of acetic anhydride added. The reaction mixture was refluxed for 2 h and 30 min, cooled, and poured into water. The precipitated material was filtered off, and washed with alcohol.

2-Acylamino-4,6-dibromo-7-hydroxy-3-ethoxycarbonylbenzo[b]thiophenes (XIX, XX). To a refluxing suspension of 0.028 mole of compounds IX or X and a catalytic amount of benzoyl peroxide in 250 ml of chloroform was slowly added a solution of 1.7 ml (0.033 mole) of bromine in 25 ml of chloroform, and the reaction mixture refluxed for 3 h and then allowed to stand at 20°C for 18 h. After washing with water, the chloroform was removed, alcohol added to the residue and the precipitated material filtered off.

2-Acylamino-4,6-dinitro-7-hydroxy-3-ethoxycarbonylbenzo[b]thiophenes (XXI-XXIII). To a suspension of 0.03 mole of compounds IX-XI in 90 ml of acetic acid was added 7 ml of nitric acid (d = 1.42 g/ml). The reaction mixture was refluxed for 5 min, cooled, and the precipitated material filtered off and washed with alcohol.

## LITERATURE CITED

1. I. A. Kharizomenova, M. V. Kapustina, A. N. Grinev, Yu. N. Sheinker, L. M. Alekseeva, and E. F. Kuleshova, Khim. Geterosikl. Soedin., No. 2, 1626 (1984).
2. K. Gewald and G. Neumann, Chem. Ber., 101, 1933 (1968).

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# SULFINYL AND SULFONYL DERIVATIVES OF ARYL SUBSTITUTED cis-1-THIADECALINS

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Individual 2α-aryl- and 2α,4α-diaryl-cis-thiadecalin-1β-oxides and 1,1-dioxides have been synthesized. The effect of sulfinyl and sulfonyl groups has been observed on the chemical shifts of carbon atoms in these conformationally homogeneous, stereochemically similar systems.

In a continuation of studies of cis-1-thiadecalins I-VII [1, 2] a number of new and previously known 2α-aryl- and 2α,4α-diaryl-cis-1-thiadecalin 1-oxides VIII-XIV and 1,1-dioxides XV-XXI were synthesized. Their $^{13}$C NMR spectra were studied in order to reveal the effect of sulfinyl and sulfonyl groups on the unusual conformationally homogeneous derivatives of cis-1-thiadecalin.

Only the $^{13}$C NMR spectra of the diastereomeric cis-1-thiadecalin-1-oxides [3], and cis-1-thiadecalin-1-N-4-chlorophenylimide and its homologs [4] have been described previously. At the same time, derivatives of trans-1-thiadecalin and its homologs, viz., sulfoxides [5], sulfones [5], and sulfimides [4], have been studied relatively fully.

The oxidant was 30% hydrogen peroxide. Individual thiadecalins I-VII [2] were oxidized in glacial acetic acid. Sulfoxides VIII-XIV were synthesized by oxidation with an equimolar amount of oxidant at 20°C; sulfones XV-XXI, with a fivefold excess of oxidant at 20-50°C. Yields were 53-73 and 70-93%, respectively (Table 1).

In the oxidation of cyclic sulfides we can expect the formation of diastereomeric sulfoxides with equatorially or axially disposed S—O groups. If the equatorial S—O in sulfoxides VIII-XIV is located in the gauche position with respect to two C—H bonds and two C—C bonds, then the axial S—O in diastereomers VIIIa-XIVa should be in gauche position to the four C—C bonds, and moreover should be substantially destablized due to the 1,3-interactions in the heterocycle.

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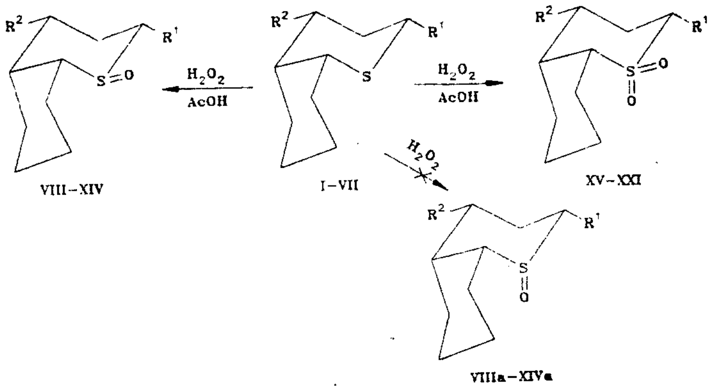
TABLE 1. 2α-$R^1$-4α-$R^2$-cis-1-Thiadecalin-1-oxides and 1,1-Dioxides

| Compound | mp, °C | IR spectrum, $cm^{-1}$ (S—O) | Found, % |  |  | Empirical formula | Calculated, % |  |  | Yield, % |
|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  | C | H | S |  | C | H | S |  |
| IX | 116—117 | 1015 | 68,9 | 8,2 | 11,3 | $C_{16}H_{22}O_2S$ | 69,1 | 8,0 | 11,5 | 53 |
| XII | 163—164 | 1020 | 74.5 | 7,5 | 9,0 | $C_{22}H_{26}O_2S$ | 74,5 | 7,4 | 9,0 | 54 |
| XIII | 128—130 | 1055 | 71,6, | 7,2 | 8,2 | $C_{23}H_{28}O_3S$ | 71,8 | 7,3 | 8,3 | 84 |
| XVI | 163—164 | 1305, 1130 | 65,0 | 7,4 | 10,4 | $C_{16}H_{22}O_3S$ | 65,3 | 7,5 | 10,9 | 70 |
| XX | 184—186 | 1300, 1135 | 68,9 | 6.9 | 7,9 | $C_{23}H_{28}O_4S$ | 69,0 | 7,0 | 8,0 | 92 |



I, VIII, XV $R^1=C_6H_5$, $R^2=H$; II, IX, XVI $R^1=C_6H_4OCH_3$-4, $R^2=H$; III, X, XVII $R^1=R^2=C_6H_5$; IV, XI, XVIII $R^1=C_6H_5$, $R^2=C_6H_4OCH_3$-4; V, XII, XIX $R^1=C_6H_4OCH_3$-4, $R^2=C_6H_5$; VI, XIII, XX $R^1=R^2=C_6H_4OCH_3$-4; VII, XIV, XXI $R^1=C_6H_5$, $R^2=C_6H_3(OCH_3)_2$-3,4

Consequently the isomers with the equatorial S—O group are predominantly formed, which are separated as individual compounds. Their diastereomers with axial sulfinyl group are evidently present in insignificant amounts in the crude products, and are detected only by TLC of the filtrates. Thus in contrast to the thiane-1-oxides, for which the predominantly axially disposed S—O is characteristic [4], we obtained sulfoxides VIII-XIV with equatorial S—O.

In the sulfinyl derivatives VIII-XIV the S—O valence vibrations appear at 1055-1015 $cm^{-1}$, while in the sulfonyl derivatives the S—O asymmetric and symmetric valence vibrations appear at 1305-1290 and 1135-1120 $cm^{-1}$.

Structural assignments for sulfoxide X were made previously on the basis of a concurrent study of the $^1H$ NMR spectra of the sulfoxide, the starting sulfide, and the 3,10-dideutero derivative of the latter [8]. The spectra of 2α-aryl- and 2α,4α-diaryl-cis-1-thiadecalins I, III-V, VII which exist in the A conformation were considered in [1]. The signals in the spectra of 1-thiadecalins II, VI, sulfoxides VIII-XIV, and sulfones XV-XXI were assigned on the basis of off-resonance data and comparison of experimental and theoretical spectra. To calculate the theoretical spectra we used the $^{13}C$ NMR spectra of cis-1-thiadecalin 1-oxides from [3] and the increments of equatorial and axial phenyl groups [2]. Table 2 shows the $^{13}C$ NMR spectra of sulfoxides VIII-XIV and sulfones XV-XXI and for comparison sulfides I-VII. Table 3 shows the effects of sulfinyl and sulfonyl groups on the $^{13}C$ chemical shifts in sulfoxides VIII-XIV and sulfones XV-XXI.

Oxidation of sulfides to sulfoxides causes a strong deshielding of the carbons adjacent to sulfinyl, due to the charge change on sulfur and to the β-effect of sulfinyl oxygen [9, 10], so that the carbon at position 9 resonates in a stronger field than does $C_{(2)}$. Such a difference is determined by the inductive effect of the aryl substituent at $C_{(2)}$ which displays electron acceptor properties. Thus for the whole series of sulfoxides VIII-XIV there is a noticeable shielding of quaternary carbons and deshielding of ortho and para carbons of the aromatic ring (Table 2).

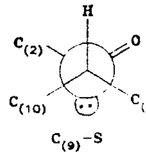
For the cis-1-thiadecalin derivatives in conformation A, in the sequence S-methylsulfonium salt [11], 1-N-4-chlorophenylimide [4, 12], and 1-oxide [3], the largest deshielding of adjacent carbons atoms is produced by the most strongly polar sulfinyl group. Further deshielding of β-carbons might be expected in going from sulfoxides VIII-XIV to sulfones XV-XXI, primarily

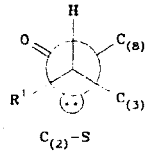
TABLE 2. Chemical $^{13}C$ Shifts of $2\alpha$-$R^1$-$4\alpha$-$R^2$-cis-1-Thiadecalin-1$\beta$-oxides (VIII-XIV), 1,1-Dioxides (XV-XXI), and Starting Sulfides I-VII

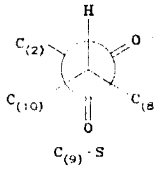
| Compound | $C_{(2)}$ | $C_{(3)}$ | $C_{(4)}$ | $C_{(5)}$ | $C_{(6)}$ | $C_{(7)}$ | $C_{(8)}$ | $C_{(9)}$ | $C_{(10)}$ | $R^1$ |  |  |  | $R^2$ |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  |  |  |  |  | quaternary | ortho | meta | para | quaternary | ortho | meta | para |
| I | 48,62 | 28,77 | 33,32 | 24,64 | 24,79 | 20,87 | 31,64 | 45,06 | 35,46 | 143,33 | 127,21 | 128,31 | 127,06 | — | — | — | — |
| VIII | 69,57 | 26,74 | 32,18 | 25,53 | 27,82 | 20,80 | 26,36 | 65,76 | 39,11 | 137,11 | 128,66 | 128,32 | 128,07 | — | — | — | — |
| XV | 67,38 | 26,59 | 31,03 | 25,13 | 25,24 | 20,69 | 23,07 | 57,98 | 37,74 | 130,54 | 129,67 | 128,07 | 128,45 | — | — | — | — |
| II | 47,76 | 28,78 | 32,26 | 24,52 | 26,72 | 18,79 | 31,52 | 44,93 | 35,28 | 134,91 | 129,14 | 113,59 | 158,39 | — | — | — | — |
| IX | 68,55 | 26,50 | 31,94 | 25,38 | 27,59 | 20,62 | 26,17 | 65,38 | 38,91 | 128,76 | 129,22 | 113,96 | 159,48 | — | — | — | — |
| XVI | 66,53 | 26,51 | 30,86 | 24,95 | 25,07 | 20,56 | 22,90 | 59,60 | 37,55 | 122,17 | 130,61 | 113,38 | 159,52 | — | — | — | — |
| III | 48,70 | 33,23 | 48,70 | 21,17 | 26,53 | 19,20 | 31,71 | 46,62 | 43,06 | 142,13 | 127,26 | 128,38 | 127,12 | 133,21 | 127,49 | 127,92 | 125,83 |
| X | 68,78 | 30,55 | 47,25 | 22,00 | 26,89 | 20,82 | 25,72 | 66,22 | 45,65 | 136,71 | 128,69 | 128,11 | 128,01 | 141,59 | 127,13 | 128,11 | 126,29 |
| XVI | 67,24 | 30,57 | 46,84 | 21,05 | 25,11 | 19,43 | 23,60 | 60,69 | 44,71 | 130,17 | 129,79 | 128,31 | 128,72 | 141,70 | 127,15 | 128,17 | 126,50 |
| IV | 48,75 | 33,46 | 47,87 | 21,21 | 26,56 | 19,16 | 31,70 | 46,60 | 43,18 | 142,28 | 127,05 | 128,11 | 126,84 | 136,12 | 128,12 | 113,21 | 157,36 |
| XI | 68,95 | 30,97 | 46,58 | 22,02 | 25,98 | 20,91 | 24,78 | 66,27 | 45,84 | 136,81 | 128,65 | 128,08 | 128,08 | 133,70 | 128,08 | 113,44 | 157,94 |
| XVIII | 67,42 | 30,97 | 46,24 | 21,12 | 25,21 | 19,46 | 23,66 | 60,77 | 44,90 | 130,29 | 129,80 | 128,22 | 128,75 | 133,84 | 128,32 | 113,64 | 158,17 |
| V | 47,05 | 33,37 | 48,73 | 21,16 | 26,53 | 19,17 | 31,69 | 46,60 | 43,03 | 134,57 | 128,24 | 113,82 | 158,65 | 144,31 | 127,50 | 127,92 | 125,85 |
| XII | 68,10 | 30,65 | 47,39 | 22,05 | 25,80 | 20,68 | 24,45 | 66,19 | 45,74 | 128,64 | 129,23 | 114,09 | 159,39 | 141,72 | 127,18 | 128,05 | 126,30 |
| XIX | 66,46 | 30,60 | 46,63 | 20,97 | 25,05 | 19,31 | 23,49 | 60,40 | 44,58 | 122,07 | 130,79 | 113,37 | 159,87 | 141,80 | 127,20 | 128,04 | 126,32 |
| VI | 47,76 | 33,50 | 47,85 | 21,06 | 26,46 | 19,03 | 31,58 | 46,43 | 43,02 | 134,52 | 128,18 | 113,67 | 158,49 | 136,37 | 128,18 | 113,23 | 157,58 |
| XIII | 68,55 | 31,18 | 46,97 | 22,33 | 26,11 | 21,23 | 26,31 | 66,55 | 46,18 | 129,05 | 129,54 | 114,40 | 159,71 | 134,13 | 128,37 | 113,74 | 158,24 |
| XX | 67,01 | 31,21 | 46.53 | 21,33 | 25,43 | 19,63 | 23,91 | 60,80 | 45,12 | 128,26 | 131,10 | 113,81 | 159,71 | 134,12 | 128,41 | 114,91 | 158,35 |
| VII | 48,70 | 33,50 | 48,20 | 21,10 | 26,50 | 19,20 | 31,60 | 46,50 | 43,10 | 142,29 | 127,12 | 128,23 | 126,93 | 136,88 | 119,33, 111,20 | 110,86, 148,98 | 147,14 |
| XIV | 68,93 | 30,98 | 46,94 | 22,11 | 25,93 | 20,86 | 25,65 | 66,22 | 46,81 | 136,77 | 128,62 | 128,13 | 128,05 | 134,25 | 118,99, 110,76 | 110,76, 148,53 | 148,45 |
| XXI | 67,39 | 31,02 | 46,67 | 21,12 | 25,26 | 19,16 | 23,12 | 60,72 | 44,97 | 130,28 | 129,84 | 128,32 | 128,79 | 134,39 | 119,30, 110,95 | 110,95, 148,76 | 147,71 |

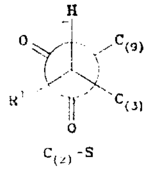
because of the increased positive charge on sulfonyl sulfur. But instead of the expected deshielding in XV-XXI, there is a shielding of β-atoms at $C_{(2)}$ averaging −1.4 ppm and at $C_{(9)}$ averaging −5.7 ppm as compared with the stereochemically similar sulfoxides VIII-XIV; this is related to the introduction of the axial S—O bond into the molecule (Tables 2 and 3).

The γ-atoms at $C_{(3)}$, $C_{(8)}$, and $C_{(10)}$ respond differently to the introduction of the equatorial sulfinyl group in going from sulfides I-VII to the respective sulfoxides VIII-XIV. $C_{(8)}$, which is in gauche position both to sulfinyl oxygen and to the free electron pair of sulfur, undergoes shielding from −5.27 to −6.92 ppm (Tables 2 and 3). $C_{(3)}$ and $C_{(10)}$, which are in γ-anti position with respect to sulfinyl oxygen and in γ-gauche position with respect to the free electron pair of sulfur, behave differently; $C_{(3)}$ is shielded from −2.03 to −2.82 ppm, while $C_{(10)}$ is deshielded from 3.15 to 3.71 ppm.









This picture is in good agreement with the data on cis-1-thiadecalin-1β-oxide [3], and with those on N-(4-chlorophenyl)-cis-1-thiadecalin-1β-imide and its homologs with a methyl group in various locations (in the A conformation) [4].

In these sulfones the γ-effect of sulfonyl on $C_{(3)}$ is practically the same as that of the SO group, viz., from −2.18 to −3.83 ppm, while at $C_{(10)}$ the deshielding effect is less than ~1 ppm (Tables 2 and 3). $C_{(8)}$ in sulfones is shielded on average 2.5 ppm more than in sulfoxides. The quaternary atoms of the aromatic substituents at $C_{(2)}$ also undergo strong shielding, from −11.79 to −12.74 ppm. Thus in general when a sulfonyl group replaces sulfinyl in aryl-substituted cis-1-thiadecalins I-VII in the A conformation, there is a strong field shift of the signals of both β- and γ-carbons [except for γ-$C_{(3)}$], due to the appearance of the second axial S—O bond. But as shown in [5] this effect cannot be entirely ascribed to the strong electrical field of sulfonyl oxygen. The reason is that the change of sulfur valence state in the sulfoxide—sulfone transition is also involved with changes of bond length and valence angles, and therefore with a change in stereoelectronic interactions in the molecule.

## EXPERIMENTAL

IR spectra were obtained in mineral oil with a UR-20 spectrometer. $^{13}C$ NMR spectra were obtained with a Varian FT-80A instrument (20 MHz) at 30°. The spectra were parametrized with respect to the signal of the secondary standard, for which the signal of $CDCl_3$ solvent was used.

Starting sulfides I-VII were obtained by hydrogenation of the respective cyclohexa[b]thiopyranes or cyclohexa[b]thiopyrilium tetrafluoroborates as described in [2]. The known sulfoxides VIII, X, XI, XIV and sulfones XV, XVII-XIX, XXI were obtained by the procedures of [2, 6, 7, 12].

TABLE 3. Effects* of Sulfinyl and Sulfonyl Groups on $^{13}C$ Chemical Shifts in Sulfoxides and Sulfones 2α-$R^1$ and 2α-$R^1$-4α-$R^2$-cis-1-Thiadecalins I-VII

| Compound | $C_{(2)}$ | | $C_{(9)}$ | | $C_{(3)}$ | | $C_{(8)}$ | | $C_{(10)}$ | | $R^1$ (quat) | | $R^2$ (quat) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\beta_{SO}$ | $\beta_{SO_2}$ | $\beta_{SO}$ | $\beta_{SO_2}$ | $\gamma_{SO}$ | $\gamma_{SO_2}$ | $\gamma_{SO}$ | $\gamma_{SO_2}$ | $\gamma_{SO}$ | $\gamma_{SO_2}$ | $\gamma_{SO}$ | $\gamma_{SO_2}$ | SO | $SO_2$ |
| I | 20,95 | 18,76 | 20,70 | 14,92 | −2,03 | −2,18 | −5,28 | −8,57 | 3,15 | 2,28 | −5,22 | −11,79 | — | — |
| II | 20,79 | 18,77 | 20,45 | 14,73 | −2,28 | −2,27 | −5,35 | −8,62 | 3,63 | 2,77 | −6,15 | −12,74 | — | — |
| III | 20,08 | 18,54 | 19,60 | 14,07 | −2,78 | −2,66 | −5,99 | −8,11 | 2,59 | 1,65 | −5,42 | −11,96 | −2,62 | −2,51 |
| IV | 20,20 | 18,67 | 19,67 | 14,17 | −2,49 | −2,49 | −6,92 | −8,04 | 2,66 | 1,72 | −5,47 | −11,99 | −2,42 | −2,28 |
| V | 21,05 | 19,41 | 19,59 | 13,80 | −2,82 | −2,77 | −5,89 | −8,20 | 2,71 | 1,55 | −5,93 | −12,50 | −2,59 | −2,51 |
| VI | 20,79 | 19,25 | 20,12 | 14,37 | −2,32 | −2,29 | −5,27 | −7,67 | 3,16 | 2,10 | −5,47 | −12,26 | −2,24 | −2,25 |
| VII | 20,23 | 18,69 | 19,72 | 14,22 | −2,58 | −2,48 | −5,95 | −8,48 | 3,71 | 1,87 | −5,52 | −12,01 | −2,63 | −2,49 |

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*Effects determined as $\Delta\delta^i = \delta^i_{(di)oxide} - \delta^i_{sulfide}$.

2α-$R^1$-4α-$R^2$-cis-1-Thiadecalin-1-oxides (IX, XII, XIII). Sulfide II, V, or VI, [2], 4 mmole, is dissolved in 10 ml of glacial acetic acid, and a 5-10% molar excess of 30% hydrogen peroxide is added dropwise with stirring. The mixture is kept at 20°C for 24 h, then poured dropwise on 200 g of crushed ice. Sulfoxides IX, XII, XIII are filtered off, dried, and reprecipitated from chloroform by hexane.

2α-$R^1$-4α-$R^2$-cis-1-Thiadecaline-1-dioxides (XVI, XX). A mixture of 2 mmole of sulfide II, VI [2], 5 ml of glacial acetic acid, and 1.4 ml of 30% hydrogen peroxide is heated in a water bath 7 min at 60° until the sulfide dissolves, then left for 24 h at 20°. Then the mixture is poured on 100 g of ice, and sulfones XVI, XX are filtered off, dried, and recrystallized from 1:1 ethanol—acetone.

The purity of the sulfones and sulfoxides was monitored by TLC (Silufol, elution by 3:2 ethyl acetate—hexane).

## LITERATURE CITED

1. S. K. Klimenko, T. V. Stolbova, T. I. Tyrina, N. N. Sorokin, I. F. Leshcheva, N. M. Sergeev, and V. G. Kharchenko, Khim. Geterotsikl. Soedin., No. 7, 898 (1984).
2. S. K. Klimenko, T. I. Tyrina, and N. N. Sorokin, Khim. Geterotsikl. Soedin., in press (1987).
3. P. K. Claus, F. W. Vierhapper, and R. L. Willer, J. Org. Chem., 44, 2863 (1979).
4. P. K. Claus and F. W. Vierhapper, and W. Rieder, Monatsh. Chem., 109, 631 (1978).
5. R. P. Roney and S. A. Evans, J. Org. Chem., 45, 180 (1980).
6. N. S. Smirnova, S. K. Klimenko, M. N. Berezhnaya, T. V. Stolbova, and V. G. Kharchenko, Zh. Org. Khim., 11, 440 (1975).
7. T. V. Stolbova, S. K. Klimenko, and V. G. Kharchenko, Zh. Org. Khim., 16, 178 (1980).
8. S. K. Klimenko, T. V. Stolbova, I. Ya. Yevtushenko, and V. G. Kharchenko, Khim. Geterotsikl. Soedin., No. 10, 1347 (1981).
9. G. Barbarella, P. Dembech, A. Garbesi, and A. Fava, Org. Magn. Reson., 8, 108 (1976).
10. T. P. Forest and G. K. Webb, Org. Magn. Reson., 12, 371 (1979).
11. E. L. Eliel and R. W. Willer, J. Am. Chem. Soc., 99, 1936 (1977).
12. S. K. Klimenko, T. I. Tyrina, N. N. Sorokin, and V. G. Kharchenko, Khim. Geterotsikl. Soedin., No. 2, 199 (1986).

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# SYNTHESIS OF AZETIDIN-3-ONES.

# STRUCTURE OF N-TOSYL-2-ETHYLAZETIDIN-3-ONE

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A one-step synthesis of azetidin-3-ones by intramolecular cyclization of 1-diazo-3-arenesulfamoylalkan-2-ones was developed. The yield of cyclic product increases to 70% in the presence of an alkyl or benzyl substituent in the hydrocarbon chain of the diazoketone. The structure of N-tosyl-2-ethylazetidin-3-one was studied by x-ray diffraction analysis and it was shown that the four-membered ring has 15° inflection.

Uncondensed azetidines with a keto group in position 3 are difficultly accessible derivatives of this heterocyclic system. Two basic synthesis routes to these compounds are known, that consist of formation of the azetidine ring followed by introduction of the carbonyl group; these are oxidation of 3-hydroxy-3-azetidinecarboxylic acid derivatives by lead tetra-

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