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# THE SYNTHESIS AND DECOMPOSITION OF 3-*p*-NITROPHENYL-3,4,5-TRIAZATRICYCLO(5.2.1.$0^{2,6endo}$)DEC-4-ENE[1]

## TRIAZOLINE THERMOLYSES

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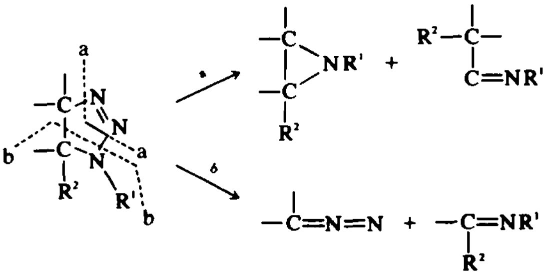
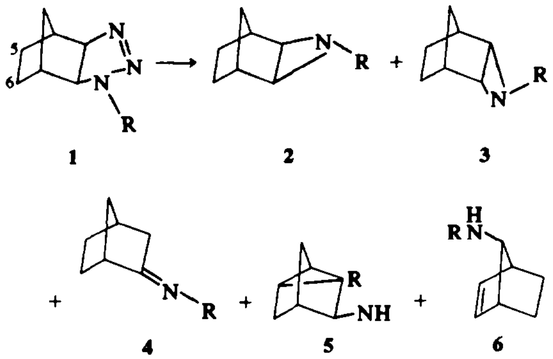
**Abstract**—A stereospecific synthesis of the *endo* triazoline **20** has been accomplished by the sequential conversion of norbornylene to the oxime of 3-*exo*-chloronorbornanone followed by reduction of its acetate or *p*-nitrobenzoate with diborane to give 2-*endo*-amino-3-*exo* chloronorbornane, then coupling of the latter with *p*-nitrobenzene diazonium chloride to give diazoamine **19**, which was cyclized with ethanolic sodium ethoxide in the presence of silver nitrate. Photolysis of *endo* triazoline **20** gave exclusively *endo* aziridine **3** (R = *p*-$NO_2C_6H_4$), while on pyrolysis in decalin at 165–170° there was obtained *endo* aziridine **3**, *exo* axiridine **2**, imine **4** and a large amount of polymer. Under identical conditions, the isomeric *exo* triazoline **1** (R = *p*-$NO_2C_6H_4$) gave *exo* aziridine **2**, *endo* aziridine **3**, imine **4** and no polymer. The "triazoline-aziridine inversion" is presumed to occur via the diazoimine intermediate **7**. While photolysis of *exo* triazolines **23** and **24** and pyrolysis of **23** gave, as expected, the corresponding *exo* aziridines **25** and **26**, pyrolysis of **24** appears to have given the isoxazoline **28**. Evidence for the intermediacy of the diazoimine **27** in the formation of **28** is presented.

Triazoline decomposition has been the subject of a recent excellent review[3] and the overall results of the thermal decompositions can be summarized as outlined in Scheme 1. Bicyclic triazolines decompose to give predominantly aziridines and/or imines as originally shown by Alder *et al.*[4] These pyrolyses are considerably more complicated than originally assumed and the product distributions appear to be dependent on a number of structural and experimental factors. Thus, in the reaction of norbornylene with benzenesulfonyl azide at room temperature, a reaction known to involve a transient *exo*-triazoline,[3] only *exo*-aziridine **2** (R = $SO_2C_6H_5$) was previously reported.[5] However, we now know that even this reaction is extremely sensitive to experimental conditions, giving substantial amounts of *endo*-aziridine and imine at elevated temperatures and in the presence of certain solvents and surfaces (Scheme 2).[6] On the other hand, the thermal reaction of norbornylene in refluxing toluene with diethyl phosphorazidate is reported to give only phosphoramidate **4** ($R = \overset{O}{\overset{\uparrow}{P}}(OEt)_2$), again via a transient *exo*-triazoline.[7] Pyrolysis of the isolatable *exo*-triazoline **1** (R = Ph) in decalin at 160° reportedly gave *exo*-aziridine **2** (49%), imine **4** (18%) *endo*-aziridine **3** (9%) and rearranged amines **5** (10%) and **6** (11%).[8] Changing the solvent to DMSO in the latter case resulted in a substantial increase in imine (42%) and decrease in *exo*-aziridine (36%). Pyrolysis of *exo*-triazoline **1** (R = $CO_2CH_3$) in decalin at 114° gave similar results: **2** (52%), **3** (7%), **4** (36%), **5** (1%), **6** (5%).[9]

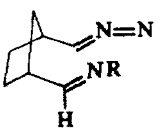


Scheme 1

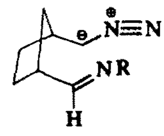


Scheme 2

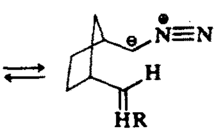
The formation of *endo*-aziridine **3** from *exo*-triazoline **1**, which we shall henceforth refer to as "triazoline-aziridine inversion" is particularly intriguing. This "inversion" was first reported in the reactions of *cis*-*endo*- and *cis*-*exo*-norbornene-5,6-dicarboxylic acid anhydrides and the corresponding *cis-exo*-dimethyl ester with benzenesulfonyl azide in refluxing carbon tetrachloride. In these cases, the inverted *endo*-aziridine was the major product (68–76%) and the *exo*-aziridine was the only other product.[10] This striking "triazoline-aziridine inversion" was not observed in the case of the isomeric 5,6-*cis-exo*-dimethyl ester, where the *exo*-aziridine was exclusively formed, apparently due to steric inhibition and unfavorable entropy.[10] Similarly, pyrolysis of the isolatable triazoline **1** (R = Ph, *exo*-anhydride at C-5, C-6) in decalin at 160° gave 46% *exo*-aziridine **2** and 54% *endo*-aziridine **3**.[10] We have previously suggested that *endo*-aziridines arise from *exo* triazolines via diazoimine intermediates **7**.



**7a**

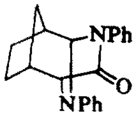


**7b**

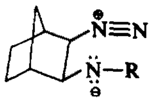


**7c**

Indeed, such a diazoimine is seen to arise by path *b* of Scheme 1, a well-established decomposition pathway in the reaction of arylsulfonyl azides with linear amines[3,11] and can be considered a "diazo transfer" process.[3,12] Similarly, Baldwin *et al.*[13] suggested a diazoimine intermediate in the formation of lactam **8**, when the phenyl azide-norbornene adduct **1**, (R = Ph) was decomposed in phenyl isocyanate.



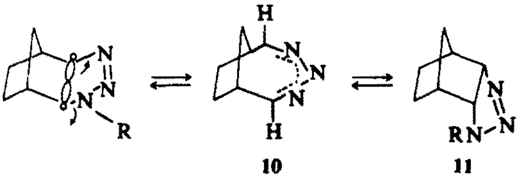
**8**



**9**

The exact mechanism(s) of the formation of the diazoimine intermediate remains in question. Thus it may arise stepwise via a diazonium betaine **9** as previously suggested[3,8–10] or directly via a thermally allowed disrotatory ring opening as illustrated in Scheme 3. On the other hand, the "triazoline-aziridine inversion" could conceivably take place by a thermally allowed electrocyclic ring opening to give first an *endo*-triazoline **11** which would then lose nitrogen to give the *endo*-aziridine (Scheme 4).

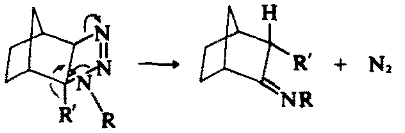
Scheme 3



Scheme 4

However, this pathway seems less likely in view of the large amount of strain to be expected in an intermediate such as **10**. Attempts to detect the conversion of an *exo*-triazoline into an *endo*-triazoline by observing the characteristic splitting patterns of the C-2, C-3 protons in the NMR have thus far failed.[14]

The formation of imine **4** may occur via the diazonium betaine intermediate **9** or by a concerted mechanism as illustrated in Scheme 5. Such a concerted mechanism has previously been postulated to account for the cyclic amidines obtained in the reaction of tosyl azide with nitrogen heterocycles such as 1,2-dimethyl-$\Delta^2$-tetrahydropyridine.[11b] On the other hand, Berlin *et al.*[15] have proposed that a 2,3-*endo-endo* migration of a methyl group occurs via a diazoimine intermediate similar to **9** in the reaction of diethyl phosphorazidate and 2-methyl-2-norbornene. In this particular case, it has been proposed that the diazonium ion is stabilized in a special manner by the highly polarized P→O function and kinetics of the related reaction with norbornene[7] clearly are not consistent with a concerted elimination of nitrogen as indicated in Scheme 5.



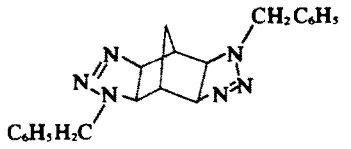
Scheme 5

In the reactions of benzenesulfonyl azide with various bicyclic olefins such as norbornene,[5] bicyclo(2.2.2)octene,[16] dicyclopentadiene,[16] norbornadiene,[16] *cis-endo-* and *cis-exo*-norbornene-5,6-dicarboxylic acid anhydrides and methyl esters,[10] no amine products such as **5** or **6** have thus far been reported. In the case of the norbornyl derivatives with ester or anhydride functions at C-5 and C-6, only aziridine products have been observed, and as previously mentioned, the product distribution in the reaction of norbornene with benzenesulfonyl azide is dependent on the nature of the solvent, the temperature and apparently trace metals.[6]

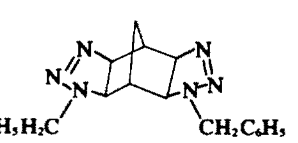
With the above mentioned background, in particular the uncertainties involved in the "*exo*-triazoline-*endo*-aziridine inversion", we undertook to develop a general synthetic route to the heretofore unknown bicyclic *endo* triazolines in order to determine if such an "inversion" would also occur in these isomeric compounds. *Endo*

(3 + 2) cycloadditions of 1,3-dipoles to norbornene are unknown.[4,17] When *exo* approach of the 1,3-dipole is blocked by substituents on the C-7 methylene group, as in the case of apobornylene, no azide addition occurs;[4] we have further verified these conclusions.[6]

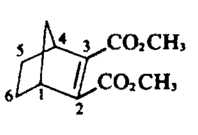
In the (3 + 2) cycloaddition of norbornadiene and phenyl azide, approx. 5% of the 1 : 1 *endo*-adduct has been reported, whereas with excess phenyl azide again only about 5% of 1 : 2 *exo* : *endo*-products were reported and no *endo* : *endo* products.[18] In spite of the previously mentioned low yields, we decided to reinvestigate the possibility of obtaining an *endo*-triazoline from norbornadiene by a (3 + 2) cycloaddition. We chose benzyl azide as the 1,3-dipole since it offered the possibility of providing an easily removable group for the potential syntheses of *endo*-triazolines by the sequence: (1) isolation of *endo*-triazoline from the (3 + 2) cycloaddition; (2) photolysis to yield the N-benzyl-aziridine;[3,17,19] (3) hydrogenolysis to give the unsubstituted aziridine and (4) isomerization of derived 1-arylazoaziridines to give 1-aryl-$\Delta^2$-1,2,3-triazolines as previously described by Heine and Tomalia.[20] In actual fact, no *endo*-triazolines could be isolated from the reactions of norbornadiene and benzyl azide under a variety of conditions and the only crystalline products obtained were the *anti*-*exo*-*exo*-ditriazoline **12** and the *syn*-*exo*-*exo*-ditriazoline **13**. That both ditriazolines (**12** and **13**) contained only *exo*-triazoline rings was apparent from the C-2—C-3 and C-5—C-6 NMR couplings in each case (J = 9 Hz) and the assignment of the *anti* arrangement in **12** was based on the equivalence of the two bridgehead protons at C-1 and C-4 (δ 2·60) in this case and their non-equivalence (δ 1·97 and 3·08) in the case of **13**. The highest observed mass spectral ion in both **12** and **13** was at *m/e* 302, corresponding to $M^+$-$2N_2$.



**12**



**13**

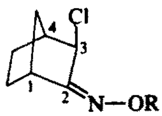


**14**: $\Delta^5$
**15**: dihydro $\Delta^5$

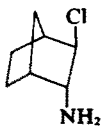
In other attempts to arrive at *endo* triazolines, N-aminophthalimide was oxidized with lead tetraacetate[21] in the presence of bornylene but no aziridine could be detected in the products. When dimethyl bicyclo(2.2.1)-hepta-2,5-diene-2,3-dicarboxylate (**14**) was treated with phenylazide, the only isolatable product was dimethyl-1-phenyl-1,2,3-triazole-4,5-dicarboxylate presumably formed by a retro (4 + 2) cycloaddition. On the other hand, the dihydro isomer **15**, as seen in the sequel, readily reacts with phenyl azide to give a triazoline which thermally decomposes by an entirely different pathway only at elevated temperatures. In the latter case the retro (4 + 2) cycloaddition pathway is not available to the triazoline. The mass spectrum of the above mentioned aromatic product, showed a large $M^+$ ion at *m/e* 261 (63%). By comparison, the much less stable triazolines we have studied, as expected, never show an $M^+$ ion, and usually only a weak ion at $M^+$-$N_2$. Not surprisingly, a (4 + 2) cycloaddition of cyclopentadiene and 1-benzyl-1,2,3-triazole failed as did the reaction of 2-imidazolone with cyclopentadiene.

With the lack of success of the preceding pathways, it was decided that an entirely different approach would be pursued which would involve constructing a norbornyl intermediate containing a C-2 *endo* amino group and an *exo* C-3 group which could be readily displaced intramolecularly either by the C-2 *endo* amino group directly or by a diazoamino group derived from the amino group. In the former case, an *endo*-aziridine would be obtained, which it was visualized could be converted into the desired *endo*-triazoline by the method of Heine and Tomilia,[20] while in the latter case, the triazoline would be obtained directly.

Since 3-*exo*-chloronorcamphor oxime (**16**) had been previously reported[22,23] this seemed the obvious starting point for our synthetic sequence. The oxime **16** was not reduced to the desired amine with rhodium on alumina and was therefore converted into its acetate **17**, which was shown to be a mixture of *syn* and *anti* forms by the presence of one bridgehead proton in two different environments (δ 3·48 (0·6) and δ 3·03 (0·4)) and an acetyl group in two different environments (δ 2·10 and δ 2·07). A word of caution must be added at this point with regard to potential users of 3-chloronorcamphor oxime acetate and the corresponding *p*-nitrobenzoate. These compounds produced severe allergic reactions in all individuals whose skins were exposed to them! Attempted hydrogenation of the oxime acetate with rhodium on carbon gave the same unidentified product as obtained from the oxime but not the desired amine, while reduction with sodium borohydride, interestingly, gave norcamphor oxime as a similar mixture of *syn* and *anti* forms. In the latter case, the intermediate anion of 3-chlororonorcamphor oxime apparently eliminates chloride ion to give 2-nitroso-2-norbornene, which rearranges to the more stable tautomer norcamphor oxime.



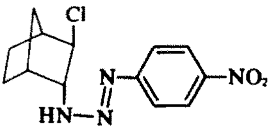
**16**: R = H (*syn* & *anti*)
**17**: R = $COCH_3$ (*syn* & *anti*)



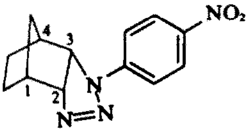
**18**

Since it had been reported that oxime esters could be reduced to amines with diborane,[24] the latter, in a stream of nitrogen, was passed through a tetrahydrofuran solution of 3-*exo*-chloronorcamphor oxime acetate. The amine product was isolated in 17% yield as its hydrochloride salt and basification gave the free amine. While the NMR spectrum of the amine indicated that it was in fact the desired 2-*endo*-amino-3-*exo*-chloronorbornane, assignment of the amino group to an *endo* configuration could not be made conclusively, at this point, since the C-2 and C-3 hydrogen signals overlapped. Conclusive proof of the stereochemical assignment, however, was found in the ultimate conversion of this chloroamine to the desired *endo*-triazoline by an intramolecular displacement of the *exo*-chloro group as discussed below. By use of the oxime *p*-nitrobenzoate instead of the corresponding acetate, the yield of chloroamine was increased to 41%.

As previously mentioned, Heine and Tomilia[20] had previously reported the coupling of aryl diazonium salts with unsubstituted aziridines to give diazoaziridines which were isomerized to the 5-membered ring triazolines via an intermediate ambident anion formed by treatment of the diazoaziridine with the nucleophilic iodide ion.[25] By coupling 2-*endo*-amino-3-*exo*-chloronorbornane with an aryldiazonium salt and treatment of the derived diazoamine with base, we would arrive at a similar intermediate ambident anion possessing the required stereochemistry for closure to an *endo* triazoline. Indeed, coupling with the diazonium salt of *p*-nitroaniline proceeded readily to give the desired diazoamine **19** in good yield (m.p. 112–115° dec). Unfortunately, we were not able to obtain a good yield of the corresponding phenyl (instead of *p*-nitrophenyl) diazoamine under similar experimental conditions. The mass spectrum of **19** was interesting in that it was very similar to that of the *endo*-triazoline **20**, ultimately obtained as described below, suggesting that **19** cyclizes to the triazoline under the mass spectrometric conditions.



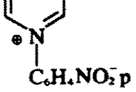
**19**



**20**

Treatment of **19** with base indeed gave the desired ambident anion as indicated by the formation of a deep red colored solution. However, the desired intramolecular displacement of chlorine was only observed (dissipation of red color) when silver nitrate was added to the solution. Formation of the desired *endo*-triazoline **20** was readily accomplished by adding an equal molar solution of ethanolic silver nitrate to an ethanolic solution of **19** containing sodium ethoxide. Upon addition of the silver nitrate solution, the deep red color changed to yellow. In this manner a 64% yield of crystalline *endo*-triazoline **20** was obtained. The NMR spectrum clearly showed that the product was indeed the *endo*-triazoline **20** by the presence of two low field multiplets (doublets of doublets) centered at $\delta$ 5·09 and $\delta$ 4·02 with coupling constants of J = 12·0, 5·50 Hz and J = 12·0, 4·25 Hz respectively. These multiplets could be assigned to the C-2 and C-3 protons of **20**, respectively, with the larger coupling of 12 Hz corresponding to $J_{2,3}$ while the smaller couplings correspond to $J_{1,2}$ = 5·50 Hz and $J_{3,4}$ = 4·25 Hz. By contrast, the isomeric *exo* triazoline (**1**, R = *p*-$NO_2C_6H_4$), prepared as previously described[26] by the (3 + 2) cycloaddition of *p*-nitrophenyl azide to norbornene shows in its NMR spectrum the C-2 and C-3 protons as a pair of doublets ($J_{2,3}$ = 9 Hz) centered at $\delta$ 4·77 and $\delta$ 3·79 respectively with $J_{1,2} \cong J_{3,4} \cong 0$ as expected.

It should be mentioned that diborane reduction of chlorooxime acetate **17** or the corresponding *p*-nitrobenzoate on a small scale appeared to be stereospecific, giving repeatedly, after coupling and cyclization, only the *endo*-triazoline, while a single attempt to scale up (10×) reduction of the *p*-nitrobenzoate of the oxime gave some *exo*-triazoline (Experimental). Photolysis of a 2:1 mixture of *endo*- and *exo*-triazolines **20** and **1** (R = *p*-$NO_2C_6H_4$), respectively, gave a 2:1 mixture of *endo*- and *exo*-aziridines **3** and **2** (R = *p*-$NO_2C_6H_4$), respectively, while photolysis of pure **1** (R = *p*-$NO_2C_6H_4$) gave, as previously reported,[19] exclusively the *exo* aziridine **2** (R = *p*-$NO_2C_6H_4$). The *endo* aziridine **3** (R = *p*-$NO_2C_6H_4$) collected by preparative gas-liquid-chromatography, from the above mentioned mixture showed the expected characteristic NMR spectrum[10] with the equivalent C-2 and C-3 protons appearing as a triplet (J = 1 Hz) centered at $\delta$ 2·93. By contrast, in the NMR spectrum of the isomeric *exo*-aziridine **2** (R = *p*-$NO_2C_6H_4$) these protons appear as a singlet at $\delta$ 2·42. Similarly, the *exo*-aziridine showed the characteristic[10] high field position of the *anti* C-8 proton ($\delta$ 0·87) which was absent in the *endo* aziridine. One interesting aspect of the mass spectra of *endo*- and *exo*-aziridines **3** and **2** (R = *p*-$NO_2C_6H_4$) was the appearance of a base peak at *m/e* 201 in each case, which may be due to ion **21**. By contrast, the isomeric imine **4** (R = *p*-$NO_2C_6H_4$), obtained as described below, showed only a very small ion at *m/e* 201.



**21**

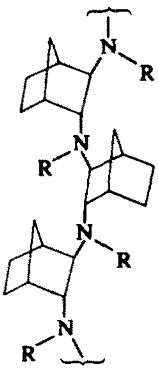
Finally, the *endo* and *exo* triazolines **20** and **1** (R = *p*-$NO_2C_6H_4$) respectively were each pyrolyzed in decalin at 165–170° for 2 hr and the results obtained are outlined in Table 1. The Table shows the percent products determined by glc analysis. The *endo*- and *exo*-aziridines were identified by GLC comparisons with authentic samples and by comparison of the NMR spectra of the pyrolysate product mixture with those of authentic samples of *endo* and *exo* aziridines. The imine was identified by GLC comparison with an authentic sample and by GLC comparison of its hydrolysis products with *p*-nitroaniline and norcamphor. From previous work it was

Table 1. Pyrolysis products (%) at 165–170° in Decalin

| Triazoline | *endo* Aziridine (3)* | Imine (4)* | *exo* Axiridine (2)* | Non-volatile products |
|---|---|---|---|---|
| *exo* (1)* | 8·8 | 42·3 | 48·5 | 0 |
| *endo* (20) | 3·7 | 10·0 | 7·3 | 79 |

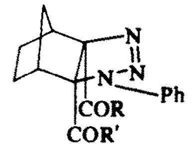
*R = $p$-NO$_2$C$_6$H$_4$

to be expected that all products from the pyrolysis of *exo*-triazoline **1** (R = $p$-NO$_2$C$_6$H$_4$) would be GLC volatile and the results of this pyrolysis correlate well with earlier observations of similar pyrolyses of *exo*-triazolines.[8-10] The large amount of GLC non-volatile material produced in the pyrolysis of the *endo*-triazoline under these conditions may be due to the formation of polymeric material such as **22**, the polymerization initiation being due to nucleophilic attack on the relatively unhindered *exo* face of the strained *endo*-aziridine or the *endo*-triazoline. It should be noted that the *endo*-triazoline was observed to lose nitrogen about thirty degrees lower (135–140°) than the *exo*-triazoline and, since it was necessary to heat the *exo*-triazoline at 165–170° to observe its decomposition, this higher temperature could account for the large amount of polymeric material produced in the case of the *endo*-triazoline. The formation of the same products in the pyrolyses of *endo*- and *exo*-triazolines **20** and **1** (R = $p$-NO$_2$C$_6$H$_4$) respectively and, in particular, the observation of the "triazoline-aziridine" inversion—that is, formation of *exo*-aziridine from *endo*-triazoline in this case adds further support to the postulation of a diazoimine intermediate (**7**) in these "triazoline-aziridine" inversions.

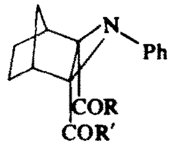


**22**

In order to gain more insight into the mechanism by which the proposed diazoimine intermediate **7** is formed in these "triazoline-aziridine" inversions and, in particular, the nature of the carbon-carbon bond fission either from **9** or directly as in Scheme 3 or Scheme 4, we decided to study the pyrolyses of triazolines **23** and **24**. Anhydride **23** was prepared by the (3 + 2) cycloaddition of phenyl azide to bicyclo(2.2.1)-2-heptene-2,3-decarboxylic anhydride as previously described[4] while the corresponding diester **24** was prepared by a similar cycloaddition to dimethyl bicyclo(2.2.1)-2-heptene-2,3-dicarboxylate. As expected, neither **23** nor **24** showed a molecular ion (M$^+$) in its mass spectrum, but **23** showed a relatively large ion at M$^+$-N$_2$ ($m/e$ 255, 69%) while the more flexible **24** showed only a small M$^+$-N$_2$ ion ($m/e$ 301, 10%). Photolysis of **23** gave, as previously reported,[19] solely the corresponding *exo*-aziridine **25**, while photolysis of **24** similarly gave a single product, identified as the dimethyl ester **26**. Similarly, pyrolysis of anhydride **23** at 163 ± 2° in decalin gave solely *exo*-aziridine **25**, indicating that "triazoline-aziridine" inversion in this non-flexible anhydride did not occur. Clearly formation of intermediate **7** (via **9** or Scheme 3) or the electrocyclic ring opening illustrated in Scheme 3 should be extremely difficult in a molecule such as **23**. It therefore was of particular interest to investigate the pyrolysis of the electronically similar but structurally more flexible molecule **24**.

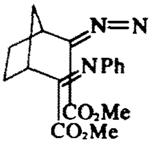


**23**: R = R' = O
**24**: R = R' = OMe



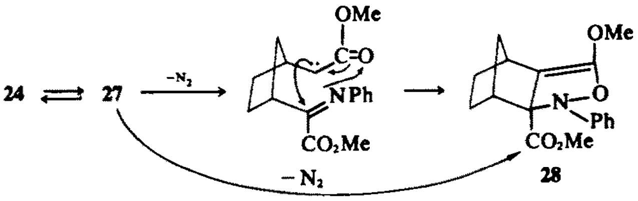
**25**: R = R' = O
**26**: R = R' = OMe

When triazoline **24** was heated in decalin at 162 ± 2°, the decalin removed at reduced pressure and the residue quickly chromatographed on silica gel, a foul-smelling yellow oil was eluted in benzene, the IR spectrum of which showed $\nu_{max}^{neat}$ 2120, 1720, 1695, 1630, 1595 cm$^{-1}$ and $\lambda_{max}^{2\text{-propanol}}$ 233, 238, 244 and 251 nm. On standing a short time at room temperature or even in the refrigerator the band at 2120 cm$^{-1}$ disappeared and all attempts to purify and characterize this material failed. However, the above spectral observations are consistent with a structure such as **27**, providing additional support for the previously suggested diazoimine type intermediate **7**.[8]



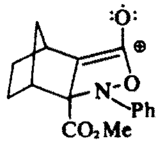
**27**

Gas chromatographic analysis of the above mentioned decalin solution after pyrolysis of triazoline **24** showed the presence of one major (75%) component and at least 7 minor components. Mixed injection with *exo* aziridine **26** showed that it was not one of the components of the product mixture. The major product decomposed when subjected to column or TLC but could be collected by preparative GLC. However, it decomposed rapidly on standing at room temperature. Its IR spectrum indicated it contained an ester CO group (1725 cm$^{-1}$) and its NMR

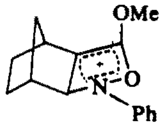


Scheme 6

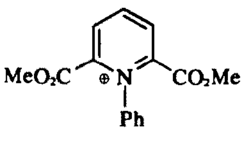
spectrum indicated it contained two non-equivalent OMe groups, only one of which was identical in chemical shift to one of the OMe groups in the starting triazoline. A comparison of the mass spectrum of this unstable product with the mass spectra of triazoline **24** and aziridine **26** under essentially identical conditions was particularly interesting and the results can be found in Table 2 in the Experimental. In order to simplify and shorten the discussion, we wish to first suggest that the major pyrolysis product should be represented by isoxaline structure **28** arising from **24** as illustrated in Scheme 6. It is tempting to suggest that the ion at *m/e* 286 present in the spectrum of **28**, but absent in the spectra of triazoline **24** and aziridine **26**, has structure **29**. It will be noticed from Table 2 that both isoxaline **28** and triazoline **24** show base peaks at *m/e* 242 which suggests this ion should be represented by the stable structure **30**. The base peak in the mass spectrum of aziridine **26** at *m/e* 272 is probably due to the ion **31** arising in a manner similar to that observed in the formation of **21** as previously mentioned from aziridines **2** and **3** ($R = p\text{-}NO_2C_6H_4$). Finally, the appearance of a relatively large ion at *m/e* 107 in the spectrum of **28**, but absent in the aziridine spectrum and present to only a small extent in the spectrum of triazoline **24**, suggests that this ion has structure **32**. While all of the mass spectral explanations are recognized to be only suggestions at this time, it does appear that the wieight of evidence tends to support structure **28**. Unfortunately, we were unable to obtain further confirmative evidence for the structure of the pyrolysis product due to its instability and particularly due to its serious adverse physiological effects (Experimental).



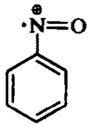
**29**



**30**

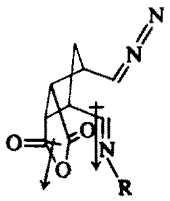


**31**

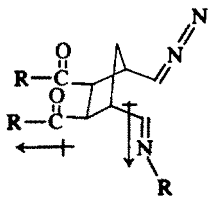


**32**

One aspect of any of the mechanisms thus far suggested to account for the "triazoline-aziridine inversion" which has continued to disturb us has been an explanation for the predominant formation of *endo* aziridines in the reactions of *cis-endo-* and *cis-exo*-norbornene-5,6-dicarboxylic acid anhydrides and the corresponding *cis-exo*-dimethyl ester with benzenesulfonyl azide and the formation of greater than 50% *endo*-aziridine in the pyrolysis of **1** ($R = C_6H_5$, *exo*-anhydride at C-5, C-6).[10] Why does one get predominantly the thermodynamically less stable product, particularly, in the case of *cis-endo*-norbornene-5,6-dicarboxylic acid anhydride? We now wish to suggest that this phenomena arises from a strong field effect exhibited by the anhydride or carbomethoxy groups at C-5 and C-6. Assuming that a diazoimine intermediate such as **7** is involved, then if the imine portion aligns itself with the dipole of the anhydride moiety in a head to tail fashion, then the preferred conformation should be as in **33** thus leading to the *endo*-aziridine. Similar arguments hold for the *exo* anhydride and dimethyl ester which might be represented as in **34**. Apparently steric effects are too great to be overcome by the dipole effect in the case of the *cis-endo*-dimethyl ester.[10] That there is indeed a field effect of the anhydride groups has been illustrated by the relative rates of nitrogen evolution in the reactions of benzenesulfonyl azide with norbornene, *exo* anhydride and *endo* anhydride (100:10:1).[10]



**33**



**34**: R = R′ = O or R = R′ = OMe

## EXPERIMENTAL

M.ps were taken on a Thomas-Hoover apparatus and are uncorrected. IR spectra were recorded with a Perkin-Elmer 237B spectrophotometer. NMR spectra were obtained with a Varian A-60 spectrometer using $CDCl_3$ as solvent and TMS as an internal standard ($\delta = 0$). Abbreviations used to report NMR spectra are as follows: s—singlet; d—doublet; t—triplet; q—quartet; b—broad; m—multiplet; c—complex. Mass spectra were obtained with a Varian M-66 mass spectrometer (70 eV).

*Preparation of 3-chloronorcamphor oxime acetate.* The crystalline dimeric nitrosochloride of norbornene was prepared in 56% yield according to the procedure of Meinwald *et al.*,[22] m.p.

155–156° (lit.[22] 155·5–156·5°); $\nu_{max}^{KBr}$ 1615, 1385, 1230, 670 $cm^{-1}$; $M^+/2$ *m/e* 159 (25%). 2-Chloro-3-nitroso-norbornane dimer was isomerized to 3-chloronorcamphor oxime in quantitative yield as previously described.[23] The mixture of *syn* and *anti* isomers[23] was isolated as a viscous oil. $\nu_{max}^{film}$ 3250, 1675, 1450 $cm^{-1}$; $M^+$ *m*/2 159 (50%); δ ($CDCl_3$) 4·40 and 4·25 (1 H, ratio 30:70; J = 2·0 Hz), 3·53 and 2·96 (1 H, ratio 70:30, m). The above oxime (2·0 g) was converted into its acetate by stirring in a mixture of $Ac_2O$ (4 ml) and pyridine (4 ml) at room temp overnight. Addition of an equal volume of ice water yielded an oily ppt which was taken up in chloroform. Sequential washing of the chloroform layer with 10% HCl aq, 5% $NaHCO_3$ aq, water and finally drying over $Na_2SO_4$ and evaporation gave 2·3 g (92%) of the acetate as a viscous oil (Found: C, 53·70; H, 6·01; Cl, 17·70; N, 7·01. Calc. for $C_9H_{12}Q_2ClN$: C, 53·73; H, 5·97; Cl, 17·64; N, 6·9%); $\nu_{max}^{film}$ 1770, 1660 $cm^{-1}$; $M^+$-$C_2H_3O_2$ *m/e* 142 (48%); δ ($CCl_4$): 4·34 (1 H, d, J = 2·5 Hz), 3·48 and 3·03 (1 H, ratio ~60:40), 2·57 (1 H, bs), 2·10 and 2·07 (total 3 H). A special note of caution is suggested for potential users of 3-chloronorcamphor oxime acetate as well as the corresponding *p*-nitrobenzoate. These compounds produced severe skin irritations and allergic reactions in individuals exposed to them!

*Preparation of the* p-*nitrobenzoate of* 3-*chloronorcamphor oxime.* To a soln of the oxime (5·86 g, 37 mmole) in anhyd ether (100 ml) and chloroform (10 ml) was added *p*-nitrobenzoyl chloride (7·58 g, 45 mmole). After stirring for 30 min, a flocculent yellow ppt began to appear and after an additional 30 min, the solvent was removed *in vacuo* and the ppt was washed with 10% $NaHCO_3$ aq and then collected by filtration. After further washing with water and air drying the solid was recrystallized from 95% EtOH to give 7·6 g (67%) of pure 3-chloronorcamphor oxime *p*-nitrobenzoate, m.p. 175–176° (Found: C, 54·45; H, 4·36; Cl, 11·35; N, 9·27. Calc. for $C_{14}H_{13}ClN_2O_4$: C, 54·47; H, 4·24; Cl, 11·48; N, 9·07%); $\nu_{max}^{KBr}$ 1750, 1660, 1530 $cm^{-1}$; $M^+$ *m/e* 308 (small); δ ($CDCl_3$): 8·25 (4 H, m), 4·53 (1 H, d, J = 2 Hz), 3·70 and 3·29 (1 H, ratio 40:60, m), 2·72 (1 H, m).

*Reduction of 3-chloronorcamphor oxime acetate.* 3-Chloronorcamphor oxime acetate was reduced with diborane according to the procedure of Feuer and Braunstein[24] using a hydroboration apparatus as described by Brown.[27] Into a soln of 4·1 ml $BF_3$-etherate in 10 ml dry diglyme was added dropwise, 0·93 g $NaBH_4$ in 35 ml dry diglyme. The generated diborane was swept by a stream of $N_2$ into a THF soln containing 1·7 g of the oxime acetate. After complete addition of the $NaBH_4$- soln to the $BF_3$, the generator was heated gradually to 60° over a period of 1 hr, then disconnected from the reaction vessel containing the THF soln. The latter soln was stirred at RT for 20 hr, then 5 ml $H_2O$ was cautiously added, after which the solvent was removed *in vacuo* to give a white solid. To this was added 20 ml of 10% HCl and the soln refluxed for 1 hr then 20 ml of 20% KOH was added and the soln was extracted with ether. After drying over $Na_2SO_4$, excess HCl gas was bubbled into the ether soln, whereupon a white, flocculent ppt formed. Compound **18**·HCl was washed several times with ether and gave m.p. 195–200° (17%) (Found: C, 45·95; H, 7·23; Cl, 39·09; N, 7·49. Calc. for $C_7H_{12}ClN \cdot HCl$: C, 46·17; H, 7·20; Cl, 38·94; N, 7·69%); $\nu_{max}^{KBr}$ 3400, 2925, 1960, 1590, 1570, 1495, 1475 $cm^{-1}$; $M^+$–HCl *m/e* 145 (67%); δ ($CF_3CO_2H$–$CDCl_3$): 7·08 (3 H, b, disappears on addition of $D_2O$), 3·63 (2 H, m), 2·50 (1 H, m), 2·32 (1 H, m), 2·0–1·0 (6 H).

The free amine was obtained as an oil upon basification of an aqueous soln with solid KOH, followed by extraction with ether, drying over $Na_2SO_4$ and removal of the solvent *in vacuo.* $\nu_{max}^{CHCl_3}$ 3380, 3300, 1610 $cm^{-1}$; deuterated amine (recovered from NMR in presence of $D_2O$); $\nu_{max}^{CHCl_3}$ 2215, 2105, 1645 $cm^{-1}$; δ ($CDCl_3$): 3·36 (1 H, t, J = 3·5), 3·20 (1 H, q?, J = 2·5), 2·23 (2 H), 2·03–1·00 (8 H), in presence of $D_2O$ δ 2·03–1·00 (6 H).

*Reduction of 3-chloronorcamphor oxime* p-*nitrobenzoate.* Diborane, generated by the dropwise addition of 1·86 g $NaBH_4$ in 70 ml dry diglyme into 8·2 ml of $BF_3$·etherate in 25 ml dry diglyme, was swept by a stream of $N_2$ into a soln of 7·9 g of 3-chloronorcamphor oxime *p*-nitrobenzoate in 125 ml THF. The soln was worked up as described above except that after acid hydrolysis, the water layer was extracted with chloroform to remove the *p*-nitrobenzoyl chloride, then the acidic soln was made alkaline, extracted with ether, etc. The amine hydrochloride was isolated in 41% yield. Attempts to scale-up the reduction 10-fold gave a yellow product of poor quality, which had to be extensively purified, before further use, as follows: dissolution in water, basification, extraction with ether, extraction with dilute acid, washing with chloroform, basification, extraction with ether, washing with water, drying, filtering and finally reacidification with gaseous hydrogen chloride.

*Preparation of* 2-endo(p-*nitrophenylazo*)*amino*-3-exo-*chloronorbornane* (**19**). To 500 mg (2·75 mmole) of 2-*endo*-amino-3-*exo*-chloronorbornane hydrochloride in 25 ml of water was added a buffered soln (pH 5·6–6·0) of *p*-nitrobenzenediazonium chloride at 0° (prepared from 180 mg, 1·30 mmole, of *p*-nitroaniline[20]). A yellow ppt formed immediately and after addition of NaCl (20 g), the soln was stirred and allowed to come to RT (1 hr). Filtration gave 234 mg (61%) of the product, **19**, m.p. 112–115° with bubbling (Found: C, 52·97; H, 5·13. Calc. for $C_{13}H_{15}ClN_4O_2$: C, 52·89; H, 5·09%); $\nu_{max}^{CHCl_3}$ 3315 $cm^{-1}$, $\nu_{max}^{KBr}$ 3380, 1600 $cm^{-1}$; $M^+$-$N_2$ *m/e* 266 (4%); δ ($CDCl_3$): 8·21 (2 H, d, J = 9), 7·26 (2 H, d, J = 9), 4·26 (1 H, m), 3·89 (1 H, t, J = 2·5), 2·54 (2 H, m), 2·22–1·10 (6 H, c). A modification of the above procedure beginning with free amine gave a somewhat higher yield (81%).

*Preparation of* 3 - p - *nitrophenyl* - 3,4,5 - *triazatricyclo* (5.2.1.$0^{2,6endo}$) - *dec* - 4 - *ene* (**20**). To 90 mg (0·307 mmole) of the above diazoamine in 20 ml abs EtOH at 60° was added 0·35 ml of a 1·08 N soln of freshly prepared NaOEt in EtOH to give a deep wine red soln. The addition of a soln of 53 mg (0·307 mmole) of $AgNO_3$ in 15 ml abs EtOH gave a bright yellow soln with a brown ppt. After cooling, the soln was filtered to remove the brown ppt, which was washed with EtOH. Evaporation of the combined EtOH fractions gave a brown-yellow solid to which was added chloroform. The chloroform soln was filtered; the brown ppt was washed with chloroform and the combined chloroform solns concentrated *in vacuo.* The residual solid was triturated with $CCl_4$, the $CCl_4$-soln filtered and evaporated to give the desired *endo* **20** (49 mg, 64%), m.p. 120–130° with bubbling. Recrystallization from EtOH gave orange crystals, m.p. 135–138° with bubbling (Found: C, 60·37; H, 5·53; N, 21·59. Calc. for $C_{13}H_{14}N_4O_2$: C, 60·45; H, 5·46; N, 21·60%); $\nu_{max}^{KBr}$ 1595, 1500, 1378, 1320 $cm^{-1}$; $M^+$-$N_2$ *m/e* 230 (84%); δ ($CDCl_3$): 8·15 (2H, d, J = 9), 7·27 (2H, d, J = 9), 5·09 (1H, d of d, J = 5·50, 12·0), 4·02 (1H, d of d, J = 4·25, 12·0), 2·80 (2 H, M), 1·65–0·75 (6H, c).

*Preparation of* 3 - p - *nitrophenyl* - 3,4,5 - *triazatricyclo*(5.2.1.$0^{2,6exo)}$*dec* - 4 - *ene* (**1**, R = p-$NO_2C_6H_4$). The *exo* triazoline was prepared by the (3 + 2) cycloaddition of *p*-nitrophenyl azide to norbornene as previously described.[26] The yellow crystals melted at 164–165° (lit.[26] 164–165°); $\nu_{max}^{KBr}$ 1595, 1500, 1375, 1320 $cm^{-1}$; δ ($CDCl_3$): 8·30 (2H, d, J = 9), 7·38 (2H, d, J = 9), 4·77 (1H, d, J = 9), 3·79 (1H, d, J = 9), 2·90 (2H, s), 1·90–0·91 (6H, c); $M^+$-$N_2$ *m/e* 230 (23%).

***Photolysis of triazolines.*** After degassing with $N_2$, an acetone (250 ml) soln containing a 2:1 mixture of the *endo* and *exo* triazolines* was photolyzed for 6 hr at 5° through a quartz filter

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*In a single attempt to scale-up (10X) the diborane reduction of the *p*-nitrobenzoate of the oxime there was isolated a crude amine hydrochloride, which was extensively purified as mentioned above to give only 13% of amine hydrochloride suitable for coupling. This purified amine hydrochloride gave, eventually, a 2:1 mixture of *endo* and *exo* triazolines!

with a 200 W Hanovia lamp. Removal of the acetone *in vacuo* gave a dark brown oil, the GLC of which showed two products in a ratio of 2:1. The minor product, of longer retention time, was identified as the *exo*-aziridine, **2** (R = *p*-$NO_2C_6H_4$) by comparison on GLC with an authentic sample (see below) and by comparison of the NMR spectrum of the dark brown oil with the NMR spectrum of an authentic sample of the *exo*-aziridine.

The major product, *endo*-**3** (R = *p*-$NO_2C_6H_4$), was collected by preparative GLC on a 15% SE-30 column and reinjection on the analytical column verified that it had not been altered in the process. The yellow, solid **3** (R = *p*-$NO_2C_6H_4$), gave m.p. 90–92°; $\nu_{max}^{KBr}$ 2960, 1590, 1497, 1345, 1325, 1285 $cm^{-1}$; δ ($CDCl_3$): 8·06 (2H, d, J = 9), 6·95 (2H, d, J = 9), 2·93 (2H, t, J = 2), 2·49 (2H, c), 2·05–1·21 (6H, c); $M^+$ *m/e* 230·0835 (4%). Calc. For $C_{13}H_{14}N_2O$: $M^+$ *m/e* 230·0969.

Photolysis of the pure *exo*-triazoline, as described above, gave exclusively *exo*-**2** (R = *p*-$NO_2C_6H_4$), m.p. 121–122° (lit.[19] 121–122°); $\nu_{max}^{KBr}$ 1590, 1500, 1385, 1325 $cm^{-1}$; δ ($CDCl_3$): 8·10 (2H, d, J = 9), 6·95 (2H, d, J = 9), 2·57 (2H, s), 2·42 (2H, s), 1·73–1·06 (5H, c), 0·87 (1H, d, J = 9·5 Hz); $M^+$ *m/e* 230 (10%).

*Pyrolysis of triazolines.* Each of the *exo* and *endo* triazolines (20 mg) were added to separate pyrex tubes containing 3 ml freshly distilled decalin. Warming on the steam both resulted only in partial solubility and the tubes were then placed in an oil bath at 165–170°. Although evolution of $N_2$ (visual observation) ceased after 15 min, heating at this temp was continued for 2 hr. Analysis of the decalin solns by GLC on a 3% XE-60 column indicated that each soln contained the same 3 volatile products in increasing order of retention times: *endo*-aziridine, N-*p*-nitrophenylbicyclo(2.2.1)hept-2-imine and *exo*-aziridine respectfully. The *endo*- and *exo*-aziridines were identified by GLC comparison with authentic samples and comparison of the NMR spectrum of the product mixture with those of authentic samples of *endo*- and *exo*-aziridines. The imine was identified from the observation that this product decomposed into *p*-nitroaniline and norcamphor (identified by GLC) when the decalin solns were exposed to moist air and by GLC comparison with an authentic sample of imine prepared by refluxing a benzene soln of norcamphor, *p*-nitroaniline and a catalytic amount of *p*-toluenesulfonic acid. The imine hydrolyzed rapidly during attempts to purify it. The ratios of products are given in Table 1 in the text.

*Reduction of 3-chloronorcamphor oxime acetate to norcamphor oxime.* To 3-chloronorcamphor oxime acetate (1·0 g) in 15 ml abs EtOH was added 0·40 g of $NaBH_4$ in 10 ml abs EtOH. After stirring for 1·75 hr, the soln was poured into 25 ml water, the water soln extracted with ether and the ether layer dried over $Na_2SO_4$, filtered and finally concentrated with a rotatory evaporator to give a quantitative yield of an oil identical with norcamphor oxime (*syn* and *anti*) prepared in the usual manner from norcamphor, except the ratio of *syn* to *anti* isomers differed as indicated in the NMR spectra. Norcamphor oxime from 3-chloronorcamphor oxime acetate: $\nu_{max}^{film}$ 3350 $cm^{-1}$; $\nu_{max}^{CCl_4}$ 3590, 3250, 2950, 1680 $cm^{-1}$; δ ($CDCl_3$): 9·20 (1H, b), 3·52 (0·6 H, s), 2·88 (0·4 H, s), 2·48 (1H, s), 2·33–1·10 (8H, c); $M^+$ *m/e* 125. Norcamphor oxime from norcamphor: b.p. 78–81°/1 mm (lit.[4] b.p. 114–6°/12 mm); $\nu_{max}^{film}$ 3350 $cm^{-1}$; $\nu_{max}^{CCl_4}$ 3590, 3250, 2950, 1680 $cm^{-1}$; δ ($CDCl_3$): 9·20 (1H, b), 3·52 (0·1H, s), 2·88 (0·9H, s), 2·48 (1H, s), 2·33–1·10 (8H, c).

### *Dimethyl-1-phenyl-1,2,3-triazole-4,5-dicarboxylate*

*Reaction of phenyl azide with dimethyl bicyclo*(2.2.1)*hepta-2,5-diene-2,3-dicarboxylate.* A soln containing phenyl azide (5·0 g) and dimethylbicyclo(2.2.1)hepta-2,5-diene-2,3-dicarboxylate (11·4 g) in 30 ml of cyclohexane was refluxed for 2 hr under $N_2$, then allowed to stand at RT for 4 days. The soln had separated into two phases, a top clear yellow phase and a lower dark brown-red phase. The upper phase was removed by pipette and the lower layer (7·8 g) crystallized. Two grams of this semi-crystalline lower layer was boiled in ether and upon cooling white crystals were deposited (0·36 g), m.p. 120–123°. Recrystallization from ether gave pure dimethyl-1-phenyl-1,2,3-triazole-4,5-dicarboxylate, m.p. 126–127° (lit.[28] m.p. 126–127°). $\nu_{max}^{KBr}$ 1720 $cm^{-1}$; δ ($CDCl_3$): 7·54 (5H, s), 3·99 (3H, s), 3·90 (3H, s); $M^+$ *m/e* 261 (63%), $(M+1)^+$ *m/e* 262 (7%); $\lambda_{max}$ 240 nm (ε 8,150), reported[29] for 1-phenyl-1,2,3-triazole $\lambda_{max}^{EtOH}$ 243 nm (log ε 4·01).

### 3,4,5,9,10,11-*Hexaazatetracyclo*(5.5.1.$0^{2,6}0^{8,12}$)*trideca* - 3,10 - *diene*(*syn* - exo - exo - *ditriazoline*) (**13**) *and anti* - exo - exo - *ditriazoline* (**12**)

*Reaction of norbornadiene with benzyl azide.* Into a refluxing soln of 3·5 g norbornadiene in 10 ml cyclohexane was added dropwise 5·0 g of benzyl azide, prepared as previously described[30] ($\nu_{max}^{film}$ 2195 $cm^{-1}$; $\delta^{CDCl_3}$: 7·15, 4·07), in 5 ml cyclohexane. After refluxing for 2·3 hr, and standing at RT for two days, 4·1 g of brown ppt appeared, which after removal by filtration was boiled in ether twice, whereupon 1·6 g of solid remained undissolved. Concentration of the ether filtrate gave 0·3 g of white needles, m.p. 154–156°, identified as the *anti exo-exo*-**12** (Found: C, 70·45; H, 6·30; N, 23·32. Calc. for $C_{21}H_{22}N_6$: C, 70·39; H, 6·15; N, 23·46%); $\nu_{max}^{KBr}$ 3050, 2940, 1465, 1445, 995, 700 $cm^{-1}$; δ ($CDCl_3$): 7·30 (10 H), 4·90 (2 H, d, J = 15), 4·61 (2 H, d, J = 15), 4·31 (2 H, d, J = 9), 3·22 (2 H, d, J = 9), 2·60 (2 H, m), 1·15 (2H, m); $M^+$-$2N_2$ *m/e* 302. The isomeric *syn-exo-exo*-**13**, m.p. 168-170°, was isolated from the 1·6 g of insoluble solid mentioned above by successive recrystallizations from $CCl_4$, n-hexane and finally ether (Found: C, 70·28; H, 6·38; N, 23·39. Calc. for $C_{21}H_{22}N_6$: C, 70·39; H, 6·15; N, 23·46%); $\nu_{max}^{KBr}$ 3050, 3030, 2975, 2920, 1490, 1475, 1350, 1120, 1105, 1000, 725 $cm^{-1}$; δ ($CDCl_3$): 7·27 (10 H), 4·79 (2 H, d, J = 15), 4·48 (2 H, d, J = 15), 4·48 (2 H, d, J = 9), 3·08 (1 H, m), 3·00 (2 H, d, J = 9), 1·97 (1 H, m), 1·10 (2 H, m); $M^+$-$2N_2$ *m/e* 302. The ratio of *anti* to *syn* triazolines, based on total recovered material, was 2·2 to 1. Varying the molar ratio of norbornadiene to benzyl azide from 1:1 (as above) to 4·1:1 decreased the amount (by weight) of isolatable crystalline products seven fold!

*Preparation of dimethyl bicyclo*(2.2.1)*hepta-2,5-diene-2,3-dicarboxylate* (**14**). Dimethyl acetylene dicarboxylate (90 g) was cautiously added to 52·3 g of freshly distilled cyclopentadiene at −78°. The vigorous reaction subsided after several seconds, giving a red soln. The product was isolated (73·0 g, 68%) by vacuum distillation, b.p. 111°/2 mm (lit.[31] 134–135°/10–11 mm). $\nu_{max}^{film}$ 2980, 2945, 1710, 1625 $cm^{-1}$; δ (neat): 6·92 (2 H, t, J = 2), 3·88 (2 H, t, J = 1·5), 3·70 (6 H, s), 2·12 (2 H, $ABX_2$ $J_{AB}$ = 7, $J_{A(B)X}$ = 1·5); $M^+$ *m/e* 208 (63%).

*Preparation of dimethyl bicyclo*(2.2.1)*-2-heptene-2,3-dicarboxylate* (**15**). The above diene (34·7 g) was hydrogenated in acetone (110 ml) in the presence of 5% Pd-C (1·75 g) at room temp and atmospheric pressure. The usual workup gave 23·5 g (67%) of the desired product, b.p. 86°/0·5 mm (lit.[31] 132–3°/12 mm); $\nu_{max}^{film}$ 1720, 1615 $cm^{-1}$; δ (neat): 3·70 (6 H, s), 3·23 (2 H, b), 2·0–1·0 (6 H, c); $M^+$ *m/e* 210 (10%).

*Preparation of bicyclo*(2.2.1)*-2-heptene-2,3-dicarboxylic acid anhydride.* A soln prepared from 3·5 g KOH, 25 ml 95% EtOH and 5 g of the above mentioned dimethyl ester was refluxed for 20 min. The usual workup' gave 4·3 g of crude diacid which was recrystallized from water to give 2·8 g (66%) of pure diacid, m.p. 213–214° (lit.[31] m.p. 212°). $\nu_{max}^{KBr}$ 2500, 1695, 1622 $cm^{-1}$; $M^+$ *m/e* 182 (9%).

A soln of 2·5 g of the above diacid in 8·4 g $Ac_2O$ was refluxed for 1·5 hr and removal of the $Ac_2O$ *in vacuo* gave a brown solid which yielded 1·5 g (68%) of the desired anhydride after recrystallizing from n-hexane, m.p. 92–94° (lit.[32] m.p. 98–99°); $\nu_{max}^{KBr}$ 1827, 1777, 1603 $cm^{-1}$; $M^+$ *m/e* 164 (45%).

*Preparation of 3-phenyl-3,4,5-triazatricyclo*(5.2.1.$0^{2,6}$)*-4-decene-2,6-*endo*-dicarboxylic anhydride* (**23**). To 1·2 g of the above mentioned anhydride in 8 ml EtOAc was added 0·87 g phenyl azide.[33] After stirring at RT for 1 day, filtration and concentration of the soln gave 1·6 g (76%) triazoline, m.p. 150–152°. Recrystallization from EtOAc-n-hexane (1 : 1) gave pure triazoline, m.p. 152–154° (lit.[4] m.p. 154°); $\nu_{max}^{KBr}$ 1870, 1780, 1590 cm$^{-1}$; M$^+$-N$_2$ *m/e* 255 (69%).

*Preparation of dimethyl-3-phenyl-3,4,5-triazatricyclo*-(5.2.1.$0^{2,6}$)-*4-decene-2,6-endo-cis-dicarboxylate* (**24**). A soln prepared by dissolving 10 g of the above mentioned dimethyl ester and 5·6 g phenyl azide in 10 ml EtOAc was stirred at RT for 15 days, at which time the precipitated solid triazoline (5·5 g), m.p. 134–142°, was removed. A total yield of 76% triazoline was obtained by such periodic filtration of the soln over a period of 3 months. The analytically pure product was obtained by recrystallization from n-hexane-EtOAc (1 : 1), m.p. 147–149°. (Found: C, 62·16; H, 5·95; N, 12·75. Calc. for $C_{17}H_{19}N_3O_4$: C, 62·06; H, 5·82; N, 12·77%); $\nu_{max}^{KBr}$ 1740, 1598, 1505, 1490, 1305, 1280, 1260, 1110, 1095, 1070 cm$^{-1}$; $\lambda_{max}^{CH_3OH}$ 298 ($\epsilon = 7840$), $\lambda_{max}^{CH_3OH}$ 285 ($\epsilon = 7130$); $\delta$ (CDCl$_3$); 7·25 & 7·44 (5 H), 3·82 (3 H, s), 3·50 (3 H, s), 3·12 (1 H, b), 2·88 (1 H, b), 2·60–1·60 (2 H, c), 1·58 (2 H, b), 1·35 (2 H, b); M$^+$–N$_2$ *m/e* 301 (10%).

### *Photolysis and pyrolysis of 3-phenyl-3,4,5-triazatricyclo*(5.2.1.$0^{2,6}$)-*4-decene*-2,6-endo-*dicarboxylic anhydride*

*Preparation of 3-phenyl-3-azatricyclo*(3.2.1.$0^{2,4}$)*octane*-2,4-endo-*dicarboxylic anhydride* (**25**). A soln of the triazoline anhydride (0·16 g) in acetone (8 ml) was photolyzed in a pyrex tube at 10 ± 1° using a 200 W Hanovia lamp for 3 hr. Removal of the acetone gave 0·14 g of crude product which on recrystallization from n-hexane-EtOAc (1 : 1) gave pure *exo*-**25**, m.p. 157–159° (lit.[19] m.p. 161–162°). $\nu_{max}^{KBr}$ 1845, 1775, cm$^{-1}$; M$^+$ *m/e* 255 (100%).

A decalin (50 ml) soln of the triazoline anhydride (0·5 g) was heated at 163 ± 2° for 2 hr. GLC analysis (3·8% UCW-98 column) of the decalin soln showed that the only product was identical, in retention time alone and on mixed injection, to the *exo*-aziridine obtained by photolysis. Removal of the decalin *in vacuo* gave *exo*-**25** identical by m.p. and IR spectrum with that obtained on photolysis of the triazoline.

### *Photolysis of dimethyl-3-phenyl-3,4,5-triazatricyclo*(5.2.1.$0^{2,6}$)-4-*decene*-2,6-endo-cis-*dicarboxylate*

*Preparation of dimethyl - 3 - phenyl - 3 - azatricyclo* - (3.2.1.$0^{2,4}$)*octane* - 2,3 - endo - cis - *dicarboxylate* (**26**). A soln of the diester triazoline (1·0 g) in 22 ml of acetone was photolyzed at 10 ± 1° in a pyrex tube using a 200 W Hanovia lamp for 3 hr. GLC analysis showed a single product. Removal of the acetone and recrystallization of the product from n-hexane-EtOAc (1 : 1) gave the pure *exo*-**26** as white plates, m.p. 106–109° (Found: C, 67·58; H, 6·31; N, 4·58. Calc for $C_{17}H_{19}NO_4$: C, 67·83; H, 6·36; N, 4·65%); $\nu_{max}^{KBr}$ 1725, 1590; $\delta$ (CDCl$_3$): 7·30–6·73 (5 H, c), 3·77 (6 H, s), 2·77 (2 H, b), 2·20–0·5 (6 H, c); M$^+$ *m/e* 301 (28%).

### *Pyrolysis of dimethyl-3-phenyl-3,4,5-triazatricyclo*(5.2.1.$0^{2,6}$)-4-*decene*-cis-endo-*dicarboxylate* (**24**)

(a) *Evidence for the diazoimine intermediate.* The triazoline (2·5 g) was placed in 200 ml decalin and the soln warmed on the steam bath until it was homogeneous, then heated in an oil bath at 162 ± 2° for 3 hr. Decalin was removed from the soln by heating on the steam bath at reduced pressure (~0·1 mm) under a slow stream of N$_2$ to give a foul-smelling yellow oil which was chromatographed on 80 g of silica gel. Benzene eluted ~0·2 g of a foul-smelling yellow oil with a characteristic IR spectrum, $\nu_{max}^{neat}$ 2120 cm$^{-1}$. This material decomposed at RT over a period of less than 2 hr with disappearance of the IR band at 2120 cm$^{-1}$. This experiment was repeated 4 times with the same results, but the illusive intermediate decomposed (even at 0°) too rapidly to be completely characterized. However, IR and UV spectra of the fractions containing the intermediate were recorded. $\nu_{max}^{KBr}$ 2120, 1720, 1695, 1630, 1595 cm$^{-1}$; $\lambda_{max}^{2\text{-propanol}}$ 233, 238, 244 and 251 nm.

(b) *Isolation of isoxazoline.* GLC analysis (3% OV-17 column) of the decalin soln after pyrolysis of the triazoline, as described above, showed the presence of one major component (75%) and at least 7 minor components. Mixed injection with the *exo*-aziridine showed that it was not one of the components of this product mixture. Attempts to isolate the major component by column or TLC on alumina or silica gel resulted in decomposition of the material as determined by GLC analysis. However, the major component survived removal of the decalin solvent and was collected as a yellow oil by preparative GLC on a 3% OV-17 column at 200°, $\nu_{max}^{CCl_4}$ 2950 (sharp), 1725, 1710, 1650(d), 1480, 1430, 1355, 1255, 1200, 1120 cm$^{-1}$.

*Warning*: The foul-smelling vapors escaping during the collection of this product caused severe headaches and dizziness to all persons exposed to them.

Data from the mass spectra of the isoxazoline, *exo* triazoline **24** and *exo*-**26** are compared in Table 2.

Table 2. Relative abundances of ions*

| *m/e* | 301 | 286 | 272 | 242 | 214 | 107 | 77 |
|---|---|---|---|---|---|---|---|
| isoxazoline **28** | 13 | 27 | 1 | 100 | 1 | 30 | 81 |
| triazoline **24** | 10 | 1 | 62 | 100 | 61 | 6 | 56 |
| aziridine **26** | 28 | 0 | 100 | 14 | 38 | 0 | 23 |

*Spectral conditions: 70 eV. Isoxazoline: 1 × 10$^{-6}$ mm, probe 90°, analyzer 125°; triazoline: 6 × 10$^{-7}$ mm, 80°, 125°; aziridine: 1·2 × 10$^{-6}$ mm, 70°, 130°.

Further attempts to elucidate the structure of the isoxazoline by use of a gas-chromatograph-mass spectrometer interface gave puzzling results. In each spectrum thus obtained the ion of highest mass observed was at *m/e* 299 (M$^+$-N$_2$-H$_2$). This observation was reproducible and was observed regardless of whether glass or stainless steel columns were used in the gas chromatograph. Direct injection of the triazoline, via an acetone soln, on the GC-MS gave a molecular ion at *m/e* 301, but in addition a peak at *m/e* 299 was observed which varied in intensity from 50–65% of the M$^+$ peak!

Another mode of pyrolysis attempted involved the use of a horizontal bubble-type short path distillation apparatus heated at 80–114° and 0·15–2·1 mm from 10 to 330 min. The resulting pyrolysis mixtures had the distinctive foul odor of the previously mentioned pyrolysate and upon standing at RT, starting triazoline crystallized from these distillates. The oily distillates were taken up in CCl$_4$, in which the triazoline is only sparingly soluble, and the NMR spectra indicated the disappearance of the triazoline methoxyl signal at $\delta$ 3·82 and the appearance of a new signal at $\delta$ 3·69 as the pyrolysis time was extended. The mass spectrum of the pyrolysate from the longest run (114°/1·4–2·1 mm, 330 min) was very similar to that of the isoxazoline described in Table 2.

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