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CYCLOADDITION REACTIONS OF NITRONES TO CYCLOOCTATETRAENE AND ITS DERIVATIVES

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Abstract—The cycloaddition of acyclic nitrones to the Diels–Alder adduct cyclooctatetraene—acetylenedicarboxylate yields three different monoadducts, whose structures are assured through NMR spectroscopy and chemical transformations. Thermolysis of these monoadducts to the new heterocyclic system of 2,3-oxazabicyclo[3.2.0]hepta-6-ene is described. Depending on the nature of the substituents on the N atom and on the stereochemistry of the isoxazolidine C-3, variable amounts of pyrrole aldehydes are also obtained.

The reaction of a cyclic nitrone with cyclooctatetraene and some of its diene adducts is also reported.

ALTHOUGH the 1,3-dipolar cycloaddition of nitrones to olefins has been extensively studied in the last years, the reactivity of nitrones toward cyclooctatetraene (COTE) and its derivatives has not been investigated. Recent studies have shown that such compounds are active dipolarophiles in the 1,3-dipolar cycloaddition to nitrile oxides and nitrile imines, thus providing a general entry to new interesting cyclobutane-condensed heterocyclic systems, e.g. 2,3-oxazabicyclo[3.2.0]hepta-3,6-dienes[1–4] and analogous pyrazoline polycyclic derivatives.[5] We report here our results on the extension of this cycloaddition reaction to the nitrones. In addition to COTE, we chose as dipolarophile the adduct COTE—dimethyl acetylenedicarboxylate (**3**), which possesses three double bonds potentially reactive with a 1,3-dipole.

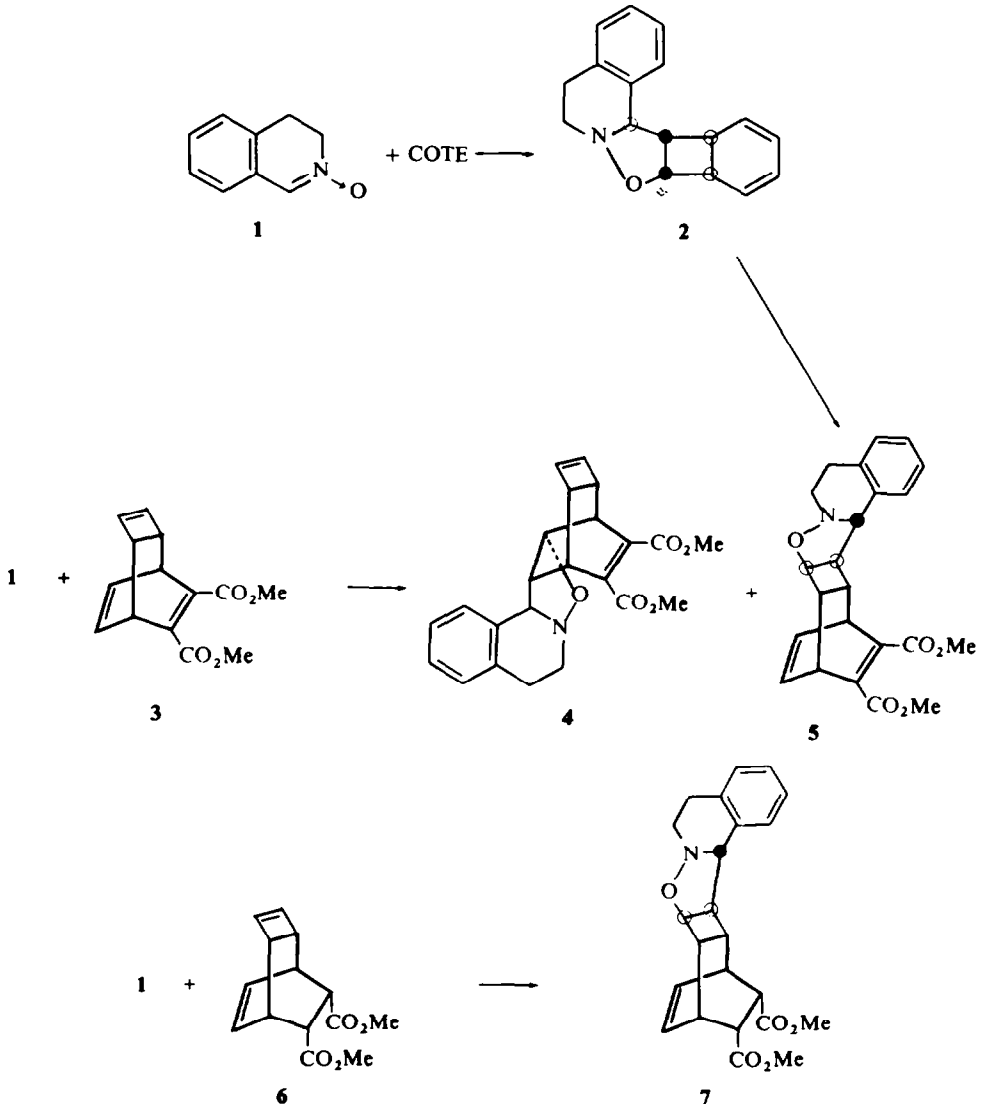
3,4-Dihydroisoquinoline N-oxide (**1**) is one of the most reactive nitrones, as shown by its relative rate constant in the cycloaddition to methyl crotonate.[6] The reaction of **1** with COTE led to the isolation of a monoadduct in 50% yield. Structure **2** was proved by the reaction with dimethyl acetylenedicarboxylate, which yielded the adduct **5** (Scheme 1). This latter compound was also obtained directly by cycloaddition of **1** to the adduct **3** of well-established stereochemistry.[7,8] In this cycloaddition reaction a second monoadduct was isolated in nearly equal amount, whose structure **4** relies on spectroscopical evidence. The dipolarophilic activities of the cyclobutene and of the cyclohexadiene unsubstituted double bonds are here competitive. As would be expected from its larger steric encumbrance, the adduct **6** reacted with **1** only on its cyclobutene double bond to give the polycondensed isoxazolidine **7**. The stereochemistry of the chiral center in position 3* of all the adducts will be discussed later.

The cycloaddition of COTE with acyclic nitrones is more sluggish and no definite product could be isolated from the reaction mixture. The Diels–Alder adduct **3** on the contrary allowed us to reach clear-cut results.

* Numbering refers to the isoxazolidine ring

Treatment of 3 with N-methyl-C-phenylnitrone (**8a**) led to the isolation of three products, whose structure of mono-adducts follows from elemental analysis and NMR spectroscopy (Table 1). Two of them are stereoisomers and result from the attack of

SCHEME 1



the 1,3-dipole to the strained cyclobutene double bond. The formation of two diastereomers in the cycloaddition of nitrones to unsaturated compounds is a common feature of the reaction.[9, 10] The third monoadduct has been assigned structure **11a** (Scheme 2) from its IR and NMR data and is thermally stable. No definite conclusion could be drawn from the NMR spectrum with regard to the stereochemistry of the chiral center, and this point will be reconsidered later.

Thermolytic breakdown of the diastereomeric monoadducts **9a** and **10a** yielded, together with dimethyl phthalate, the diastereomeric 3-methyl-4-phenyl-2,3-oxazabicyclo[3.2.0]hept-6-enes **12a** and **13a** respectively. No other by-product could be found. The configurational assignment to the epimeric pairs **9a/12a** and **10a/13a** respectively relies on the following considerations. Spin–spin coupling of protons on C-3 and C-4 of isoxazolidine ring is known from previous examples[9a–d, 10] to be larger for *cis* isomers than for *trans* isomers. With the adducts diarylnitrone/N-phenylmaleimide the coupling constant was found to be zero for the *trans* isomer and as large as 8·4–9·0 for the *cis* isomer,[10] whereas with less rigid condensed systems (e.g. the adduct diphenylnitrone/norbornene) the difference is less pronounced.[9a]

The significant NMR data of our compounds are summarized in Table 1. Compounds **10a** and **13a** show doublets for H-3, with a coupling constant J_{34} of 6·0 c/s, whereas the signal of H-3 in the picrate of **9a** and **12a** appears as a singlet. Therefore,

TABLE 1. NMR PARAMETERS OF CONDENSED ISOXAZOLIDINES[a]

Compound	H-3	H-4	H-5	O—Me	N—Me	H H	J_{34}
2[b]	4·12 s	[c]	4·37 m	—	—	5·66 m	<0·5
4	4·13 d	[c]	4·85 q	3·79; 3·84 s	—	6·30; 6·39 dd[e]	8·6
7	4·37 s	[c]	3·99	3·63 s	—	6·47 m	<0·5
9a picrate[d]	4·81 s	[c]	4·54	3·74 s	2·58 s	6·62 m	<0·5
9b	4·76 s	[c]	[c]	3·78 s	—	6·55 m	<0·5
9c	4·70 s	[c]	[c]	3·78 s	—	6·54 m	<0·5
10a	3·43 d	[c]	[c]	3·68; 3·77 s	2·64 s	6·49 m	6·0
10b	4·31 d	[c]	[c]	3·66; 3·77 s	—	6·52 m	6·4
10c	4·25 d	[c]	[c]	3·68; 3·77 s	—	6·53 m	6·4
11a	3·24	[c]	4·63 q	3·80; 3·88 s	2·44 s	6·24; 6·41 dd[e]	8·1
11b[b]	4·26 d	[c]	4·78 q	3·41; 3·48 s	—	5·90; 5·56 dd[e]	8·1
11c	[c]	[c]	4·83 q	3·86; 3·84 s	—	6·30; 6·48 dd[e]	
12a[b]	3·75 d	3·60	5·03	—	2·49 s	6·07 m	1·0
12a picrate	5·15 s	4·20 m	5·72 m	—	2·81 s	6·14; 6·44 m[e]	<0·5
12b	4·9 s	3·88 m	5·35 m	—	—	6·00; 6·23 m[e]	<0·5
12c[b]	4·57 s	3·52 m	4·98 m	—	—	5·63; 5·76 m[e]	<0·5
13a	3·19 d	3·88 m	4·82 m	—	2·64 s	6·04; 6·31 m[e]	6·0
13b[b]	3·87 d	3·65 m	4·92 m	—	—	5·67; 6·15 m[e]	6·6
13c[b]	3·69 m		4·88 m	—	—	5·67; 6·13 m[e]	

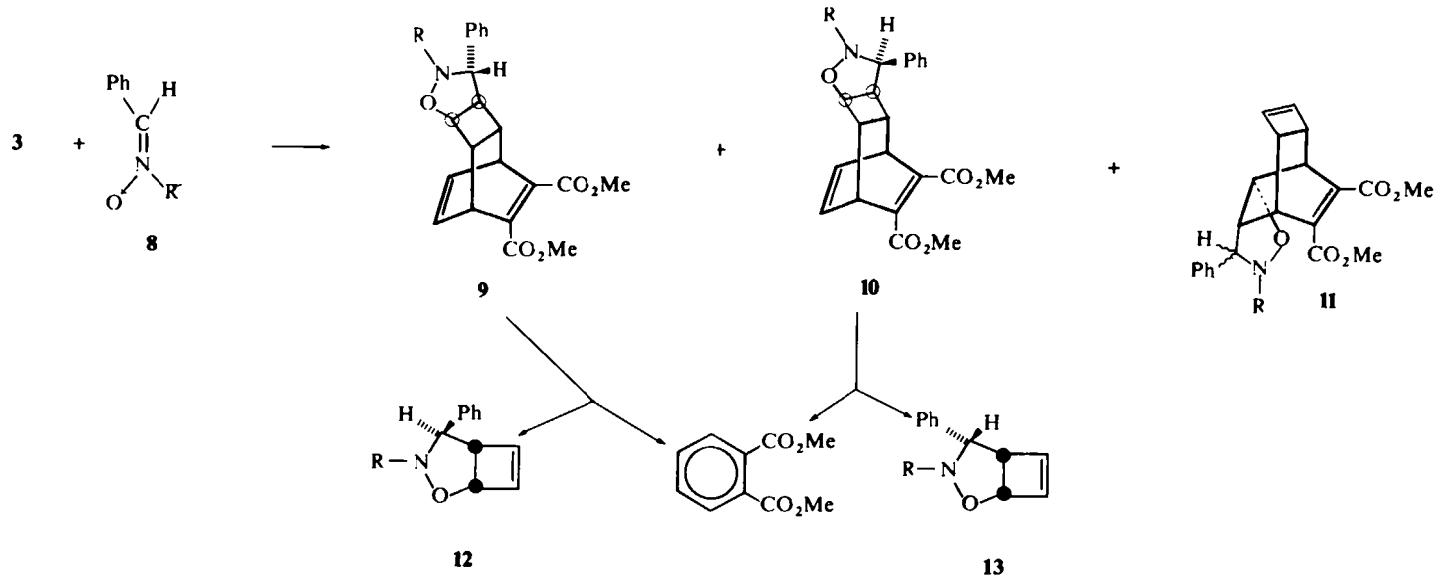
[a] Numbering refers to isoxazolidine ring; [b] In C_6D_6; [c] Signal cannot be identified with certainty; [d] In DMSO; [e] J = 2·68

we assign configuration *cis* to the couple **10a/13a** and configuration *trans* to the couple **9a/12a**. Analogously, the presence of the C-3 protons as singlets both in **2** and in **7** presumes a *trans* relationship between H-3 and H-4 in these compounds and in the related adduct **5**.

The isomeric adduct **4** shows for H-3 a doublet with J_{34} = 8·6 c/s. Since H-4 belongs also to 6-membered rings no definite conclusion on the stereochemistry of the C-3/C-4 junction can be drawn from the spectral data.

Analogous results have been obtained by reacting N,C-diphenylnitrone (**8b**) or

SCHEME 2



a: R = Me
b: R = Ph
c: R = p-ClC_6H_4

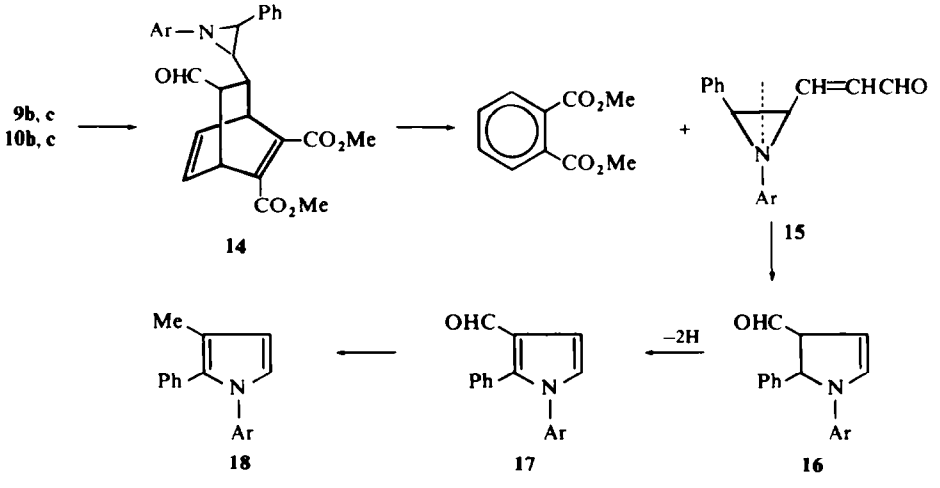
N-*p*-chlorophenyl-C-phenylnitrone (**8c**) with **3**: in both cases three monoadducts (**9**, **10**, **11b** and **c**) were obtained. In the latter case, however, the adduct **11c** was present only in traces and could not be purified. The compounds **9b** and **9c** show a singlet as signal of the C-3 proton, and were assigned the *trans* configuration with regard to the protons in 3 and 4 positions. On the contrary coupling constants J_{34} of 6·4 were ascertained for **10b** and **10c**, and therefore a *cis* configuration was deduced for them.

The presence of only one signal for the two OMe groups in the *trans*-isomers **9a–c**, is noteworthy whereas the *cis* isomers **10a–c** show two separate singlets. This latter fact may be attributed to a long-range shielding effect of the favourable sited phenyl ring at C-3 on one of the two OMe groups. This consideration confirms the above stereochemical assignments. Consistent with these facts, the same splitting of the —OMe signal is observed in the triphenylderivative **19** (see below).

Interestingly, the yield ratios of the two epimers are reversed passing from an N-methyl-nitrone (**9a/10a** = 2·4) to an N-aryl-nitrone (**9b/10b**/or **9c/10c** = 0·5). If we assume a one-step four-center process with a "two-planes" activated complex[9b] and take account of the *trans* relationship of the substituents in aldonitrones,[11] the higher steric demand of the N-aryl group in comparison with the N-methyl group, already noticed in the cycloaddition of nitrones with styrene, pushes the former group in a *transoid* position to the cyclobutene ring, whereas in the latter case a *cisoid* arrangement is preferred, the steric encumbrance of the C-phenyl group here prevailing. If we take this observation as a general rule, then an isoxazolidine H-3/H-4 *trans* relationship for **11a** and an H-3/H-4 *cis* configuration for **11b** and **11c** can be tentatively inferred.

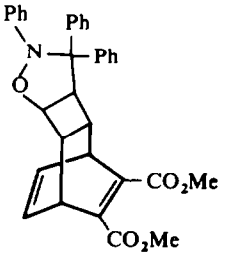
The retro-diene thermolysis of **9b** and **10b** led to dimethyl phthalate, to the epimers **12b** and **13b** respectively and to a new product, obtained from both starting compounds in yields up to 36%. Elemental analysis, IR and NMR spectral data, as well as Wolff-Kishner reduction to the known 1,2-diphenyl-3-methylpyrrole (**18**), identified the product as 1,2-diphenyl-3-formylpyrrole (**17a**). Starting from **9c** or **10c**, the aldehyde **17b** was analogously obtained, together with **12c** and **13c** respectively.

SCHEME 3

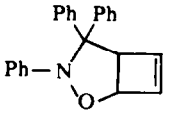


Although the formation of pyrrole derivatives by thermal ring opening and recyclization of 4-isoxazolines has been reported,[12-15] the thermal behaviour of isoxazolidines has been studied less. A plausible mechanism for the formation of **17** is given in Scheme 3. The valence rearrangement to the aziridine **14** would be followed by a retro-diene reaction to give the vinylogous formylaziridine **15**. This latter compound would undergo cleavage of the C—C bond to yield **16**, which finally dehydrogenates to the pyrrole aldehyde **17**. Therefore, when the nitrogen is aryl-substituted, the rate of the heterocyclic ring cleavage competes with the rate of the retrodiene reaction and even prevails in the case of the *cis* isomers **10b–c**. Although the few terms hitherto studied do not allow general conclusions, the thermolysis of cyclobutane-condensed isoxazolidines seems to be influenced strongly both by the nature of the substituent on the N atom and by the stereochemistry of the C-3 chiral center. The former influence has already been noted during a study on the thermolysis of the 4-isoxazolines.[12] Further experiments are in progress in order to study the nature of this substituent effect and to substantiate the cleavage mechanism.*

The cycloaddition of **3** to N,C,C-triphenylnitrone was more sluggish, and only a 16% yield of the monoadduct **19** was obtained, together with an equal amount of its



19



20

thermolytic product **20**. No by-product could be isolated in this case.

Our experimental results allow us to conclude that the nitrones, like nitrile oxides,[4] do not react with the carbethoxy-conjugated double bond of **3**. Contrary to nitrile oxides, which react faster with the cyclohexadiene double bond, acyclic nitrones add preferentially the cyclobutene double bond. This preference should mainly depend on the higher sensibility of the nitrones to steric factors. Consistent with this point of view is the large increase of the ratio between the total amount of **9** + **10** and the amount of **11** when the 1,3-dipole changes from N-methyl-C-phenylnitrone (3:1) to N,C-diphenylnitrone (13:1).

EXPERIMENTAL

All m.ps are uncorrected. IR spectra were recorded on a Perkin–Elmer 257 spectrophotometer as nujol mulls, the UV spectra on a Perkin–Elmer 135 recording spectrophotometer in 95% solns, and the NMR spectra on a Perkin–Elmer R-12A spectrometer with TMS as internal standard. Mycroanalyses were performed by Dr Lucia Maggi Dacrema. TLC were run on precoated silica gel G (Merck) plates and developed with H_2SO_4 (1:1; 100 ml)—CrO_3 (3 g). When a mixture of products was obtained, column

* An alternative pathway might consider **12** and **13** respectively as intermediates. This seems less probable, at least as exclusive route, since the thermal breakdown of **12** and **13** under similar experimental conditions led to different results, on which we will report later

TABLE 2. CHARACTERIZATION DATA OF POLYCYCLIC ISOXAZOLIDINES

Compd	M.p. °C	Recrystal. solvent	% Yield	Elemental analyses						
				Calc. %			Formula	Found %		
				C	H	N		C	H	N
2	99–100	Petrol ether	50	81·2	6·8	5·6	$C_{17}H_{17}NO$	80·9	6·9	5·6
4	153–154	EtOH-cyclohexane	37·5	70·2	5·9	3·6	$C_{23}H_{23}NO_5$	70·2	5·8	3·6
5	152–153	EtOH-cyclohexane	43	70·2	5·9	3·6	$C_{23}H_{23}NO_5$	70·3	5·9	3·8
7	165–166	EtOH	82	69·9	6·4	3·5	$C_{23}H_{25}NO_5$	69·6	6·5	3·5
9a	131–132	Cyclohexane	43	69·3	6·1	3·7	$C_{22}H_{23}NO_5$	69·7	6·3	3·7
9b	158–159	EtOH	26·7	73·1	5·7	3·2	$C_{27}H_{25}NO_5$	72·7	5·7	3·3
9c	183–184	EtOH-benzene	25	67·8	5·1	2·9	$C_{27}H_{24}ClNO_5$	67·3	5·2	3·1
10a	134	Cyclohexane	17·7	69·3	6·1	3·7	$C_{22}H_{23}NO_5$	69·65	6·2	3·7
10b	142–143	EtOH	54·4	73·1	5·7	3·2	$C_{27}H_{25}NO_5$	72·9	5·8	3·4
10c	156–157	EtOH	57	67·8	5·1	2·9	$C_{27}H_{24}ClNO_5$	67·4	5·2	2·9
11a	128–129	Cyclohexane	22	69·3	6·1	3·7	$C_{22}H_{23}NO_5$	68·9	6·2	3·6
11b	162–163	EtOH	6	73·1	5·7	3·2	$C_{27}H_{25}NO_5$	72·7	5·5	3·2
12a picrate	178–179 dec.	EtOH	78	51·9	3·9	13·5	$C_{18}H_{16}N_4O_8$	52·1	4·1	13·4
12b	143–144	MeOH	*	81·9	6·1	5·6	$C_{17}H_{15}NO$	82·4	5·8	5·5
12c	88–90	Petrol ether	*	72·0	5·0	4·9	$C_{17}H_{14}ClNO$	72·3	5·2	5·0
13a	38–39	Petrol ether	73	77·0	7·0	7·5	$C_{12}H_{13}NO$	77·2	7·0	7·4
13b	80–81	Petrol ether	*	81·9	6·1	5·6	$C_{17}H_{15}NO$	82·1	6·1	5·7
19	185–192	EtOH	16	76·3	5·6	2·7	$C_{33}H_{29}NO_5$	76·1	5·7	2·7
20	152–153	EtOH	17	84·9	5·9	4·3	$C_{23}H_{19}NO$	84·6	6·3	4·5

* See Experimental

chromatography was carried out on silica gel H (Merck) with one of the following cyclohexane/AcOEt eluant systems: A (7:3), B (4:1), C (9:1). Characterization and analytical data of unknown compounds are collected in Table 2.

Cycloaddition of 3,4-*dihydroisoquinoline* N-*oxide to COTE.* 3,4-Dihydroisoquinoline N-oxide (0·85 g) and COTE in excess were heated under N_2 at 65° for 26 hr. The crude mixture was separated by column chromatography (eluant C). Besides a by-product, m.p. 117–118° (0·165 g), which was not further investigated, the adduct **2** (0·73 g) was thus obtained; λ_{max} 268·5 nm (1 g ε 3·50) and 274 nm (1 g ε 3·54).

Reaction of **2** *with dimethyl acetylenedicarboxylate.* A mixture of dimethyl acetylenedicarboxylate (0·07 g) and **2** (0·07 g) in benzene (3 ml) was left for 48 hr at r.t. After evaporation of the solvent, the residue was slurried with little EtOH. The separated solid (0·08 g; 73%) was identical (IR and mixed m.p.) with **5** obtained as described.

Dimethyl tricyclo[4.2.2.0^{2,5}]*deca*-3,7,9-*triene*-7,8-*dicarboxylate.* (**3**) The method was adapted from a known procedure.[16] COTE (23 g) and dimethyl acetylenedicarboxylate (28 g) were heated for 7 hr at 140°. Distillation under reduced press (124–128°/0·4 mm) followed by column chromatography (eluant C) gave pure **3** (40%; m.p. 52–53°, lit.[7] 50–53°).

Reaction of dimethyl tricyclo[4.2.2.0^{2,5}]*deca*-3,7,9-*triene*-7,8-*dicarboxylate* (**3**) *with nitrones*

(a) 3,4-*Dihydroisoquinoline* N-*oxide* (**1**). A soln of **1** (0·36 g) and **3** (1·2 g) in benzene (10 ml) was refluxed for 5 hr. The mixture was separated by column chromatography (eluant A). Adducts **4** (0·36 g) and **5** (0·41 g) were thus obtained.

(b) N-*Methyl*-C-*phenylnitrone* (**8a**). A soln of **8a** (1·0 g) and **3** (3·65 g) in benzene (15 ml) was refluxed for 150 hr. The solvent was evaporated and the residue separated by column chromatography (eluant A). The following products were successively eluted: unreacted **3**, **10a** (0·50 g), **11a** (0·62 g) and **9a** (1·22 g). Compounds **9a**, **10a** and **11a** gave the corresponding yellow picrates m.p. 169–171°, 168–169° and 180–181° respectively.

(c) N,C-*Diphenylnitrone* (**8b**). A soln of **8b** (3·0 g) and **3** (7·5 g) in benzene (30 ml) was refluxed for 31 hr. The mixture was separated by column chromatography (eluant B). The following compounds were successively eluted: **11b** (0·4 g), **9b** (1·8 g) and **10b** (3·67 g).

(d) N-p-*Chlorophenyl*-C-*phenylnitrone* (**8c**). A soln of **8c** (1·15 g) and **3** (2·46 g) was refluxed in benzene (15 ml) for 41 hr. After evaporation of the solvent, the residue was dissolved in MeOH (30 ml), yielding **9c** (0·41 g) as an insoluble solid. The concentrated mother liquor gave a further crude ppt which, after crystallization from MeOH, yielded **10c** (0·93 g). The residue from the combined mother liquors were subjected to column chromatography (eluant B), thus yielding, besides some unreacted **3**, further amounts (0·19 g) of **9c** and **10c** (0·43 g). Traces of a third isomer (**11c**) were also detected by NMR analysis (Table 1).

(e) N,C,C-*Triphenylnitrone.* N,C,C-Triphenylnitrone (0·55 g) and **3** (0·5 g) were refluxed in toluene (10 ml) for 240 hr. The crude mixture was separated by column chromatography (eluant C), yielding unreacted starting nitrone (0·07 g), unreacted **3** (0·2 g), **20** (0·1 g) and **19** (0·15 g). Small amounts of by-products were isolated but not further investigated; NMR of **19**: 3·66 and 3·77 s (6H; —OMe), 6·58 m (2H, = C—H) ppm.

Reaction of **1** *with* **6**. A soln of **1** (0·5 g) and **6** (0·85 g) in benzene (15 ml) was refluxed for 18 hr. After evaporation of the solvent, the residue was slurried with a little MeOH and **7** (1·10 g) was filtered off.

(1RS, 4RS, 5RS)-3-*Methyl*-2,3-*oxaza*-4-*phenylbicyclo*[3.2.0]*hept*-6-*ene* (**13 a**). Compound **10 a** (0·51 g) was heated under reflux in xylene (15 ml) under N_2 for 24 hr. Column chromatography (eluant B) gave **13a** (0·18 g) and dimethyl phthalate (0·2 g).

(1RS, 4SR, 5RS)-3-*Methyl*-2,3-*oxaza*-4-*phenylbicyclo*[3.2.0]*hept*-6-*ene* (**12a**). Compound **9a** (0·81 g) was heated under reflux in xylene (15 ml) for 72 hr. Column chromatography (eluant A) gave **12a** (0·31 g), an oily product, and dimethyl phthalate (0·3 g). The picrate of **12a** was crystallized from EtOH to give yellow needles, m.p. 178–179°.

(1RS, 4RS, 5RS)-3,4-*Diphenyl*-2,3-*oxazabicyclo*[3.2.0]*hept*-6-*ene* (**13b**). Compound **10b** (0·50 g) was heated in a sublimator at 140°/0·2 mm (oil bath temp) for several hr. The sublimate was separated by chromatography (eluant C) to give **13b** (0·06 g; 22%), **17a** (0·07 g; 26%) and dimethyl phthalate. Spectral data of **17a**: M^+ 247; IR: ν_{max} 2760 w and 1665 s (—CHO cm^{-1}); UV: λ_{max} 241 nm (1 g ε 4·23) and 271 nm (1 g ε 4·19); NMR: δ 6·9 m (2H, H-4 and H-5 of the pyrrole ring), 7·0–7·5 m (10H, aromatics), 9·76 s (1H, —CHO) ppm.

Thermolysis of **10b** in boiling xylene for 12 hr under N_2 gave **13b** and **17a** in 18% and 36% yields respectively, along with dimethyl phthalate.

(1RS, 4SR, 5RS)-3,4-*Diphenyl*-2,3-*oxazabicyclo*[3.2.0]*hept*-6-*ene* (**12b**). Compound **9b** (0·4 g) was heated at 160°/0·2 mm (oil bath temp) for several hr in a sublimator. Chromatographic separation (eluant C) gave **12b** (0·1 g, 44·5%), **17a** (0·03 g, 13%) and dimethyl phthalate. Compounds **12b** (28%) and **17a** (24%) were also obtained together with dimethyl phthalate by boiling **9b** in xylene for 26 hr.

Thermolysis of **9c** *and* **10c**. Compounds **9c** and **10c** were heated in sublimator under a pressure of 0·1 mm with an oil bath temp of 180° and 155–160° resp. Chromatographic separation of the sublimate from **10c** gave **13c**, m.p. 104° (0·05 g, 16%) and **17b** (0·1 g, 32%), whereas **9c** gave **12c** (0·14 g, 47%) and **17b** (0·035 g, 12·5%). From both cases dimethyl phthalate was isolated. Spectral data of **17b**: IR: ν_{max} 2760 w, 1665 s (—CHO) cm^{-1}; UV: λ_{max} 243·5 nm (1 g ε 4·23) and 270 nm (1 g ε 4·20); NMR: δ 6·91 s (2H, H-4 and H-5 of pyrrole ring), 7·0–7·5 m (9H, aromatics), 9·73 s (1H, —CHO) ppm.

3,4,4-*Triphenylbicyclo*[3.2.0]*hept*-6-*ene* (**20**). By boiling **19** for 17 hr in xylene, **20** was obtained in 80% yield. Compound **20** was easily separated from the accompanying dimethyl phthalate by chromatography (eluant A); NMR: δ 4·44 m (1H, H-1), 5·5 m (2H, H-5 and =CH—), 6·32 m (1H, =CH—) ppm.

1,2-*Diphenyl*-3-*methylpyrrole*. 1,2-Diphenylpyrrole-3-carboxyaldehyde (0·2 g) was added at r.t. with a mixture of KOH (0·5 g), 90% hydrazine hydrate (0·4 ml) and diethylene glycol (10 ml). The mixture was refluxed for 15 min and then distilled. The distillate (8 ml) was diluted with water and extracted with ether. The ethereal extract was dried over $MgSO_4$, distilled and 1,2-diphenyl-3-methylpyrrole (0·05 g) was obtained as an oily product (lit.[17] m.p. 37–38°). 1,2-Diphenyl-3-methylpyrrole was shown to be identical with an authentic sample obtained by the known method by IR and NMR. NMR: δ 6·25 d (1H, H-5, $J_{4,5}$ = 2·6 c/s), 6·88 d (1H, H-4), 7·0–7·4 m (10H, aromatics), 2·19 d (3H, Me, J_{Me-4} = 0·5 c/s) ppm

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