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Regioselectivity of the (Ethoxycarbonyl)nitrene Insertion Reaction on Monochloro- and Dichloroalkanes and Cycloalkanes

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Ethyl azidoformate has been thermolyzed in 1,1-dichloropentane, 1,1-dichlorohexane, 1,1-dichlorocyclohexane, 7,7-dichlorobicyclo[4.1.0]heptane, 1-chlorohexane, 1-chlorooctane, and chlorocyclohexane. All substrates showed a distribution of the insertion products quite different from the statistical one. The general trend was the preferential introduction of the functional group far from the chlorine atom(s). Inversely, chlorocyclohexane gave a large amount (33.5%) of *trans*-1-chloro-2-[(ethoxycarbonyl)amino]cyclohexane. The results are discussed in terms of probable coordination of the nitrene by heteroatom lone-pair electrons, in addition to polar and steric effects.

In recent years we and other authors have focused attention on the problem of interaction between solvents containing heteroatoms, such as fluorine, chlorine, oxygen, and nitrogen, and (ethoxycarbonyl)nitrene,[1] carbonylnitrenes,[2] or other nitrenes.[3] Data have been collected which point to the possible formation of a nitrene–solvent complex, whose stability depends on the nature of the solvent heteroatom and on the conditions, thermolysis or photolysis, for nitrene generation.

We also considered the possibility of using the supposed ability of coordination of nitrene by chlorine atoms contained in a substrate as a tool for attempting regioelective functionalization. We obtained encouraging results when we chose to test the thermolysis of ethyl azidoformate in *trans*-1,2-dichlorocyclohexane. We isolated only the product of functionalization at C-4 in good yield.[4] This result, compared with the product mixtures resulting from the thermolysis of ethyl azidoformate in several α,ω-dichloroalkanes, strengthened the hypothesis of a complex between the nitrene and a heteroatom lone pair.

However, we believed it necessary to undertake a more systematic study before drawing general conclusions. We decided to study the thermolysis of ethyl azidoformate in monochloroalkanes, *gem*-dichloroalkanes, and cycloalkanes, in particular 1,1-dichloropentane (**1**), 1,1-dichlorohexane (**2**), 1,1-dichlorocyclohexane (**3**), 7,7-dichlorobicyclo[4.1.0]heptane (**4**), 1-chlorohexane (**5**), 1-chlorooctane (**6**), and chlorocyclohexane (**7**).

Thermolyses were run with an excess of substrate, usually ten times (in volume) the azide, in a sealed glass tube. The reaction mixtures were analyzed by IR, NMR, and GC/MS techniques. The identity of urethanes was usually established by the fragmentation pattern in the mass spectra (especially for straight-chain ones). Actually the main fission involved the C–C bonds next to the nitrogen atom. In addition the urethane mixtures coming from 1,1-dichlorocyclohexane were hydrolyzed and compared with products derived from the thermolysis in cyclohexanone.[5] The reaction mixture from 7,7-dichlorobicyclo[4.1.0]heptane was reduced with lithium in liquid ammonia, and the products thus obtained were compared with the urethanes generated by the thermolysis of ethyl azidoformate in bicyclo[4.1.0]heptane.[6]

Results and Discussion

Results from the thermolysis of ethyl azidoformate in chloroalkanes have been collected in Table I according to the substrate structure. The reported figures come from multiple area calculation on triplicate experiments. It is immediately clear that the general trend is the preferential introduction of the functional group far from the chlorine atom(s). In more detail, for *gem*-dichloroalkanes we found small amounts of functionalization product (4.3 and 4.9%) of C-2. In the case of *gem*-dichlorocyclohexane we have not been able to detect the corresponding product of functionalization of C-2, and the main product found (80%) is that coming from insertion of (ethoxycarbo-

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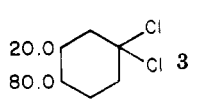
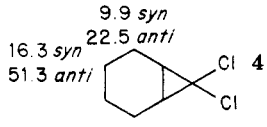
Table I. Relative Percentage of Functionalization of Chloroalkanes by (Ethoxycarbonyl)nitrene[a]

$CH_3—CH_2—CH_2—CH_2—CHCl_2$ 1
13.2 64.5 18.0 4.3
(1.0) (7.3) (2.1) (0.5)

$CH_3—CH_2—CH_2—CH_2—CH_2—CHCl_2$ 2
5.7 40.1 36.8 11.4 4.9
(1.0) (10.5) (9.7) (3.0) (1.3)



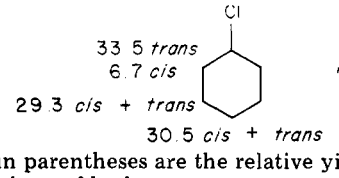
3



4

$CH_3—CH_2—CH_2—CH_2—CH_2—CH_2Cl$ 5
5.6 36.5 32.8 18.3 6.8
(1.0) (9.8) (8.8) (4.9) (1.8)

$CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2Cl$ 6
5.7 22.5 20.0 18.7 11.0 17.8 4.3
(1.0) (5.9) (5.3) (4.9) (2.9) (4.7) (1.1)



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[a] Values in parentheses are the relative yields corrected for the numbers of hydrogens.

nyl)nitrene in the most remote (from chlorine atoms) C–H bonds, despite the unfavorable statistical factor (0.5) compared with that of other annular positions. A similar behavior was observed also in the reaction in 7,7-dichlorobicyclo[4.1.0]heptane. Here the statistical factor for the 2- and 3-positions is one: the difference in reactivity between these two positions is smaller than in the case of 1,1-dichlorocyclohexane, while there is evident a large steric preference for anti attack (22.5% anti and 9.9% syn for the 2-position and 51.3% anti and 16.3% syn for the 3-position). The product distribution for 1-chlorohexane is similar to that obtained for 1,1-dichlorohexane. Higher chloroalkanes such as 1-chlorooctane (**6**) and 1-chlorodecane did not show a substantial change in product distribution; however, the reaction mixture from 1-chlorodecane was not completely resolved by GC, even on a capillary column, where the first three peaks partially overlapped. Interestingly, chlorocyclohexane gave a peculiar result: the main product is the one resulting from the nitrene insertion into a C–H bond adjacent to the chlorine atom, with a large preference for the trans position (33.5%) with respect to the cis (6.7%). The other two positions undergo functionalization in a pattern quite different from the statistical distribution, with a preference for nitrene insertion at C-4. The behavior of straight-chain chloroalkanes in reacting with (ethoxycarbonyl)nitrene resembles that of radical chlorination of straight-chain carboxylic acids.[7] In both cases the selectivity is lower than that reached in the chlorination reactions of chloroalkanes reported by Minisci et al., using protonated *N*-haloamines.[8] This comparison suggests that probably similar factors operate in the present reaction and in radical chlorination of alkanoic acids. The first factor that may be involved is a polar effect of the chlorine atom resulting in a deactivation of neighboring (C-2 and C-3) C–H bonds. However, this effect does not seem to be reflected by NMR chemical shift values: actually only the C-2 methylene group suffers this effect. Steric hindrance of chlorine atoms might be an additional effect to consider, especially in the hypothesis of a nitrene complexation by chlorine atoms. In the case of chlorocyclohexane the high quantity of the insertion product into the trans C–H bond in the 2-position (33.5%) does not seem to be in agreement with the assumption that a polar effect is operative, and it might be consistent with the hypothesis of nitrene coordination by chlorine. Here, probably as a consequence of a favorable geometry, the coordinated (ethoxycarbonyl)nitrene is released to the nearest C–H bond.[9] In addition to the above considerations on the polar and steric effects of the chlorine atoms for the reactions on flexible straight-chain chloroalkanes, it is possible to consider the intramolecular release of a coordinated nitrene to the properly positioned C–H bonds, as well as the intermolecular attack by "free" or "coordinated" nitrene on the same less hindered C–H bonds.

Experimental Section

General Procedures. ^1H NMR spectra were recorded with tetramethylsilane as an internal standard on either a Perkin-Elmer R 32 90-MHz or a JEOL C-60 HL spectrometer. IR spectra were obtained from a Perkin-Elmer 257 Infracord instrument. Mass spectra were taken on an AEI-MS 12 spectrometer at 70 eV; the GS/MS data were obtained by using the same spectrometer coupled to a Varian 1400 gas chromatograph, using a column of 2% OV 17 (2 m × 2 mm). GC analyses were performed on a Perkin-Elmer F 11 gas chromatograph equipped with a column of 2% OV 17 (2 m × 2 mm) or on a Carlo Erba Fractovap GI gas chromatograph equipped with a capillary glass column of 5% Apiezon "L". Monochloroalkanes were commercial products: **5** and **7** were from Fluka and **6** was from Merck. *gem*-Dichloroalkanes were synthesized by reported procedures: **1** and **2** were from the corresponding aldehydes,[10] **3** was from cyclohexanone,[11] and **4** was from cyclohexene.[12] Ethyl azidoformate was a known compound.[13]

Thermolyses. A volume of ethyl azidoformate and ten volumes of the appropriate chloride were placed in a sealed tube and heated at 100 °C overnight. The crude mixture was analyzed by GC (for the relative percentages, see Table I) and by GC/MS. The retention times of products coming from the straight-chain mono- and dichlorides increase as the introduced function moves from C-2 to C-8. A chromatographic separation of excess substrate from reaction products (isomeric positional urethanes) was made on silica gel, using benzene/ethyl acetate (9:1). The yield calculated on collected products ranged from 48 to 67%. IR and NMR spectra showed nothing inconsistent with the structures of the halourethanes.

(a) In 1,1-Dichloropentane (1). Mass spectra [*m/e* (relative intensity)] follow. 1,1-Dichloro-2-[(ethoxycarbonyl)amino]pentane: 186 (6), 184 (8, $Cl_2CHCHNH^+CO_2Et$), 144 (100, $CH_3CH_2CH_2CHNH^+CO_2Et$), 98 (44), 72 (58, 144 - CO_2 - $CH_2=CH_2$), 41 (100), 36 (100). 1,1-Dichloro-3-[(ethoxycarbonyl)amino]pentane: 202 (10), 200 (66), 198 (100, $Cl_2CHCH_2CHNH^+CO_2Et$), 130 (96, $CH_3CH_2CHNH^+CO_2Et$), 128 (34), 126 (54, 198 - CO_2 - $CH_2=CH_2$), 58 (56, 130 - CO_2 - $CH_2=CH_2$), 41 (72). 1,1-Dichloro-4-[(ethoxycarbonyl)amino]-pentane: 214 (1), 212 (2, $Cl_2CHCH_2CH_2CHNH^+CO_2Et$), 142 (2), 140 (3, 212 - CO_2 - $CH_2=CH_2$), 116 (100, $CH_3CHNH^+CO_2Et$), 44 (28, 116 - CO_2 - $CH_2=CH_2$). 1,1-Dichloro-5-[(ethoxycarbonyl)amino]pentane: 194 (6), 192 (20, M - Cl), 102 (100, $CH_2NH^+CO_2Et$), 56 (20), 41 (28), 30 (57, 102 - CO_2 - $CH_2=CH_2$).

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(b) In 1,1-Dichlorohexane (2). 1,1-Dichloro-2-[(ethoxycarbonyl)amino]hexane: 184 (5, $Cl_2CHCHNH^+CO_2Et$), 158 (100, $CH_3CH_2CH_2CH_2CHNH^+CO_2Et$), 86 (50, 158 - CO_2 - CH_2=CH_2). 1,1-Dichloro-3-[(ethoxycarbonyl)amino]hexane: 202 (10), 200 (60), 198 (98, $Cl_2CHCH_2CHNH^+CO_2Et$), 144 (100, $CH_3CH_2CH_2CHNH^+CO_2Et$), 130 (6), 128 (36), 126 (60, 198 - CO_2 - CH_2=CH_2), 72 (42, 144 - CO_2 - CH_2=CH_2). 1,1-Dichloro-4-[(ethoxycarbonyl)amino]hexane: 216 (8), 214 (40), 212 (58, $Cl_2CHCH_2CH_2CHNH^+CO_2Et$), 144 (4), 142 (21), 140 (34, 212 - CO_2 - CH_2=CH_2), 130 (100, $CH_3CH_2CHNH^+CO_2Et$), 58 (77, 130 - CO_2 - CH_2=CH_2. 1,1-Dichloro-5-[(ethoxycarbonyl)amino]-hexane: 116 (100, $CH_3CHNH^+CO_2Et$), 44 (72, 116 - CO_2 - CH_2=CH_2). 1,1-Dichloro-6-[(ethoxycarbonyl)amino]hexane: 241 (1, M^+), 208 (2), 206 (6, M - Cl), 102 (100, $CH_2NH^+CO_2Et$), 30 (90, 102 - CO_2 - CH_2=CH_2).

(c) In 1-Chlorohexane (5). 1-Chloro-2-[(ethoxycarbonyl)-amino]hexane: 158 (100, $CH_3CH_2CH_2CH_2CHNH^+CO_2Et$), 152 (12), 150 (32, $ClCH_2CHNH^+CO_2Et$), 86 (31, 158 - CO_2 - CH_2=CH_2), 80 (19), 78 (52, 150 - CO_2 - CH_2=CH_2). 1-Chloro-3[(ethoxycarbonyl)amino]hexane: 166 (33), 164 (100, $ClCH_2CH_2CHNH^+CO_2Et$), 94 (27), 92 (81, 164 - CO_2 - CH_2=CH_2), 72 (53, 144 - CO_2 - CH_2=CH_2). 1-Chloro-4-[(ethoxycarbonyl)amino]hexane: 180 (26), 178 (86, $ClCH_2CH_2CH_2CHNH^+CO_2Et$), 130 (100, $CH_3CH_2CHNH^+CO_2Et$), 108 (19), 106 (63, 178 - CO_2 - CH_2=CH_2), 58 (96, 130 - CO_2 - CH_2=CH_2). 1-Chloro-5-[(ethoxycarbonyl)amino]hexane: 116 (100, $CH_3CHNH^+CO_2Et$), 44 (94, 116 - CO_2 - CH_2=CH_2). 1-Chloro-6-[(ethoxycarbonyl)amino]hexane: 207 (2, M^+), 172 (13, M - Cl), 102 (87, $CH_2NH^+CO_2Et$), 30 (100, 102 - CO_2 - CH_2=CH_2).

(d) In 1-Chlorooctane (6). 1-Chloro-2-[(ethoxycarbonyl)-amino]octane: 186 (100, $CH_3(CH_2)_5CHNH^+CO_2Et$), 152 (12), 150 (41, $ClCH_2CHNH^+CO_2Et$), 114 (22, 186 - CO_2 - CH_2=CH_2), 80 (8), 78 (25, 150 - CO_2 - CH_2=CH_2). 1-Chloro-3-[(ethoxycarbonyl)amino]octane: 172 (62, $CH_3(CH_2)_4CHNH^+CO_2Et$), 166 (33), 164 (100, $ClCH_2CH_2CHNH^+CO_2Et$), 94 (15), 92 (51, 164 - CO_2 - CH_2=CH_2). 1-Chloro-4-[(ethoxycarbonyl)amino]octane: 180 (30), 178 (100, $ClCH_2CH_2CH_2CHNH^+CO_2Et$), 158 (86, $CH_3CH_2CH_2CH_2CHNH^+CO_2Et$), 142 (28, 178 - HCl), 108 (16), 106 (52, 178 - CO_2 - CH_2=CH_2), 70 (40, 142 - CO_2 - CH_2=CH_2. 1-Chloro-5-[(ethoxycarbonyl)amino]octane: 194 (24), 192 (74, $Cl(CH_2)_4CHNH^+CO_2Et$), 144 (100, $CH_3CH_2CH_2CHNH^+CO_2Et$), 122 (10), 120 (29, 192 - CO_2 - CH_2=CH_2), 72 (30, 144 - CO_2 - CH_2=CH_2). 1-Chloro-6-[(ethoxycarbonyl)amino]octane: 208 (16), 206 (50, $Cl(CH_2)_5CHNH^+CO_2Et$), 136 (6), 134 (19, 206 - CO_2 - CH_2=CH_2), 130 (100, $CH_3CH_2CHNH^+CO_2Et$), 58 (48, 130 - CO_2 - CH_2=CH_2). 1-Chloro-7-[(ethoxycarbonyl)amino]octane: 235 (<1, M^+), 222 (1), 220 (3, $Cl(CH_2)_6CHNH^+CO_2Et$), 116 (100, $CH_3CHNH^+CO_2Et$), 44 (41, 116 - CO_2 - CH_2=CH_2). 1-Chloro-8-[(ethoxycarbonyl)amino]octane: 235 (<1, M^+), 200 (17, M - Cl), 102 (100, $CH_2NH^+CO_2Et$), 30 (54, 102 - CO_2 - CH_2=CH_2).

(e) In 1,1-Dichlorocyclohexane (3). Two products in a 20:80 ratio were obtained and analyzed by mass spectral fragmentation. Minor product: 243 (1), 241 (6), 239 (10, M^+), 214 (1), 212 (6), 210 (10), 206 (5), 204 (16), 168 (7), 128 (100), 115 (9), 56 (50). Major product: 243 (1), 241 (5), 239 (8, M^+), 206 (15), 204 (46), 168 (22), 128 (100), 115 (51), 56 (66). The mixture of the two products was then exposed to concentrated sulfuric acid at 40 °C for 1 h, in the same conditions described for the transformation of 1,1-dichlorocyclohexane in cyclohexanone,[11] and converted into a 20:80 mixture of 3-[(ethoxycarbonyl)amino]cyclohexanone and 4-[(ethoxycarbonyl)amino]cyclohexanone.[14,15]

(f) In 7,7-Dichlorobicyclo[4.1.0]heptane (4). Four products in yields of 9.9, 16.3, 22.5, and 51.3% in order of increasing retention times were obtained. Their identification was possible after reduction with lithium in liquid ammonia to the corresponding known bicyclo[4.1.0]heptylurethanes.[6] *syn*-7,7-Dichloro-2-[(ethoxycarbonyl)amino]bicyclo[4.1.0]heptane: 251 (1, M^+), 218 (4), 216 (14), 168 (100), 140 (42), 90 (28), 79 (42), 67 (28), 55 (38). *syn*-7,7-Dichloro-3-[(ethoxycarbonyl)amino]bicyclo-[4.1.0]heptane: 253 (5), 251 (7, M^+), 218 (12), 216 (38), 168 (80), 164 (28), 162 (45), 129 (65), 128 (48), 127 (78), 91 (100), 90 (88), 57 (100), 56 (93), 36 (60). *anti*-7,7-Dichloro-2-[(ethoxycarbonyl)amino]bicyclo[4.1.0]heptane: 253 (4), 251 (6, M^+), 218 (9), 216 (27), 129 (33), 128 (45), 127 (70), 91 (78), 90 (100), 62 (58), 57 (55), 56 (93), 36 (44). *anti*-7,7-Dichloro-3-[(ethoxycarbonyl)amino]bicyclo[4.1.0]heptane: 253 (8), 251 (11, M^+), 224 (10), 222 (16), 218 (6), 216 (18), 180 (11), 178 (10), 164 (16), 162 (24), 129 (29), 128 (100), 127 (82), 115 (39), 101 (42), 91 (74), 90 (100), 65 (53), 62 (69), 56 (99), 36 (34).

(g) In Chlorocyclohexane (7). Six products in yields of 6.7, 33.5, 10.8, 13.0, 19.7, and 16.3% in order of increasing retention times were obtained. The last four isomers were identified by comparison with authentic samples prepared by $SOCl_2$ treatment of the known *cis*- and *trans*-3-[(ethoxycarbonyl)amino]cyclohexanol and *cis*- and *trans*-4-[(ethoxycarbonyl)amino]cyclohexanol;[15] the 33.5% product was identified as *trans*-2-chloro-1-[(ethoxycarbonyl)amino]cyclohexane[13] (and the first product was deduced to be *cis*-2-chloro-1-[(ethoxycarbonyl)amino]-cyclohexane). All products showed the same fragmentation pattern of the mass spectrum but for minor differences in the relative abundance of the peaks: 207, 205 (M^+), 178, 176, 170, 128 (generally the base peak), 90, 81, 67, 62, 56.

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Registry No. 1, 820-55-3; 2, 62017-16-7; 3, 2108-92-1; 4, 823-69-8; 5, 544-10-5; 6, 111-85-3; 7, 542-18-7; 1,1-dichloro-2-[(ethoxycarbonyl)amino]pentane, 71118-69-9; 1,1-dichloro-3-[(ethoxycarbonyl)-amino]pentane, 71118-70-2; 1,1-dichloro-4-[(ethoxycarbonyl)-amino]pentane, 71118-71-3; 1,1-dichloro-5-[(ethoxycarbonyl)-amino]pentane, 71118-72-4; 1,1-dichloro-2-[(ethoxycarbonyl)-amino]hexane, 71118-73-5; 1,1-dichloro-3-[(ethoxycarbonyl)-amino]hexane, 71118-74-6; 1,1-dichloro-4-[(ethoxycarbonyl)-amino]hexane, 71118-75-7; 1,1-dichloro-5-[(ethoxycarbonyl)-amino]hexane, 71118-76-8; 1,1-dichloro-6-[(ethoxycarbonyl)-amino]hexane, 71118-77-9; 1-chloro-2-[(ethoxycarbonyl)amino]hexane, 71118-78-0; 1-chloro-3-[(ethoxycarbonyl)amino]hexane, 71118-79-1; 1-chloro-4-[(ethoxycarbonyl)amino]hexane, 71118-80-4; 1-chloro-5-[(ethoxycarbonyl)amino]hexane, 71118-81-5; 1-chloro-6-[(ethoxycarbonyl)amino]hexane, 71118-82-6; 1-chloro-2-[(ethoxycarbonyl)-amino]octane, 71118-83-7; 1-chloro-3-[(ethoxycarbonyl)amino]octane, 71118-84-8; 1-chloro-4-[(ethoxycarbonyl)amino]octane, 71118-85-9; 1-chloro-5-[(ethoxycarbonyl)amino]octane, 71118-86-0; 1-chloro-6-[(ethoxycarbonyl)amino]octane, 71118-87-1; 1-chloro-7-[(ethoxycarbonyl)amino]octane, 71118-88-2; 1-chloro-8-[(ethoxycarbonyl)-amino]octane, 71118-89-3; 3-[(ethoxycarbonyl)amino]cyclohexanone, 38031-97-9; 4-[(ethoxycarbonyl)amino]cyclohexanone, 39244-24-1; *syn*-7,7-dichloro-2-[(ethoxycarbonyl)amino]bicyclo[4.1.0]heptane, 71118-90-6; *syn*-7,7-dichloro-3-[(ethoxycarbonyl]amino]bicyclo-[4.2.1]heptane, 71118-91-7; *anti*-7,7-dichloro-2-[(ethoxycarbonyl)-amino]bicyclo[4.2.1]heptane, 71118-92-8; *anti*-7,7-dichloro-3-[(ethoxycarbonyl)amino]bicyclo[4.2.1]heptane, 71129-30-1; *cis*-3-[(ethoxycarbonyl)amino]cyclohexanol, 71118-93-9; *trans*-3-[(ethoxycarbonyl)amino]cyclohexanol, 71118-94-0; *cis*-4-[(ethoxycarbonyl)-amino]cyclohexanol, 71118-95-1; *trans*-4-[(ethoxycarbonyl)amino]-cyclohexanol, 71118-96-2; *trans*-2-chloro-1-[(ethoxycarbonyl)-amino]cyclohexane, 18296-24-7; *cis*-2-chloro-1-[(ethoxycarbonyl)-amino]cyclohexane, 18296-25-8; (ethoxycarbonyl)nitrene, 2655-26-7; ethyl azidoformate, 817-87-8.

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