

trans-Cycloalkenes. Part 10.¹ Reactions of Bicyclic *trans*-Cyclo-octenes constrained in Chair and Twist Conformations

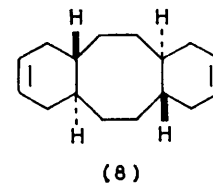
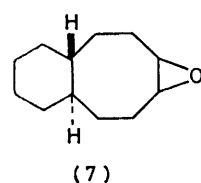
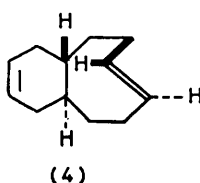
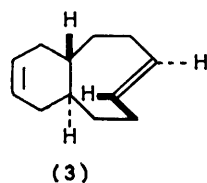
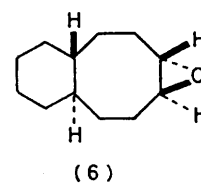
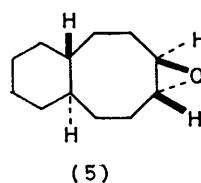
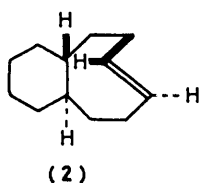
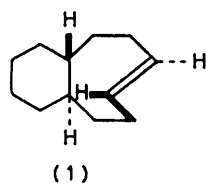
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The following reactions of twist and chair bicyclic *trans*-cyclo-octenes (1) and (2), and (3) and (4) have been investigated: isomerisation with iodine, epoxidation, Diels-Alder addition of butadiene, addition of phenyl azide and pyrolysis of the resulting triazolines, and addition of iodine azide. In most cases diastereoisomeric products were produced from each olefin and in one case, addition of iodine azide, constitutionally different products were obtained. The chair isomer (4) is converted to the twist isomer (3) at 150 °C, and from ΔG^\ddagger for this process it is estimated that the twist isomer is some 14 kJ mol⁻¹ thermodynamically more stable than the chair form.

THE previous two papers have been concerned with the preparation and proof of configuration of the bicyclic twist and chair *trans*-cyclo-octenes (1) and (2) and their unsaturated analogues (3) and (4). We now describe some of their properties and reactions.

verifies the high symmetry of these molecules and in turn confirms the structures of (3) and (4).

A classic diagnostic test for compounds containing a strained double bond is 1,3-dipolar addition of phenyl



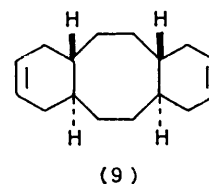
RESULTS AND DISCUSSION

The high reactivities of the olefins (1), (2), (3), and (4) were immediately apparent from their ease of polymerisation. Thus, whereas *trans*-cyclo-octene itself is stable for long periods as the neat liquid at 0 °C, the chair forms (2) and (4) readily precipitated opaque polymer at 0 °C when neat, and slowly in solution. The twist forms (1) and (3) could be kept for a few hours as the neat material, and for a few weeks in light petroleum at 0 °C with little loss.

The bicyclic *trans*-cyclo-octenes (1)–(4) were rapidly isomerised to the corresponding *cis*-isomers by iodine catalysts.¹ This was used in proofs of structure and configuration in the previous papers.

The bicyclic olefins (1) and (2) formed the diastereoisomeric epoxides (5) and (6) respectively on treatment with peracetic acid. As required for molecules with a C₂ axis of symmetry, (5) and (6) showed only six carbon signals in ¹³C n.m.r. spectra in contrast to the *cis*-epoxide (7) which showed ten carbon signals.

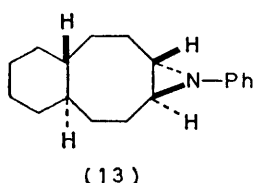
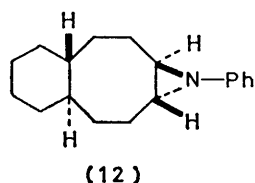
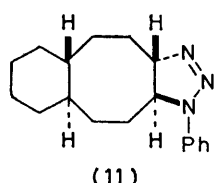
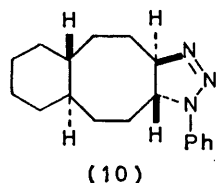
Diels-Alder addition of butadiene (at 50 °C) to (3) and (4) has already been described¹ as part of the evidence for structural assignments. The presence of only four signals in the ¹³C n.m.r. spectra of (8) and (9)



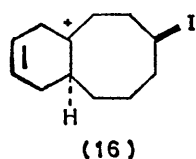
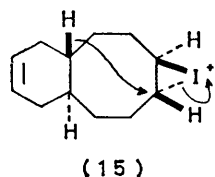
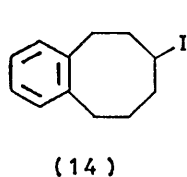
azide to give triazolines.² Both twist (1) and chair (2) olefins reacted rapidly with phenyl azide in light petroleum. Unfortunately second-order rate constants for addition could not be obtained as the reactions, particularly in the case of (2), were not kinetically well behaved. However initial rates of addition of phenyl azide in cyclohexane at 25 °C showed that the twist olefin (1) was about three times more reactive than *trans*-cyclo-octene itself³ and the chair olefin (2) about ten times more reactive. Crystalline adducts were isolated and assigned the triazoline structures (10) and (11) respectively. On pyrolysis, (10) and (11) lost nitrogen, in an analogous fashion to the triazoline from *trans*-cyclo-octene,⁴ to give aziridines which are considered to have the stereochemistry shown in (12) and (13) respectively. Apart from the aromatic absorption, only signals due to six carbons were present in the ¹³C n.m.r. spectra of (12) and (13); this confirms the

retention of the *trans*-stereochemistry of the ring fusion of the heterocyclic ring in the nitrogen elimination process. No imine or *cis*-aziridine were detected as pyrolysis products. On pyrolysis of the triazoline from *cis*-cyclo-octene both aziridine and imine are formed.⁵ The extrusion of nitrogen from heterocyclic azo-compounds is often mechanistically complex⁶ and the formation of common products from stereoisomeric triazolines is frequently observed⁷ e.g. *exo*- and *endo*-norbornyl-triazolines give both *exo*- and *endo*-aziridines on pyrolysis.⁸ The high stereospecificity observed in the formation of (12) and (13) is thus quite striking.

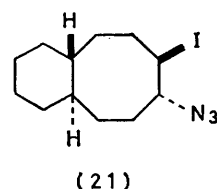
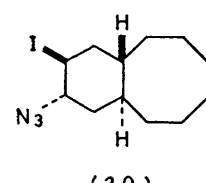
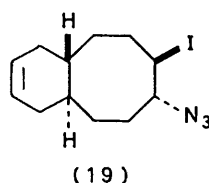
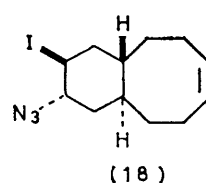
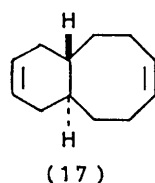
One of the very few instances of *trans*-cyclo-octene undergoing a transannular addition is the reaction with iodine azide to give *trans*-1-azido-4-iodocyclo-octane,⁹ considered to be derived by 1,5-hydride shift. The bicyclic *trans*-cyclo-octenes (3) and (4) were therefore treated with iodine azide in acetonitrile at -20 to -30 °C. In the case of the twist olefin (3) the major product was an aromatic compound, assigned structure (14) on the basis of its mass spectrum and i.r. and n.m.r. spectra. Inspection of molecular models shows the



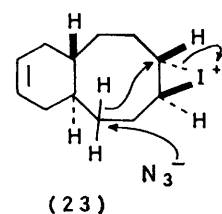
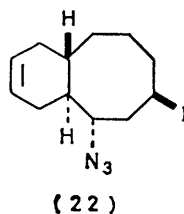
two bridgehead hydrogens of (3) to point into the eight-membered ring very close to the rear face of the *trans*-double bond. Transannular 1,5-hydride migration [cf. (15)] similar to that proposed for *trans*-cyclo-octene itself, is then not surprising, giving (16), followed by proton loss and oxidation to (14).



Addition of iodine azide to the chair olefin (4) was more complex. The major product contained both I and N_3 groups and the cyclohexene double bond was still present. To confirm that isomerisation of the *trans*-double bond, e.g. by iodine, was not preceding addition,



the *cis,cis*-diene (17) was treated with iodine azide under the same conditions and gave as major product (18) together with a minor product considered to be (19). The distinction between (18) and (19) was made on the basis of n.m.r. comparisons with the adducts (20) and (21) from the corresponding mono-olefins.



A tentative assignment of structure (22) to the adduct from the chair olefin was made on the basis that: (a) n.m.r. decoupling experiments indicated that there was no spin-coupling between the proton α to I and that α to N_3 ; (b) treatment with potassium *t*-butoxide gave an unsaturated azide assigned an allylic structure on the basis of the CHN_3 proton at τ 5.75; and (c) of the two possible 1,3-iodoazides, given the location of iodine at one of the original double-bond carbons, (22) is mechanistically more plausible as being produced *via* a 1,4-hydride migration (23). Nevertheless it is surprising that migration of a bridgehead hydrogen to give (14) does not occur since these hydrogens appear to be more favourably placed than those involved in (23). The re-

action thus provides a clear, if inexplicable chemical distinction between the twist and chair olefins (3) and (4).

The original incentive behind our work on bicyclic twist and chair *trans*-cyclo-octenes was that they might provide indirect information about the configurational and conformational situation for *trans*-cyclo-octene itself,¹⁰ and the actual isolation of (1) and (2), and (3) and (4), provides evidence that rotation of the double-bond unit through the ring is a relatively high-energy process. We therefore examined the thermal behaviour of one of these diastereoisomeric pairs in the hope of obtaining quantitative data. It was decided to work with (3) and (4) since they were more stable to polymerisation than (1) and (2), and they were also separable by g.l.c.

It was found that on heating in mesitylene at *ca.* 150 °C in the presence of 2,6-di-*t*-butylphenol as a radical scavenger, and in the absence of oxygen, the twist isomer (3) was stable for several hours while the chair isomer (4) underwent isomerisation to (3) and to the *cis*-isomer (17). The latter reaction showed satisfactory kinetic behaviour for two competing first-order processes, thereby enabling the first-order rate constant for isomerisation of (4) to (3) to be obtained (see Experimental section). Approximate values of ΔG^\ddagger could then be calculated. Results from three runs are: $k = 1.15 \times 10^{-4}$, ΔG^\ddagger 133 at 141 °C; $k = 2.2 \times 10^{-4}$, ΔG^\ddagger 132 at 146 °C; and $k = 4.5 \times 10^{-4} \text{ s}^{-1}$, ΔG^\ddagger 131 kJ mol⁻¹ at 150 °C.

The results clearly demonstrate the greater stability of twist isomer (3) and by implication confirms that the twist is the preferred conformation for *trans*-cyclo-octene itself. Cope had found ΔG^\ddagger for racemisation of *trans*-cyclo-octene to be 145 kJ mol⁻¹ at 155.3 °C.¹¹ As discussed earlier,¹⁰ this should be the free-energy barrier on going from, *e.g.* the (*R*)-twist to (*S*)-chair conformation, so that 145 – 131, *i.e.* 14 kJ mol⁻¹, should represent the free-energy difference between twist and chair *trans*-cyclo-octenes, on the rather drastic assumption that one can extrapolate from our bicyclic system to the parent olefin. Clearly this value is consistent with our observation (by g.l.c.) that no chair olefin (4) can be detected in equilibrium with (3).

Ermer¹² has performed some calculations for the bicyclic *trans*-cyclo-octenes (1) and (2) with a saturated six-membered ring. The chair form (2) (with also a chair six-membered ring) was predicted to be some 15.1 kJ mol⁻¹ higher energy than the twist form (1) (with a boat six-membered ring). Values of 10¹³ and 13¹⁴ kJ mol⁻¹ have been calculated for the energy difference between twist and chair for *trans*-cyclo-octene. Our experimental results are thus in reasonable if perhaps fortuitous agreement with the values derived from molecular mechanics calculations.

EXPERIMENTAL

For general points see ref. 10.

(1RS,4RS,6RS,9RS)-5-Oxatricyclo[7.4.0.0^{4,6}]tridecane (5).—The *trans*-olefin (1) (from precursor hydroxyphosphine

oxide,¹⁰ 1.05 mmol) in methylene chloride (10 ml) containing sodium carbonate (200 mg) was epoxidised with peracetic acid (0.5 ml, 42%). Work-up and distillation gave the epoxide (5) (115 mg, 61% based on phosphine oxide), b.p. 100 °C (bath) at 0.2 mmHg (Found: C, 80.3; H, 11.4. C₁₂H₂₀O requires C, 79.9; H, 12.2%); $\tau(\text{CCl}_4)$ 7.2–7.5 (2 H, m, CHO), 7.6–8.0 (2 H, m, 3-H and 6-H), and 8.1–9.2 (16 H, m); δ_{C} 59.3 (d, C-4), 42.5 (d, C-1), and 35.6, 31.6, 30.0, and 20.6 (t, C-2, C-3, C-10, and C-11).

(1RS,4SR,6SR,9RS)-5-Oxatricyclo[7.4.0.0^{4,6}]tridecane (6).—The *trans*-olefin (2) (from precursor phosphine oxide,¹⁰ 1.3 mmol) was epoxidised as above. Distillation gave the epoxide (6) (130 mg, 55% based on phosphine oxide), b.p. 100 °C (bath) at 0.2 mmHg (Found: C, 80.3; H, 11.3%); $\tau(\text{CCl}_4)$ 7.25–7.5 (2 H, m, CHO), 7.6–9.0 (18 H, m); δ_{C} 57.8 (d, C-4), 42.5 (d, C-1), and 37.5, 37.3, 27.3, and 26.2 (t, C-2, C-3, C-10, and C-11).

(1RS,4RS,8RS,11RS)-7-Phenyl-5,6,7-triazatricyclo[9.4.0.0^{4,8}]pentadec-5-ene (10).—A solution of the *trans* olefin (1) (190 mg, 1.16 mmol) and phenyl azide (150 mg, 1.25 mmol) in light petroleum (4 ml; b.p. 40–60 °C) was set aside at 18 °C for 4 h. The needles were collected by filtration to give the triazoline (10) (266 mg, 81%), m.p. 110–112 °C (decomp.) (Found: C, 76.6; H, 8.65; N, 14.7. C₁₈H₂₅N₃ requires C, 76.3; H, 8.9; N, 14.8%); λ_{max} (cyclohexane) 280 nm (ϵ 9 030), τ 2.5–3.1 (5 H, m, Ph), 5.4–5.9 (1 H, m, 4-H), 6.1–6.6 (1 H, m, 8-H), and 7.1–9.2 (18 H, m).

(1RS,4RS,6RS,9RS)-5-Phenyl-5-azatricyclo[7.4.0.0^{4,6}]tridecane (12).—The triazoline (10) (130 mg) was heated under nitrogen at 120 °C for 30 min, then the residue was purified by p.l.c., eluting with ethyl acetate–benzene (1 : 10), to give the *aziridine* (12) (70 mg, 60%) as a pale yellow oil (Found: C, 84.5; H, 9.75; N, 5.4. C₁₈H₂₅N requires C, 84.65; H, 9.9; N, 5.5%); τ 2.7–3.3 (5 H, m, Ph), 7.6–8.0 (2 H, m, CHN), and 8.1–9.3 (18 H, m); *m/e* 255 (34, M⁺) and 119 (100); δ_{C} 151.4, 128.8, 121.6, and 120.9 (aromatic), 45.2 (d, C-4), 43.6 (d, C-1), and 35.3, 32.5, 28.8, and 23.5 (t, C-2, C-3, C-10, and C-11).

(1RS,4SR,8SR,11RS)-7-Phenyl-5,6,7-triazatricyclo[9.4.0.0^{4,8}]pentadec-5-ene (11).—A solution of the *trans* olefin (2) (180 mg, 1.1 mmol) and phenyl azide (150 mg, 1.25 mmol) in light petroleum (4 ml; b.p. 40–60 °C) was set aside at 18 °C for 4 h, then the crystals were collected to give the triazoline (11) (166 mg, 53%), m.p. 109 °C (decomp.) (Found: C, 76.6; H, 8.7; N, 14.9. C₁₈H₂₅N₃ requires C, 76.3; H, 8.9; N, 14.8%); λ_{max} (cyclohexane) 280 nm (ϵ 9 020); τ 2.5–3.0 (5 H, m, Ph), 5.65–6.1 (1 H, m, 4-H), 6.4–6.8 (1 H, m, 8-H), and 7.1–9.0 (18 H, m).

(1RS,4SR,6SR,9RS)-5-Phenyl-5-azatricyclo[7.4.0.0^{4,6}]tridecane (13).—The procedure described for (12) was repeated using (11) (130 mg). P.l.c. followed by distillation gave the *aziridine* (13) as an oil, b.p. 120 °C (bath) at 0.05 mmHg (Found: C, 84.5; H, 9.7; N, 5.3. C₁₈H₂₅N requires C, 84.65; H, 9.9; N, 5.5%); τ 2.7–3.3 (5 H, m, Ph), 7.7–8.2 (2 H, m, CHN), and 8.2–9.2 (18 H, m); *m/e* 255 (38, M⁺) and 119 (100); δ_{C} 151.6, 128.9, 121.6, and 121.1 (aromatic), 44.6 (d, C-4), 42.6 (d, C-1), and 36.5, 37.1, 26.8, and 25.4 (t, C-2, C-3, C-10, and C-11).

Reaction of the trans Olefin (3) with Iodine Azide.—The *trans* olefin (3) (130 mg, 0.8 mmol) in ether (10 ml) was added to a solution of iodine azide¹⁵ (1 mmol) in acetonitrile (20 ml) at –30 °C. The mixture was stirred at –20 to –30 °C for 1 h, then poured into water (50 ml) and extracted with ether (3 × 30 ml). The extracts were washed with

aqueous sodium thiosulphate (20 ml), then brine (2×20 ml), combined, and dried (MgSO_4). Removal of the solvent gave the *iodide* (14) (140 mg, 60%), a sample of which was distilled, b.p. 70°C (bath) at 0.1 mmHg (Found: C, 50.6; H, 5.4. $\text{C}_{12}\text{H}_{15}\text{I}$ requires C, 50.4; H, 5.3%); m/e 286 (8, M^+) and 159 (79, $M - \text{I}$); $\tau(\text{CCl}_4)$ 2.96 (4 H, s, aromatic), 5.9 (1 H, m, CHI), and 7.0–9.0 (10 H, m).

Reaction of the trans-Olefin (4) with Iodine Azide.—The *trans* olefin (4) (170 mg, 1.05 mmol) in ether (5 ml) was added to iodine azide (1.2 mmol) in acetonitrile (20 ml) as described for (3). Work-up gave the crude product (280 mg) which was purified by p.l.c., eluting twice with light petroleum. The major band gave the adduct (22) (110 mg) (Found: C, 45.5; H, 5.6; N, 12.55. $\text{C}_{12}\text{H}_{18}\text{IN}_3$ requires C, 43.5; H, 5.5; N, 12.7%); m/e 176 (23, $M^+ - \text{N}_2 - \text{I}$); $\tau(\text{CCl}_4)$ 4.43 (2 H, s, $\text{CH}=\text{CH}$), 5.3 (1 H, m, CHI), 6.3 (1 H, m, CHN_3), and 7.1–9.0 (14 H, m).

The minor product from the p.l.c. had i.r. and n.m.r. spectra identical to those of the elimination product below.

*Treatment of the Adduct (22) with Potassium *t*-Butoxide.*—To a solution of the adduct (22) (120 mg) in dry ether (10 ml) was added potassium *t*-butoxide (55 mg) and the mixture was stirred at 15°C for 3 d. Monitoring by t.l.c. showed little change; ether (10 ml) and more potassium *t*-butoxide (20 mg) were added and the solution was heated under reflux for 6 d, then poured into water (50 ml) and extracted with ether (2×20 ml). The extracts were washed with water, dried (MgSO_4), and evaporated to give the crude product (80 mg), which was purified by p.l.c., eluting with light petroleum. The major band gave the *allylic azide* (40 mg) which was distilled, b.p. 80°C (bath) at 0.1 mmHg (Found: C, 70.8; H, 8.6; N, 20.5. $\text{C}_{12}\text{H}_{17}\text{N}_3$ requires C, 70.9; H, 8.4; N, 20.7%); $\tau(\text{CCl}_4)$ 4.2–4.6 (4 H, m, olefinic H), 5.7 (1 H, m, CHN_3), and 7.2–9.0 (12 H, m).

Reaction of the Diene (17) with Iodine Azide.—The diene (17) (200 mg, 1.2 mmol) in dry ether (10 ml) was added to iodine azide (1.4 mmol) as described for (3). Work-up followed by p.l.c., eluting with light petroleum, gave as the major product the *adduct* (18) (168 mg) as a white solid, m.p. $63\text{--}64^\circ\text{C}$ (Found: C, 43.7; H, 5.6; N, 12.5. $\text{C}_{12}\text{H}_{18}\text{IN}_3$ requires C, 43.5; H, 5.5; N, 12.7%); ν_{max} 1 009 and 728 cm^{-1} ; τ 4.4 (2 H, m, $\text{CH}=\text{CH}$), 5.45 (1 H, m, CHI), 5.87 (1 H, m, CHN_3), and 7.1–8.8 (14 H, m). Minor bands on p.l.c. gave unreacted diene (49 mg), and a minor adduct (19) which showed τ 4.44 (2 H, m, $\text{CH}=\text{CH}$), 5.4–6.4 (2 H, m, CHI and CHN_3), and 7.2–9.0 (14 H, m).

Reaction of Bicyclo[6.4.0]dodec-10-ene with Iodine Azide.—The olefin (200 mg) in ether (5 ml) was added to iodine azide (1.4 mmol) in acetonitrile. Work-up gave the adduct (310 mg) which was purified by p.l.c. to give (20) as an oil (160 mg); ν_{max} (film) 2 100, 1 240, and $1 070\text{ cm}^{-1}$; $\tau(\text{CCl}_4)$ 5.45 (1 H, m, CHI), 5.92 (1 H, m, CHN_3), and 7.4–8.9 (18 H, m).

Reaction of Bicyclo[6.4.0]dodec-4-ene with Iodine Azide.—The olefin (200 mg, 1.22 mmol) was treated with iodine azide as above. Work-up and p.l.c. gave a mixture of stereoisomers (92 mg) which was separated by further p.l.c., eluting three times with light petroleum, to give a major band (42 mg) (Found: C, 44.4; H, 6.1; N, 12.4. $\text{C}_{12}\text{H}_{20}\text{IN}_3$ requires C, 43.25; H, 6.05; N, 12.6%); $\tau(\text{CCl}_4)$ 5.7 (1 H, ddd, CHI), 6.6 (1 H, ddd, CHN_3), 7.4–9.2 (18 H, m); and a minor band (27 mg), $\tau(\text{CCl}_4)$ 5.7 (1 H, dt, CHI), 6.1 (1 H, dt, CHN_3), and 7.5–9.2 (18 H, m).

Cyclo-oct-2-enyl Azide.—A solution of cyclo-oct-2-enyl bromide **18** (200 mg, 1.05 mmol) in DMF (5 ml) and sodium azide (100 mg, 1.54 mmol) was stirred at 25°C for 15 h.

Water (100 ml) was added, the mixture was extracted with ether (3×50 ml), and the extracts were washed with water (3×30 ml). The combined organic layer was dried (MgSO_4), the solvent was removed, and the residue was distilled to give the *allylic azide* (130 mg, 81%), b.p. 50°C (bath) at 2 mmHg (Found: C, 63.5; H, 8.95; N, 27.4. $\text{C}_8\text{H}_{13}\text{N}_3$ requires C, 63.5; H, 8.7; N, 27.8%); ν_{max} (film) $3 010$, $2 100$, $1 450$, $1 250$, and 927 cm^{-1} , τ 4.1–4.7 (2 H, m, $\text{CH}=\text{CH}$), 5.7 (1 H, m, CHN_3), and 7.6–8.9 (10 H, m).

Thermal Isomerisation of the trans-Olefin (4).—A solution of the *trans*-olefin (4) (34 mg), 2,6-di-*t*-butylphenol (100 mg), and bicyclo[6.4.0]dodec-4-ene (14 mg, internal standard) in mesitylene (6 ml) was placed in a flask sealed with a vaccine cap, and flushed with nitrogen. The flask was placed in an oil-bath at 141°C , and samples of the mixture (*ca.* 0.2 ml) were removed at intervals by syringe and analysed by g.l.c. (column A). Peak areas, standardised relative to the phenol, were assumed to be proportional to component concentration in the range examined. A good first order plot of $\ln([4])$ against time t gave $k = 3.38 \times 10^{-4}\text{ s}^{-1}$. *cis*-Olefin (17) and twist olefin (3) were produced in parallel first-order reactions, and the rate constant for the appearance of (3), $k_1 = 1.15 \times 10^{-4}\text{ s}^{-1}$, was obtained from the straight-line plot of concentration against $(1 - e^{-kt})$.¹⁷ Experiments at 149 and 146°C similarly gave values for k_1 of 4.5×10^{-4} and $2.21 \times 10^{-4}\text{ s}^{-1}$, respectively.

Thermal Stability of trans-Olefin (3).—A solution of the *trans*-olefin (3) containing 2,6-di-*t*-butylphenol from one of the above isomerisations was divided into Pyrex test tubes sealed with vaccine caps, which were flushed out with nitrogen and placed in an oil-bath at 149°C . The tubes were removed at intervals and the mixture analysed by g.l.c. (A). From a first-order plot of $\ln[(3)]$ against time t the rate constant for isomerisation of (3) to *cis*-olefin (17) was found to be $1.85 \times 10^{-5}\text{ s}^{-1}$.

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