The Unusual Formation of Methyl α-(5,6-Dimethoxycarbonyl-2,3-Dimethoxyazepin-7-ylidene)-α-[5-methoxycarbonyl-2,3-Dimethoxypyrid-6-yl)acetate During the Pyrolysis of "Azido-*meta*-hemipinate"

First Example of a Reaction Involving a Concomitant Ring Expansion and Ring Extrusion

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The *ortho* methoxycarbonyl substituent constitutes a sole exception in the ring closure reactions of *ortho* substituted aryl azides, as it provides no rate acceleration to this reaction. Pyrolysis of "azido-*meta*-hemipinate", an aryl azide containing such a substituent, led us to the title compound, a new azepinylidene-pyridylacetic ester, whose structure has been established unambiguously by a single crystal X-ray diffraction study. This is the first report of a reaction involving both a ring expansion to an azaheptafulvalene and a ring extrusion to a pyridyl ring residue.

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Introduction.

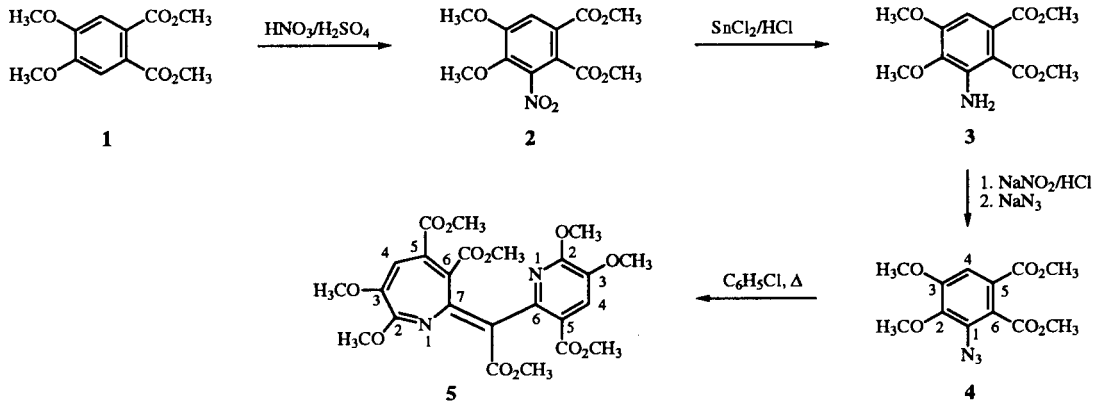
Aryl azides are important photoresists and photoaffinity labeling agents [1] and the therapeutic value of azidothymidine [2] (AZT) in the treatment of AIDS is well known. The lively debate on the role of substituents on the ring closure reaction of *ortho* substituted aryl azides also came to our notice. Dyall and Kemp [3] have advocated an electrocyclic mechanism for this reaction, while Hall, Behr and Reed [4] suggested the alternative 1,3-cycloaddition pathway. Smith [5], on the other hand, emphasised that charge separation is more important in the transition state than in the parent azide itself. Among the substituents the *ortho*-methoxycarbonyl group constitutes a sole exception as it provides no rate acceleration to the ring closure reaction and it is known that methyl *o*-azidobenzoate "reacts in other ways" [6]. In this context, the product obtained by us during the pyrolysis of 1-azido-5,6-dimethoxycarbonyl-2,3-dimethoxybenzene ("azido-*meta*-hemipinate"), an aryl azide containing an *ortho*-methoxycarbonyl substituent, was clearly most unusual. Since the product arises out of a series of rather involved rearrangement reactions, there were obvious limitations in establishing the structure of the product by spectroscopic methods alone. The structure and conformation of the molecule were established unambiguously by single crystal X-ray diffraction study of the compound which showed the most unexpected azepinylidene-pyridylacetic ester structure. No example of a compound of this class has been described before in the literature.

Our report constitutes the first example of the reaction of an aryl azide where ring expansion to an azaheptafulvalene [7] and ring extrusion to a pyridine [8,9] both occur simultaneously in the same reaction. In the present example, ring expansion to an azaheptafulvalene is accompanied by a ring extrusion reaction, which leads to the simultaneous formation of a pyridine ring *via* the extrusion of the C-6 carbon atom of the parent azide. A myriad of possible intermediates [10], including nitrene-carbene interconversions, have been invoked in the past to explain the diverse products obtained. These have even involved cycloperambulation of the nitrogen atom of the initially formed nitrene intermediate.

Results.

1-Azido-5,6-dimethoxycarbonyl-2,3-dimethoxybenzene **4** ("azido-*meta*-hemipinate") was prepared from 1,2-dimethoxycarbonyl-4,5-dimethoxybenzene **1** (dimethyl-*meta*-hemipinate) by nitration, reduction of the nitro compound **2** with stannous chloride-hydrochloric acid to the amine **3** followed by diazotisation and displacement with sodium azide. Thermolysis of azido-*meta*-hemipinate **4** was carried out in chlorobenzene for four hours at 130°. The yellow product obtained was purified by column chromatography to give the title compound **5** [Scheme I]. Its ir spectrum showed absorption bands for the carbonyl groups at 1700 and 1645 cm^{-1}. No absorption due to the N-H group was observed. The uv spectrum showed an absorption maximum in methanol at 289.8 nm and in chloroform at 293.8 nm. The ^1H nmr spectrum, however, clearly pointed to its rather unusual structure. Eight different signals were seen in the region δ 3.33 to δ 4.01 ppm, which indicated its dimeric nature. A one proton signal was observed at δ 7.8 and another at δ 5.6 ppm, showing that while the former lies in

Scheme I: Steps involved in the synthesis of **5**



the aromatic region, the latter is in the olefinic region. Mass spectrum of the new compound showed the molecular ion at m/z 534. The base peak appeared at m/z 475 and is formed by the loss of a methoxycarbonyl group. Single crystal X-ray study of the compound established its structure to be methyl α-(5,6-dimethoxycarbonyl-2,3-dimethoxyazepin-7-ylidene)-α-(5-methoxycarbonyl-2,3-dimethoxypyrid-6-yl)-acetate **5**. Crystal data for the compound are given in Table 1. The coordinates of non-hydrogen atoms along with the B-equivalent values are listed in Table 2. Bond lengths are given in Table 3, while bond angles are given in Table 4.

Table 1
Crystal Data of 5

Formula	$C_{24}H_{26}N_2O_{12}$
Mr	534
Space Group	$P2_1/c$
a	11.934(1) Å
b	14.290(2) Å
c	15.638(3) Å
β	105. 16 (1)°
Volume	2574.23 Å^3
Z	4
Dcalc	1.378 gm/cc
λ (CuKα)	1.5418 Å
μ (CuKα)	8.59 mm^{-1}
F (000)	1120
T	292 K

Discussion.

The presence of eight signals in the ^{1}H nmr spectrum of the new compound, four signals each for the methoxy and methoxycarbonyl groups, clearly pointed to an unusual structure and ruled out a symmetrical azobenzene structure for the 'dimeric' compound. The one proton signal at δ 5.6 ppm was very highly characteristic and this proton was clearly attached to a ring which was no longer aromatic in nature, and could be explained by assuming that a ring expansion had occurred. Ring expansion to azepines presumably occur *via* singlet nitrenes, whereas triplet nitrenes lead to amines and azobenzenes. It was initially assumed by us that a ring expansion to an azepine had occurred.

Table 2
The Coordinates of Non-hydrogen Atoms along with B- Equivalent Values in **5**

Atomic Coordinates Atom	X/a	Y/b	Z/c	B- Equivalent
N1	0.84940(30)	0.41790(20)	0.40910(20)	3.12(0.09)
C1	0.81150(30)	0.32510(20)	0.41100(30)	2.80(0.11)
C2	0.69530(40)	0.31790(30)	0.42830(30)	3.14(0.12)
C3	0.60260(40)	0.35020(30)	0.36520(30)	3.27(0.12)
C4	0.60950(40)	0.39350(30)	0.28400(30)	3.26(0.12)
C5	0.69740(40)	0.44750(30)	0.27200(30)	3.20(0.12)
C6	0.79850(40)	0.47100(30)	0.34630(30)	3.30(0.12)
C7	0.68470(40)	0.27660(30)	0.51210(30)	3.75(0.14)
O1	0.78560(30)	0.28190(20)	0.57390(20)	4.62(0.11)
C8	0.79130(90)	0.23940(60)	0.65910(40)	6.34(0.27)
O2	0.59840(30)	0.24390(30)	0.52510(30)	6.31(0.13)
C9	0.48100(40)	0.34060(30)	0.37420(30)	4.14(0.15)
O3	0.45730(30)	0.40640(20)	0.42680(20)	4.99(0.11)
C10	0.33990(70)	0.40870(70)	0.43590(80)	7.71(0.30)
O4	0.41270(30)	0.28450(30)	0.33470(30)	6.59(0.13)
O5	0.70120(30)	0.49130(20)	0.19720(20)	4.41(0.10)
C11	0.60340(60)	0.48480(60)	0.12040(50)	5.77(0.21)
O6	0.83210(30)	0.56030(20)	0.34190(20)	4.57(0.09)
C12	0.93480(70)	0.58760(40)	0.41090(50)	6.29(0.23)
Cl 3	0.87540(40)	0.24990(20)	0.40320(30)	2.99(0.12)
C14	0.98820(40)	0.25790(30)	0.38380(30)	3.19(0.11)
O7	1.02230(30)	0.17560(20)	0.35640(20)	4.13(0.10)
C15	1.12820(50)	0.17750(40)	0.33020(50)	5.17(0.19)
O8	1.04640(30)	0.32760(20)	0.38740(20)	4.72(0.11)
C16	0.82180(30)	0.15420(20)	0.40350(30)	2.96(0.11)
C17	0.85730(40)	0.08930(20)	0.47020(30)	3.04(0.12)
C18	0.80170(40)	0.00050(30)	0.46050(30)	3.62(0.14)
C19	0.71540(40)	-0.01710(30)	0.38610(30)	3.79(0.13)
C20	0.68110(40)	0.05470(30)	0.32400(30)	3.66(0.13)
N2	0.73290(30)	0.13740(20)	0.33160(20)	3.48(0.10)
C21	0.95060(40)	0.10900(30)	0.55190(30)	3.34(0.13)
O9	0.95100(30)	0.04610(20)	0.61420(20)	4.36(0.10)
C22	1.03610(60)	0.05610(40)	0.69870(40)	5.11(0.19)
O10	1.01780(30)	0.17330(20)	0.56070(20)	4.70(0.09)
O11	0.65490(30)	-0.09920(20)	0.36500(20)	5.46(0.11)
C23	0.68850(80)	-0.17730(40)	0.42210(70)	7.21(0.29)
012	0.59110(30)	0.03610(20)	0.25370(20)	5.33(0.11)
C24	0.54040(90)	0.11270(50)	0.19680(60)	8.14(0.28)

However, a single crystal X-ray diffraction study showed the presence of an azaheptatulvalene ring and unambiguously established the methyl azepinylidenepyridylacetate

Table 3

Bond Lengths (Angstrom) in **5**

Bond Distances (Angstrom)
[Corrections Following Busing and Levy, Acta Cryst., **17**, 142 (1964)].

			Uncorrected Distance
N1	-	C1	1.4046
N1	-	C6	1.2635
C1	-	C2	1.4846
C1	-	C13	1.3421
C2	-	C3	1.3560
C3	-	C4	1.4336
C4	-	C5	1.3547
C5	-	C6	1.4778
C13	-	C16	1.5110
C16	-	C17	1.3769
C16	-	N2	1.3498
C17	-	C18	1.4222
C18	-	C19	1.3599
C19	-	C20	1.3983
C20	-	N2	1.3251

Table 4

Bond Angles (Degrees) in **5**

Bond Angles (Degrees)
[E.S.D. Following Cruickshank, Internat. Tables, II, 1959, P.331].

C1	-	N1	-	C6	119.5
N1	-	C1	-	C13	124.1
N1	-	C1	-	C2	113.0
C2	-	C1	-	C13	122.8
C1	-	C2	-	C7	119.5
C1	-	C2	-	C3	117.9
C3	-	C2	-	C7	122.7
C2	-	C3	-	C9	121.7
C2	-	C3	-	C4	124.5
C4	-	C3	-	C9	113.8
C3	-	C4	-	C5	126.5
C4	-	C5	-	O5	126.3
C4	-	C5	-	C6	121.6
C6	-	C5	-	O5	111.9
N1	-	C6	-	C5	127.0
C5	-	C6	-	O6	111.6
N1	-	C6	-	O6	121.4
C1	-	C13	-	C16	118.3
C1	-	C13	-	C14	122.2
C14	-	C13	-	C16	119.1
C13	-	C16	-	N2	113.6
C13	-	C16	-	C17	124.5
C17	-	C16	-	N2	122.0
C16	-	C17	-	C21	122.4
C16	-	C17	-	C18	118.6
C18	-	C17	-	C21	119.0
C17	-	C18	-	C19	119.0
C18	-	C19	-	O11	126.7
C18	-	C19	-	C20	118.4
C20	-	C19	-	O11	114.9
C19	-	C20	-	O12	116.6
C19	-	C20	-	N2	123.2
N2	-	C20	-	O12	120.2
C16	-	N2	-	C20	118.7

structure. Thus ring expansion to an azaheptafulvalene and ring extrusion to a pyridyl residue were occurring simultaneously in the present case. Cyclisation to an isoxazole was ruled out based on the earlier work by Purvis *et al.* (*loc. cit.*) on photolysis of methyl *o*-azidobenzoate. The possible formation of an isoxazole ring after an initial ring expansion, *via* the azanorcaradiene intermediate suggested by Abramowitch [11], was also duly considered.

A PLUTO view of **5** along with the atom numbering scheme is shown in Figure 1. All the bonds in the ring have partial double bond character. The seven membered ring is strained, with the bond angle at C3, C4 and C6 being 125.0°, 126.0° and 126.7° respectively which is significantly more than 120° seen for sp^2 carbon atoms. As seen in the packing diagram (Figure 2) the pyridine ring folds over the azaheptafulvalene ring with the dihedral angle between the least squares planes being 29.6(1)°. The azaheptafulvalene ring assumes a boat conformation with puckering parameters, Q_T = 0.767(5)Å (puckering amplitude) and θ 2 = 74.0° (3) (phase angle) (Cremer and Pople [12]). The carbon atoms C1, C4 and C5 are 0.66Å, 0.56Å, and 0.60Å, respectively above the least squares plane of the remaining atoms in the seven membered ring. The methoxy groups attached to the pyridine ring are *ortho* to each other in the plane of the aromatic ring as evident from the torsion angles C19-C20-O12-C24 169.3(5)°; C20-C19-O11-C23 176.6(5)° and O11-C19-C20-O12 2.5(6)°. In the azaheptafulvalene ring the methoxy groups are once again *ortho* to each other with the torsion angles C5-C6-O6-C12 and C6-C5-O5-C11 being -177.4(4)° and -173.2(5)° respectively. The methoxycarbonyl substituent at the pyridine ring is almost in plane with the aromatic ring (C16-C17-C21-O9, 165.4 (4)°).

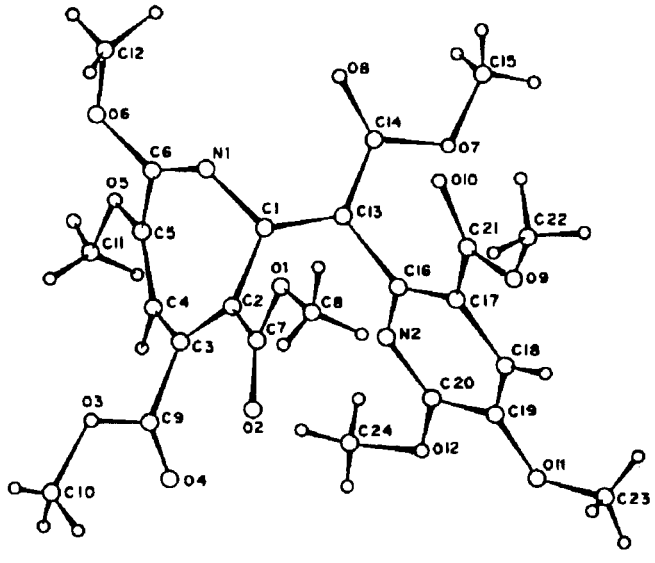


Figure 1. Molecular diagram of **5** along with the atomic numbering scheme.

Figure 1 shows that ring expansion to an azaheptafulvalene has occurred. An azaheptafulvalene has been described in literature only once previously [7]. This compound was

prepared in 5% yield by flow pyrolysis of pentafluorophenylazide. However, ring expansion in **5** is accompanied by a ring extrusion, while the diazaheptafulvalene obtained earlier arose out of yet another concomitant ring expansion.

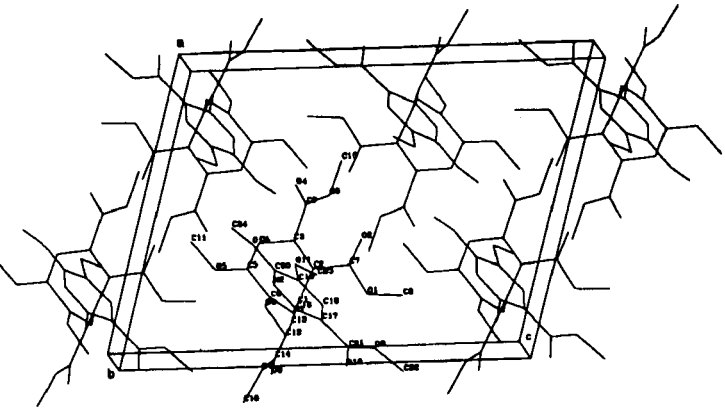


Figure 2. Packing diagram of **5** as seen down the crystallographic b axis.

In the formation of **5**, extrusion of the C-6 carbon atom is observed, while Sundberg *et al* [8] discussed the extrusion of the C-4 carbon atom during the photolysis of *o*-substituted aryl azides. Yields of 2-6% of the corresponding pyridines were obtained, as against a yield of 19%, in the present case. During studies on formation of *N*-(*o*-tolyl)-2-acetimidylpyridine in 2-5% yield during deoxygenation of *o*-nitrosotoluenes using triethylphosphite, a speculative mechanism was proposed by Sundberg [9], who rationalised the formation of the products in terms of a 7-azabicyclo[4.1.0]hepta-2,4,6-triene intermediate.

EXPERIMENTAL

All melting points are uncorrected. The uv spectra were recorded on Shimadzu UV-260 spectrophotometer. Infrared spectra were recorded on Perkin-Elmer 1710 FT-IR and Shimadzu IR-435 spectrophotometers. The ^{1}H nmr spectra were recorded on JEOL JNM-FX 100 and FX 200 FT-NMR spectrometers. Mass spectra were recorded at the Max-Planck-Institute for Biochemistry, Munich. Satisfactory elemental analysis were obtained on Heraus CHN-RAPID instrument.

2,3-Dimethoxycarbonyl-4,5-dimethoxynitrobenzene (**2**).

A cold mixture of fuming nitric acid and concentrated sulphuric acid (1:1, 12 ml) was added gradually in small amounts to dimethyl *meta*-hemipinate **1**, [13] 2.2 g (86 mmoles) at -5° to 0° over 10 minutes with stirring. It was allowed to stand for another 10 minutes at the same temperature. The reddish solution obtained was poured into ice-water and the yellow solid obtained was collected by filtration, washed with water, aqueous bicarbonate, again with water and then dried to give 1.95 g of the crude product. This was crystallised from a minimum amount of ethyl alcohol to give the nitro ester **2**, 1.4 g (54%) as yellow needles, mp 112°; ir (potassium bromide): ν_{max} 2940 cm^{-1} (m), 1720 (s), 1600 (s), 1535 (s), 1500 (w), 1428 (s), 1400 (w), 1370 (s), 1325 (s), 1295 (s), 1260 (s), 1215 (s), 1160 (m), 1075 (w), 995 (s), 980 (m), 868 (w), 800 (m); uv (chloroform): λ_{max} 245 nm (ε_{max} 15464), 300 (2705); ^{1}H nmr (deuteriochloroform): δ 7.5 (s, Ar, 1H), 4.03 (s, OCH_3, 6H), 3.91 (s, OCH_3, 3H), 3.87 (s, OCH_3, 3H); cmr (deuteriochloroform): 164.8 (s), 164.3 (s), 154.1 (s), 144 (s), 125.6 (s), 120.9 (s), 120.1 (s), 114.8 (d), 62.2 (q), 56.5 (q), 53.2 (q), 52.9 (q) ppm; ms: m/z (relative intensity) 300 (M + 1, 16.7), 299 (M$^+$, 100), 268 (100), 253 (2.9), 240 (2.1), 136 (16), 106 (10.2), 77 (20), 59 (80).

Anal. Calcd. for $C_{12}H_{13}NO_8$: C, 48.16; H, 4.34; N, 4.68. Found: C, 47.8; H, 4.1; N, 4.9.

2,3-Dimethoxycarbonyl-5,6-dimethoxyaniline (**3**).

To a stirred mixture of stannous chloride dihydrate 3.0 g (13.3 mmoles) and concentrated hydrochloric acid (20 ml) was added the nitro ester, **2**, 0.55 g (1.8 mmoles) in small quantities over half an hour at room temperature. The mixture was diluted with water and extracted with ethyl acetate and chloroform. The organic layers were washed with water and dried over anhydrous sodium sulphate. After filtration and removal of the solvents the combined residue, was dissolved in minimum amount of ethanol, and water added and allowed to stand overnight at 10-15°. Cream coloured crystals precipitated out, which where filtered and dried to give the amino ester **3**, 0.3 g (61%). The amino ester showed blue fluorescence under a uv lamp, mp 90°; ir (potassium bromide): ν_{max} 3440 cm^{-1} (s), 3350 (s), 2900 (s), 1700 (s), 1600 (s), 1405 (s), 1345 (s), 1265 (s), 1210 (w), 1190 (s), 1120 (s), 995 (m), 985 (m), 910 (m), 825 (m); uv (methanol): λ_{max} 234.2 nm (ε_{max} 18500), 270.8 (4922), 332.6 (4273); ^{1}H nmr (deuteriochloroform): δ 6.50 (s, Ar, 1H), 5.57 (br, s, NH_2, 2H, deuterium oxide exchangeable), 3.89 (s, OCH_3, 3H), 3.85 (s, OCH_3, 3H), 3.82 (s, OCH_3, 6H); cmr (deuteriochloroform): 169.4 (s), 167.5 (s), 153.8 (s), 143.4 (s), 136.2 (s), 131 (s), 105.7 (s), 101.9 (d), 59.9 (q), 56 (q), 52.6 (q), 52 (q) ppm; ms: m/z (relative intensity) 270 (M+1, 13), 269 (M$^+$, 100), 254 (17.2), 238 (39.5), 236 (28.6), 222 (88.5), 208 (21), 194 (13.4), 179 (8.9), 162 (17.5), 151 (30.2), 137 (7.9), 65 (5.4), 28 (26.7).

Anal. Calcd. for $C_{12}H_{15}NO_6$: C, 53.53; H, 5.57; N, 5.20. Found: C, 53.54; H, 5.59; N, 5.19.

1-Azido-2,3-dimethoxycarbonyl-5,6-dimethoxybenzene (**4**).

A cold solution of sodium nitrite, 0.75 g (10.8 mmoles) in water (2 ml) was added dropwise with stirring to a mixture of amino ester **3**, 0.25 g (0.92 mmole) in concentrated hydrochloric acid (2 ml) at 0-8° over 10 minutes. It was allowed to stand for another 30 minutes at the same temperature, the mixture was removed from ice-bath and a cold freshly prepared solution of sodium azide, 0.75 g (11.5 mmoles) dissolved in water (2 ml) was then added slowly with constant stirring and the mixture allowed to stand at 10-15° for two hours. A pale yellow solid precipitated out which was filtered and dried. It was then crystallised from petroleum ether to give the azido ester **4**, 0.1 g (36%) as pale yellow prisms, mp 67°; ir (potassium bromide): ν_{max} 2925 cm^{-1} (s), 2090 (s), 1720 (s), 1585 (s), 1487 (s), 1405 (s), 1340 (s), 1245 (w), 1080 (s), 1025 (s), 990 (m), 935 (w), 855 (s); uv (chloroform): λ_{max} 245 nm (ε_{max} 28861), 305 (2405), 317 (1763); ^{1}H nmr: (deuteriochloroform): δ 7.2 (s, Ar, 1H), 3.96 (s, OCH_3, 3H), 3.93 (s, OCH_3, 6H), 3.84 (s, OCH_3, 3H); cmr (deuteriochloroform): 169 (s), 166.4 (s), 153.2 (s),

147.2 (s), 132.2 (s), 124 (s), 123 (s), 110.4 (d), 61.2 (q), 56.1 (q), 52.8 (q), 52.6 (q) ppm; ms: m/z (relative intensity) 296 (M+1, 1.6), 295 (M^+, 7.6), 244 (24.8), 220 (29.3), 196 (24.8), 194 (31.2), 189 (19.1), 177 (34.4), 166 (35.9), 150 (100), 137 (12.7), 122 (19.7), 93 (12.7), 78 (15.3), 95 (55.1), 51 (12.7), 43 (4.7), 28 (39.8), 27 (3.8).

Anal. Calcd. for $C_{12}H_{13}N_3O_6$: C, 48.8; H, 4.4; N, 14.2. Found: C, 48.7; H, 4.5; N, 14.0.

Methyl-α-(5,6-Dimethoxycarbonyl-2,3-dimethoxyazepin-7-ylidene)-α-(5-methoxycarbonyl-2,3-dimethoxypyrid-6-yl)acetate (**5**).

A solution of the azido ester **4**, 0.3 g (1 mmole) in chlorobenzene (10 ml) was heated for 4 hours at 130°. Most of the solvent was removed under reduced pressure and the residue chromatographed on a silica gel column. Elution with benzene-ethyl acetate (90:10) followed by removal of the solvent and crystallisation of the residue from chloroform-petroleum ether gave the title compound **5**, 0.05 g (19%) as yellow needles, mp 181°; ir (potassium bromide): ν_{max} 2925 cm^{-1} (s), 1700 (s), 1645 (s), 1590 (s), 1545 (w), 1480 (s), 1425 (m), 1410 (w), 1380 (m), 830 (s), 800 (w); uv (methanol): λ_{max} 245.2 nm (ε_{max} 24454), 293.8 (26923); ^1H nmr (deuteriochloroform): δ 7.57 (s, Ar, 1H), 5.98 (s, 1H), 4.01 (s, OCH_3, 3H), 4.0 (s, OCH_3, 3H), 3.90 (s, OCH_3, 3H), 3.85 (s, OCH_3, 3H), 3.80 (s, OCH_3, 3H), 3.72 (s, OCH_3, 3H), 3.64 (s, OCH_3, 3H), 3.33 (s, OCH_3, 3H); ms: m/z (relative intensity) 535 (M+1, 2.6), 534 (M^+, 10.7), 519 (4.1), 503 (3.8), 475 (100), 460 (28.1), 417 (32.5), 401 (5.3), 389 (2.5), 373 (3.3), 357 (2.4), 343 (3.3), 327 (2.3), 315 (2.3), 283 (1.6), 255 (1.8), 238 (2.3), 222 (4.1), 215 (4.3), 193 (5), 174 (4.1), 163 (5), 149 (3.6), 129 (2), 105 (2.1), 93 (1.8), 83 (2), 69 (3), 59 (9.5).

Anal. Calcd. for $C_{24}H_{26}N_2O_{12}$: C, 53.93; H, 4.86; N, 5.24. Found: C, 53.40; H, 4.90; N, 5.30.

X-ray Crystal Structure Determination of (**5**).

Colourless transparent cuboidal crystals of the compound were grown for X-ray study by slow evaporation of the solvent in acetone-benzene mixture. A single crystal of good quality was mounted on a glass fibre on a CAD4 Enraf Nonius diffractometer. Monochromated CuKα radiation was used. Cell constants were obtained by a least squares procedure of 25 reflections with θ values in the 0 to 30° range. A total of 3368 unique reflections were measured using w(omega) - 2θ scan mode. Diffraction data were collected up to 60° with ±h, k, l. The structure was solved using direct methods. All the non hydrogen atoms were located using RANTAN option in MULTAN80 [14] and refined anisotropically. The hydrogen atoms were fixed by stereochemical considerations and were refined isotropically. 2621 observed reflections with $|F|>3\ \sigma(F)$ were used for the refinement. The Weighting scheme used for the refinement was:

$$\text{Weight} = 1.0000/(\sigma^2(F) + 0.001\ |F|^2).$$

The R-factor and the R_W values converged at 0.0685 and 0.0658 respectively. The maximum shift/ESD for non-hydrogen atom coordinates was 0.314 while it was 0.224 for the anisotropic temperature factors. The maximum positive and negative residual Fourier peak were +0.25 e/Å^3 and -0.35 e/Å^3 respectively. All the computations were done on a VAX11/785 computer.

Conclusion.

Thermal and photochemical reactions of aryl azides in the presence of nucleophiles like aliphatic bases and alcohols lead to azepines *via* ring expansion. These reactions remain one of the "most enigmatic reactions" of aryl azides. Such reactions when carried out in inert solvents like aromatic hydrocarbons or their halogenated derivatives, allow us to observe unusual reactions like the one described in this paper and point towards a more complex reaction pathway than previously suggested.

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Supplementary Materials.

Tables of thermal parameters, complete torsion angles, fitting of planes with respect to selected sets of atoms, calculated and observed structure factors.

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