# Claisen Rearrangement of Tropolone Ethers. Part II.[1]

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Thermal isomerisations of 3-methylbut-2-enyl ethers of tropolone and 3,5,7-trimethyltropolone proceed in refluxing n-nonane with migration of the ether residue to both 3- and 5-positions. Where enolisation of the resulting cycloheptadienediones cannot occur the 5,5-disubstituted cyclohepta-3,6-diene-1,2-dione predominates in the resulting equilibrium.

CLAISEN rearrangements of tropolone allyl ethers generally result in a straightforward [3,3] sigmatropic migration of the allyl residue to give cyclohepta-3,5-diene-1,2-diones, which, when enolisation regenerating the tropolone system is prevented by the presence of a substituent, can undergo intramolecular electrocyclisation to tricyclic α-diketones.[1] Further rearrangement to the 5-position was not observed in the case of 3,5,7-trimethyltropolone allyl ether,[1] but an early report[2] of the synthesis in low yield of the naturally occurring nootkatin (V) by thermolysis of the mixed 3-methylbut-2-enyl ethers of 4-isopropyltropolone indicated that,

(I)

(II)

(IV) R = H
(V) R = Pr^i

(III)
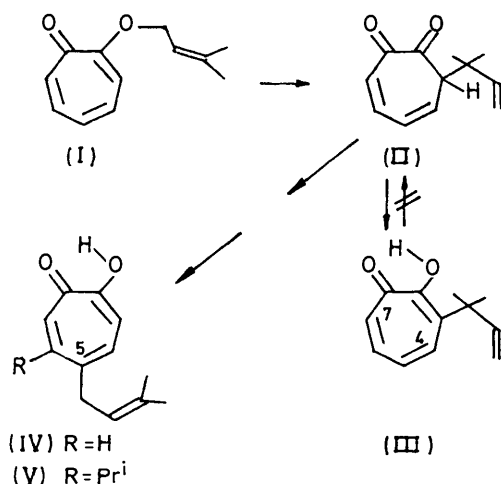
as is well known in the benzenoid series,[3] a double rearrangement could be expected where sufficient steric compression existed in the initial 3-substituted product. That this is the case is further demonstrated by the following studies on thermolysis of 3-methylbut-2-enyl ethers of tropolone and 3,5,7-trimethyltropolone.

Rearrangement of the ether (I) proceeded slowly in refluxing n-nonane (150°); t.l.c. showed that reaction was complete only after 5 h and two isomeric products were formed which were easily separated. The n.m.r. spectrum (solvent C_6D_6) of the major component (82%) showed signals characteristic of the 3-methylbut-2-enyl residue, together with a pair of doublets (J 11·5 Hz) at low field, attributed to the A_2B_2 system of a 5-substituted tropolone (IV), in which rapid prototropic equilibration results in averaging of chemical shifts of protons on opposite sides of the ring. The spectrum of the minor product (III) (13%), most clearly resolved in carbon tetrachloride solution, showed evidence for a 1,1-dimethylallyl side-chain by the presence of a sharp singlet due to the two methyl groups together with a well-defined ABX pattern arising from the vinyl protons. A low field doublet (J 9·7 Hz), probably due to the 4- rather than the 7-proton of (III),[4] was clearly differentiated from signals for the other ring protons which showed the complex pattern expected for a 3-substituted tropolone.

Curiously, thermolysis of the ether (I) for a limited time gave a mixture containing 33% of (III) and only 28% of (IV), in spite of the fact that n-nonane solutions of pure samples of either compound, maintained at 150° for up to 12 h, gave no indication (t.l.c. or g.l.c.) of significant interconversion. The mechanism by which the eventual predominance of (IV) in the rearrangement products is reached is at present obscure, and can only attributed to unknown factors influencing the tautomeric equilibrium between (II) and (III). The ' ortho '-product (III) probably owes its thermal stability to the strong intramolecular hydrogen bonding present in the tropolone system, which would be expected to inhibit ketonisation to (II), and hence equilibrium to the probably more stable 5-substituted product (IV). This recalls the parallel failure of the xanthone deriv-

[1] Part I. R. M. Harrison, J. D. Hobson, and M. M. Al Holly, *J. Chem. Soc.* (C), 1971, 3084.
[2] Y. Kitahara and M. Funamizu, *Bull. Chem. Soc. Japan*, 1958, **31**, 782.

[3] *Cf.* A. Jefferson and F. Scheinmann, *Quart. Rev.*, 1968, **22**, 391.
[4] D. J. Bertelli, T. G. Andrews, and P. O. Crews, *J. Amer. Chem. Soc.*, 1969, **91**, 5286.

ative (VI) to undergo further rearrangement even after lengthy heating,[5] and the same reason doubtless also accounts for the lack of ' abnormal ' Claisen rearrange-

(VI)
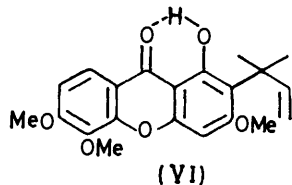
ment products arising from (III) , in contrast with benzenoid analogues.[6]

As in the benzenoid series,[3] steric compression caused by the presence of additional ring substituents results in substantial elimination of a dimethylallyl residue, and thermolysis of the ether (VII) in n-nonane at 150° gave a **64%** recovery of 3,5,7-trimethyltropolone, together with two other products which were separated by preparative g.l.c. and identified by their spectra as the cycloheptadienediones (VIII) and (IX).

The u.v. spectrum of the 3,5-diene-1,2-dione (VIII) closely resembled that of the corresponding α-diketone produced by isomerisation of 3,5,7-trimethyltropolone allyl ether,[1] but the spectrum of its congener showed a maximum at 267 nm of moderate intensity, evidently characteristic of the chromophore of (IX), together with weak absorption near 400 nm typical of a cisoid α-dike-

(VII)　(VIII)

(IX)
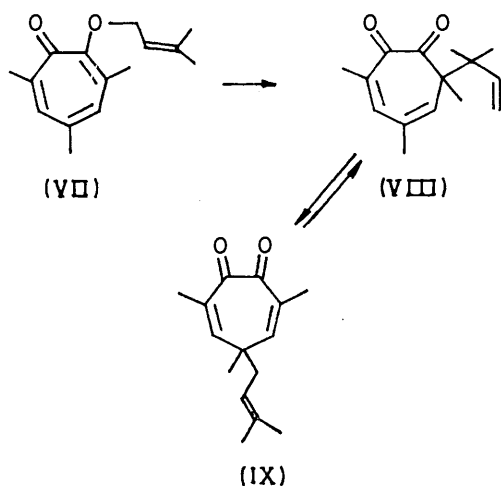
tone.[1] Prolonged heating of n-nonane solutions of either pure diketone resulted in interconversion, the ultimate composition of the equilibrium mixture being approximately 1 : 6 in favour of (IX). The predominance of the latter was thus not overwhelming in spite of the evident steric strain in the 3-substituted isomer (VIII), and it seems likely that the cross-conjugated dienedione system of (IX) is also destabilised to some extent by electronic factors. This would be consistent with the failure of the ether residue of 3,5,7-trimethyl-

tropolone allyl ether to undergo double migration to the 5-position.[1]

EXPERIMENTAL

Spectra were determined using Unicam SP 800 and SP 200 G, and Perkin-Elmer R14 (100 MHz) machines; n.m.r. data were measured using tetramethylsilane as internal reference. Mass spectra were recorded on an A.E.I. MS-9 spectrometer with direct insertion of samples (ionising energy 70 eV).

2-(3-*Methylbut-2-enyloxy*)*tropone* (I).—Anhydrous potassium carbonate (3 g) was added to a stirred solution of tropolone (1 g) in dimethylformamide (15 ml), followed by 3-methylbut-2-enyl bromide (1 ml). Stirring was continued for 36 h at 50—60°, with the addition of more bromide (1·0 ml) after 15 h. Dilution with water and continuous extraction with ether gave, after evaporation *in vacuo*, an oil which was extracted with boiling light petroleum. The concentrated extract was chromatographed on silica; elution with ether and distillation at 70° (bath) and 0·1 mmHg gave the *ether* (I) (0·96 g, 62%) as a pale yellow oil (Found: C, 76·1; H, 7·2. $C_{12}H_{14}O$ requires C, 75·8; H, 7·4%), $\lambda_{max.}$ (EtOH) 236, 320, 348, and 364sh nm (ε 24,000, 8700, 7200, and 4800); $\nu_{max.}$ (film) 3010, 2912, 2895, 1679, 1628, 1590, 1282, 1232, 1193, 1078, 777, and 715 cm^{-1}; τ (C_6D_6) 2·83 (1H, d, J 12·1 Hz, 7-H), 3·2—3·8 (4H, m, other ring protons), 4·46br (1H, t, J 6·5 Hz, C:CH·CH$_2$), 5·65br (2H, d, J 6·5 Hz, ·CH$_2$·O·), 8·47 (3H, d, J 1 Hz), and 8·55 (3H, s, Me groups); m/e 190 (M$^+$), 175, 147, 122, 105, 94, 69, and 41; m* 161·2 (M$^+$ —→ 175).

3,5,7-*Trimethyl-2-(3-methylbut-2-enyloxy)tropone* (VII).—Alkylation of 3,5,7-trimethyltropolone[1] sodium salt with 3-methylbut-2-enyl bromide (0·75 ml) was carried out as just described, giving the *ether* (VII) (0·35 g, 41%) as an oil distilling at 65° (bath) and 0·02 mmHg (Found: C, 77·8; H, 9·0. $C_{15}H_{20}O_2$ requires C, 77·6; H, 8·7%), $\lambda_{max.}$ 244 and 325 nm (ε 21,800 and 7500), $\nu_{max.}$ (film) 3115, 2920, 1673, 1582, 1183, 1023, and 960 cm^{-1}; τ (CCl$_4$) 2·94 and 3·33 (2 × 1H, 2 × s, ring protons), 4·65 (1H, t, J 7·0 Hz, C:CH·CH$_2$·), 5·39 (2H, d, J 7·0 Hz, ·O·CH$_2$·), 7·76br and 7·78br (9H, 2 × s, ring Me groups), and 8·29br (6H, s, ·HC:CMe$_2$); m/e 232 (M$^+$), 164, 136, 121, and 91.

Claisen Rearrangement of 2-(3-Methylbut-2-enyloxy)tropone.—(a) A solution of the ether (195 mg) in n-nonane (30 ml) was refluxed under nitrogen for 5 h, cooled, diluted with ether, and shaken with 2N-sodium hydroxide (4 × 20 ml). The alkaline extract was acidified to pH 5 with 2N-hydrochloric acid and the liberated products were isolated with ether; the pasty solid was freed from oil by washing with cold (0°) n-pentane, crystallised from the same solvent at −20°, and then sublimed at 90—100° and 0·03 mmHg to give plates, m.p. 100—101° of 5-(3-*methylbut-2-enyl*)-*tropolone* (IV) (160 mg, 82%) (Found: C, 75·5; H, 7·2. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·4%), $\lambda_{max.}$ (EtOH) 234, 325, and 354sh nm (ε 28,400, 11,000, and 7200), $\nu_{max.}$ (Nujol) 1670, 1613, 1552, 1263, 1213, 1080, and 787 cm^{-1}, τ (C_6D_6) 1·35br (1H, s, OH), 2·99br and 3·41br (2 × 2H, 2 × d, J 11·5 Hz, tropolone A$_2$B$_2$ system), 4·99br (1H, t,

[5] E. D. Burling, A. Jefferson, and F. Scheinmann, *Tetrahedron*, 1965, **21**, 2653; A. Dyer, A. Jefferson, and F. Scheinmann, *J. Org. Chem.*, 1968, **33**, 1259.

[6] *Cf.* H.-J. Hansen, in ' Mechanisms of Molecular Migrations,' ed. B. S. Thyagarajan, Wiley-Interscience, New York, 1971, p. 177.

J 7 Hz, $CH_2 \cdot CH \colon CMe_2$), 7·18br (2H, d, J 7 Hz, $\cdot CH_2 \cdot CH \colon$), 8·39 (3H, d, J 1 Hz, Me) and 8·55br (3H, s, Me); m/e 190 (M^+), 175, 161, 147, 107, 77, and 41.

Evaporation of the combined n-pentane washings and mother liquors and chromatography of the residue on silica afforded 3-(1,1-dimethylallyl)tropolone (III) (26 mg, 13%) identical with a sample obtained as described in (b).

(b) A solution of the ether (I) (0·52 g) in n-nonane (35 ml) was refluxed under nitrogen for 1 h. Work-up as described in (a) gave 5-(3-methylbut-2-enyl)tropolone (IV) (149 mg, 28%) and 3-(1,1-*dimethylallyl*)*tropolone* (III) (173 mg, 33%), obtained, after distillation at 50° (bath) and 0·05 mmHg, as a pale yellow oil (Found: C, 75·8; H, 7·2%), $\lambda_{max.}$ 244, 322, 356, and 373 nm (ε 25,000, 7300, 7000, and 6400), $\nu_{max.}$ (film) 3188, 3085, 3008, 2968, 2871, 1620, 1590, 1553, 1295, 1248, and 750 cm^{-1}; τ (CCl$_4$) 2·37 (1H, d, J 9·7 Hz, ring proton), 2·8—3·3 (3H, m, ring protons), 3·78 (1H, q, $\cdot CH \colon CH_2$), 4·96 (1H, m), and 5·09 (1H, q) (vinyl ABX: J_{AX} 18·0, J_{BX} 10·4, J_{AB} −1·2 Hz), and 8·47 (6H, s, Me groups); m/e 190 (M^+), 175, 161, 147, 91, 77, and 65.

Solutions of either compound (15 mg) in n-nonane (1 ml) were refluxed under nitrogen. Examination after 1, 6, and 12 h by t.l.c. and g.l.c. (5 ft × 3/16 in of 5% QF-1 on Supasorb at 135°) gave no indication of any significant interconversion.

Claisen Rearrangement of 3,5,7-*Trimethyl*-2-(3-*methylbut-2-enyloxy*)*tropone* (VII).—A solution of the ether (300 mg) in n-nonane (30 ml) was refluxed under nitrogen for 7 h; t.l.c. then indicated the disappearance of all starting material. The cooled mixture was diluted with ether and shaken with 2N-sodium hydroxide; the alkaline layer was separated and acidified to pH 5, and the product isolated with ether. Crystallisation from aqueous methanol gave crystals (136 mg, 64%), m.p. 96°, identical with an authentic specimen of 3,5,7-trimethyltropolone.

Evaporation of the ether–nonane mother liquors gave a dark yellow oil (67 mg) shown by g.l.c. to consist of residual 3,5,7-trimethyltropolone and two other components. Preparative g.l.c. (5 ft × 3/16 in of 20% QF-1 on Supasorb at 148°) gave 3,5,7-*trimethyl*-5-(3-*methylbut-2-enyl*)-*cyclohepta*-3,6-*diene*-1,2-*dione* (IX) as pale yellow crystals, m.p. 45—46°, $\lambda_{max.}$ 267, 318, and 405 nm (ε 4300, 1000, and 80), $\nu_{max.}$ (film) 1747, 1650, 1448, 1378, and 896 cm^{-1}; m/e 232 (M^+), 217, 204, 189, 164, 136, 121, 91, and 69; and 7-(1,1-*dimethylallyl*)-3,5,7-*trimethylcyclohepta*-3,5-*diene*-1,2-*dione* (VIII) as a yellow oil, $\lambda_{max.}$ 225sh, 313, and 446 nm (ε 5800, 3200, and 100); $\nu_{max.}$ (film) 2980, 2923, 1715, 1660, 1452, 1370, and 816 cm^{-1}; m/e 232, 189, 164, 142, 136, 121, 91, and 69.

Samples (1 mg) of the α-diketones (VIII) and (IX) in n-nonane (0·05 ml) were sealed under nitrogen in glass ampoules and heated by immersion in refluxing nonane in the absence of light. Examination after 8 and 12 h by t.l.c. and g.l.c. indicated equilibration to a mixture containing the diketones (IX) and (VIII) in the ratio 6 : 1, together with 3,5,7-trimethyltropolone.