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Singlet Ethoxycarbonylnitrene Stabilization by Dichloromethane. Thermolysis of Ethyl Azidoformate in Adamantane and Ethylbenzene

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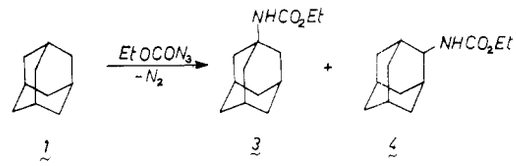
Some evidence was gained in favor of the formation of a solvent–singlet ethoxycarbonylnitrene complex. It has been reported that dichloromethane,[1,2] hexafluorobenzene,[3,4] and 1,4-dioxan[5] stabilize the singlet state of EtOCON, generated by ethyl azidoformate, during the C–H insertion reaction. Quite recently Takeuchi et al.[6] discussed the situation for EtOCON generated in the THF–CH_2Cl_2–cyclohexane system and their conclusions were against a stabilizing effect during thermolysis.

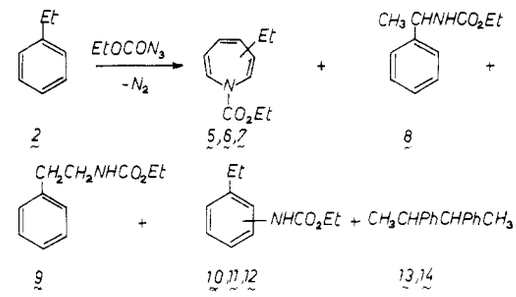
We now report on some more data supporting our opinion on this matter for the thermal decomposition of $EtOCON_3$ in adamantane (**1**) and in ethylbenzene (**2**). This choice was suggested for the former hydrocarbon by the low steric hindrance for the bridgehead C–H bonds compared to that of the CH_2 groups and for the latter one by the high stability of the radical $Ph\dot{C}HCH_3$, in connection with the possibility of the triplet EtOCON participation in the C–H insertion reaction.[7] The reaction between adamantane and $EtOCON_3$ in CH_2Cl_2 has been reported and a 6.0 tertiary/secondary reactivity ratio was found.[8]

We confirmed this figure and found a 23% yield (based on ethyl azidoformate) of 1-adamantylurethan (**3**) and 2-adamantylurethan (**4**). The reactivity ratio for the thermolysis of $EtOCON_3$ in a cyclohexane solution[9] of adamantane was 4.0. In this case the absolute yield of **3** and **4** was 7% while a 11% yield of cyclohexylurethan was found. The decrease in the reactivity ratio and in the yield is in agreement with the formation of a dichloromethane–singlet nitrene complex with a steric demand larger than that of a free nitrene, and it is consistent with our first results on decalins[1] as well as with Belloli's finding on *trans*-1,2-dimethylcyclohexane.[2] In fact in the case of *cis*- and *trans*-decalin, where the tertiary C–H bonds are the most crowded ones, we observed an increased tertiary/secondary reactivity ratio when the thermolysis was run in the absence of CH_2Cl_2. The above interpretation is corroborated by the results we obtained in the photolysis of $EtOCON_3$ in a cyclohexane solution of adamantane. Under these conditions the value of reactivity ratio was 4.1 which was quite close to that (4.0) of the thermolysis in cyclohexane. Since it is known that about 30% of the photolytically generated EtOCON is formed in the triplet state, this should not be involved in the insertion reaction giving the 1- or 2-adamantylurethan.

Scheme I



Scheme II



The thermolysis of $EtOCON_3$ in ethylbenzene has been previously described by Photis[10] and azepines **5–7** were recognized as the main products. We reinvestigated the above thermolysis and compared the results with those of the thermolysis carried out in the presence of CH_2Cl_2. From careful GC analysis, GC–MS study, and comparison with authentic samples we are able to give a more complete picture of the actual situation. Observed products **5–14** are indicated in Scheme II and their relative amounts and absolute yields are shown in Table I.

N-Ethylphenylurethans **10–12** are the isomerization[11] products of azepines **5–7** in the reaction with CH_2Cl_2, as confirmed by heating the products of the thermolysis of $EtOCON_3$ in ethylbenzene after addition of CH_2Cl_2. Urethan **8** arising from EtOCON insertion into benzylic CH_2 is formed in low yield (5%) in thermolysis with CH_2Cl_2, i.e., under the stabilization conditions of the singlet ethoxycarbonylnitrene. The amount of this urethan rises to 16% in the thermolysis without solvent. It is noteworthy that the parallel increase from 6 to 23% of hydrocarbons **13** and **14** comes from the coupling of $Ph\dot{C}HCH_3$ in the absence of dichloromethane. In our opinion this trend is confirmed by the consideration that the ratio of insertion product **8** to the sum of **5, 6, 7, 10, 11,** and **12** products, derived from the singlet EtOCON addition to the benzene ring,[12] goes from 0.056 to 0.26 and seems to indicate

Table I. Thermolysis of $EtOCON_3$ in Ethylbenzene

Reaction conditions	Products, %[a] 5 + 6 + 7	8	10 + 11 + 12	13 + 14	Ratio 8/(5 + 6 + 7 + 10 + 11 + 12)
90 °C, 15 h, CH_2Cl_2	9 (4.5)	5 (2.5)	80 (41)	6 (3)	0.056
90 °C, 15 h, neat	61 (21.5)	16 (5.5)		23 (8)	0.26

[a] Relative yields; absolute yields are given in parentheses (see Experimental Section).

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the participation of the triplet EtOCON in the insertion reaction.[13]

In conclusion, the above results indicate in both cases the formation of a dichloromethane–singlet ethoxycarbonylnitrene complex and the probable involvement of triplet EtOCON in the insertion reaction in the benzylic C–H bonds.

Experimental Section

GC analyses were performed on a Perkin-Elmer F 11 gas chromatograph equipped with a column of 2% OV 17 (2 m × 2 mm). Absolute yields have been evaluated by comparison of the peaks of the reaction mixture with those of standard solutions. Infrared spectra (in CCl_4) were obtained on a Perkin-Elmer 257 Infracord instrument. Nuclear magnetic resonance spectra were recorded on a Perkin-Elmer R32 90 MHz spectrometer, using Me_4Si as an internal standard and CCl_4 as solvent. GC–MS were obtained on an AEI-MS 12 spectrometer at an ionization potential of 70 eV, coupled to a Varian 1400 gas chromatograph using a column of 2% OV 17 (2 m × 2 mm).

Ethyl azidoformate was prepared from ethyl chloroformate and sodium azide.[14] Adamantane was obtained from EGA. **3** and **4** were prepared according to a reported procedure.[8] **3:** IR 3440 (NH) and 1725 cm^{-1} (CO); NMR δ 1.2 (t), 1.6–2.2 (m), 4.0 (q), 4.2 (broad). **4:** IR 3450 (NH) and 1720 cm^{-1} (CO); NMR δ 1.2 (t), 1.6–2.0 (m), 4.0 (q), 4.2 (broad). Ethylbenzene was obtained from Fluka.

Thermolysis of Ethyl Azidoformate in Adamantane. (a) In Cyclohexane. Adamantane (204 mg; 1.5 mmol), 144 mg (1.25 mmol) of ethyl azidoformate, and 504 mg (6 mmol) of cyclohexane were placed in a sealed tube and heated at 90 °C for 15 h. GC analysis of the crude product showed that the ratio of **3** to **4** was 4.0 (corrected for numbers of H). The other reaction product cyclohexylurethan does not interfere in the area calculations, showing a shorter retention time.

(b) In Dichloromethane. Adamantane (204 mg; 1.5 mmol), 29 mg (0.25 mmol) of ethyl azidoformate, and 2.5 mL of dichloromethane were placed in a sealed tube and heated at 90 °C for 15 h. The observed tertiary/secondary reactivity ratio was 6.0.

Photolysis of Ethyl Azidoformate in a Cyclohexane Solution of Adamantane. Adamantane (204 mg; 1.5 mmol), 315 mg (2.75 mmol) of ethyl azidoformate, and 1.625 mL (15 mmol) of cyclohexane were photolyzed[7] in a quartz vessel using a medium pressure Hanovia PCR lamp for 6 h. The observed tertiary/secondary reactivity ratio was 4.1.

Thermolysis of Ethyl Azidoformate in Ethylbenzene. Ethylbenzene (1 mL) and 0.1 mL of ethyl azidoformate were placed in a sealed tube and heated at 90 °C for 15 h. The crude mixture was analyzed by GC–MS. The first three peaks (61) were attributed to the isomeric azepines **5–7;** their mass spectra were very similar and the only prominent peaks were at *m/e* 193 (M), 120 (M − EtOCO), and 91 (tropylium ion). The following peak (16) had the same retention time and coincident MS with **8,** synthesized by EtOCOCl treatment of 1-phenylethylamine, obtained by Na/EtOH reduction of acetophenone oximes: *m/e* 193 (M, 36), 178 (92), 164 (73), 147 (16), 132 (37), 120 (58), 106 (100), 105 (71), 91 (12), 79 (92), 77 (60). For synthesized **8:** IR 3440 (NH) and 1720 cm^{-1} (CO); NMR δ 1.2 (t), 1.5 (d), 4.0 (q), 4.8 (broad), 7.3 (s). The following two peaks (23) had the same retention time and coincident MS with meso and *d,l* mixtures of 2,3-diphenylbutanes (**13** and **14**) reported:[15] *m/e* 210 (M), 105 (base peak). The last peak (<0.5%) had the same retention time and coincident MS with **9,** synthesized by EtOCOCl treatment of commercial 2-phenylethylamine (Fluka): *m/e* 193 (M, 16), 164 (7), 120 (7), 104 (38), 102 (100), 91 (74), 77 (10), 65 (10). For synthesized **9:** IR 3450 (NH) and 1725 cm^{-1} (CO); NMR δ 1.2 (t), 2.8 (t), 3.4 (sextet), 4.0 (q), 4.5 (broad), 7.3 (s).

Thermolysis of Ethyl Azidoformate in Ethylbenzene and Dichloromethane. Ethyl azidoformate (0.1 mL), 1 mL of ethylbenzene, and 10 mL of dichloromethane were placed in a sealed tube and heated at 90 °C for 15 h. The crude mixture was analyzed by GC–MS. The major peaks (80%) were the isomeric *N*-ethylphenylurethans **10–12,** as confirmed by the identity of retention times and MS with those obtained by EtOCOCl treatment of the amines coming from Sn/HCl reduction of the isomeric nitroethylbenzenes:[16] *m/e* 193 (M), 178, 147, 134, 132, 120, 106, 91, 77, 65.

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Registry No.—**1,** 281-23-2; **2,** 100-41-4; **3,** 25192-03-4; **4,** 17778-75-5; **5,** 31536-49-9; **6,** 66085-10-7; **7,** 66085-11-8; **8,** 1623-51-4; **9,** 6970-83-8; **10,** 28352-95-6; **11,** 66085-12-9; **12,** 28238-56-4; **13,** 4613-11-0; **14,** 2726-21-8; ethyl azidoformate, 817-87-8; dichloromethane, 75-09-2.

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2,3-Bis(trimethylsilyloxy)-1,3-butadiene as a Useful Reactive Diene in the Diels–Alder Reaction[1]

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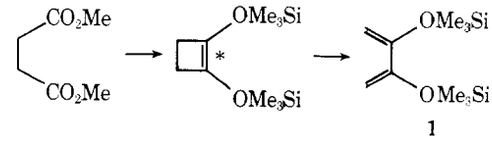
In the course of our present work we have needed to synthesize a number of substituted phthalimides, among them 4,5-dimethoxyphthalimide (**5**) (methahemipinimide). Our synthetic approach to **5** employs a Diels–Alder reaction utilizing the novel diene 2,3-bis(trimethylsilyloxy)-1,3-butadiene (**1**).[2] Further investigation has demonstrated that **1** is indeed a synthetically useful, versatile diene in the Diels–Alder reaction.

2,3-Bis(trimethylsilyloxy)-1,3-butadiene was prepared by the method of Bloomfield and co-workers (Scheme I) although we were able to increase the yield of **1** from 76 to 84% by the addition of 2% by weight hydroquinone to inhibit polymerization during the pyrolysis of the cyclobutene.

The diene **1** was found to readily cycloadd to the dienophiles listed in Table I with the indicated yields. The cisoid conformation of **1** is apparently easily attained since the Diels–Alder cycloadditions occurred under fairly mild conditions. In a typical experiment, 1 equiv each of **1** and the dienophile were either refluxed in dry toluene under a nitrogen atmosphere or heated to 150–200 °C in a sealed combustion tube for 24 h. The products were isolated by fractional vacuum distillation or fractional sublimation.

Our original aim was the synthesis of methahemipinimide (**5**), so the cycloadduct **2** was oxidized and further transformed

Scheme I



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