Reactions of Enamines from *trans*-Decalin-2-ones with β-Nitrostyrene and Phenyl Vinyl Ketone, and *X*-Ray Analysis of 2-*p*-Bromophenyl-4a,5,5a,6,7,8,9,9a,10,10a-decahydro-5a-methyl-10a-morpholino-4*H*-naphtho[2,3-*b*]pyran

By **M. Forchiassin, A. Risaliti,* and C. Russo,** Laboratorio di Chimica Organica, Università, 34127 Trieste, Italy
M. Calligaris and G. Pitacco, Laboratorio di Strutturistica Chimica, Università, 34127 Trieste, Italy

Only the Δ^2-isomers of the morpholine enamines from *trans*-decalin-2-one (1) and 4a-methyl-*trans*-decalin-2-one (9) react with β-nitrostyrene and phenyl vinyl ketone to give the enaminic adducts (2) and (13), and the naphthopyran derivatives (5) and (16a), respectively. The structures of the products (2), (5), and (13) were assigned from spectral data and their hydrolysis products, while that of (16a) was made through *X*-ray analysis. The enamine (9) displays reduced reactivity with respect to enamine (1) in the foregoing reactions.

We have previously reported that both Δ^1- (1a) and Δ^2- (1b) isomers of 2-morpholino-*trans*-octalin, existing as a 21 : 79 mixture, react with azodicarboxylates, though by a different stereochemical route, to give new trisubstituted enamine derivatives.[1] In continuation of our investigation, the reaction of these enamines with electrophilic olefins has now been studied, to ascertain whether (1a) and (1b) also react similarly with these reagents. Unexpectedly we found that only the Δ^2-isomer (1b) reacted quantitatively with β-nitrostyrene and phenyl vinyl ketone, the starting ketone (*trans*-decalin-2-one) being recovered in both cases from the hydrolysed mother liquor of the reaction mixture, in amounts corresponding to the percentage of the Δ^1-isomer (1a).

From the reaction with β-nitrostyrene, 2-morpholino-3β-(2-nitro-1-phenylethyl)-Δ^1-*trans*-octalin (2) was obtained in 75% yield. Its structure was deduced from spectral and chemical data. The i.r. spectrum showed a band at 1630 cm^{-1}, due to a conjugated enamine double-bond and the ^1H n.m.r. spectrum showed a rather broad signal at τ 5·24, typical of the C-1 olefinic proton.[1] The axial orientation of the substituent at C-3 was established by consideration that the ketone obtained by hydrolysis of (2) under non-equilibrating conditions, could be readily equilibrated into the more stable isomer. Thus structures (3) and (4) were assigned to the two ketones (Scheme 1). This possibility of facile equilibration is important, since chemical equilibration is one of the most reliable methods of configurational study.

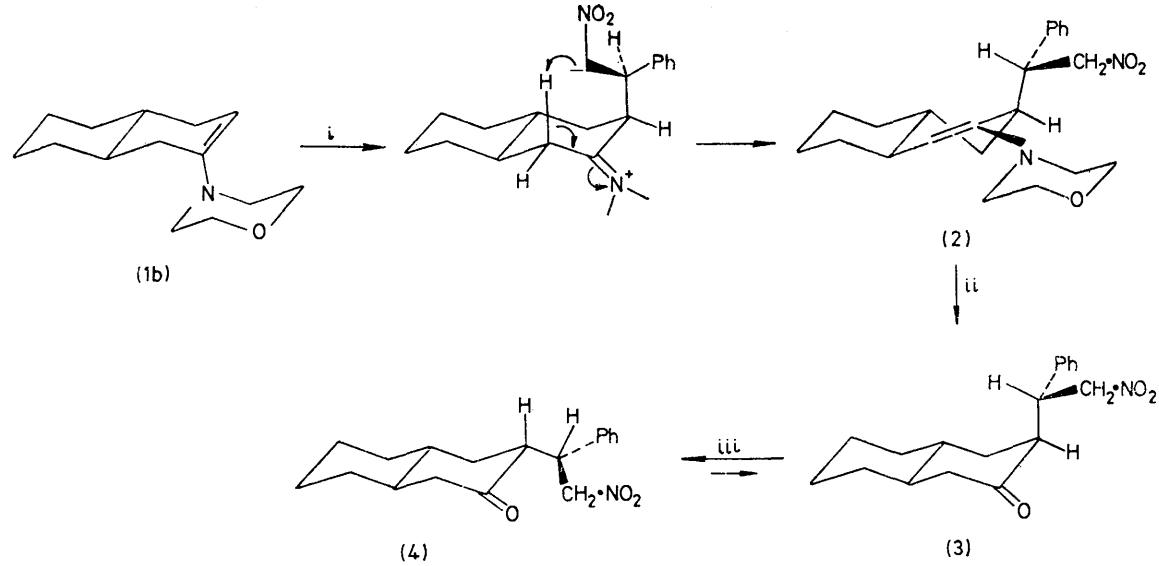
The configurational assignment to C-1 of the side-chain of (2) was made by analogy with the results of the reaction between morpholinocyclohexene and the same olefin.[2]

The reaction with phenyl vinyl ketone furnished a naphthopyran derivative (5) with the three rings *cis-anti-trans* fused (Scheme 2). In fact, the absence of carbonyl bands in the i.r. spectrum allowed us to discard both a cyclobutane and an enamine structure, and the band at 1655 cm^{-1} in the i.r. spectrum was therefore attributed to an enol ether double-bond, and the ill-defined multiplet at τ 4·75 (1H) in the ^1H n.m.r. spectrum was assigned to the vinyl proton of the dihydropyran ring. Once again the fact that hydrolysis of (5) gave ketone (6) which could be smoothly converted into the thermodynamically more stable isomer (7), confirmed that the heterocyclic and carbocyclic rings were *cis*-fused, and that a normal axial attack of the reagent had taken place. These results exactly parallel those for the reaction of the same olefin with 1-morpholino-4-t-butylcyclohexene.[3] By prolonged heating in anhydrous benzene, the adduct (5) rearranged quantitatively into a mixture of alkylated enamines (8) (Scheme 2), the tetrasubstituted form (8b) predominating (80%), as calculated from the ^1H n.m.r. spectrum of the mixture. This showed the C-1 vinylic resonance at τ 5·45 as a signal of area 0·2, indicating the presence of only 20% of the trisubstituted isomer (8a). This result can be readily accounted for by the greater stability of the Δ^2- with respect to the Δ^1-isomers [4,5] and/or by the lack of bulky substituents at the electrophilic carbon atom of the olefin, a feature which can favour the formation of more substituted enamines.[3] On the other hand, the i.r. spectrum contains not only the band due to the carbonyl group conjugated to the benzene ring ($\nu_{max.}$ 1685 cm^{-1}), but also two N·C:C stretching absorptions ($\nu_{max.}$ 1632 and

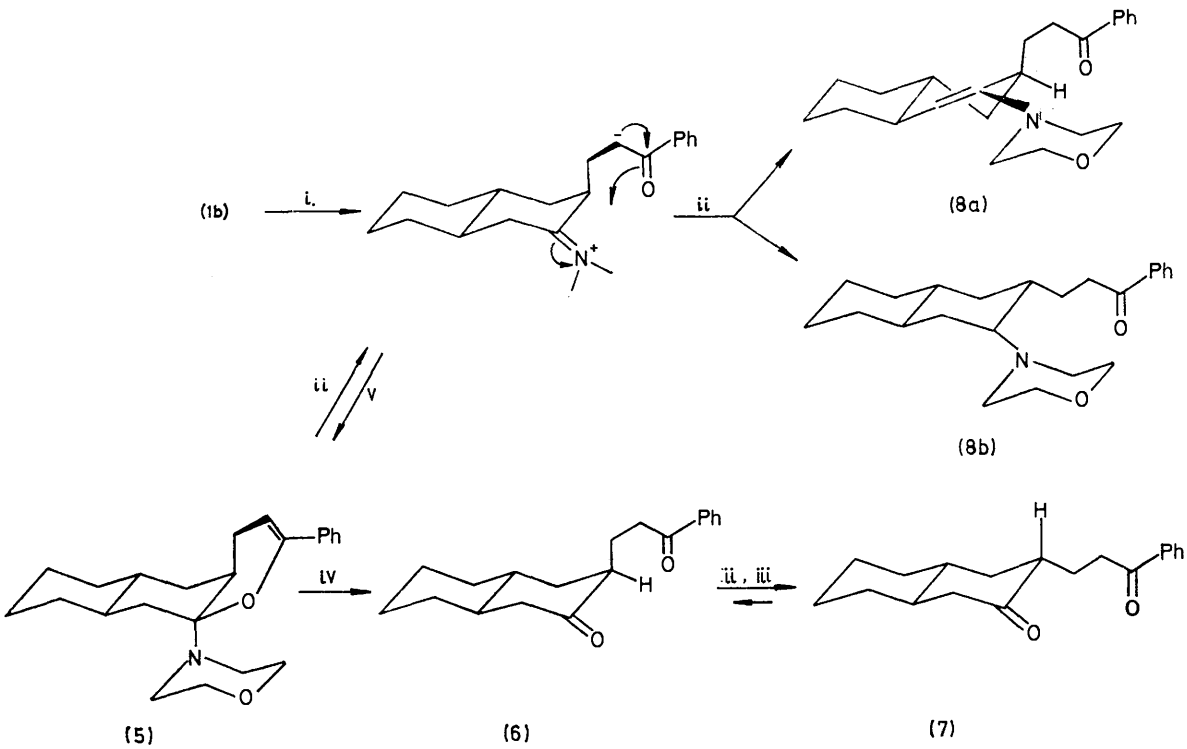
[1] M. Forchiassin, C. Russo, and A. Risaliti, *Gazzetta*, 1972, **102**, 607.
[2] A. Risaliti, L. Marchetti, and M. Forchiassin, *Ann. Chim. (Italy)*, 1966, **56**, 317; A. Risaliti, M. Forchiassin, and E. Valentin, *Tetrahedron Letters*, 1966, 6331.
[3] F. P. Colonna, S. Fatutta, A. Risaliti, and C. Russo, *J. Chem. Soc. (C)*, 1970, 2377.
[4] E. J. Corey and R. A. Sneen, *J. Amer. Chem. Soc.*, 1955, **77**, 2505; R. B. Turner, W. R. Meador, and R. W. Winkler, *ibid.*, 1957, **79**, 4122.
[5] S. K. Malhotra, D. F. Moakley, and F. Johnson, *Chem. Comm.*, 1967, 448.

1651 cm^{-1}) corresponding to the tri- and tetra-substituted enamine double-bond, respectively.[6]

The lack of reactivity of the Δ^1-isomer could be due to the fact that at the C-1 centre a rear electrophilic attack must take place, presumably because of steric hindrance of the C-6 and C-8 axial hydrogen atoms,[1] besides, of course, that of the C-4a axial H and of the C-3 quasi-axial H. While this reaction occurs with azodicarboxylates because of their high electrophilic character, for β-nitrostyrene and phenyl vinyl ketone, which are less reactive, the reaction which takes place is the easier antiparallel regiospecific attack at the C-3 centre.



SCHEME 1
Reagents: i, PhCH:CH·NO_2; ii, H_3O^+, 25 °C; iii, H^+, 80 °C

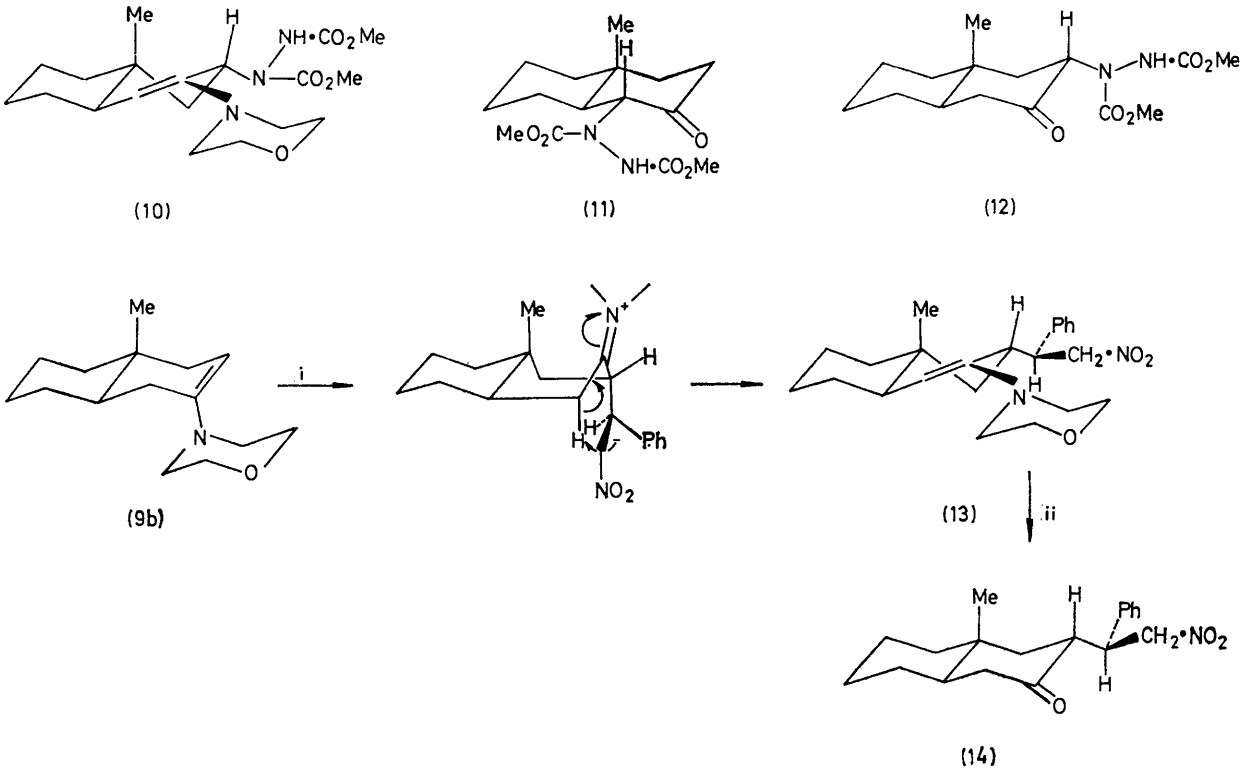


SCHEME 2
Reagents: i, CH_2:CH·COPh; ii, 80 °C; iii, H^+; iv, H_3O^+, 25 °C; v, 5 °C

In order to study the behaviour of these olefins when there is no competition between two different modes of

[6] A. G. Cook, 'Enamines: Synthesis, Structure and Reactions,' Marcel Dekker, New York and London, 1969, p. 38.

attack, the morpholine enamine from 4a-methyl-*trans*-decalin-2-one (9a + b), which exists almost exclusively as the Δ^2-isomer (9b) (≥90%),[7] was chosen. In this compound, the presence of the angular methyl group completely prevents the usual axial approach, the only possible mode of reaction being therefore a parallel attack of the electrophile. The reaction of this enamine with dimethyl azodicarboxylate led to the adduct (10), in only 60% yield. The C-3 substituent was assigned an equatorial position from the pattern of the proton signal at the same C-3.[1] After hydrolysis and column chromatography of the residue from this reaction, 1α- (11) The stretching frequency, however, indicated a rather low degree of conjugation of the enamine system, attributable to the equatorial orientation of the C-3 substituent, which prevents perfect coplanarity of the morpholine ring with the C:C bond. However, hydrolysis of (13) confirmed this expected configuration at C-3, since a ketone (14), which did not epimerise, was always obtained (Scheme 3) regardless of the conditions used. The configuration of C-1 of the side-chain in (13) was assigned as that most favoured for the same carbon atom in the corresponding dipolar intermediate, with the phenyl group pointing outside the ring.[2]



SCHEME 3
Reagents: i, PhCH:CH·NO_2; ii, H_3O^+

(5%) and 3α-(*NN'*-bismethoxycarbonylhydrazino)-4a-methyl-*trans*-decalin-2-one (12) (18%) were isolated from the mother liquor (Scheme 3).

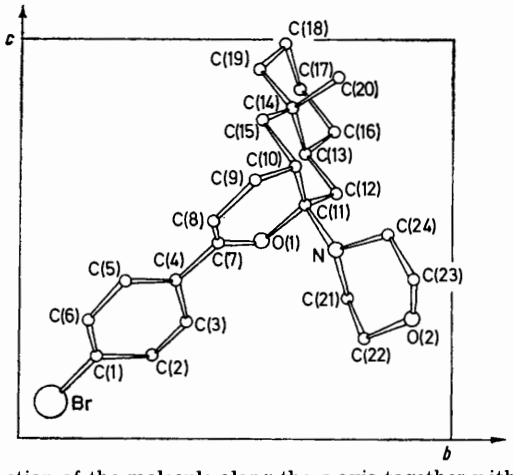
For β-nitrostyrene and phenyl vinyl ketone, the reaction occurred only with the Δ^2-isomer, the product yields, compared with those of the analogous reactions with enamine (1b), being always much lower than the percentage of this isomer in the starting enamine mixture.

The 1 : 1 adduct isolated (68%) from the reaction between (9) and β-nitrostyrene was 4a-methyl-2-morpholino-3α-(2-nitro-1-phenylethyl)-Δ^1-*trans*-octalin (13), its structure being assigned from spectroscopic data and its hydrolysis product. In the ^{1}H n.m.r. spectrum a rather broad signal at τ 5·54 was assigned to the C-1 vinyl proton, and the i.r. spectrum established the presence of an enamine double-bond ($\nu_{max.}$ 1640 cm^{-1}).

The reaction of the enamine (9) with phenyl vinyl ketone afforded a naphthopyran derivative, as evidenced by its i.r. spectrum, which showed a strong enol ether double-bond absorption at 1658 cm^{-1}, and by its ^{1}H n.m.r. spectrum, which displayed an ill-resolved multiplet (1H) centred at τ 4·67, characteristic of the vinyl proton of the heterocyclic ring. This product, which was shown by t.l.c. to consist of a single component, always gave the same ketone (17) after hydrolysis under various conditions. This result confirmed only that the thermodynamically more stable equatorial group was present both in the ketone and in the parent adduct, but gave no evidence about the type of ring closure (Scheme 4). To establish unequivocally the structure of this product, an *X*-ray crystallographic study was undertaken on a

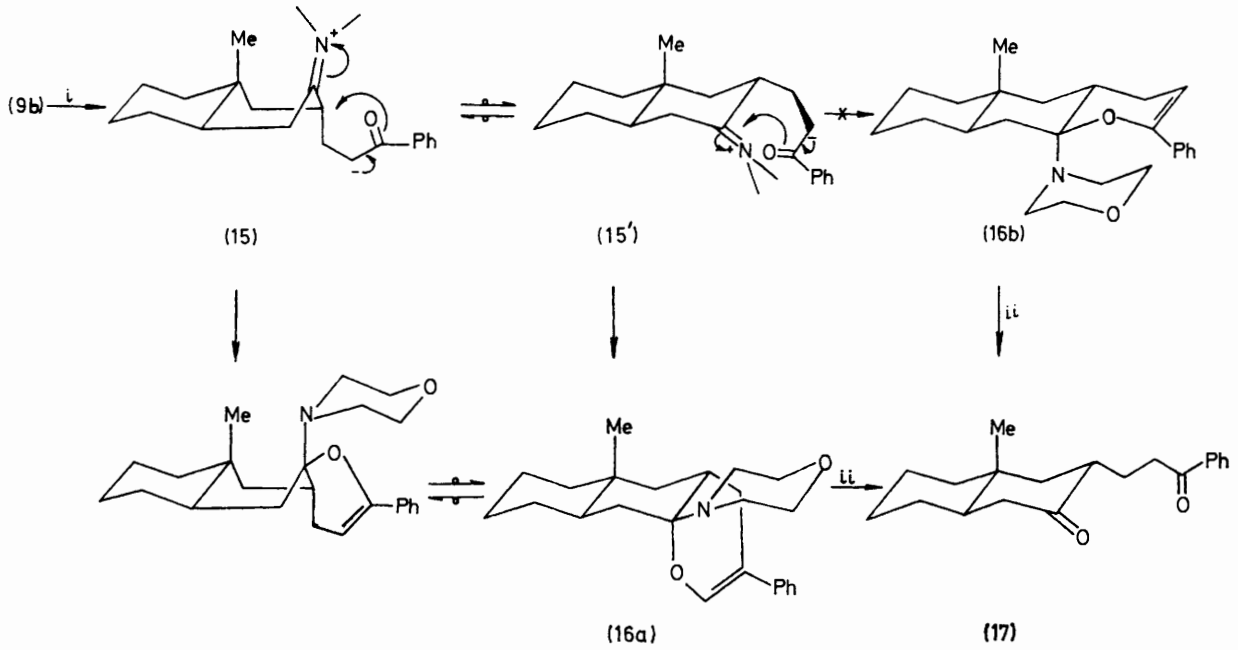
[7] M. E. Kuehne and T. J. Giacobbe, *J. Org. Chem.*, 1968, **33**, 3359.

single crystal of the model compound (16'), having a bromine atom in the *para*-position of the aromatic ring. The results showed it to have the structure depicted in the Figure, with the methyl group at C(14) *trans* to the dihydropyran ring. In the *cis*-fused heterocyclic ring the oxygen atom is axially oriented and the morpholine ring occupies an equatorial position. Steric hindrance is further reduced by rotation of the same ring around the C(11)–N bond, so that the lone pair of the nitrogen atom is *endo* with respect to the dihydropyran ring. The latter has a nearly half-chair conformation (see Table 1),



Projection of the molecule along the *a* axis together with the atom numbering scheme used in the crystallographic analysis

whereas the two rings of the decalin system as well as the morpholine ring are in the classic chair conformation. All bond lengths and angles (Table 2) have the expected values. The presence of the double bond between C(7) and C(8) causes the O(1), C(4), and C(7)—(9) to be coplanar, with a maximum displacement of 0·02 Å. The best molecular plane passing through these atoms is only slightly twisted with respect to the aromatic ring, the torsion angle around the C(4)–C(7) bond being 16·0°. Such a conformation is not too different from that found for the molecule of biphenyl in its crystalline state.[8] This may arise from a compromise between two



SCHEME 4
Reagents: i, CH_2:CH·COPh; ii, H_3O^+

opposing tendencies: planarity, which lowers the π-electron energy, and non-planarity, as required by steric repulsion between H(5) and H(8). This consideration is supported by π-molecular orbitals and potential-energy calculations on biphenyl and other compounds such as *trans*-β-methylstyrene.[9] On the other hand, just as in the case of biphenyl, the planar structure may also be stabilised by intermolecular interactions, mainly involving the carbon atoms of the benzene ring (see Table 3).

Thus the structure of the tricyclic adduct is *cis-syn-trans* (16a). The product can be derived from the dipolar intermediate (15), if cyclisation precedes the boat-chair conformational inversion: (15) ⇌ (15'). However, it is much more probable that such inversion is faster than ring closure, so that it would be expected that intermediate (15') would give the adduct (16a), together with isomer (16b). In the latter, the three rings are *trans-syn-trans* fused, and this system of annulation is favoured with respect to *cis-syn-trans*, by analogy with the perhydroanthracene systems.[10] The stereospecific formation of the naphthopyran derivative (16a)

[8] G. B. Robertson, *Nature*, 1961, **191**, 593.
[9] T. H. Goodwin and D. A. Morton-Blake, *Theor. Chim. Acta*, 1963, **1**, 458; G. Favini and M. Simonetta, *ibid.*, 1963, **1**, 294.
[10] E. L. Eliel, 'Stereochemistry of Carbon Compounds,' McGraw-Hill, New York, 1962, p. 284.

seems to be direct evidence that the driving force in the closure of the heterocyclic ring is the orientation of the rather hindering morpholine ring, which must then occupy an equatorial position in the product.

The fact that no products were isolated which could result from attack at C-1 might also be due, in this case, to the lower electrophilicity of the olefins with respect to the azodicarboxylate, but it is likely that this is not the only reason. On the basis of the already reported mechanism [1] for attack of electrophile at this centre, and from inspection of Dreiding molecular models, a controlling factor could be hindrance of the C-8 centre itself, which would render more difficult, or completely prevent, the approach of reagent.

TABLE 1

Some significant torsion angles (°)

O(1)–C(11)–N–C(21)	56·5
O(1)–C(11)–N–C(24)	357·6
O(1)–C(11)–C(12)–C(13)	63·7
O(2)–C(22)–C(21)–N	301·2
N–C(11)–C(12)–C(13)	357·9
N–C(24)–C(23)–O(2)	61·3
C(3)–C(4)–C(7)–C(8)	344·0
C(4)–C(7)–C(8)–C(9)	358·3
C(7)–O(1)–C(11)–C(10)	311·8
C(7)–C(8)–C(9)–C(10)	12·4
C(8)–C(9)–C(10)–C(11)	316·6
C(8)–C(9)–C(10)–C(15)	78·6
C(9)–C(10)–C(11)–O(1)	61·0
C(9)–C(10)–C(15)–C(14)	357·5
C(10)–C(11)–O(1)–C(7)	311·8
C(10)–C(11)–C(12)–C(13)	308·3
C(10)–C(15)–C(14)–C(20)	294·6
C(11)–N–C(21)–C(22)	347·3
C(11)–N–C(24)–C(23)	12·6
C(11)–C(10)–C(15)–C(14)	302·4
C(11)–C(12)–C(13)–C(14)	56·6
C(12)–C(13)–C(14)–C(15)	301·9
C(12)–C(13)–C(14)–C(19)	355·8
C(12)–C(13)–C(14)–C(20)	62·8
C(12)–C(13)–C(16)–C(17)	7·2
C(13)–C(14)–C(15)–C(10)	59·1
C(13)–C(14)–C(19)–C(18)	303·8
C(13)–C(16)–C(17)–C(18)	56·6
C(14)–C(13)–C(16)–C(17)	301·2
C(16)–C(17)–C(18)–C(19)	305·2
C(17)–C(18)–C(19)–C(14)	54·2
C(18)–C(19)–C(14)–C(15)	353·4
C(18)–C(19)–C(14)–C(20)	68·0
C(21)–N–C(24)–C(23)	297·0
C(22)–C(21)–N–C(24)	61·5
C(23)–O(2)–C(22)–C(21)	55·8
C(24)–C(23)–O(2)–C(22)	303·7

EXPERIMENTAL

I.r. spectra were recorded for Nujol mulls, unless otherwise noted, with a Perkin-Elmer 225 spectrophotometer. ^{1}H n.m.r. spectra were recorded with a JEOL JNM 60 HL spectrometer, with tetramethylsilane as internal standard, for $CDCl_3$ solutions, unless otherwise noted. Analytical t.l.c. plates were spread with silica gel G (Merck–Stahl). Yields, and physical and analytical data are reported in Tables 4—6.

Reaction With β-Nitrostyrene.—Equimolecular quantities of morpholine enamine, from *trans*-decalin-2-one (1) [1] or from 4a-methyl-*trans*-decalin-2-one (9),[7] and β-nitrostyrene[11] were allowed to react in anhydrous ether at 5 °C for 72 h. 2-*Morpholino*-3β-(2-*nitro*-1-*phenylethyl*)-Δ^1-trans-*octalin* (2) and its 4a-*methyl derivative* (13) were obtained, respectively. Both adducts gave a single spot on t.l.c. analysis (benzene–few drops of acetone).

* Prepared by a variation of the method of ref. 12, by steam distillation of 3-piperidinopropiophenone or *p*-bromo-3-piperidinopropiophenone hydrochlorides, respectively.

TABLE 2

Bond lengths (Å) and angles (°), with their estimated standard deviations in parentheses

(*a*) Distances			
Br–C(1)	1·90(1)	C(8)–C(9)	1·52(2)
O(1)–C(7)	1·38(2)	C(9)–C(10)	1·57(2)
O(1)–C(11)	1·45(2)	C(10)–C(11)	1·56(2)
O(2)–C(22)	1·41(2)	C(10)–C(15)	1·57(2)
O(2)–C(23)	1·37(2)	C(11)–C(12)	1·53(2)
N–C(11)	1·44(2)	C(12)–C(13)	1·56(2)
N–C(21)	1·43(2)	C(13)–C(14)	1·50(2)
N–C(24)	1·45(2)	C(13)–C(16)	1·56(2)
C(1)–C(2)	1·38(2)	C(14)–C(15)	1·52(2)
C(1)–C(6)	1·44(2)	C(14)–C(19)	1·54(2)
C(2)–C(3)	1·35(2)	C(14)–C(20)	1·56(2)
C(3)–C(4)	1·41(2)	C(16)–C(17)	1·45(2)
C(4)–C(5)	1·41(2)	C(17)–C(18)	1·55(3)
C(4)–C(7)	1·45(2)	C(18)–C(19)	1·50(3)
C(5)–C(6)	1·33(2)	C(21)–C(22)	1·52(2)
C(7)–C(8)	1·35(2)	C(23)–C(24)	1·54(2)
(*b*) Angles			
Br–C(1)–C(2)	120·8(10)	C(8)–C(9)–C(10)	110·5(11)
Br–C(1)–C(6)	118·7(10)	C(9)–C(10)–C(11)	108·2(12)
O(1)–C(7)–C(4)	113·0(10)	C(9)–C(10)–C(15)	109·8(12)
O(1)–C(7)–C(8)	121·4(11)	C(10)–C(11)–C(12)	108·9(11)
O(1)–C(11)–N	108·0(10)	C(10)–C(15)–C(14)	111·6(12)
O(1)–C(11)–C(10)	108·5(10)	C(11)–N–C(21)	114·4(10)
O(1)–C(11)–C(12)	103·5(10)	C(11)–N–C(24)	117·2(12)
O(2)–C(22)–C(21)	112·5(10)	C(11)–C(10)–C(15)	111·7(11)
O(2)–C(23)–C(24)	110·9(10)	C(11)–C(12)–C(13)	113·2(11)
N–C(11)–C(10)	110·8(10)	C(12)–C(13)–C(14)	112·3(11)
N–C(11)–C(12)	116·5(10)	C(12)–C(13)–C(16)	112·3(11)
N–C(21)–C(22)	108·5(12)	C(13)–C(14)–C(15)	108·6(12)
N–C(24)–C(23)	108·6(13)	C(13)–C(14)–C(19)	106·6(12)
C(1)–C(2)–C(3)	119·8(13)	C(13)–C(14)–C(20)	114·2(13)
C(1)–C(6)–C(5)	118·3(12)	C(13)–C(16)–C(17)	109·2(13)
C(2)–C(1)–C(6)	120·5(12)	C(14)–C(13)–C(16)	113·2(12)
C(2)–C(3)–C(4)	121·4(13)	C(14)–C(19)–C(18)	115·8(17)
C(3)–C(4)–C(5)	117·5(12)	C(15)–C(14)–C(19)	109·4(13)
C(3)–C(4)–C(7)	121·7(12)	C(15)–C(14)–C(20)	108·3(13)
C(4)–C(5)–C(6)	122·4(12)	C(16)–C(17)–C(18)	113·9(15)
C(4)–C(7)–C(8)	125·5(11)	C(17)–C(18)–C(19)	107·5(14)
C(5)–C(4)–C(7)	120·8(11)	C(19)–C(14)–C(20)	109·7(13)
C(7)–O(1)–C(11)	118·9(10)	C(21)–N–C(24)	106·6(12)
C(7)–C(8)–C(9)	123·3(12)	C(22)–O(2)–C(23)	110·7(12)

TABLE 3

Intermolecular distances (Å) < 4 Å, with estimated standard deviations in parentheses

Br · · · O(1^{II})	3·94(1)	C(5) · · · C(9^{IV})	3·62(2)
Br · · · C(3^{II})	3·77(1)	C(5) · · · C(10^{IV})	3·74(2)
Br · · · C(13^{II})	3·98(1)	C(5) · · · C(17^{VI})	3·79(2)
Br · · · C(16^{II})	3·96(1)	C(5) · · · C(18^{VI})	3·62(2)
Br · · · C(23^{IV})	3·82(2)	C(6) · · · C(9^{IV})	3·99(2)
O(2) · · · C(5^{III})	3·99(2)	C(6) · · · C(18^{VI})	3·53(2)
O(2) · · · C(6^{III})	3·27(2)	C(6) · · · C(24^{IV})	3·89(2)
C(1) · · · C(18^{VI})	3·68(2)	C(7) · · · C(9^{IV})	3·93(2)
C(2) · · · C(18^{VI})	3·96(2)	C(8) · · · C(15^{IV})	3·84(2)
C(3) · · · C(9^{IV})	3·84(2)	C(8) · · · C(22^{I})	3·80(2)
C(4) · · · C(9^{IV})	3·52(2)	C(16) · · · C(19^{V})	3·94(2)
C(4) · · · C(18^{IV})	3·90(2)		

Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z:

I $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$	IV $\frac{1}{2} - x, 1 - y, -\frac{1}{2} + z$
II $-x, -\frac{1}{2} + y, \frac{1}{2} - z$	V $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$
III $x, 1 + y, z$	VI $1 - x, -\frac{1}{2} + y, \frac{3}{2} - z$

*Reaction With Phenyl Vinyl Ketone and p-Bromophenyl Vinyl Ketone.**—Enamines (1) or (9), reacted with equi-

[11] *Org. Synth.*, Coll. Vol. I, 1941, p. 413.
[12] H. Schäfer and B. Tollens, *Ber.*, 1906, **39**, 2187.

TABLE 4

Physical and analytical data for enamines and naphthopyran derivatives

Compound	Yield (%)	M.p./°C	Formula	Found (%) C	Found (%) H	Found (%) N	Required (%) C	Required (%) H	Required (%) N
(2)	75	136—138 [a]	$C_{32}H_{30}N_2O_3$	70·75	8·05	7·3	71·3	8·15	7·55
(5)	77	128—130 [b]	$C_{23}H_{31}NO_2$	77·8	8·8	3·95	78·15	8·85	3·95
(8)	100	88—90 [a]	$C_{23}H_{31}NO_2$	78·5	8·8	3·95	78·15	8·85	3·95
(13)	68	134—136 [a]	$C_{23}H_{32}N_2O_3$	72·2	8·45	7·15	71·85	8·4	7·3
(16a)	68	133—134 [b]	$C_{24}H_{33}NO_2$	78·9	8·9	3·7	78·45	9·05	3·8
(16′)	43	134—136 [a]	$C_{24}H_{32}BrNO_2$	64·3	7·25	3·2	64·55	7·2	3·15

[a] From ligroin. [b] Triturated with light petroleum.

TABLE 5

Physical and analytical data for *trans*-decalin-2-one and 4a-methyl-*trans*-decalin-2-one derivatives

Compound	M.p./°C	Formula	Found (%) C	Found (%) H	Found (%) N	Required (%) C	Required (%) H	Required (%) N
(3)	174—176 [a]	$C_{18}H_{23}NO_3$	71·6	7·75	4·65	71·75	7·7	4·65
(4)	97—99 [b]	$C_{18}H_{23}NO_3$	71·1	7·7	4·55	71·75	7·7	4·65
(6)	107—108 [b]	$C_{19}H_{24}O_2$	79·5	8·6		80·25	8·5	
(7)	111—112 [b]	$C_{19}H_{24}O_2$	80·0	8·5		80·25	8·5	
(11)	111—112 [b]	$C_{15}H_{24}N_2O_5$	58·2	7·9	8·9	57·7	7·75	8·95
(12)	104—105 [b]	$C_{15}H_{24}N_2O_5$	57·65	7·7	8·85	57·7	7·75	8·95
(14)	124—125 [b]	$C_{19}H_{25}NO_3$	72·35	8·1	4·3	72·35	8·0	4·45
(18)	183—185 [c]	$C_{26}H_{30}N_4O_5$	65·25	6·35	11·75	65·25	6·3	11·7

[a] From ethanol. [b] From ligroin. [c] Triturated with hot methanol.

molecular amounts of phenyl vinyl ketone, in light petroleum at 5 °C for 60 h, to give 4a,5,5a,6,7,8,9,9a,10,10a-*decahydro*-10a-*morpholino*-2-*phenyl*-4H-*naphtho*[2,3-b]*pyran* (5) and its 5a-*methyl derivative* (16a), respectively. Enamine

TABLE 6

I.r. and ^{1}H n.m.r. data for compounds reported in Tables 4 and 5

Compound	$\nu_{max.}$/cm^{-1}	Chemical shifts (τ)
(2)	1555 (NO_2), 1630 (N·C:C)	5·24br (1H, N·C:C*H*) [a]
(3)	1550 (NO_2), 1700 (CO)	5·3—5·53 (2H, m, C*H*$_2$·NO_2)
(4)	1549 (NO_2), 1702 (CO)	5·1 (2H, d, C*H*$_2$·NO_2)
(5)	1655 (O·C:C)	4·65—4·88 (1H, m, O·C:*H*)
(6)	1682, 1701 (CO)	
(7)	1675, 1703 (CO)	
(8)	1632, 1651 (N·C:C)	5·45br (0·2H, N·C:C*H*)
(11)	1716, 1730sh, 1765 (CO)	5·2—5·75 (1H, m, C*H*·N)
(12)	1715, 1730, 1765 (CO) [b]	4·67—5·34 (1H, m, C*H*·N)
(13)	1551 (NO_2), 1640 (N·C:C)	5·54br (1H, N·C:C*H*)
(14)	1545 (NO_2), 1705 (CO)	4·75—5·55 (2H, m, C*H*$_2$·NO_2)
(16a)	1658 (O·C:C)	4·47—4·7 (1H, m, O·C:C*H*)
(16′)	1659 (O·C:C)	4·43—4·7 (1H, m, O·C:C*H*)
(18)	1620 (C:N), 1680 (COPh)	

[a] For CD_3·CO·CD_3 solution. [b] For CCl_4 solution.

(9), reacted under the same conditions with *p*-bromophenyl vinyl ketone, to give the 2-*p*-bromophenyl adduct (16′). The adducts (5), (16a), and (16′) gave a single spot on t.l.c. analysis (benzene–acetone 95 : 5).

Thermal Rearrangement of (5).—A solution of the naphthopyran derivative (5) in anhydrous benzene was heated under reflux for 22 h, under dry nitrogen. After removal of the solvent *in vacuo*, a mixture (2 : 8) of 3β-(2-*benzoylethyl*)-2-*morpholino*-Δ^1-trans-*octalin* (8a) and the Δ^2-*isomer* (8b) was obtained.

Hydrolysis of (2), (5), (10), *and* (13).—To a stirred solution of the adducts in acetone and water at room temperature, was added an equimolecular quantity of glacial acetic acid. After 48 h, solvent was removed *in vacuo* and subsequent work-up gave quantitatively the corresponding substituted ketones: 3β-(2-*nitro*-1-*phenylethyl*)-trans-*decalin*-2-*one* (3), 3β-(2-*benzoylethyl*)-trans-*decalin*-2-*one* (6), 3α-(NN′-*bismethoxycarbonylhydrazino*)-4a-*methyl*-trans-*decalin*-2-*one* (12), and 4a-*methyl*-3α-(2-*nitro*-1-*phenylethyl*)-trans-*decalin*-2-*one* (14). The adduct (16a), under the same conditions, was virtually unchanged (i.r. spectrum). After 12 days hydrolysis was complete (absence of 1658 cm^{-1} band, appearance of 1685 and 1703 cm^{-1} bands due to side-chain and decalinone CO, respectively) and furnished a very viscous product identified as 3α-(2-*benzoylethyl*)-4a-*methyl*-trans-*decalin*-2-*one* (17) through its 2,4-*dinitrophenylhydrazone* (18). The same result was obtained when hydrolysis was carried out with hydrochloric acid, both at room temperature or when heated under reflux in ethanol. Attempts to obtain the pure ketone (17) by distillation or chromatography (column and preparative t.l.c.) were unsuccessful.

When the mother liquor from the reaction between enamine (9) and dimethyl azodicarboxylate was hydrolysed with aqueous 10% hydrochloric acid for 48 h, a solid was obtained, after removal of solvent, which showed three spots on t.l.c. analysis. The faster one corresponded to 4a-*methyl*-trans-*decalin*-2-*one* and the slower to the ketone (12) (by comparison with authentic samples). The third product isolated by column chromatography through silica gel (70—325 mesh ASTM Merck) with ligroin–ethyl acetate (1 : 1) as eluant, was 1α-(NN′-*bismethoxycarbonylhydrazino*)-4a-*methyl*-trans-*decalin*-2-*one* (11). The equatorial orientation of the substituent at C-1 resulted from the pattern of the hydrogen atom geminal to the *NN*′-bismethoxycarbonylhydrazino-group in the ^{1}H n.m.r. spectrum.[1]

Epimerisation of (3) *and* (6).—Ketones (3) and (6), were heated under reflux in ethanol containing a few drops of hydrochloric acid for 10 h, and were converted quantitatively into the more stable 3α-epimers (4) and (7), respectively. Under these conditions ketones (12) and (14) were unchanged, even when heated for 24 h

Crystallography

Crystal Data for (16′).—$C_{24}H_{32}NO_2Br$, $M = 446{\cdot}4$. Orthorhombic, $a = 2{\cdot}275(7)$, $b = 10{\cdot}713(4)$, $c = 10{\cdot}248(4)$ Å, $U = 2225{\cdot}9$ Å^3, $Z = 4$, $D_c = 1{\cdot}333$. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) = 19·8 cm^{-1}. Space group $P2_12_12_1$ (D_2^4).

Cell parameters were determined from Weissenberg photographs taken with Co-K_α radiation and refined with an on-line automated single-crystal Siemens diffractometer with Mo-K_α radiation.

TABLE 7

Fractional co-ordinates ($\times 10^4$), with estimated standard deviations in parentheses; hydrogen atoms are numbered according to the carbon atom to which they are bonded

	x	*y*	*z*
Br	665(1)	704(2)	978(2)
O(1)	1199(4)	5543(8)	5112(8)
O(2)	2401(5)	9085(10)	3068(11)
N	1839(5)	7335(11)	4817(12)
C(1)	965(6)	1934(12)	2176(13)
C(2)	658(7)	3077(12)	2260(14)
C(3)	874(6)	3929(13)	3129(14)
C(4)	1413(6)	3677(12)	3965(13)
C(5)	1720(6)	2500(12)	3852(13)
C(6)	1525(7)	1650(13)	2993(14)
C(7)	1641(6)	4581(11)	4913(13)
C(8)	2227(6)	4550(13)	5530(12)
C(9)	2434(7)	5505(14)	6545(15)
C(10)	1826(7)	6318(14)	6978(15)
C(11)	1428(6)	6678(12)	5733(14)
C(12)	789(6)	7331(13)	6146(14)
C(13)	385(7)	6576(13)	7180(15)
C(14)	780(7)	6295(14)	8376(15)
C(15)	1391(7)	5565(14)	7975(15)
C(16)	−295(8)	7192(14)	7486(15)
C(17)	−675(9)	6364(16)	8319(21)
C(18)	−320(10)	6007(19)	9611(18)
C(19)	341(9)	5469(16)	9256(16)
C(20)	1006(10)	7473(17)	9146(17)
C(21)	1525(7)	7614(14)	3598(13)
C(22)	2051(9)	8031(15)	2632(16)
C(23)	2674(9)	8868(16)	4268(19)
C(24)	2143(8)	8481(15)	5261(17)
H(2)	241	3272	1600
H(3)	622	4804	3287
H(5)	2111	2239	4524
H(6)	1792	784	2852
H(8)	2559	3793	5272
1-H(9)	2639	5061	7410
2-H(9)	2826	6127	6152
H(10)	1992	7196	7419
1-H(12)	921	8214	6618
2-H(12)	500	7508	5306
H(13)	266	5704	6669
1-H(15)	1252	4683	7508
2-H(15)	1695	5349	8816
1-H(16)	−210	8094	7951
2-H(16)	−569	7380	6571
1-H(17)	−1138	6869	8553
2-H(17)	−791	5552	7781
1-H(18)	−265	6804	10287
2-H(18)	−625	5309	10173
1-H(19)	233	4603	8724
2-H(19)	603	5243	10131
1-H(20)	1268	7224	10046
2-H(20)	569	8034	9470
3-H(20)	1311	8071	8572
1-H(21)	1261	6790	3229
2-H(21)	1159	8362	3697
1-H(22)	2391	7231	2541
2-H(22)	1826	8194	1704
1-H(23)	3035	8089	4142
2-H(23)	2934	9679	4542
1-H(24)	1780	9205	5403
2-H(24)	2371	8296	6234

Intensity Measurements.—Three-dimensional intensity data were collected on the Siemens diffractometer by the θ—2θ scan technique and Mo-K_α radiation up to 2θ(max), 50°. The crystal used was sealed under nitrogen in a thin-walled capillary tube to prevent decomposition. A total of 1009 reflexions was collected and corrected for the Lorentz polarisation factors. Because of the large value of μ ($\mu R \simeq 1$) an absorption correction was applied, assuming a rough cylindrical shape. No correction was applied for the anomalous scattering of bromine or for extinction effects.

Structure Determination and Refinement.—The structure was solved by conventional Patterson and Fourier methods and refined by the block-diagonal matrix least-squares technique. The function minimised was $\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|)^2$ where $w = 1/(20 + |F_o| + 0{\cdot}0030\ |F_o|^2)$ so that

TABLE 8

Anisotropic temperature factors * ($\times 10^4$) with estimated standard deviations in parentheses

	B_{11}	B_{12}	B_{13}	B_{22}	B_{23}	B_{33}
Br	42(0)	−34(2)	−4(2)	122(1)	−84(3)	168(2)
O(1)	21(2)	−7(8)	−7(9)	77(8)	−42(18)	107(10)
O(2)	39(3)	5(12)	16(12)	135(12)	67(24)	173(14)
N	30(3)	3(10)	−18(11)	95(11)	0(21)	95(12)
C(1)	26(3)	−32(11)	20(14)	80(12)	−59(25)	99(14)
C(2)	30(4)	−14(16)	−10(17)	89(12)	−16(26)	118(15)
C(3)	23(3)	26(12)	−4(14)	101(14)	−6(26)	104(16)
C(4)	21(3)	−22(11)	8(13)	80(11)	−23(25)	80(13)
C(5)	24(3)	7(12)	−9(14)	81(12)	−8(26)	79(14)
C(6)	27(4)	−8(12)	36(15)	80(13)	9(26)	118(16)
C(7)	21(3)	−23(10)	7(13)	58(11)	9(22)	107(15)
C(8)	26(3)	24(13)	−1(13)	101(16)	−51(26)	88(15)
C(9)	34(4)	−21(17)	−36(16)	109(16)	23(35)	133(17)
C(10)	30(4)	5(15)	−26(16)	96(13)	−36(31)	136(19)
C(11)	25(3)	−10(12)	−24(14)	84(12)	−48(26)	92(15)
C(12)	29(4)	14(13)	−11(16)	95(13)	−4(27)	127(17)
C(13)	31(4)	8(14)	13(16)	81(14)	−18(28)	106(16)
C(14)	37(5)	−14(15)	−3(16)	95(14)	−30(28)	116(15)
C(15)	34(4)	66(14)	−35(15)	106(15)	−46(33)	136(18)
C(16)	41(5)	31(15)	44(18)	105(15)	−17(30)	116(19)
C(17)	45(6)	−1(21)	57(25)	96(16)	−31(40)	271(26)
C(18)	57(6)	−8(21)	37(21)	152(23)	−29(42)	148(21)
C(19)	59(6)	68(18)	3(20)	146(20)	−33(39)	132(20)
C(20)	60(6)	−1(22)	−7(24)	143(19)	−112(40)	140(20)
C(21)	36(4)	−7(14)	21(15)	88(14)	−17(26)	104(15)
C(22)	56(6)	−6(18)	28(21)	100(15)	−13(32)	127(20)
C(23)	42(5)	−41(17)	−29(23)	136(17)	90(39)	213(26)
C(24)	43(5)	−55(15)	−33(20)	110(15)	10(34)	170(21)

* In the form: $\exp[-(B_{11}h^2 + B_{12}hk + B_{13}hl + B_{22}k^2 + B_{23}kl + B_{33}l^2)]$.

$w(|F_o| - |F_c|)^2$ was maintained essentially constant over all ranges of $|F_o|$ and (sin θ/λ).

After anisotropic refinement R was 0·061. At this stage a three-dimensional Fourier synthesis was calculated to locate the hydrogen atoms. Estimated positions for these atoms all occurred in regions of positive electron density. Hydrogen atoms were included at calculated positions and final anisotropic least-squares refinement reduced R to 0·051. The co-ordinates and the thermal factors (set at 5 Å^2) of the hydrogen atoms were held constant. During data collection the crystal assumed a pink colour, but there were no significant variations in reference reflexions. No fundamental alteration in the crystal structure had occurred, since the powder pattern calculated from the final atomic parameters was shown to be identical with the experimental spectrum. Final atomic parameters are listed in Tables 7 and 8 together with their estimated standard deviations, calculated from the residuals and the diagonal elements of

the inverse matrix of the final least-squares cycle. The atom numbering scheme used in the crystallographic analysis is shown in Figure. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20872 (5 pp).* Atomic scattering factors were calculated according to ref. 13.

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

[13] F. H. Moore, *Acta Cryst.*, 1963, **16**, 1169.

This work was supported by a grant from the C.N.R. Rome.

[3/1444 *Received*, 10*th July*, 1973]