Ltd. fluorosilicone oil FS1265 (QF-1), Carbowax 20M, and silicone gum E301, all supported on B.D.H. silanised Supasorb.

2-(*Prop*-2-*ynyloxy*)*tropone*.—A suspension of anhydrous sodium tropolonate (0·90 g) in dimethylformamide (8 ml) containing prop-2-ynyl bromide (0·70 ml) was stirred at 50° for 36 h. More bromide (0·2 ml) was added after 24 h. The mixture was diluted with water and acidified to pH 5 with N-hydrochloric acid, and the product was isolated by continuous extraction with ether. Evaporation of the solvents *in vacuo* gave 2-(*prop*-2-*ynyloxy*)*tropone* (0·87 g, 87%), crystallising from light petroleum (b.p. 60—80°) as needles, m.p. 87—88° (Found: C, 74·7; H, 5·3. $C_{10}H_8O_2$ requires C, 75·0; H, 5·0%), $\lambda_{max.}$ (EtOH) 237, 319, and 343sh nm (ε 23,800, 8500, and 6700), $\nu_{max.}$ (hexachlorobutadiene) 3252 (:CH), 2962, and 2120 cm^{-1} (C:C); $\nu_{max.}$ (Nujol) 1620 (C:C), 1591, 1561 (C:O), 1175 (C·O·C), 1085, and 775 cm^{-1}; τ (C_6D_6) 2·97 (1H, d, *J* 12·5 Hz, 7-H), 3·4—3·9 (4H, m, ring protons), 5·50 (2H, d, *J* 2·5 Hz, O·CH_2), and 7·94 (1H, t, *J* 2·5 Hz, :CH); *m/e* 160 (M^+), 132, 131, 106, 105, 78, and 51.

Treatment of the ether with ethereal picric acid afforded a *hemipicrate*, obtained from ethyl acetate–light petroleum (b.p. 60—80°) as yellow needles, m.p. 68—70° (Found: C, 57·2; H, 4·0; N, 7·3. $C_{26}H_{19}N_3O_{11}$ requires C, 56·8; H, 3·5; N, 7·65%).

Allyl 3-*Bromotropolone Ethers*.—A 20% solution of silver nitrate (10 ml) was added to a cold stirred solution of 3-bromotropolone sodium salt (2·5 g); the precipitated silver salt was collected, washed with water, and dried *in vacuo*. The dry salt (3·1 g) and allyl bromide (2·4 g) in acetonitrile (10 ml) were refluxed for 16 h; the cooled mixture was filtered and the residue was washed with more hot solvent. Evaporation of the filtrate gave an oil which was extracted three times with boiling n-pentane (15 ml); the residue was recrystallised from light petroleum (b.p. 40—60°) giving 2-allyloxy-7-bromotropone (I) (0·51 g) as yellow needles, m.p. 77—78° (lit.,[2] 69·5—70°), $\lambda_{max.}$ 256, 328, 360, and 374sh nm (ε 27,000, 8300, 7800, and 5900), $\nu_{max.}$ (CCl_4) 3095, 3030, 2920, 2875, 1625, 1275, 1188, and 935 cm^{-1}; τ (C_6D_6) 2·44br (1H, d, *J* 8·7 Hz, 6-H), 3·6—4·1 (3H, m, other ring protons), 4·1—4·5 (1H, m, ·C*H*:CH_2), 4·78 and 5·00 (2 × 1H, dd, *J* 10·2 and 16·5 Hz, ·CH:CH_2), and 5·95br (2H, d, *J* 4·9 Hz, ·OCH_2·); *m/e* 242 and 240 (M^+), 213 and 211 [$(M - CHO)^+$], 212 and 210, 161 [$(M - Br)^+$], 105, and 41.

The combined n-pentane and petroleum mother liquors were concentrated to *ca.* 30 ml and shaken with saturated aqueous copper(II) acetate. After filtration, the organic layer was dried and evaporated, and the residual oil was chromatographed on silica. Elution with 2 : 1 ether–light petroleum afforded the isomeric ether (II) (0·48 g), obtained after distillation at 70—90° (bath) and 0·05 mmHg as a pale yellow oil, m.p. 0—3° (Found: C, 49·5; H, 3·6. Calc. for $C_{10}H_9BrO_2$: C, 49·8; H, 3·8%), $\lambda_{max.}$ 253·5 and 326 cm (ε 19,000 and 6700), $\nu_{max.}$ (film) 3085, 3015, 2985, 2925, 1625, 1590, 1228, 1184, 991, 937, and 805 cm^{-1}; τ (C_6D_6) 3·11br (1H, d, *J* 12·0 Hz, 4-H), 3·30br (1H, d, *J* 11·9 Hz, 7-H), 3·87 (1H, q, *J* 11·9 and 8·4 Hz, ring proton), 4·2 (1H, m, ·C*H*:CH_2), 4·35br (1H, q, *J* 12·0 and 8·4 Hz, ring proton), 4·77 and 5·01 (2H, dd, *J* 10·4 and 17·4 Hz, ·CH:CH_2), and 5·21br (2H, d, *J* 5·9 Hz, O·CH_2); *m/e* 242 and 240 (M^+), 212 and 210, 186 and 184, 161, 105, and 41.

The freshly prepared allylation mixture, freed from starting material with copper(II) acetate solution, was shown to contain approximately equal amounts of the ethers by either u.v. or n.m.r. analysis.

3-*Bromotropolone Prop*-2-*ynyl Ethers*.—3-Bromotropolone sodium salt (dried over P_2O_5 *in vacuo* for 2 days) (4·05 g), anhydrous potassium carbonate (5 g), and prop-2-ynyl bromide (2·0 ml) in dimethylformamide (50 ml) were stirred at 50—60° for 36 h. The cooled mixture was poured into water (250 ml) and ether (30 ml) and the crystals (0·84 g) which separated were collected and washed with ether. Recrystallisation from ethyl acetate–light petroleum (b.p. 60—80°) and sublimation at 95—105° and

* Since the yields of product (XIa) from either of the two ethers were less than quantitative, other processes may proceed concurrently, and this ratio must be regarded as an upper limit.

[11] R. M. Harrison, A. W. Midgley, and J. D. Hobson, unpublished work.

[12] A. A. Frost and R. G. Pearson, ' Kinetics and Mechanism,' Wiley, New York, 1961, p. 66.

0·05 mmHg gave 2-*bromo*-7-(*prop*-2-*ynyloxy*)*tropone* (Va), m.p. 152—153° (Found: C, 50·5; H, 3·1. $C_{10}H_7BrO_2$ requires C, 50·2; H, 3·0%), $\lambda_{max.}$ (EtOH) 255·5, 327, 358, and 372sh nm (ε 26,000, 8400, 7600, and 5200); $\nu_{max.}$ (Nujol) 1607, 1585, 1277, 1240, 1198, 968, and 759 cm^{-1}; τ ($CDCl_3$) 1·75br (1H, d, *J* 9·3 Hz, 6-H), 2·7—3·3 (3H, m, other ring protons), 5·04 (2H, d, *J* 2·4 Hz, ·O·CH_2·), and 7·43 (1H, t, 2·4 Hz, :CH); *m/e* 240 and 238 (M^+), 186 and 184, 145, 105, 77, 63, and 51.

The combined ether extracts and washings were evaporated giving an oily solid from which a further crop (0·6 g) of the ether (Va) was isolat ' by crystallisation from ethyl acetate–light petroleum.] :tional crystallisation of the residue obtained from the mother liquors from light petroleum (b.p. 60—80°) gave 3-*bromo*-2-(*prop*-2-*ynyloxy*)-*tropone* (VIa) (0·52 g, 12%), m.p. 100—101° (Found: C, 50·4; H, 3·1%), $\lambda_{max.}$ (EtOH) 253 and 324br nm (ε 20,200 and 6300); $\nu_{max.}$ (Nujol) 1625, 1573, 1237, 1182, 1003, 804, and 788 cm^{-1}; τ (C_6D_6) 3·07 (1H, d, *J* 11·9 Hz, 4-H), 3·22 (1H, d, *J* 12·0 Hz, 7-H), 3·81br (1H, q, *J* 8·4 and 12·0 Hz, 6-H), 4·28br (1H, q, *J* 8·4 and 11·9 Hz, 5-H), 4·94 (2H, d, *J* 2·4 Hz ·OCH_2·), and 7·99 (1H, t, *J* 2·4 Hz, :C*H*); *m/e* 240 and 238 (M^+), 211 and 209 [$(M - CHO)^+$], 186 and 184, 159 [$(M - Br)^+$], 145, 143, 105, 77, 64, and 63.

Continuous extraction of the aqueous mother liquors with ether gave an intensely yellow solution from which 2-*bromo*-7-*dimethylaminotropone* (0·13 g) was isolated, giving, after crystallisation from light petroleum (b.p. 40—60°) and sublimation at 80° and 0·05 mmHg, yellow needles, m.p. 95—96° (Found: C, 47·6; H, 4·4; Br, 35·3; N, 6·5. $C_{19}H_{10}BrNO$ requires C, 47·4; H, 4·4; Br, 35·0; N, 6·1%), $\lambda_{max.}$ (EtOH) 266, 359, and 437 nm (ε 15,300, 11,300, and 8800); $\nu_{max.}$ (Nujol) 1584, 1551, 1318, 1248, 1050, 906, 837, and 751 cm^{-1}; τ (C_6D_6) 2·31br (1H, d, *J* 9·6 Hz, 3-H), 3·46br (1H, q, *J* 9·7 and 11·7 Hz, 5-H), 4·2 (2H, m, ring protons), and 7·55 (6H, s, NMe_2); *m/e* 229 and 227 (M^+), 214 and 212, 186 and 184, 105, 77, 60, and 44.

3-*Methyltropolone*.—A solution of 3-bromotropolone (2·01 g) and morpholine (2·7 g) in methanol (10 ml) was treated with 40% aqueous formaldehyde (1·65 ml), and after stirring at 40° for 40 h the yellow precipitate (0·85 g) was collected, washed with methanol, and dried. Pure 3-*bromo*-7-*morpholinomethyltropolone* was obtained from dimethyl formamide as yellow crystals, m.p. 181—182° (decomp.) (Found: C, 48·2; H, 4·7; Br, 26·4; N, 4·9. $C_{12}H_{14}BrNO_3$ requires C, 48·0; H, 4·7; Br, 26·4; N, 4·7%), $\lambda_{max.}$ (EtOH) 257, 335br, 383, and 419 nm (ε 18,700, 3900, 3300, and 3100); $\nu_{max.}$ (Nujol) 2620 ($>\overset{+}{N}H$), 1588, 1528, 1075, 960, 860, and 765 cm^{-1}; τ [$(CD_3)_2SO$] 2·00 (1H, d, *J* 10 Hz), 2·30 (1H, d, *J* 10 Hz), and 3·30 (1H, t, *J* 10 Hz) (three ring protons), and 6·2—7·6 (10H, m, morpholinomethyl); *m/e* 301 and 299 (M^+), 243 and 241, 187 and 185, 105, 86, 77, and 51.

After removal of the monosubstituted product, evaporation of the methanolic mother liquors followed by trituration with ether and crystallisation from dimethylformamide gave crystals (1·2 g, 30%) of 3-bromo-5,7-bismorpholinomethyltropolone, m.p. 161—162° (decomp.) (lit.,[13] 157—158°); $\nu_{max.}$ (Nujol) 1600, 1532, 1114, 910, 864, 802 and 790 cm^{-1}; *m/e* 401 and 399 (M^+), 315 and 313, 230 and 228, and 86.

[13] E. Hartwig, *Angew. Chem.*, 1954, **66**, 605.
[14] T. Nozoe, T. Mukai, M. Kumori, T. Muroi, and K. Matsui, *Sci. Reports Tohoku Univ.* (*I*), 1952, **35**, 242.

To a solution of 3-bromo-7-morpholinomethyltropolone (0·5 g) in glacial acetic acid (10 ml) stirred at 65—70° was added zinc dust (0·5 g) in small portions during 5 min. Stirring was continued for 10 min, the excess of zinc was filtered off and the filtrate was diluted with water. Isolation with ether and crystallisation of the residue from isopentane at 0°, followed by sublimation at 50—70° and 10 mmHg, gave 3-methyltropolone, m.p. 47—49° (lit.,[9] 46—47°; lit.,[14] 50—51°), $\lambda_{max.}$ 236, 321, 355, and 370 nm (ε 23,100, 5600, 4900, and 4700).

3-*n*-*Propyltropolone*.—Tropolone (2·0 g), allyl bromide (2·1 ml), and anhydrous potassium carbonate (3 g) in dimethylformamide (20 ml) were stirred at 50—60° for 36 h. Dilution with water and continuous extraction with ether afforded 2-*allyloxytropone* (1·96 g, 74%) as an oil, b.p. 80° (bath) at 0·1 mmHg, $\lambda_{max.}$ (EtOH) 238, 320, and 347 nm (ε 23,500, 8800, and 7200) (Found: C, 73·7; H, 6·5. $C_{10}H_{10}O_2$ requires C, 74·1; H, 6·5%); *m/e* 162 (M^+), 133, 106, 105, 65, and 51. Treatment of this compound with ethereal picric acid afforded a *hemipicrate*, m.p. 85—86° (Found: C, 56·2; H, 4·3; N, 7·5. $C_{26}H_{23}N_3O_{11}$ requires C, 56·4; H, 4·2; N, 7·6%).

After 4 h in refluxing n-nonane under nitrogen the allyl ether was converted into 3-allyltropolone (91%), giving pale yellow plates, m.p. 44—45° (from n-pentane at −20°) (Found: C, 73·7; H, 6·4%); τ (C_6D_6) 0·3br (1H, s, OH), 2·9—3·8 (4H, m, ring protons), 3·8—5·1 (3H, m, vinyl), and 6·51 (2H, d, *J* 7 Hz, O·CH_2·); *m/e* 162 (M^+), 147, 115, 105, 91, 77, and 51.

Hydrogenation of 3-allyltropolone over 10% palladium–charcoal gave 3-n-propyltropolone in quantitative yield.

3-*Methyltropolone Prop*-2-*ynyl Ethers*.—A solution of 3-methyltropolone (1·05 g) in ethanol (10 ml) was neutralised by addition of aqueous N-sodium hydroxide (1 equiv.). Evaporation to dryness *in vacuo* followed by azeotropic distillation of benzene (80 ml) from the residue gave the dry sodium salt, which was stirred with anhydrous potassium carbonate (3 g) and prop-2-ynyl bromide (1·0 ml) in dimethylformamide (10 ml) for 24 h. Dilution with water (40 ml) and isolation with ether gave a crude oily product (0·71 g), shown by t.l.c. to contain two components. Extraction with boiling light petroleum (b.p. 40—60°), concentration, and cooling to −10° resulted in the separation of 2-*methyl*-7-(*prop*-2-*ynyloxy*)*tropone* (Vb) (0·46 g, 42%), m.p. 76—77° (Found: C, 75·9; H, 6·0. $C_{11}H_{10}O_2$ requires C, 75·8; H, 5·8%), $\lambda_{max.}$ 237, 320, and 342sh nm (ε 28,400, 8400, and 7400); $\nu_{max.}$ (Nujol) 1598, 1577, 1280, 1212, 1032, and 753 cm^{-1}; τ (C_6D_6) 3·1—3·8 (4H, m, ring protons), 5·42 (2H, d, *J* 2·4 Hz, ·O·CH_2·), 7·7br (3H, s, Me), and 7·93 (1H, t, *J* 2·4 Hz); *m/e* 174 (M^+), 146 [$(M - CO)^+$], 145 [$(M - CHO)^+$], 120, 119, 91, 77, and 65.

Evaporation of the mother liquors from the isolation of the isomer (Vb) gave an oil which was chromatographed on silica (15 g). Elution with 1 : 1 ether–light petroleum (b.p. 40—60°) gave 3-*methyl*-2-(*prop*-2-*ynyloxy*)*tropone* (VIb) (65 mg, 6%), obtained after sublimation at 90° (bath) and 0·02 mmHg as pale yellow crystals, m.p. 79—80° (Found: C, 75·6; H, 6·0%), $\lambda_{max.}$ 241 and 322 nm (ε 21,000 and 6900); $\nu_{max.}$ (Nujol) 3190, 2122, 1631, 1577, 1190, 1145, 1010, and 798 cm^{-1}; τ 3·03br (1H, d, *J* 12·0 Hz, 7-H), 3·5—4·1 (3H, m, ring protons), 4·95 (2H, d, *J* 2·3 Hz, O·CH_2), 7·90 (3H, s, Me), 8·03 (1H, t, *J* 2·3 Hz, :CH); *m/e* 174 (M^+), 136, 135, 120, 91, 77, and 39.

3-*n*-*Propyltropolone Prop*-2-*ynyl Ethers*.—Preparation and separation of these ethers was accomplished as already

described. From 3-n-propyltropolone (1·07 g) was obtained *2-propyl-7-(prop-2-ynyloxy)tropone* (Vc) (0·68 g, 58%), crystallising from light petroleum (b.p. 40—60°), m.p. 53° (Found: C, 76·9; H, 7·0. $C_{13}H_{14}O_2$ requires C, 77·2; H, 7·0%); $\lambda_{max.}$ (EtOH) 238 and 322 nm (ε 30,380 and 9050); $\nu_{max.}$ (Nujol) 1590, 1568, 1273, 1255, 1202, 1025, and 751 cm^{-1}; τ (C_6D_6) 3·14—3·75 (4H, m, ring protons), 5·42 (2H, d, *J* 2·4 Hz, O·CH_2), 6·31 (2H, t, *J* 7·2 Hz, ·CH_2·CH_2·CH_3), 7·87 (1H, t, *J* 2·4 Hz, :CH), 8·15—8·51 (2H, m, ·CH_2·CH_2·CH_3), and 9·04 (3H, t, *J* 7·3 Hz, ·CH_2·CH_2·CH_3); *m/e* 202 (M^+), 174, 173, 163, 148, 147, 91, 77, and 73; together with the isomer, *3-propyl-2-(prop-2-ynyloxy)tropone* (VIc) (98 mg, 9%), obtained as a yellow oil, b.p. 100° (bath) at 0·08 mmHg (Found: C, 77·6; H, 7·1%); $\lambda_{max.}$ (EtOH) 243 and 321 nm (ε 23,400 and 7260); $\nu_{max.}$ (film) 3293 (:CH), 3240, 2958, 2120 (C:C), 1628 (C:C), 1575 (CO), 1177, 1138, 1020, and 805 cm^{-1}; τ (C_6D_6) 3·02br (1H, d, *J* 11·6 Hz, ring proton), 3·50—4·01 (3H, m, ring protons), 4·88 (2 H,d, *J* 2·4 Hz, O·CH_2), 7·46 (2H, t, *J* 7·5 Hz, CH_2·CH_2·CH_3), 8·01 (1H, t, *J* 2·4 Hz, :CH), 8·30—8·67 (2H, m, CH_2·CH_2·CH_3), and 9·11 (3H, t, *J* 7·3 Hz, ·CH_2·CH_2·CH_3); *m/e* 202 (M^+), 174, 173, 164, 163, 149, 133, 131, 120, 91, 85, 83, and 77.

Claisen Rearrangements.—(a) *Of 2-(prop-2-ynyloxy)tropone.* A solution of the ether (0·20 g) in n-nonane (35 ml) was refluxed under nitrogen for 8 h. Recrystallisation of the product from light petroleum (b.p. 60—80°) at −20° gave 2-methylcyclohepta[*b*]furan-8-one (XI; R = H) (0·15 g) as needles, m.p. 58—59° (lit.,[6] 49—50·5°) (Found: C, 74·7; H, 5·2. Calc. for $C_{10}H_8O_2$: C, 75·0; H, 5·0%), $\lambda_{max.}$ (EtOH) 264, 270·5, 300, 338, and 350sh nm (ε 26,800, 27,200, 7200, 3800, and 2500) [lit.,[6] 251, 300, and 335 nm (30,200, 7900, and 4200)]; $\nu_{max.}$ (Nujol) 1625, 1582, 1545, 1248, 1161, 945, and 822 cm^{-1}; τ (C_6D_6) 2·79br (1H, d, *J* 12·5 Hz, ring proton), 3·2—3·8 (3H, m, ring protons), 4·21 (1H, d, *J* 1 Hz, furan ring proton), and 8·12 (3H, d, *J* 1 Hz, Me); *m/e* 160 (M^+), 132, 131, 105, 77, and 43. The compound was deliquescent, and wet samples exhibited a substantially different i.r. spectrum.

A suspension of the furotropone (120 mg) in 2N-sodium hydroxide (10 ml) was stirred under nitrogen at 80—90° for 4·5 h. The cooled and acidified solution was extracted with ether, and the product (110 mg, 82%) crystallised from light petroleum (b.p. 40—60°) giving 3-acetonyltropolone as needles, m.p. 92·5—93·5° (lit.,[6] 86—87°) (Found: C, 67·7; H, 5·5. Calc. for $C_{10}H_{10}O_3$: C, 67·4; H, 5·7%), $\lambda_{max.}$ (EtOH) 242, 322, 355, and 367sh nm (ε 24,000, 7400, 6700, and 6200); $\nu_{max.}$ (Nujol) 3197, 1710, 1630, 1600, 1548, 1429, 1234, 1010, 789, and 752 cm^{-1}; τ ($CDCl_3$) 1·7br (1H, s, OH), 2·9—3·8 (4H, m, ring protons), 6·54 (2H, s, CH_2·CO), and 8·09 (3H, s, Me); *m/e* 178 (M^+), 136, 108, 77, and 43.

(b) *Of 3-bromotropolone allyl ethers.* Solutions of the ether in n-nonane (20 ml) were refluxed for 4 h under nitrogen. The cooled solution was diluted with ether and shaken with N-sodium hydroxide, and the alkaline layer was separated and washed with ether. Acidification and isolation with ether afforded 3-allyl-7-bromotropolone (III), crystallising from n-pentane at −20° as plates, m.p. 55—56° (lit.,[2] 55—55·5°), $\lambda_{max.}$ (EtOH) 260, 328, and 374 nm (ε 35,800, 6700, and 6400); $\nu_{max.}$ (CCl_4) 3390, 3090, 2990, 2930, and 1640 cm^{-1}; τ ($CDCl_3$) 2·00 (1H, d, *J* 10·5 Hz), 2·56 (1H, d, *J* 10·3 Hz), and 3·21 (1H, t, *J* 10·4 Hz) (ring protons), 3·8—4·2 (1H, m, ·CH:CH_2), 4·7—5·0 (2H, m, ·CH:CH_2), and 6·40 (2H, d, *J* 7 Hz, CH_2·CH:CH_2).

From 2-allyloxy-7-bromotropone (I) (90 mg) and 2-allyloxy-3-bromotropone (II) (61 mg) the yields of product (III) were 73 (81%) and 22 mg (36%), respectively.

After refluxing for 4 h in *p*-cymene 3-allyl-7-bromotropolone was almost completely recovered, and no conversion into any other product was detected by t.l.c.

(c) *Of 3-bromotropolone prop-2-ynyl ethers.* Solutions of either ether in *p*-cymene (35 ml) were refluxed for 2 h under nitrogen. The solvent was removed *in vacuo* and the residue crystallised from light petroleum (b.p. 60—80°) giving *7-bromo-2-methylcyclohepta*[b]*furan-8-one* (XIa), m.p. 125—126° (Found: C, 50·2; H, 3·05; Br, 33·7. $C_{10}H_7BrO_2$ requires C, 50·2; H, 3·0; Br, 33·4%), $\lambda_{max.}$ (EtOH) 237·5, 244, 275, 306sh, 321, 332sh, 349, and 366 nm (ε 11,600, 11,300, 32,800, 6200, 5500, 4000, 4100, and 3100); $\nu_{max.}$ (Nujol) 1626, 1588, 1248, 1160, 962, and 830 cm^{-1}; τ ($CDCl_3$) 2·34br (1H, d, *J* 9·4 Hz), 3·39br (1H, d, *J* 10·7 Hz), 4·06br (1H, q, *J* 9·4 and 10·7 Hz), 4·32 (1H, d, *J* 1 Hz), and 8·17 (3H, d, *J* 1 Hz); *m/e* 240 and 238 (M^+), 212 and 210, 211 and 209, 159, 131, 103, 77, and 51.

From 7-bromo-2-(prop-2-ynyloxy)tropone (Va) (300 mg) and 3-bromo-2-(prop-2-ynyloxy)tropone (VIa) (150 mg) were obtained 250 (83%) and 100 mg (67%), respectively, of the furotropone (XIa). No other thermolysis product was detected in either reaction.

Hydrogenation of this bromo-compound (20 mg) in ethanol (10 ml) over 10% palladium–charcoal gave 2-methylcyclohepta[*b*]furan-8-one (XI; R = H), identical with material prepared as described previously.

(d) *Of 3-methyltropolone prop-2-ynyl ethers.* Solutions (*ca.* 1%) of the ethers in *p*-cymene were refluxed under nitrogen for 2 h; the solvent was removed *in vacuo*, and the residue was chromatographed on silica (10 g per 100 mg product).

Elution of the products from 7-methyl-2-(prop-2-ynyloxy)tropone (Vb) with 35% ether in light petroleum (b.p. 40—60°) afforded *5-methyl-9-methylenetricyclo*[3.3.1.$0^{2,8}$]*non-6-ene-3,4-dione* (Xb) (8 mg, 4%), obtained from n-pentane as yellow crystals, m.p. 86—87°, $\lambda_{max.}$ 260sh and 427 nm (ε 870 and 90); $\nu_{max.}$ (film) 3025, 2925, 1730, 1710, 1640, 1239, 1005, 905, 831, and 752 cm^{-1}; *m/e* 174 (M^+), 146, 131, 118, 117, 105, 103, 91, 77, and 51; *m** 95·3 (146 ⟶ 118).

Ether–light petroleum (3 : 1) eluted 2,7-dimethylcyclohepta[*b*]furan-8-one (XIb) (172 mg, 82%), obtained by crystallisation from light petroleum (b.p. 60—80°) and sublimation at 70° and 0·02 mmHg as yellow crystals, m.p. 62—63° (lit.,[6] 62—64°) (Found: C, 75·5; H, 6·05. Calc. for $C_{11}H_{10}O_2$: C, 75·8; H, 5·8%), $\lambda_{max.}$ (EtOH) 223, 264, 270, 300sh, 324, 337, and 352 nm (ε 15,400, 30,800, 30,600, 6300, 4900, 4800, and 3500); $\nu_{max.}$ (Nujol) 3090, 1627, 1573, 1549, 1248, 1142, 962, 798, and 680 cm^{-1}; τ (C_6D_6) 3·13 and 3·27 (2H, 2 × d, *J* 9·0 and 10·8 Hz, respectively, 6- and 4-H), 3·68br (1H, q, *J* 9·0 and 10·8 Hz, 5-H), 4·21 (1H, d, *J* 1 Hz, 3-H), 7·61 br (3H, s, 7-Me), and 8·09 (3H, d, *J* 1 Hz, 2-Me); *m/e* 174 (M^+), 146, 145, 131, 91, and 77.

From the isomeric ether (VIb) (36 mg) similarly were obtained *2-methyl-9-methylenetricyclo*[3.3.1.$0^{2,8}$]*non-6-ene-3,4-dione* (XIIIb) (29 mg, 81%) as an oil, b.p. 50° (bath) at 0·02 mmHg (Found: C, 76·0; H, 6·1%), $\lambda_{max.}$ 268, 275sh, and 429 nm (ε 780, 750, and 70); $\nu_{max.}$ (film) 3050, 2970, 2932, 1738, 1709, 1651, 1455, 891, 832, and 770 cm^{-1}; τ (C_6D_6) 4·29br (1H, q, *J* 8·9 and 5·5 Hz) and 4·86br (1H, q, *J* 8·9 and 7·2 Hz) (olefinic protons), 5·28 and 5·34 (2H, 2 × s, :CH_2), 6·27 [1H, q, *J* 7·1 and 2·2 Hz (long-range coupling to cyclopropane proton), >C*H*·C:O], 8·29 (1H, q,

J 7·3 and 2·2) and 8·53 (1H, q, *J* 7·3 and 5·3) (cyclopropane protons), and 9·01 (3H, s, Me); *m/e* 174 (M^+), 146, 118, 117, 103, 91, 77, 65, and 51; *m** 95·3 (146 ⟶ 118).

Ether–light petroleum (3 : 7) eluted a solid (1 mg) shown by spectroscopic and g.l.c. examination to be starting material; continued elution with ether–light petroleum (3 : 1) gave an oily solid (2 mg) shown by g.l.c., t.l.c., and u.v. and i.r. spectroscopy to be mainly 2,7-dimethylcyclohepta[*b*]furan-8-one (XIb).

A solution of the α-diketone (XIIIb) (5 mg) in glacial acetic acid (0·5 ml) containing sulphuric acid (0·1 ml) was kept for 16 h; the mixture was diluted with water and the product, isolated with ether, was recrystallised from light petroleum (b.p. 40—60°) giving crystals (2 mg), m.p. 96—97°, which gave a dark green colouration with ethanolic iron(III) chloride.

(e) *Of 3-propyltropolone prop-2-ynyl ethers.* Rearrangements in *p*-cymene were carried out as already described.

From 7-propyl-2-(prop-2-ynyloxy)tropone (Vc) was obtained 2-*methyl*-7-*propylcyclohepta*[b]*furan*-8-*one* (XIc) as yellow crystals (from light petroleum) (290 mg, 90%), m.p. 119—120° after sublimation at 100° and 0·05 mmHg (Found: C, 77·6; H, 6·7. $C_{13}H_{14}O_2$ requires C, 77·2; H, 7·0%), $\lambda_{max.}$ (EtOH) 226, 266, 271, 339, and 354 (ε 13,450, 29,250, 29,150, 4345, and 2990); $\nu_{max.}$ (Nujol) 3100, 1625, 1573, 1547, 1250, 1180, 1150, 970, 847, and 685 cm^{-1}; τ (C_6D_6) 3·03br (1H, d, *J* 8·9 Hz) and 3·22br (1H, d, *J* 10·2 Hz) (6- and 4-H, respectively), 3·55br (1H, q, *J* 8·9 and 10·2 Hz, 5-H), 4·16 (1H, d, *J* 1·2 Hz, 3-H), 7·14 (2H, t, *J* 7·6 Hz, ·C*H*$_2$Et), 8·09 (3H, d, *J* 0·9 Hz, Me), 8·19—8·48 (2H, m, CH_2·C*H*$_2$·CH_3), and 9·07 (3H, t, *J* 7·1 Hz, CH_2·CH_2·C*H*$_3$); *m/e* 202 (M^+), 187, 174, 145, 131, 115, 91, and 77.

From 3-propyl-2-(prop-2-ynyloxy)tropone (90 mg) was obtained, after chromatography and elution with 20% ether–light petroleum, 9-*methylene*-2-*propyltricyclo*-[3.3.1.0^{2,8}]*non*-6-*ene*-3,4-*dione* (XIIIc) as a yellow oil (62 mg, 69%), purified by distillation at 70° (bath) and 0·08 mmHg; $\lambda_{max.}$ 272 and 430 nm (ε 735 and 94); $\nu_{max.}$ (film) 2960, 2930, 1743, 1708, 1650, 1465, 1020, 905, and 770 cm^{-1}; τ (C_6D_6) 4·17br (1H, q, *J* 9·0 and 5·7 Hz) and 4·77br (1H, q, *J* 9·0 and 7·3 Hz) (olefinic protons), 5·24 and 5·15 (2H, 2 × s, :CH_2), 6·18 (1H, q, *J* 7·3 and 2·3 Hz, ·C*H*·C:O), 8·09 (1H, q, *J* 7·3 and 2·3 Hz, cyclopropane proton), 8·43—8·22 (2H, m, ·C*H*$_2$·CH_2·CH_3), 8·83—8·60 (2H, m, ·CH_2·C*H*$_2$·CH_3), 8·92—9·10 (1H, m, cyclopropane ring proton), and 9·25 (3H, t, *J* 7·1 Hz, ·CH_2·CH_2·C*H*$_3$); *m/e* 202 (M^+), 174, 162, 146, 131, 117, 87, 85, 83, and 47.

Further elution with ether–light petroleum (up to 75% ether) gave starting material (5 mg, 6%), followed by crystals (10 mg, 9%), shown by m.p., g.l.c., and u.v. spectra to be 2-methyl-7-propylcyclohepta[*b*]furan-8-one (XIc).

Kinetics of Rearrangement of 3-Bromotropolone Prop-2-ynyl Ethers.—Stock solutions (1% w/v) of the ethers (Va) and (VIa) in redistilled *p*-cymene containing di-n-butyl phthalate (0·33%) as internal standard were prepared and samples (0·1 ml) were sealed in glass ampoules after flushing with nitrogen. Preheated samples were immersed in refluxing *p*-cymene (176 ± 1°) and after measured time intervals were quenched in cold water and analysed by g.l.c. [5 ft × 3/16 in of 5% QF-1 on 100—120 mesh silanised Supasorb (B.D.H.); temp. 155°, N_2 carrier flow 80 ml min^{-1}]. Chromatograph detector responses of the two ethers were calibrated against di-n-butyl phthalate as internal standard for a wide range of concentrations of each compound. Graphical determination of the slopes of plots of ln (c_0/c_t) *vs.* *t* (four half-lives) gave k_{obs} (±5%) for the disappearance of the ethers (see text); half-lives for (Va) and (VIa) were 6·2 and 8·6 min, respectively.

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