Tetrahedron Vol. 42, No. 18, pp. 5081 to 5088, 1986
Printed in Great Britain.

0040-4020/86 $3.00+.00
Pergamon Journals Ltd.

SYNTHESIS OF HETEROCYCLIC PROPELLANES. PREPARATION AND TRANSANNULAR REACTIONS OF 5-ETHOXYCARBONYLMETHYLENE-CYCLOOCTANONE AND THE CORRESPONDING OXIMES AND HYDRAZONES

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(*Received in UK* 4 *July* 1986)

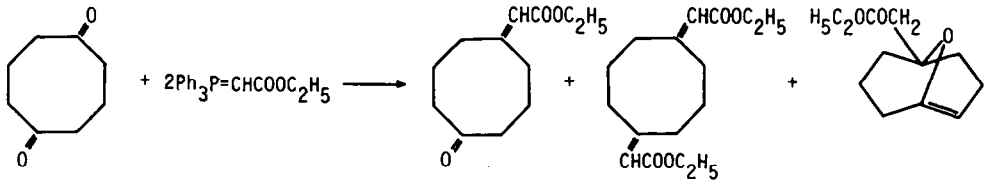
Abstract: 5-Ethoxycarbonylmethylene-cyclooctanone (3) is prepared by Wittig monoolefination of dione 1 with phosphorus ylide 2. Thermal transannular cyclization of oxime 6 and phenylhydrazone 12 of the ketone 3 affords 3-oxa-2-aza- and 2,3-diaza[3.3.3]propellanes 7 and 14 respectively. Irradiation of ketone 3, its oxime 9, and its dimethylhydrazone 16 furnish 9-oxa-, and 9-aza[3.3.2]propellanes 11, 10, and 17, respectively. In addition to the propellane 14, phenylazo-bicyclo compound 13 is also obtained from phenylhydrazone 12. The acetyl derivatives 8 and 15 of propellanes 7 and 14 are also prepared and studied.

Cyclooctane-1,5-dione (1) and its simple derivatives have been shown to exist predominantly in the boat-chair conformation with the carbonyl groups, or with their unsaturated analogs, in a parallel orientation[1,2]. The existence of through-space transannular interaction between formally non-conjugated methylene and carbonyl π-electrons in some suitable 1,5-disubstituted cyclooctanes has been recently demonstrated by ^{13}C NMR spectroscopy[3]. Dione 1 undergoes a double Wittig reaction with methylenetriphenylphosphorane to give 1,5-dimethylene-cyclooctane[4,5], which is readily transformed into bridgehead substituted bicyclo[3.3.1]nonane derivatives via transannular addition of some nucleophiles[4,6,7], or bicyclo[4.3.1]decane derivatives by a catalytic Pd^{II} mediated oxidation reaction[7], or [3.3.2]propellane by a photocyclization reaction[5].

We have recently reported preparation of some bis(arylhydrazones)of cyclooctane-1,5-dione (1) and their oxidation with lead tetraacetate to the corresponding 1,5-bis(arylazo)-bicyclo-[3.3.0]octanes[8]. In connection with this study and our previous work on the Wittig reactions of o-quinones with phosphorus ylides[9], we now wish to report our results on the reactions of dione 1, and cyclodecane-1,6-dione (18) with ethoxycarbonylmethylenetriphenylphosphorane (2). We also report some reactions of ketone 3, obtained from dione 1, which lead to heterocyclic propellanes, as depicted in Schemes 2-6.

RESULTS AND DISCUSSION

When a mixture of dione 1 and two equivalents of ylide 2 was heated at 170-180 °C for 2,5 h and the reaction mixture was then subjected to column chromatography, compound 3, 1,5-bis-(ethoxycarbonylmethylene)-cyclooctane (4) and a compound isomeric to 3 were isolated in 25%, 57% and 12% yield, respectively (Scheme 1). The proposed structures for compounds 3 and 4 were confirmed by elemental analyses and spectral data.

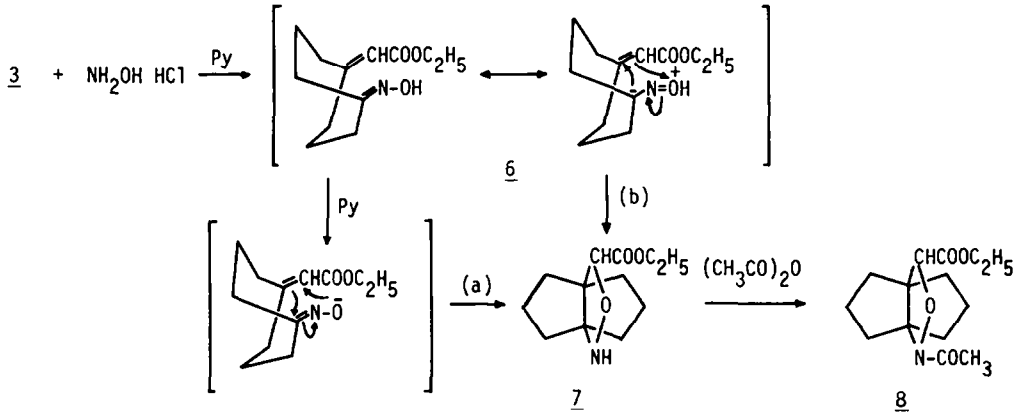


1 2 3 4 5

Scheme 1

The third product isolated from the reaction mixture showed in the mass spectrum a molecular ion at m/z 210. The ^{1}H NMR spectrum of the compound in question exhibited, in addition to the signals for ethyl and cyclooctane protons, one proton multiplet at δ 5.87-5.40 and a two proton singlet at δ 2.97, while the IR spectrum showed absorptions at 1722, 1700 cm^{-1}. On the basis of these data, the structure of 9-oxa-5-ethoxycarbonylmethyl-bicyclo-[3.3.1]non-1-ene (5) may be proposed for this product. We note that when the reaction between compounds 1 and 2 was repeated at a lower temperature and for a shorter period of time, the yields of compounds 4 and 5 were reduced to 20 and 3%, respectively, whereas the yield of compound 3 was increased to 60%. The structure of compound 5 is under further consideration.

Subsequently, we studied the reactions of compound 3 depicted in Schemes 2-6. Treatment of compound 3 with hydroxylamine hydrochloride in boiling pyridine for 20 min afforded 4-ethoxycarbonyl-3-oxa-2-aza[3.3.3]propellane (7) in 85% yield (Scheme 2). This obviously



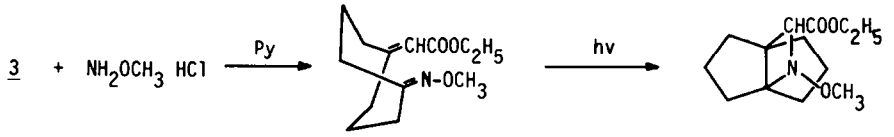
Scheme 2

occurs through a transannular cyclization of the initially formed oxime 6, via abstraction of the oxime proton by pyridine and further Michael-type addition (route a, as suggested by referee), or by analogy to the previously reported synthesis of 5-methoxycarbonylisoxazolidine, which was proposed to proceed via 1,3-dipolar cycloaddition of formaldoxime to methyl acrylate[10] (route b). The spectral data of compound 7 are in agreement with the proposed structure and similar to those reported for 5-methoxycarbonylisoxazolidine. The ^{1}H NMR spectrum displayed an one proton singlet at δ 4.17 (C_4-H) and an one proton broad singlet at δ 5.88 (N-H, exchangeable with deuterium oxide).

Treatment of compound 7 with acetic anhydride gave the acetyl-derivative 8. The mass spectrum of compound 8 showed correct molecular ion and an abudant ion M - 42, followed by a fragmentation pattern very similar to that of compound 7. The IR spectrum exhibited

an absorption at 1671 cm^{-1}, indicative of the presence of the N-$COCH_3$ group and in agreement with the proposed isoxazolidine structure for compounds 7 and 8.

In order to avoid the transannular cyclization of the initially formed oxime 6 and to shed more light into the mechanism proposed for the formation of propellane 7, we attempted preparation of the O-methyl derivative 9. Treatment of compound 3 with O-methyl-hydroxylamine hydrochloride in boiling pyridine for 1 h afforded oxime 9 as a mixture of two stereoisomers, as indicated by the ^1H NMR spectrum, which showed a broad singlet at δ 5.65 (=CH) and two singlets for OCH_3 at δ 3.71 and 3.76 with a total ratio of 1:3. Efforts to separate the mixture by chromatographic methods (column, p.t.l.c.) were unfruitful. Oxime 9 was recovered unchanged after heating at 110 °C for 14 h. Irradiation of oxime 9 with a 125 W medium pressure mercury arc in benzene solution for 2,5 h furnished 9-methoxy-10-ethoxycarbonyl-9-aza[3.3.2]propellane (10) in 71% yield (Scheme 3), by analogy to the previously reported synthesis of azetidines

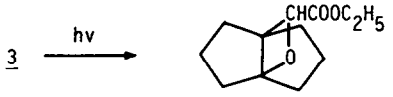


9 10

Scheme 3

through photochemical reaction of the [2+2] type [11]. The spectral data of the azetidine derivative 10 are very similar to those reported for cis- and trans-1-t-butyl-2-carbomethoxy-4-methyl-azetidines[12] and they are in good agreement with the proposed structure. The mass spectrum of compound 10 gave the correct molecular ion with the more abudant fragment at m/z 108 (100%), corresponding to the bicyclooctane fragment of the propellane. The ^1H NMR spectrum showed an one proton singlet at δ 3.8 for the C_2-H of the azetidine ring, and the IR spectrum exhibited strong absorptions at 1750 (ester ν_1 C=O) and 1723 cm^{-1} (ester ν_2 C=O).

It is well known that the photochemical reaction of carbonyl compounds and alkenes is one of the two most used methods for oxetane synthesis and that the major product corresponds to the more stable ether-diradical intermediate [13]. In accordance with that, irradiation of compound 3 in benzene solution gave 10-ethoxycarbonyl-9-oxa[3.3.2]propellane (11) in 70% yield (Scheme 4). The mass spectrum of compound 11 showed the correct molecular ion at m/z 210

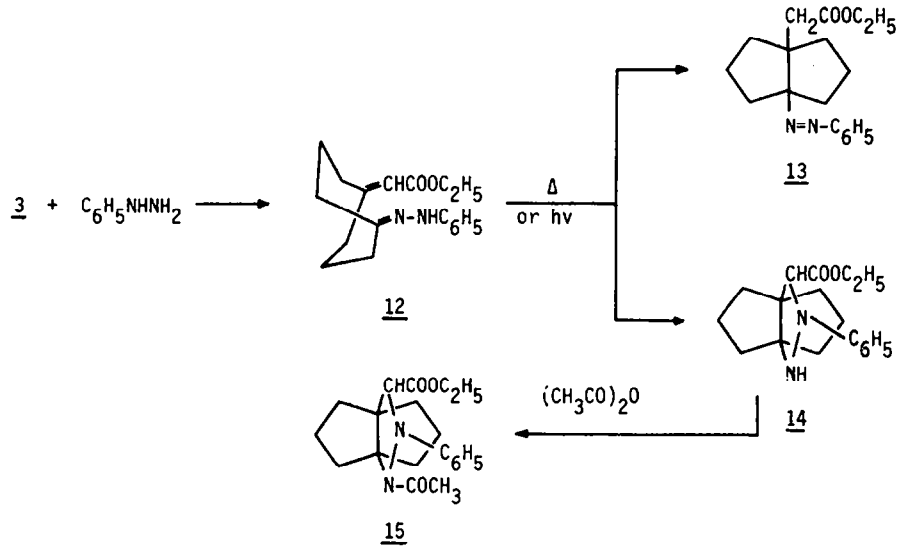


11

Scheme 4

(~1%) and an abudant fragment at m/z 108 (26%), arising from the expected cross-ring cleavage of the oxetane ring[13]. The ^1H NMR spectrum displayed an one proton singlet at δ 4.70 for the C_{10}-H, and the same value (4.73) is reported for the α-protons of the oxetane[14]. The signal at 4.70 appearing at higher field than that expected for a proton next to a carbethoxy substituent can be attributed to the participation of the oxetane ring in the propellane system, since introduction of alkyl substituents in the oxetane ring, as with other small rings, often causes special shielding effects, due to proximity effects[14].

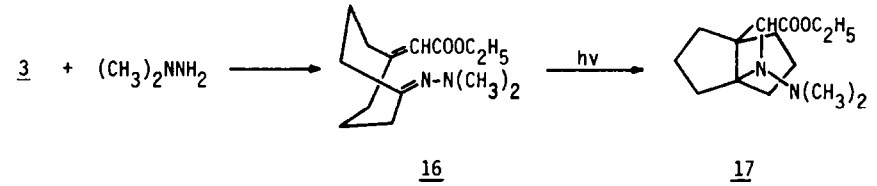
Treatment of ketone 3 with phenylhydrazine in ethanol solution at room temperature for 2 h, gave phenylhydrazone 12 and 4-ethoxycarbonyl-3-phenyl-2,3-diaza[3.3.3]propellane (14) in 40, and 23% yield, respectively. Heating of compound 12 in benzene solution for 9 h afforded propellane 14 and 1-phenylazo-5-ethoxycarbonylmethyl-bicyclo[3.3.0]octane (13) in 70, and 14% yield, respectively (Scheme 5). The same products, 14 (43%) and 13 (35%), were also obtained



Scheme 5

by irradiation of compound 12 in benzene solution for 2,5 h. Treatment of compound 14 with acetic anhydride and pyridine gave the acetyl-derivative 15 in 57% yield. The structures of compounds 12, 13, 14 and 15 were confirmed by their elemental analyses and spectral data. The olefinic proton of compound 12 resonates at about the same field as the corresponding proton of compounds 3, 4 and 9. The chemical shift values of the C_4-H of compounds 14 and 15 are very similar to those observed for the C_4-H of compounds 7 and 8. A two-proton upfield singlet for compound 13 is attributed to the methylene protons attached to the carbethoxy-group, in agreement with the proposed structure for this product.

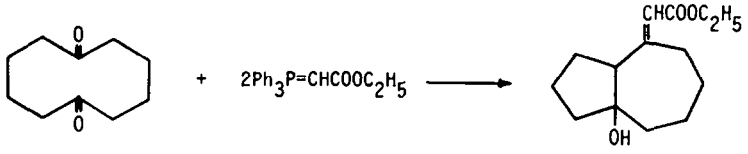
A mechanism similar to that proposed for the formation of compound 7, may also explain the transformation of compound 12 to propellane 14, whereas a transannular cyclization with concomitant transfer of the N-hydrogen atom to the exomethylene carbon atom of compound 12 may account for the formation of phenylazo-derivative 13. The proposed mechanism for the formation of propellane 14 is further supported by the fact that treatment of compound 3 with N,N-dimethyl-hydrazine in boiling ethanol afforded only the hydrazone 16, as indicated by the ^1H NMR spectrum of the concentrated reaction mixture, which exhibited the characteristic singlet at δ 5.7 for the olefinic proton. Compound 16 was not isolated in pure form due to



Scheme 6

gradual decomposition on standing, or during column chromatography. Irradiation of a crude sample of 16, immediately after it was prepared, afforded 9-dimethylamino-10-ethoxycarbonyl-9-aza[3.3.2]propellane 17 (Scheme 6). The spectral data for azetidine 17 are similar to those of the azetidine 10, in agreement with the proposed structure.

Finally, heating of a mixture of cyclodecane-1,6-dione 18 and ylide 2 at 160-170 °C for 3,5 h and separation of the reaction mixture by column chromatography, gave two isomeric 6-ethoxycarbonylmethylene-bicyclo[5.3.0]decan-1-ols (19) in 34% total yield (Scheme 7). This is analogous



18 2 19

Scheme 7

to the previously reported tendency of compound 18 and of its derivatives to be transformed into bicyclo[5.3.0]decane derivatives[8,15]. The analytical and spectral data of the two isomeric products are in good agreement with the proposed structure 19.

EXPERIMENTAL

M.p.s. are uncorrected and were determined on a Kofler hot-stage apparatus. IR spectra were obtained with a Perkin-Elmer 297 spectrophotometer as films or Nujol mulls. UV spectrum was recorded on a Shimadzu UV-210A spectrophotometer in 95% ethanol. ^{1}H NMR spectra were recorded with deuteriochloroform as the solvent on a Varian A60-A spectrometer, with tetramethylsilane as the internal standard. Mass spectra were determined on a Hitachi Perkin-Elmer RMU-6L mass spectrometer. The ionisation energy was maintained at 70 eV. Light petroleum refers to the fraction of 40-60 °C.

Reaction of Cyclooctane-1,5-dione (1) with Ethoxycarbonylmethylenetriphenylphosphorane (2). Preparation of compounds (3), (4) and (5). A mixture of compounds 1 (1.4 g, 10 mmol) and 2 (7.25 g, 20.8 mmol) was heated in an oil bath maintained at 170-180°C under nitrogen for 2.5 h and the reaction mixture was then chromatographed on silica gel. The column was eluted with light petroleum containing increasing amounts of ethyl acetate (from 20 to 35%) to give a total of three fractions. The first fraction was found to be 1,5-bis(ethoxycarbonylmethylene)-cyclooctane (4) as an oil (1.6 g, 57%); Found: C, 68.35; H, 8.7. $C_{16}H_{24}O_4$ requires C, 68.54; H, 8.63%; ν_{max}(film) 1720, 1710, 1638 cm^{-1}; δ ($CDCl_3$) 1.25 (6 H, t, J=7 Hz), 1.62-2.42 (8 H, m), 2.52-2.95 (4 H, m), 4.12 (4 H, q, J=7 Hz) and 5.63 (2 H, br s); m/z 280 (M$^+$, 27%), 252 (37), 235 (23), 234 (26), 207 (13), 206 (48), 193 (8), 192 (15), 188 (18), 161 (19), 160 (15), 147 (20), 146 (10), 133 (25), 119 (27), 108 (5), 105 (31), 91 (29), 41 (40) and 29 (100).
The second fraction was compound 5 (0.252 g, 12%), obtained as an oil; Found: C, 68.45; H, 8.5. $C_{12}H_{18}O_3$ requires C, 65.54; H, 8.63%; ν_{max} (film) 3030, 1722, 1700, 1625$_{sh}$ cm^{-1}; δ ($CDCl_3$) 1.25 (3 H, t, J=7 Hz), 1.5-2.15 (3 H, m), 2.15-2.63 (7 H, m), 2.97 (2 H, s), 4.12 (2 H, q, J=7 Hz) and 5.40-5.87 (1 H, m); m/z 210 (M$^+$, 16%), 195 (3), 182 (29), 165 (10), 154 (10), 137 (23), 123 (8), 108 (14), 107 (11), 95 (15), 93 (17), 91 (13), 79 (38), 55 (56), 41 (74), 29 (100).
The third fraction was 5-ethoxycarbonylmethylene-cyclooctanone (3) (0.525 g, 25%) obtained in oily form; Found: C, 68.3; H, 8.7. $C_{12}H_{18}O_3$ requires C, 68.54; H, 8.63%; ν_{max} (film) 3035, 1720$_{sh}$, 1708, 1638 cm^{-1}; δ ($CDCl_3$) 1.27 (3 H, t, J=7 Hz), 1.83-2.93 (12 H, m), 4.12 (2 H, q, J=7 Hz) and 5.72 (1 H, s); m/z 210 (M$^+$, 4%), 182 (3), 165 (10), 164 (15), 137 (10), 136 (17), 123 (10), 119 (13), 108 (20), 107 (11), 95 (13), 94 (10), 93 (12), 91 (9), 79 (32), 55 (69), 43 (36), 41 (78) and 29 (100).

When the above reaction was repeated by heating a mixture of compounds 1 (1.4 g, 10 mmol) and 2 (7.25 g, 20.8 mmol) at 160-170°C for 1.5 h compounds 4 (0.56 g, 20%), 5 (63 mg, 3%) and 3 (1.26 g, 60%) were obtained. Efforts to crystallize compounds 3, 4, 5 were unsuccessful.

Reaction of compound (3) with Hydroxylamine Hydrochloride. Preparation of 4-Ethoxycarbonyl-3-oxa-2-aza[3.3.3]propellane (7). A solution of compound 3 (0.21 g, 1.5 mmol) and hydroxylamine hydrochloride (0.15 g, 2.15 mmol) in pyridine (3 ml) was heated at reflux for 20 min. Water (20 ml) was then added and the mixture was extracted with methylene chloride. The organic layer was separated, dried (Na_2SO_4), the solvent was removed under reduced pressure, and the residue

was chromatographed on silica gel, using light petroleum-ethyl acetate (1:1) as eluant, to give, as an oil, compound 7 (0.19 g, 85%); Found: C, 64.0; H, 8.4; N, 6.1. $C_{12}H_{19}NO_3$ requires C, 63.97; H, 8.50; N, 6.22%; ν_{max} (film) 3215, 1750, 1735 cm^{-1}; δ ($CDCl_3$) 1.31 (3 H, t, J=7 Hz), 1.50-2.43 (12 H, m), 4.17 (1 H, s), 4.27 (2 H, q, J=7 Hz) and 5.88 (1 H, br s, removed by D_2O, NH); m/z 225 (M^+, 72%), 208 (24), 197 (6), 193 (6), 180 (9), 179 (25), 162 (15), 152 (58), 151 (11), 150 (13), 147 (34), 134 (28), 124 (66), 123 (15), 122 (33), 121 (38), 119 (40), 108 (25), 107 (46), 96 (48), 95 (28), 93 (30), 91 (30), 79 (56), 67 (46), 55 (53), 43 (33), 41 (92) and 29 (100).

When the above reaction was carried out at room temperature compound 3 was recovered unchanged.

Preparation of 2-Acetyl-4-ethoxycarbonyl-3-oxa-2-aza[3.3.3]propellane (8). To a solution of propellane 7 (50 mg, 0.22 mmol) in dry benzene (2 ml) was added acetic anhydride (30 mg, 0.29 mmol) and the mixture was stirred at room temperature for 2 h. Water (2 ml) was then added and the mixture was heated at reflux for 10 min. The organic layer was separated, washed with water, dried (Na_2SO_4) and concentrated under reduced pressure. Preparative t.l.c. of the residue on silica gel (light petroleum-ethyl acetate 2:1) gave compound 8 as an oil (53 mg, 89%); Found: C, 62.6; H, 7.75; N, 5.0. $C_{14}H_{21}NO_4$ requires C, 62.90; H, 7.92; N, 5.24%; ν_{max} (film) 1750, 1728, 1671, 1660 cm^{-1}; δ ($CDCl_3$) 1.32 (3 H, t, J=7 Hz), 1.50-2.50 (12 H, m), 2.13 (3 H, s), 4.27 (1 H, s) and 4.29 (2 H, q, J=7 Hz); m/z 267 (M^+, 14%), 225 (100), 208 (12), 197 (2), 193 (3), 179 (15), 162 (5), 152 (18), 147 (12), 134 (10), 124 (15), 123 (7), 122 (11), 121 (15), 119 (12), 108 (11), 107 (18), 96 (13), 95 (11), 93 (13), 91 (12), 79 (19), 67 (16), 55 (18), 43 (77), 41 (38) and 29 (41).

Reaction of compound (3) with O-Methyl-hydroxylamine Hydrochloride. Preparation of 5-Ethoxycarbonylmethylene-cyclooctanone-oxime Methyl Ether (9). A solution of compound 3 (0.21 g, 1.5 mmol) and O-methyl-hydroxylamine hydrochloride (0.168 g, 2 mmol) in pyridine (3 ml) was heated at reflux for 1 h. Water (20 ml) was then added and the mixture was extracted with methylene chloride. The organic layer was separated, dried (Na_2SO_4), the solvent was removed under reduced pressure and the residue was chromatographed on silica gel. The column was eluted with light petroleum containing increasing amounts of ethyl acetate (from 9 to 15%) to give compound 9 as an oily mixture of two stereoisomers (0.186 g, 78%). Efforts to separate the isomers by p.t.l.c. on silica gel were unsuccessful. Found: C, 65.25; H, 8.7; N, 5.6. $C_{13}H_{21}NO_3$ requires C, 65.24; H, 8.85; N, 5.85%; ν_{max} (film) 1735, 1710, 1638 cm^{-1}; δ ($CDCl_3$) 1.25 (3 H, t, J=7 Hz), 1.57-2.87 (12 H, m), 3.71 and 3.76 (3 H, two singlets, O-CH_3), 4.13 (2 H, q, J=7 Hz) and 5.65 (1 H, br s); m/z 239 (M^+, 10%), 211 (5), 208 (17), 194 (8), 166 (12), 162 (7), 134 (20), 126 (22), 120 (12), 119 (9), 112 (31), 108 (7), 107 (11), 106 (10), 93 (20), 91 (17), 79 (27), 57 (14), 55 (24), 41 (76) and 29 (100).

When compound 9 in toluene solution was heated at reflux for 14 h, it was recovered unchanged.

Preparation of 9-Methoxy-10-ethoxycarbonyl-9-aza[3.3.2]propellane (10). A solution of the isomeric mixture 9 (80 mg, 0.33 mmol) in benzene (32 ml) was irradiated in a quartz cell with a 125 W medium pressure mercury arc for 2.5 h. The solution was concentrated and the residue was chromatographed on silica gel. Elution of the column with light petroleum containing increasing quantities of ethyl acetate (from 9 to 15%) gave two fractions. The first fraction was an oil identified as 10 (57 mg, 71%); Found: C, 64.9; H, 8.6; N, 5.6. $C_{13}H_{21}NO_3$ requires C, 65.24; H, 8.85; N, 5.85%; ν_{max} (film) 1750, 1723 cm^{-1}; δ ($CDCl_3$) 1.28 (3 H, t, J=7 Hz), 1.40-2.60 (12 H, m), 3.49 (3 H, s), 3.80 (1 H, s) and 4.21 (2 H, q, J=7 Hz); m/z 239 (M^+, 9%), 223 (3), 166 (37), 134 (6), 132 (8), 120 (5), 119 (14), 109 (14), 108 (100), 107 (63), 93 (19), 91 (21), 80 (55), 79 (53), 77 (20), 67 (20), 57 (17), 55 (18), 43 (25), 41 (48) and 29 (69). The second fraction was starting material (8 mg, 10%).

Preparation of 10-Ethoxycarbonyl-9-oxa[3.3.2]propellane (11). A solution of compound 3 (0.1 g, 0.48 mmol) in benzene (40 ml) was irradiated in a quarz cell with a 125 W medium pressure mercury arc for 5 h. After evaporation of the solvent the residue was chromatographed on silica gel with light petroleum-ethyl acetate (4:1 up to 3:1) as eluant to give a total of two fractions. The first fraction was found to be an oily product identified as 11 (70 mg, 70%); Found: C, 68.7; H, 8.5. $C_{12}H_{18}O_3$ requires C, 68.54; H, 8.63%; ν_{max} (film) 1750, 1722 cm^{-1}; δ ($CDCl_3$) 1.25 (3 H, t, J=7 Hz), 1.35-3.03 (12 H, m), 4.23 (2 H, q, J=7 Hz) and 4.70 (1 H, s); m/z 210 (M^+, 0.7%), 166 (3), 165 (24), 138 (17), 137 (16), 126 (5), 123 (3), 119 (25), 109 (10), 108 (26), 107 (12), 93 (18), 91 (24), 79 (45), 67 (30), 55 (40), 41 (69) and 29 (100). The second fraction was identified as starting material 3 (25 mg, 25%).

Reaction of compound (3) with Phenylhydrazine. Preparation of compounds (12) and (14). To a solution of compound 3 (0.21 g, 1.5 mmol) in ethanol (2 ml) was added phenylhydrazine (0.216 g, 2 mmol) and the mixture was stirred at room temperature for 2 h. Phenylhydrazone 12 was precipitated as white crystals (0.12 g, 40%), m.p. 130-134°C; Found: C, 71.8; H, 8.1; N, 9.4. $C_{18}H_{24}N_2O_2$ requires C, 71.97; H, 8.05; N, 9.33%; ν_{max} (Nujol) 3345, 1693, 1640, 1603 cm^{-1}; δ ($CDCl_3$) 0.98 (3 H, t, J=7 Hz), 1.83-2.90 (12 H, m), 3.87 (2 H, q, J=7 Hz), 5.58 (1 H, br s)

and 6.73-7.43 (5 H, m); m/z 300 (M^+, 28%), 255 (2), 227 (100), 195 (12), 192 (5), 141 (7), 121 (14), 108 (14), 107 (80), 105 (16), 93 (74), 92 (29), 91 (22), 79 (50), 77 (78), 67 (26), 65 (44), 41 (50) and 29 (66). The filtrate was concentrated under reduced pressure and the residue was chromatographed on silica gel with light petroleum-ethyl acetate (6:1) as eluant to give white crystals of 4-ethoxycarbonyl-3-phenyl-2,3-diaza[3.3.3]propellane (14) (70 mg, 23%), m.p. 75-77°C (from ethanol); Found: C, 71.7; H, 8.2; N, 9.4. $C_{18}H_{24}N_2O_2$ requires C, 71.97; H, 8.05; N, 9.33%; ν_{max} (Nujol) 3190, 1728, 1603 cm^{-1}; δ ($CDCl_3$) 1.22 (3 H, t, J=7 Hz), 1.30-2.47 (12 H, m), 4.18 (2 H, q, J=7 Hz), 4.27 (1 H, s) and 6.55-7.53 (5 H, m); m/z 300 (M^+, 33%), 227 (100), 107 (3), 105 (7), 93 (5), 92 (4), 91 (9), 79 (9), 77 (40), 67 (8), 65 (10), 55 (12), 41 (21) and 29 (35).

Thermal (A) and Photochemical (B) Transformation of compound (12) into compounds (13) and (14). A. A solution of compound 12 (50 mg, 0.16 mmol) in benzene (3 ml) was heated at reflux for 9 h. The solvent was evaporated and the residue was chromatographed on silica gel using light petroleum-ethyl acetate (6:1) as eluant to give a total of two fractions. The fraction eluted first was an oil identified as 1-phenylazo-5-ethoxycarbonylmethyl-bicyclo[3.3.0]octane (13) (7 mg, 14%); Found: C, 71.65; H, 8.1; N, 9.0. $C_{18}H_{24}N_2O_2$ requires C, 71.97; H, 8.05; N, 9.33%; λ_{max} (95% EtOH) 215, 265 and 413 nm (log ε 4.68, 4.60 and 2.24); ν_{max} (film) 1730, 1360, 1170 cm^{-1}; δ ($CDCl_3$) 1.18 (3 H, t, J=7 Hz), 1.38-2.33 (12 H, m), 2.37 (2 H, s, CH_2-COOEt), 4.04 (2 H, q, J=7 Hz) and 7.22-7.83 (5 H, m); m/z 300 (M^+, 2%), 255 (3), 227 (2), 195 (M - $C_6H_5N_2$, 36%), 167 (4), 141 (4), 121 (15), 108 (15), 107 (100), 105 (14), 93 (16), 91 (17), 79 (54), 77 (49), 67 (16), 55 (20), 44 (57), 41 (42) and 29 (52). The second fraction was identical to compound 14 (35 mg, 70%).

B. When a solution of compound 12 (90 mg, 0.3 mmol) in benzene (40 ml) was irradiated in a quarz cell with a 125 W medium pressure mercury arc for 2.5 h and the reaction mixture was separated as above, compounds 13 (31 mg, 35%) and 14 (39 mg, 43%), identical to those obtained before, were eluted.

Preparation of 2-Acetyl-3-phenyl-4-ethoxycarbonyl-2,3-diaza[3.3.3]propellane (15). To a solution of compound 14 (0.1 g, 0.33 mmol) in pyridine (1 ml) was added acetic anhydride (50 mg, 0.49 mmol) and the mixture was heated at reflux for 2 h. Water (1 ml) was then added and the reaction mixture was refluxed for 15 min. The mixture was extracted with ether, the organic layer was washed successively with dilute hydrochloric acid, water, and it was dried (Na_2SO_4). The solvent was evaporated and the residue was chromatographed on silica gel with light petroleum-ethyl acetate (3:1) as eluant to give compound 15 as an oil (65 mg, 57%); Found: C, 70.0; H, 7.75; N, 8.05. $C_{20}H_{26}N_2O_3$ requires C, 70.15; H, 7.65; N, 8.18%; ν_{max} (film) 1745, 1728, 1665 cm^{-1}; δ ($CDCl_3$) 1.35 (3 H, t, J=7 Hz), 1.45-2.75 (12 H, m), 2.08 (3 H, s), 4.30 (2 H, q, J=7 Hz), 4.33 (1 H, s) and 6.60-7.47 (5 H, m); m/z 342 (M^+, 5%), 300 (8), 299 (M - $COCH_3$, 32%), 269 (3), 227 (5), 204 (10), 141 (11), 105 (15), 91 (16), 86 (39), 84 (68), 77 (61), 57 (42), 55 (56), 43 (100), 41 (87) and 29 (71).

Reaction of compound (3) with N,N-Dimethyl-hydrazine. Preparation of compound (16) and its subsequent Irradiation to compound (17). To a solution of compound 3 (0.1 g, 0.48 mmol) in ethanol (3 ml) was added N,N-dimethylhydrazine (46 mg, 0.76 mmol) and the mixture was heated at reflux for 4 h. The solvent was evaporated to give an oil which was found to be unstable on standing and during column chromatography. This was tentatively assigned structure 16, by ^1H NMR [δ 5.70 (=CH, s)], IR (1662 cm^{-1}) and mass spectrometry [m/z 252 (M^+, 28%), 224 (M-28, 57%), 207 (M - OC_2H_5, 7%), 179 (M - $CO_2C_2H_5$, 18%), 165 (M - $CH_2CO_2C_2H_5$, 100%)].

A solution of the crude oil 16, obtained above, in benzene (20 ml) was irradiated in a quartz cell with a 125 W medium pressure mercury arc for 8 h. After evaporation of the solvent the residue was chromatographed on silica gel with light petroleum-ethyl acetate (3:1 up to 2:1) as eluant to give an oily fraction. This was further purified by preparative t.l.c. on silica gel (light petroleum-ethyl acetate 2:1) to give 9-dimethylamino-10-ethoxycarbonyl-9-aza[3.3.2]-propellane (17) as an oil (45 mg, 37%, based on compound 3); Found: C, 67.0; H, 9.65; N, 10.75. $C_{14}H_{24}N_2O_2$ requires C, 66.63; H, 9.59; N, 11.10%; ν_{max} (film) 1740, 1715 cm^{-1}; δ ($CDCl_3$) 1.27 (3 H, t, J=7 Hz), 1.35-2.90 (12 H, m), 2.28 (6 H, s), 3.85 (1 H, s) and 4.20 (2 H, q, J=7 Hz); m/z 252 (M^+, 11%), 210 (3), 179 (10), 165 (3), 145 (19), 144 (13), 137 (8), 119 (4), 108 (20), 107 (11), 103 (18), 102 (13), 99 (61), 93 (13), 91 (15), 80 (25), 79 (39), 77 (19), 74 (24), 71 (20), 67 (19), 59 (74), 44 (100), 43 (66), 41 (48) and 29 (81).

Reaction of compound (18) with ylide (2). Preparation of 6-Ethoxycarbonylmethylene-bicyclo-[5.3.0]decan-1-ol (19). A mixture of compounds 18 (0.315 g, 1.87 mmol) and 2 (1.3 g, 3.74 mmol) was heated in an oil bath maintained at 160-170°C under nitrogen for 3.5 h and the reaction mixture was chromatographed on silica gel. The column was eluted with light petroleum-ethyl acetate (5:1) to give two fractions, obtained as oils, considered to be stereoisomers of structure 19. First fraction: 90 mg (20%); Found: C, 70.2; H, 9.0. $C_{14}H_{22}O_3$ requires C, 70.55; H, 9.31%; ν_{max} (film) 3500, 1705, 1690, 1625 cm^{-1}; δ ($CDCl_3$) 1.32 (3 H, t, J=7 Hz), 1.38-3.30 (15 H, m), 4.18 (2 H, q, J=7 Hz) and 5.82 (1 H, br s); m/z 238 (M^+, 10%), 220 (28), 193 (34), 192 (100), 174 (22), 164 (20), 151 (32), 147 (46), 146 (40), 133 (35), 132 (48), 91 (35), 79 (39), 77 (81), 67 (35), 55 (49), 43 (28) 41 (51) and 29 (48). Second fraction: 60 mg (14%);

Found: C, 70.3; H, 9.2. $C_{14}H_{22}O_3$ requires C, 70.55; H, 9.31%; ν_{max} (film) 3460, 1712, 1695, 1635 cm^{-1}; δ ($CDCl_3$) 1.28 (3 H, t, J=7 Hz), 1.42-3.27 (15 H, m), 4.16 (2 H, q, J=7 Hz) and 5.63 (1 H, br s); m/z 238 (M^+, 12%), 220 (8), 193 (23), 192 (69), 174 (17), 164 (13), 151 (18), 147 (24), 133 (14), 132 (19), 91 (20), 77 (100), 67 (15), 55 (21), 51 (43), 50 (30), 43 (17), 41 (23) and 29 (23).

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