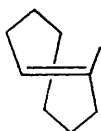


trans-Cycloalkenes. Part V.¹ 1-Methyl-*trans*-cyclo-octene

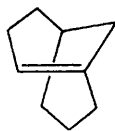
By Alexander J. Bridges and Gordon H. Whitham,* The Dyson Perrins Laboratory, South Parks Road, Oxford OX1 3QY

The reactions of 1-methyl-*trans*-cyclo-octene (I) with a number of reagents have been investigated for comparison with the reactions of bicyclo[3.3.1]non-1-ene (II) and *trans*-cyclo-octene. Towards cycloadditions and addition of alkyl-lithium, 1-methyl-*trans*-cyclo-octene (I) is no more reactive than *trans*-cyclo-octene, indicating similar strain energies, but appreciably less reactive than the bicyclononene (II), which is considerably more strained. In electrophilic additions however, the methyl derivative (I) reacts more rapidly than *trans*-cyclo-octene owing to the presence of the electron-releasing methyl group. Treatment of compound (I) with 4-phenyl-1,2,4-triazoline-3,5-dione gave rapidly the product (X) of an 'ene' reaction.

In earlier papers of this series we have discussed the chemistry of *trans*-cyclo-octene † itself and of certain of its derivatives, but we have not so far been concerned with compounds bearing an alkyl substituent on the double bond. Such compounds are relatively inaccessible and 1-methyl-*trans*-cyclo-octene² and 3-methoxy-2-methyl-*trans*-cyclo-octene³ have been described only recently. In neither case was a study of the reactions of the compound reported, and since our β -hydroxyphosphine oxide route made 1-methyl-*trans*-cyclo-octene readily available from 1-methyl-*cis*-cyclo-octene⁴ we decided to carry out a brief survey of its chemistry. A particular reason for such an investigation was to compare 1-methyl-*trans*-cyclo-octene (I) with bicyclo[3.3.1]non-1-ene⁵ (II) in order to assess how



(I)



(II)

much of the unusual reactivity of (II) was attributable to its bicyclic character ('anti-Bredt') rather than being effectively a 1-alkyl-*trans*-cyclo-octene.

† We shall continue to use the terms *cis*- and *trans*- in this series of papers to designate the way in which the ring system is joined to the double bond. This avoids any possible confusion arising out of a change from *E*- to *Z*- when groups of high priority in the sequence rule are attached to the double bond.

‡ A sample kept in the refrigerator for 6 months was unchanged.

RESULTS AND DISCUSSION

1-Methyl-*trans*-cyclo-octene (I) is a colourless stable ‡ liquid with the smell characteristic of a *trans*-cyclo-octene. The n.m.r. spectrum shows a singlet at τ 8.29 (Me), a doublet (J 10 and 5.5 Hz) at 4.74 (:CH coupled to the adjacent non-equivalent allylic protons), and a complex multiplet at 9.0—9.5 (attributable to two protons at C-5 and C-6 as in *trans*-cyclo-octene¹). For comparison, *trans*-cyclo-octene shows :CH absorption at τ 4.6 and bicyclo[3.3.1]non-1-ene⁵ at 4.38. Compound (I) shows i.r. absorption (C=C str.) at 1654 cm^{-1} [*cf.* *trans*-cyclo-octene 1658, and (II) 1620 cm^{-1}]; in addition there are two prominent bands at 1202 and 880 cm^{-1} . The differences between (I) and (II) in the above respects presumably reflect the greater strain in (II).

1-Methyl-*trans*-cyclo-octene has been postulated as a transient intermediate in the photoinduced addition of methanol to its *cis*-isomer.⁶ This possibility was supported in that treatment of (I) with acidic methanol (0.25% w/v H_2SO_4 ⁶) gave 1-methoxy-1-methylcyclo-

¹ Part IV, K. T. Burgoine, S. G. Davies, M. J. Peagram, and G. H. Whitham, *J.C.S. Perkin I*, 1974, 2629.

² E. Vedejs, K. A. J. Snoble, and P. L. Fuchs, *J. Org. Chem.*, 1973, **38**, 1178.

³ M. S. Baird, *J.C.S. Chem. Comm.*, 1974, 196.

⁴ A. J. Bridges and G. H. Whitham, *J.C.S. Chem. Comm.*, 1974, 142.

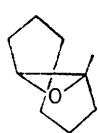
⁵ J. R. Wiseman and W. A. Pletcher, *J. Amer. Chem. Soc.*, 1970, **92**, 956; J. A. Marshall and H. Faubl, *ibid.*, p. 948; G. L. Buchanan, *Chem. Soc. Rev.*, 1974, **3**, 41.

⁶ P. J. Kropp, E. J. Reardon, Z. L. F. Gaikel, K. F. Williard, and J. H. Hattaway, *J. Amer. Chem. Soc.*, 1973, **95**, 7058.

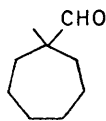
octane as major product. Under these conditions the half-life of (I) at 20 °C was 2 min. In contrast, treatment of (I) with acetic acid (under reflux) gave only 1-methyl-*cis*-cyclo-octene. This should be compared with the *syn*-addition of acetic acid to *trans*-cyclo-octene itself,¹ and to formation of the bridgehead acetate from the bicyclic olefin (II).⁵ Presumably protonation of (I) to give the 1-methylcyclo-octyl cation is followed by solvent capture in the case of the more nucleophilic solvent methanol and by proton loss in the acetic acid. The bridgehead cation from (II) can only give a less strained product by solvent capture.

In contrast to the bromination of the bicyclic olefin (II) which gave a single dibromide,⁵ addition of bromine to (I) gave a mixture containing at least eight products (g.l.c.) and in this respect it is much more like *trans*-cyclo-octene which also gives a complex mixture.⁷

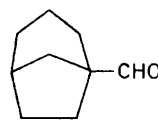
Epoxidation of (I) with buffered peracetic acid gave the epoxide (III). The latter rearranged to 2-methylene-cyclo-octanol on treatment with lithium isopropylcyclo-hexylamide,* and to the ring contracted aldehyde (IV)



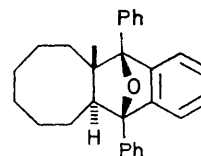
(III)



(IV)



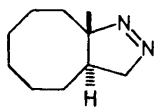
(V)



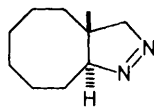
(VI)

with ethereal magnesium iodide. This reaction is analogous to the rearrangement of the epoxide from (II) to the aldehyde (V). However the epoxide from (II) was reduced by lithium aluminium hydride to 1-hydroxybicyclo[3.3.1]nonane⁵ while (III) gave a mixture of products which did not contain significant amounts of 1-methylcyclo-octanol.

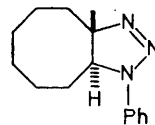
1-Methyl-*trans*-cyclo-octene (I) readily took part in diene and 1,3-dipolar additions, albeit appreciably more slowly than the olefin (II).⁵ Thus the adduct (VI) †



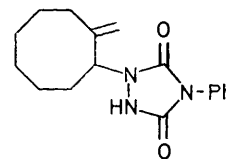
(VII)



(VIII)



(IX)



(X)

was obtained with 1,3-diphenylisobenzofuran, the pyrazolines (VII) and (VIII) ‡ (formed in the ratio 14 : 1) were the result of addition of diazomethane in ether, and the triazoline (IX) was produced on treatment with phenyl azide.

* The same product is formed from 1-methyl-*cis*-cyclo-octene oxide.⁸

† Stereochemistry assigned on the basis of the sterically less demanding transition state.

‡ Tentative structure.

§ We also prepared the 'ene' adduct from caryophyllene (a 1-methyl-*trans*-cyclononene) and *N*-phenyltriazoledione for comparison purposes, but the yield was less satisfactory in this case.

It was expected that 1-methyl-*trans*-cyclo-octene would be an excellent substrate for an 'ene' reaction,⁹ since a concerted transition state involving one of the hydrogen atoms of the allylic methyl group would benefit from considerable release of strain. In fact, treatment of (I) with 4-phenyl-1,2,4-triazoline-3,5-dione,¹⁰ a powerful enophile,¹¹ led to instantaneous decolourisation with formation of the expected 'ene' product (X).§ The triazolidione also reacted rapidly with *trans*-cyclo-octene, but a complex mixture of products was formed. *trans*-Cyclo-octene is structurally less well suited to participate in a concerted 'ene' reaction than (I) and the formation of many products may reflect a stepwise process.

One of the remarkable reactions of the bicyclic olefin (II) is the addition of methyl- (or phenyl-) lithium to give bridgehead-substituted bicyclo[3.3.1]nonanes after hydrolysis,⁵ and it has been our experience that addition of alkyl-lithium to *trans*-cycloalkenes is a sensitive indicator of degree of strain in the olefin. Thus *trans*-cyclo-octene only undergoes very slow addition of

n-butyl-lithium in hydrocarbon solvents whereas rapid reaction occurs with *cis,trans*-cyclo-octa-1,5-diene.¹² 1-Methyl-*trans*-cyclo-octene was unchanged after exposure to methyl-lithium in ether at 20 °C for 20 days; apparently the reactivity of the bicyclic olefin (II) is a consequence of greater ring strain.

Although only qualitative rate data are available for comparisons it is clear that in concerted cycloaddition reactions and in addition of alkyl-lithium, 1-methyl-*trans*-cyclo-octene is at least ten times less reactive than

the bicyclic analogue (II) and indeed comparable in reactivity to *trans*-cyclo-octene itself. We consider that the greater reactivity of (II) in such reactions is a

⁷ N. L. Allinger and L. A. Tushaus, *Tetrahedron*, 1967, **23**, 2051.

⁸ J. K. Crandall and L. C. Lin, *J. Org. Chem.*, 1968, **33**, 2375.

⁹ H. M. R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 556.

¹⁰ R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, *J. Chem. Soc. (C)*, 1967, 1905.

¹¹ W. H. Pirkle and J. C. Stickler, *Chem. Comm.*, 1967, 760.

¹² J. N. Hines, M. J. Peagram, E. J. Thomas, and G. H. Whitham, *J.C.S. Perkin I*, 1973, 2332.

manifestation of its considerably more strained double bond.*

The most marked reactivity difference between (I) and *trans*-cyclo-octene occurs in electrophilic addition reactions where the combined effects of strain and stability of the incipient tertiary cation conspire to make (I) comparable in reactivity to (II) [compare acid-catalysed addition of methanol to (I) with that of ethanol to (II)⁵]. Presumably the postulated greater strain in (II) than in (I) is compensated by the diminished stability of the bridgehead tertiary cation which would be involved in electrophilic addition to (II).

EXPERIMENTAL

Instruments were (i.r.) Perkin-Elmer 257, (¹H n.m.r.) Perkin-Elmer R32 (90 MHz), R14 (100 MHz), or R10 (60 Hz) (Me₄Si as internal standard; solvent CCl₄ for liquid samples, CDCl₃ for solids), (¹³C n.m.r.) Bruker HF X90 (22.63 MHz) with broad band proton decoupling (solvent CDCl₃; chemical shifts in p.p.m. downfield from Me₄Si), (g.l.c.) Pye 104 with 5 ft × 4 mm Carbowax 20M (15%) on Diatomite or (for *trans*-cyclo-octenes) 1,2,3-tris-(2-cyanoethoxy)propane on Embacel.

1-Methyl-*trans*-cyclo-octene, prepared from *trans*-2-hydroxy-2-methylcyclo-octyl(diphenyl)phosphine oxide,⁴ had ν_{\max} (film) 1 654, 1 202, and 880 cm⁻¹, τ 4.71 (1 H, q), 7.6—8.8 (10 H, m, ring methylenes with characteristic fine structure), 8.29 (3 H, s, CH₃), and 8.9—9.5 (2 H, m, shielded 5- and 6-H), δ_{C} (off-resonance decoupled) 137.67 (s, C-1), 127.43 (d, C-2), 41.88 (t, C-8), 36.98 (t, C-3), 33.67, 33.15, 30.48, and 28.15 (all t, C-4 to C-7), and 18.27 (q, CH₃).

Reaction of 1-Methyl-trans-cyclo-octene with Acidified Methanol.—The olefin (0.25 g) and decane (0.05 g; g.l.c. standard) were dissolved in methanol (20 ml) at 20 °C. The g.l.c. properties of the system were established, sulphuric acid (0.05 ml) was added, and the reaction was monitored by g.l.c. Two products in a 15 : 85 ratio were formed; the faster moving (minor) product had a retention time identical with that of 1-methyl-*cis*-cyclo-octene. After 1 h the solution was poured onto water (50 ml) and extracted with light petroleum (2 × 20 ml). The organic phase was washed with water, dried (MgSO₄), and evaporated. The residual liquid (0.27 g) was purified by preparative g.l.c. and the major product was identified as 1-methoxy-1-methylcyclo-octane,⁶ ν_{\max} 2 960, 2 820, 1 480, 1 365, 1 125, and 1 080 cm⁻¹, τ 6.92 (3 H, s, OCH₃), 8.1—8.7 (14 H, m, ring methylenes), and 8.95 (3 H, s, CMe).

Reaction of 1-Methyl-trans-cyclo-octene with Acetic Acid.—1-Methyl-*trans*-cyclo-octene (0.25 g, 0.002 mol) was heated to reflux in acetic acid (5 ml). G.l.c. after 1 h showed no starting material, but a single product which coinjection confirmed was 1-methyl-*cis*-cyclo-octene. The solution was poured into an excess of dilute sodium carbonate solution and the mixture was extracted with light petroleum (2 × 20 ml). The organic extracts were washed with water, dried (MgSO₄), and evaporated. The residual liquid was shown by n.m.r. and i.r. spectroscopy to be 1-methyl-*cis*-cyclo-octene.

Reaction of 1-Methyl-trans-cyclo-octene with Bromine.—1-Methyl-*trans*-cyclo-octene (0.25 g) in carbon tetrachloride (25 ml) was added to bromine (0.96 g, 0.06 mol) in carbon

tetrachloride (25 ml) at 20 °C. G.l.c. after 10 min showed no starting material but six major products. The solvent was removed under reduced pressure (HBr fumes) to give a light yellow oil (0.24 g), the n.m.r. spectrum of which confirmed the presence of a complex mixture.

1-Methyl-9-oxa-trans-bicyclo[6.1.0]nonane.—Peracetic acid (40%; 7 ml) was added dropwise to 1-methyl-*trans*-cyclo-octene (2.48 g, 0.02 mol) and sodium carbonate (7 g) suspended in stirred dichloromethane (60 ml) at 0 °C. The mixture was allowed to warm to 20 °C, and after 20 h was poured onto water (100 ml). The aqueous layer was decanted and extracted with dichloromethane (40 ml). The combined organic extracts were washed with water and saturated aqueous sodium carbonate, dried (Na₂CO₃), and evaporated. Distillation of the waxy residue at 92—94° and 26 mmHg gave 1-methyl-9-oxa-*trans*-bicyclo[6.1.0]nonane (1.96 g, 70%) as a waxy impure solid, m.p. ca. 30° (the material could not be purified further, as chromatography led to rapid decomposition); ν_{\max} 2 920, 1 455, 910, 810, and 780 cm⁻¹, τ 7.25 (1 H, dd, \int 12 and 3 Hz, 8-H), 7.85—9.1 (12 H, m, ring methylenes), 8.74 (3 H, s, Me), and 9.01 (s, Me of impurity) (impurity ca. 10%).

1-Methylcycloheptanecarbaldehyde.—Magnesium (0.06 g, 0.0025 mol) and iodine (0.508 g, 2 mmol) were refluxed together in ether (10 ml) for 3 h. 1-Methyl-9-oxa-*trans*-bicyclo[6.1.0]nonane (0.28 g, 0.002 mol) was added, and a brown oil immediately separated. The ethereal layer was washed with water and brine and dried (MgSO₄). The solvent was removed to give 1-methylcycloheptanecarbaldehyde (0.28 g, 100%) as a light yellow liquid with a sharp smell, ν_{\max} 2 920, 2 800, 2 690, 1 730, 1 460, and 1 370 cm⁻¹, τ 0.72 (1 H, s, CHO), 8—8.7 (12 H, m, ring methylenes), and 9.07 (3 H, s, Me); its 2,4-dinitrophenylhydrazone (0.24 g, 37%) afforded bright orange needles, m.p. 147—148° (Found: C, 56.25; H, 6.35; N, 17.5. C₁₅H₂₀N₄O₄ requires C, 56.25; H, 6.30; N, 17.5%), ν_{\max} (CHCl₃) 3 300, 2 920, 1 620, 1 590, 1 510, 1 335, and 1 310 cm⁻¹, τ 1.02 (1 H, d, $J_{3,5}$ 2.5 Hz, phenyl H-3), 1.86 (1 H, dd, $J_{3,5}$ 2.5, $J_{5,6}$ 10 Hz, phenyl H-5), 2.14 (1 H, d, $J_{5,6}$ 10 Hz, phenyl H-6), 2.64 (1 H, s, CH₃N), 7.9—8.6 (12 H, m, ring methylenes), and 8.84 (3 H, s, Me), M^+ 320.

Reaction of 1-Methyl-9-oxa-trans-bicyclo[6.1.0]nonane with Lithium N-Isopropylcyclohexylamide.—*n*-Butyl-lithium (2.5N, 1.2 ml) was added to *N*-isopropylcyclohexylamine (0.49 g, 0.0035 mol), followed by 1-methyl-9-oxa-*trans*-bicyclo[6.1.0]nonane (0.25 g, 0.0018 mol). After 10 min the mixture was acidified with dilute hydrochloric acid, and extracted with light petroleum (5 ml). The extract was washed with water, dried (MgSO₄), and evaporated to leave 2-methylenecyclo-octanol (0.14 g, 56%), identified by spectroscopic comparison with an authentic sample.

5,5a,6,7,8,9,10,11,11a,12-Decahydro-5a-methyl-5,12-di-phenyl-5-epoxycyclo-octa[b]naphthalene (VI).—1-Methyl-*trans*-cyclo-octene (0.25 g, 0.02 mol) and 1,3-diphenylisobenzofuran (0.60 g, 0.0023 mol) were mixed in benzene (10 ml) at 20 °C for 24 h. The solvent was removed under reduced pressure and the residual gum was crystallised from ethanol to give the adduct (0.355 g, 46%) as pale yellow hexagonal plates, m.p. 130—132° (lit.,² 125.5—127°) (Found: C, 88.35; H, 7.6. Calc. for C₂₅H₃₀O: C, 88.25; H, 7.75%), ν_{\max} (CCl₄) 2 920, 1 445, 1 010, 1 000, 985, and 705 cm⁻¹, τ 2.25—3.1 (14 H, m, aromatic), 7.13 (1 H, d, J 10 Hz, 11a-H), 8—9.2 (12 H, m, ring methylenes), and

* The strain energy differences (alkene minus alkane) for *trans*-cyclo-octene and bicyclo[3.3.1]non-1-ene have been calculated to be 6.3 and 13.1 kcal mol⁻¹, respectively.¹³

¹³ N. L. Allinger and J. T. Sprague, *J. Amer. Chem. Soc.*, 1972, **94**, 5734.

9.23 (3 H, s, Me), *m/e* 270 (diphenylisobenzofuran; base peak) (no M^+).

8-Methyl-9,10-diaza-trans-bicyclo[6.3.0]undec-9-ene.— A distilled solution of diazomethane in ether was prepared from *N*-nitroso-*N*-methylurea in the usual way.¹⁴ 1-Methyl-trans-cyclo-octene (0.25 g, 0.002 mol) was added, and the flask was covered in foil, stoppered, and left for 5 days at 20 °C. It was then left uncorked overnight, to allow the excess of diazomethane to evaporate. The remaining ether was removed under reduced pressure and the residual oil was chromatographed on silica gel (10 g) with 1 : 1 light petroleum-ether as eluant. The solvent was removed to give the pyrazoline (VII) (0.27 g, 81%) as an unstable yellow oil, ν_{\max} . 2 920, 1 550, 1 445, and 1 370 cm^{-1} , τ 5.31 (1 H, dd, J_{gem} 17 Hz, $J_{1,11}$ 8 Hz, 11-H), 6.40 (1 H, dd, J_{gem} 17 Hz, $J_{1,11'}$ 11 Hz, 11-H'), 7.3—7.7 (1 H, m, deshielded methylene proton), 8.0—8.8 (11 H, m, ring methylenes), and 9.08 (3 H, s, Me) {irradiation at τ 8.38 caused signals at τ 5.31 and 6.40 to collapse to doublets, confirming orientation of addition; a minor peak at τ 9.26 (s) was tentatively assigned to the methyl group of the other adduct, 1-methyl-9,10-diaza-trans-bicyclo[6.3.0]-undec-9-ene (VIII), *ca.* 7% of the product}, M^+ 166.

8-Methyl-11-phenyl-9,10,11-triaza-trans-bicyclo[6.3.0]-undec-9-ene (IX).—1-Methyl-trans-cyclo-octene (0.25 g, 0.002 mol) and phenyl azide¹⁵ (0.24 g, 0.002 mol) were dissolved in ether (10 ml) in a foil-covered vessel at 20 °C. After 24 h the solvent was removed and the residue was chromatographed on alumina (50 g), eluted initially with 2% ether-light petroleum, changing to 25% ether. The major product was isolated as a white crystalline solid, which on recrystallisation gave the triazoline (0.075 g, 16%) as flakes, m.p. 81° (decomp.) (Found: C, 74.2; H, 8.9; N, 17.3. $\text{C}_{15}\text{H}_{21}\text{N}_3$ requires C, 74.05; H, 8.7; N, 17.25%), ν_{\max} . (CCl_4) 2 930, 1 660, 1 595, 1 485, 1 450, 1 280, 1 090, 1 030, 870, and 695 cm^{-1} , τ 2.7—2.9 (5 H, m, Ph), 6.15 (1 H, dd, J 10 and 1.5 Hz, 1-H), 7.2—8.8 (12 H, m, ring methylenes), and 9.21 (3 H, s, Me) [the orientation of addition was assigned on the basis of the low τ value of the bridgehead proton (6.15)], *m/e* 215 ($M^+ - \text{N}_2$) (no M^+).

1-(2-Methylenecyclo-octyl)-4-phenyl-1,2,4-triazolidine-3,5-dione (X)—*t*-Butyl hypochlorite (0.595 g, 0.005 mol) was added dropwise to 4-phenyl-1,2,4-triazolidine-3,5-dione

(0.885 g, 0.005 mol) in dioxan (25 ml) at 20°. After 10 min the solvent was removed under reduced pressure at 20° leaving a pink crystalline solid, which was dissolved in tetrahydrofuran (20 ml). 1-Methyl-trans-cyclo-octene (*ca.* 0.6 g) was added dropwise until the red colour of the triazolinedione was completely discharged. The solvent was removed under reduced pressure and the residual gum produced a white solid on trituration with ether. The solid was recrystallised from benzene-petroleum to give the adduct (X) (0.9 g, 60%) as needles, m.p. 103—105° (Found: C, 68.25; H, 7.1; N, 14.2. $\text{C}_{17}\text{H}_{21}\text{N}_3\text{O}_2$ requires C, 68.25; H, 7.05; N, 14.05%), ν_{\max} . (Nujol) 3 160, 3 060, 1 775, 1 695, 1 500, 770, 715, and 695 cm^{-1} , τ 0.65 (1 H, s, NH), 2.4—2.7 (5 H, m, Ph), 4.67 and 4.93 (1 H and 1 H, 2s, exocyclic CH_2), 5.33 (1 H, dd, J 12 and 4 Hz, 2'-H), 7.6—7.8 (2 H, m, allylic methylene), and 8—8.7 (10 H, m, ring methylenes), M^+ 299.

1-(11,11-Dimethyl-4,8-dimethylene-trans-bicyclo[7.2.0]-undecan-5-yl)-4-phenyl-1,2,4-triazolidine-3,5-dione.— *N*-Phenyltriazolinedione was prepared from *t*-butyl hypochlorite (0.595 g, 0.005 mol) and 4-phenyl-1,2,4-triazolidine-3,5-dione (0.885 g, 0.005 mol) as in the previous experiment. The red solid was dissolved in stirred tetrahydrofuran (25 ml) and crude β -caryophyllene (*ca.* 1.2 g) was added dropwise until the red colouration was discharged. The solvent was removed and the foamy residue produced a white solid on trituration with petroleum. The solid was recrystallised with difficulty from benzene-petroleum to give the 'ene' adduct (0.53 g, 28%) as a white microcrystalline compound, m.p. 148—156° (Found: C, 72.55; H, 7.75; N, 10.85. $\text{C}_{23}\text{H}_{29}\text{N}_3\text{O}_2$ requires C, 72.8; H, 7.7; N, 11.1%), ν_{\max} . (Nujol) 3 170, 3 080, 1 775, 1 765, 1 680, 1 505, 1 420, and 770 cm^{-1} , τ 0.9—1.8 (1 H, s, NH), 2.4—2.7 (5 H, m, Ph), 4.81, 4.90, 4.96, and 5.05 (4 \times 1 H, 4s, exocyclic methylenes), 5.39 (1 H, dd, J 15 and 3 Hz, 6'-H), 7.5—8.9 (12 H, m, ring protons), and 9.04 and 9.06 (3 H and 3 H, 2s, C-11' methyls), M^+ 379.

We thank the S.R.C. for a research studentship (to A. J. B.).

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¹⁴ F. Arndt, *Org. Synth.*, Coll. Vol. 2, 1943, p. 165.

¹⁵ R. O. Lindsay and C. F. H. Allen, *Org. Synth.*, Coll. Vol. 3, 1955, p. 710.