# MASS-SPECTROMETRIC STUDY OF THE CYCLIZATION OF DIAZO KETONES.

# 3.* CYCLIZATION OF o-(p-PHENYLSULFAMOYL)-ω-DIAZOACETOPHENONES TO N-(p-PHENYLSULFONYL)INDOXYLS

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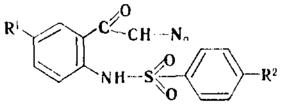
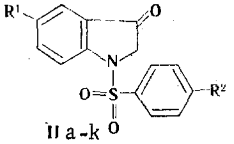
UDC 543.51:547.755'541.52'235.42:542.953.1

A comparison of the mass spectra of o-(p-phenylsulfamoyl)-ω-diazoacetophenones and N-(p-phenylsulfonyl)indoxyls makes it possible to conclude that under the conditions of electron impact and chemical ionization the molecular ions of the examined diazo ketones lose a molecule of nitrogen and under cyclization to the corresponding N-substituted derivatives of indoxyls without undergoing the Wolff rearrangement.

We have recently shown [1, 2] that 1-diazo-2-sulfonylaminopropan-2-ones and 1-diazo-4-sulfonylaminobutan-2-ones in the gas phase in the ionization chamber of a mass spectrometer undergo partial cyclization to N-sulfonylazetidin-3-ones and N-sulfonylpyrrolidin-3-ones, respectively, by eliminating a molecule of nitrogen. In order to investigate the possibility of the cyclization of o-(p-phenylsulfonyl)-ω-diazoacetophenones (I) to N-(p-phenylsulfonyl)-indoxyls (II) in the gas phase we studied the mass spectra of a series of I and II under conditions of electron impact (EI) and chemical ionization (CI).†


I a-j


II a-k

a $R^1=R^2=H$; b $R^1=H$, $R^2=CH_3$; c $R^1=H$, $R^2=OCH_3$; d $R^1=CH_3$, $R^2=H$; e $R^1=OCH_3$, $R^2=H$; f $R^1=R^2=CH_3$; g $R^1=OCH_3$, $R^2=CH_3$; h $R^1=OCH_3$, $R^2=Cl$; i $R^1=Cl$, $R^2=OCH_3$; j $R^1=Br$, $R^2=OCH_3$; k $R^1=Br$, $R^2=CH_3$

Proceeding from the data in [4-7] one might have expected that the molecular ions ($M^+$) of diazo ketones I under the experimental conditions would eliminate a molecule of nitrogen and undergo the Wolff rearrangement. In this case product A (see Scheme 1) could subsequently undergo fragmentation with the ejection of a molecule of CO (ion radical B) or undergo cyclization to oxindole ring C. The Wolff rearrangement was not observed in [1, 2] in the mass-spectrometric fragmentation of diazo ketones; this is evidently associated with the remoteness of the carbonyl group from the benzene ring, as well as with the competitive cyclization process, which leads to the formation of a stable heteroring. In the case of I the carbonyl group is bonded directly to the aromatic ring, and the probability of the Wolff rearrangement consequently increases, although the possibility of cyclization is retained. A detailed analysis of the mass spectra makes it possible to assert that diazo ketones I do not undergo the Wolff rearrangement but rather undergo cyclization to indoxyl derivatives II. The absence in the mass spectra of the peak of $[M - N_2, -CO]^+$ ions that was observed in all cases when the investigated diazo ketones underwent the Wolff rearrangement without subsequent cyclization constitutes evidence that the $[M - N_2]^+$ ions do not exist in the B form. The peaks of ions that are characteristic for the fragmentation of the indoxyl

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*See [1] for Communication 2.

†The cyclization of I to II under the influence of acidic agents was described in [3].

M. V. Lomonosov Moscow State University, Moscow 117234. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1056-1063, August, 1982. Original article submitted November 23, 1981.

0009-3122/82/1808-0804$07.50

TABLE 1. Intensities of the Peaks of the Characteristic Fragment Ions in the Mass Spectra of I and II in Percent of the Total Ion Current*

| Compound | $M^+$ $[M-N_2]^+$ | $F_1$ | $F_2$ | $F_3$ | $F_4$ | $F_5$ | $F_6$ | $F_8$ | $F_7$ | $F_9$ | $F_{10}$-$F_{14}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Ia | 1,3 | 9,9 | 0,5 | 0,9 | 0,9 | 0,5 | 9,0 † | | 8,6 † | | 0,3 |
| IIa | 1,7 | 10,2 | 0,5 | 1,0 | 1,2 | 0,4 | 8,3 † | | 7,5 † | | 0,2 |
| Ib | 1,4 | 7,3 | 1,1 | 0,6 | 0,8 | 0,4 | 4,3 | 4,3 | 2,8 | 1,9 | 0,7 |
| IIb | 1,9 | 9,2 | 1,1 | 0,8 | 0,8 | 0,4 | 4,9 | 4,1 | 2,9 | 1,7 | 0,2 |
| Ic | 1,2 | 4,0 | 4,0 | 0,5 | 0,7 | 0,4 | 5,6 | 2,3 | 2,6 | 1,2 | 1,6 |
| IIc | 1,7 | 4,3 | 4,8 | 0,7 | 0,7 | 0,5 | 6,4 | 2,6 | 2,7 | 1,1 | 1,3 |
| Id | 1,0 | 7,6 | 0,2 | 0,3 | 0,7 | 0,7 | 2,7 | 3,6 | 2,3 | 3,5 | 0,5 |
| IId | 2,0 | 9,8 | 0,2 | 0,4 | 0,5 | 0,4 | 3,7 | 2,0 | 3,2 | 2,5 | 0,2 |
| Ie | 2,4 | 13,9 | 0,2 | 0,4 | 0,8 | 0,3 | 0,8 | 8,3 | 2,2 | 6,2 | 0,2 |
| IIe | 1,4 | 10,0 | 0,1 | 0,2 | 0,4 | 0,2 | 0,4 | 3,5 | 1,0 | 2,1 | 0,4 |
| If | 1,0 | 8,8 | 0,6 | 0,3 | 0,8 | 0,8 | 5,6 † | | 3,6 † | | 0,4 |
| IIf | 1,9 | 9,6 | 0,5 | 0,4 | 0,5 | 0,5 | 5,9 † | | 4,0 † | | 0,3 |
| Ig | 0,9 | 7,3 | 0,1 | 0,2 | 0,3 | 0,3 | 0,4 | 2,6 | 1,7 | 2,4 | 0,9 |
| IIg | 1,5 | 9,8 | 0,1 | 0,2 | 0,4 | 0,2 | 0,4 | 1,6 | 1,0 | 1,8 | 0,1 |
| Ih | 0,6 | 7,8 | — | 0,2 | 0,4 | 0,4 | 0,9 | 0,3 | 0,9 | 0,4 | 0,1 |
| IIh | 0,4 | 5,8 | — | 0,2 | 0,3 | 0,3 | 0,3 | 0,4 | 0,7 | 0,4 | 0,1 |
| Ii | 1,5 | 1,8 | 5,1 | 0,3 | 0,3 | 0,1 | 1,7 | 3,5 | 0,9 | 0,4 | 2,2 |
| IIi | 0,9 | 1,6 | 5,7 | 0,2 | 0,3 | 0,5 | 1,6 | 3,0 | 0,7 | 0,4 | 1,7 |
| Ij | 1,2 | 1,3 | 5,9 | 0,1 | 0,2 | 0,1 | 0,9 | 3,1 | 0,7 | 0,5 | 1,9 |
| IIj | 0,8 | 1,1 | 5,1 | 0,1 | 0,3 | 0,5 | 0,8 | 2,5 | 0,8 | 0,4 | 1,5 |
| IIk | 1,7 | 3,2 | 1,7 | 0,1 | 0,2 | 0,2 | 1,3 | 5,5 | 0,9 | 2,2 | 0,2 |

*The total ion current was calculated with a computer over the range from the ion with m/z 40 to the ion with m/z 449; more than 50% of the total ion current is due to the current of the background ions.

†The $F_6$ and $F_8$ ions, as well as the $F_7$ and $F_9$ ions, have the same m/z value.

ring but not for the oxindole ring (see below) constitute evidence that structure C is also inapplicable for the $[M - N_2]^+$ ions of diazo ketones I. Since the analysis of the electron impact (EI) mass spectra repudiates both possible structures due to the Wolff rearrangement, it may be concluded that the o-(p-phenylsulfamoyl)-ω-diazoacetophenones after elimination of a molecule of nitrogen by their molecular ions do not undergo rearrangement via the Wolff mechanism. It is evident that in this case also the cyclization of the $[M - N_2]^+$ ion proves to be more favorable than rearrangement [1, 2]. The fact that the diazo keto and sulfamoyl groups are ortho-oriented with respect to one another and the so-called "ortho effect" [8] is exerted also possibly plays a definite role.

As in [1, 2], $M^+$ peaks are not observed in the EI mass spectra of any of the I, and the intensities of the peaks of the $[M - N_2]^+$ ions, as well as the $M^+$ peaks in the case of II, range from 1 to 2% of the total ion current (see Table 1). This fact may serve as evidence that these ions have a common structure — in all likelihood, an indoxyl structure.

Since the indoxyl system can be regarded as benzopyrrolidin-3-one, it should have been expected that the splitting out of a molecule of CO that is characteristic for pyrrolidin-3-ones [1]* would be one of the possible pathways of the fragmentation of $M^+$. However, we were unable to record peaks of these ions in any of the mass spectra. The pyrrolidinone ring is consequently stabilized due to annelation with the benzene ring, and the primary fragmentation of all of the investigated compounds is associated exclusively with cleavage of the S—N bond to give $F_1$ and $F_2$ fragments, the subsequent fragmentation of which determines the entire pattern of the dissociative ionization.

The principal pathways in the mass-spectral fragmentation of I and II under electron impact can be represented by the general scheme

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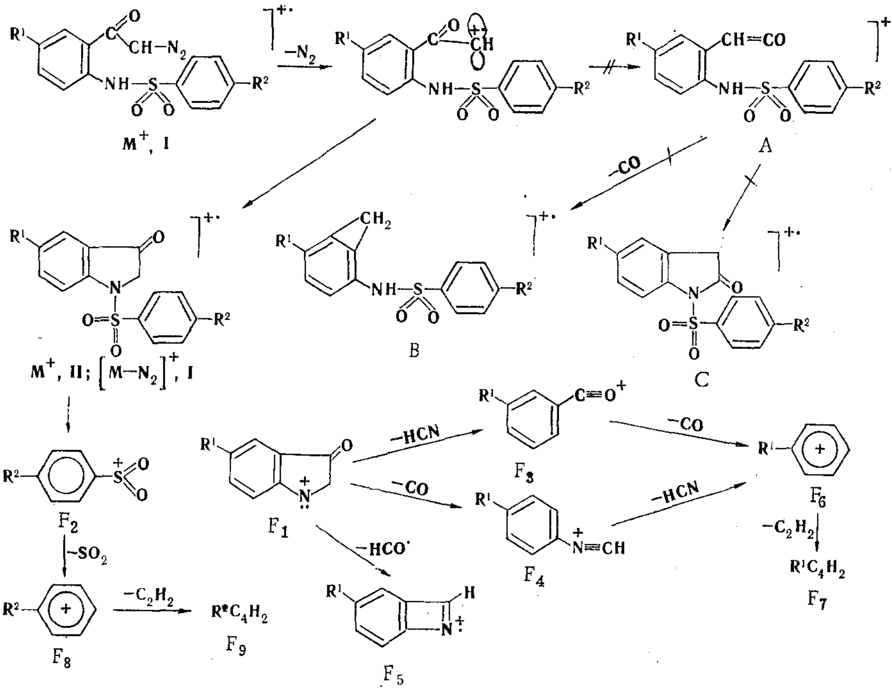
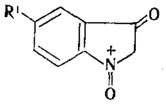
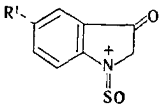
*Low-intensity peaks of $[M - CO, -SO_2]^+$ ions that are characteristic for the fragmentation of pyrrolidin-3-ones [1] are observed in the mass spectra of some compounds. It is possible in this case that the sequence of the elimination of molecules of CO and $SO_2$ is reversed [9, 10].



In addition to the indicated ions, the EI mass spectra also contain low-intensity peaks of ions that are due to processes involving the rearrangement of the sulfo group, viz.,

$R^2-C_6H_4-SO^+$ ($F_{10}$), $R^2-C_6H_4-S^+$ ($F_{11}$), $R^2-C_6H_4-O^+$ ($F_{12}$),

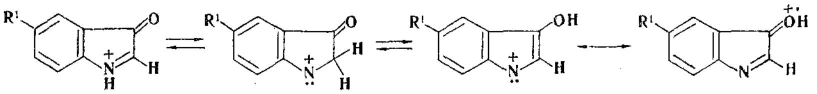

($F_{13}$),


($F_{14}$),

however, their overall intensity does not exceed 1% in the total ion current. More intense peaks of $F_{12}$ ions (1-1.5%) are observed only in the mass spectra of the compounds with $R^2 = OCH_3$ (I and IIc, i, k).

The ratio of the intensities of the peaks of $F_1$ and $F_2$ ions to one another ($I_{F_1}/I_{F_2} = X$) in the mass spectrum of IIa ($R^1 = R^2 = H$) is 20. This ratio is the same for IIf, where $R^1 = R^2 = CH_3$. When $R^1 \neq R^2$, X changes substantially. Electron-donor $R^1$ substituents in the benzene ring of indoxyl lead to an increase in this ratio, while similar $R^2$ substituents in the aromatic ring of the phenylsulfonyl grouping lead to a decrease. Electron-acceptor substituents have the opposite effect. We decided to ascertain the quantitative dependence of the X value on the algebraic sum of the Hammett $\sigma$ constants of substituents $R^1$ and $R^2$; the $\sigma$ constant of substituent $R^1$ had the tabular value, while the $\sigma$ constant of substituent $R^2$ was taken with the opposite sign. The graph of this dependence is presented in Fig. 1.* Correlation coefficient $r = 0.98$ (a satisfactory correlation), while reaction constant $\rho = 3.21 \pm 0.03$. Proceeding from the large absolute value of the reaction constant, it may be concluded that the X value is very sensitive to the electronic parameters of both substituents. The electronic properties of the substituents evidently have a pronounced effect on the stabilities of fragments $F_1$ and $F_2$. Thus small changes in the electron density under the influence of the substituents have a pronounced effect on the X value, and, in accordance with Stevenson's rule [11], the ionization potentials of these fragments are consequently very close.

The $F_1$ ion subsequently undergoes fragmentation via several pathways: splitting out of a molecule of HCN leads to the $F_3$ ion, splitting out of a molecule of CO leads to the $F_4$ ion, and splitting out of an $HCO^{\cdot}$ radical leads to the $F_5$ ion. The formation of this series of ions is associated with the possibility of tautomeric transformations in the $F_1$ ion.



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*The log X value for IIg deviates from the general dependence and is not measurable for IIh.

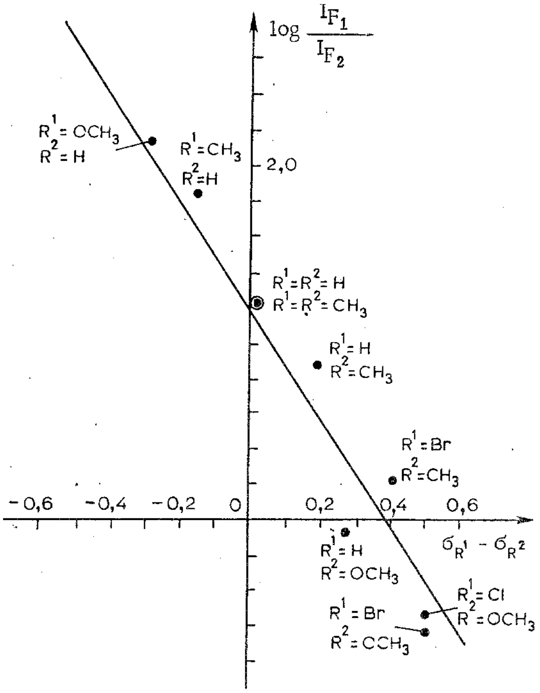

Fig. 1. Dependence of log X on the algebraic sum of the Hammett σ constants of substituents $R^1$ and $R^2$.

TABLE 2. Intensities of the Peaks of the Characteristic Fragment Ions in the Mass Spectra of I and II in Percent of the Total Ion Current*

| Compound | MH [MH—$N_2$] | $F_1$ | $F'_1$ | $F''_1$ | $F_2$ | $F''_2$ | $F_{10}$ | $F'_{10}$ | $F''_{10}$ | $F_{11}$ | $F''_{11}$ | $F_{12}$ | $F''_{12}$ | $F_{13}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ia | 27,2 | 1,0 | 0,4 | 5,5 | 0,1 | 9,1 | 0,6 | 0,3 | 0,7 | — | 0,1 | — | — | 0,6 |
| IIa | 35,6 | 1,0 | 0,2 | 2,8 | 0,1 | 0,5 | 0,1 | 0,2 | 0,3 | — | 0,1 | — | 0,1 | 0,1 |
| Ib | 4,8 | 3,2 | 1,5 | 9,4 | 0,1 | 1,9 | 0,1 | 1,1 | 3,0 | 0,2 | 0,1 | 0,1 | 0,1 | 0,1 |
| IIb | 25,8 | 2,7 | 0,4 | 3,1 | 0,3 | 0,7 | 0,3 | 0,9 | 0,9 | — | 0,1 | — | 0,1 | 0,3 |
| c | 3,8 | 6,4 | 1,0 | 6,8 | 1,0 | 8,9 | 2,6 | 2,1 | 1,6 | 1,0 | 1,0 | 0,6 | — | 0,2 |
| IIc | 20,9 | 2,9 | 0,2 | 2,6 | 0,5 | 0,6 | 0,5 | 0,8 | 0,5 | 0,3 | 0,3 | 0,1 | — | 0,1 |
| Id | 6,9 | 3,0 | 3,1 | 17,6 | 0,8 | 3,0 | 0,5 | 1,4 | 2,0 | 0,2 | 0,4 | 0,2 | 0,8 | 0,5 |
| IId | 24,4 | 3,5 | 1,0 | 7,8 | 0,2 | 1,0 | 0,2 | 0,8 | 0,6 | — | 0,1 | 0,1 | 0,3 | 0,1 |
| Ie | 32,1 | 0,6 | 0,7 | 2,8 | 0,2 | 9,0 | 0,8 | 2,7 | 4,3 | 0,1 | 0,4 | 0,1 | 0,4 | 0,1 |
| IIe | 21,1 | 4,5 | 2,1 | 8,5 | 0,3 | 1,4 | 0,1 | 0,7 | 0,5 | — | 0,1 | 0,1 | 0,3 | 0,1 |
| If | 8,8 | 1,1 | 1,9 | 14,0 | 1,5 | 16,5 | 4,3 | 3,3 | 4,4 | 0,6 | 0,5 | 0,1 | — | 0,3 |
| IIf | 1,8 | 4,0 | 0,9 | 5,9 | 0,1 | 0,4 | 0,1 | 0,5 | 0,4 | 0,3 | 0,2 | 0,1 | 0,1 | — |
| Ig | 11,9 | 4,8 | 2,2 | 7,9 | 0,3 | 2,0 | 0,5 | 2,4 | 3,4 | 0,3 | 0,5 | — | 0,1 | 0,7 |
| IIg | 27,3 | 3,7 | 1,1 | 3,0 | 0,1 | 1,0 | 0,2 | 0,6 | 0,8 | 0,1 | 0,2 | — | 0,1 | 0,1 |
| Ih | 26,9 | 5,7 | 3,1 | 4,0 | 0,1 | 1,8 | 0,1 | 0,2 | 0,3 | 0,7 | 0,1 | 0,2 | — | 0,6 |
| IIh | 16,4 | 5,7 | 1,1 | 2,4 | — | 0,5 | 0,1 | 0,5 | 0,5 | — | — | — | — | 0,3 |
| Ii | 2,2 | 4,3 | 2,2 | 6,7 | 0,2 | 0,7 | 0,7 | 0,8 | 1,0 | 0,6 | 1,1 | 0,1 | 0,1 | 1,0 |
| IIi | 1,5 | 2,8 | 0,1 | 1,7 | 0,4 | 0,9 | 0,9 | 3,8 | 0,7 | 0,6 | 0,8 | 0,2 | 0,2 | 0,2 |
| Ij | 13,7 | 1,1 | 0,7 | 1,9 | 1,0 | 7,5 | 3,8 | 2,8 | 2,3 | 1,5 | 1,6 | 0,3 | 0,3 | 1,3 |
| IIj | 25,2 | 1,6 | 0,6 | 2,0 | 0,5 | 3,0 | 2,4 | 1,4 | 0,6 | 0,5 | 0,3 | 0,1 | — | 0,1 |
| IIk | 29,6 | 1,8 | 0,6 | 2,3 | 0,2 | 2,7 | 0,9 | 0,9 | 1,3 | 0,1 | 0,1 | — | 0,1 | 0,1 |

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*The total ion current was calculated with a computer over the range from the ion with m/z 60 to the ion with m/z 449; more than 50% of the total ion current is due to the current of the background ions.

TABLE 3. Mass Spectra of Ia-j and IIa-k

| Compound | m/z values (relative intensities of the ion peaks in percent of the maximum peak) |
|---|---|
| 1 | 2 |
| | 1. Electron impact |
| Ia | 273 (13,0), 133 (12,0), 132 (100), 105 (8,8), 104 (8,7), 91 (10,4), 77 (90,4), 76 (24,2), 51 (87,6), 50 (18,3) |
| Ib | 287 (18,0), 132 (100), 92 (16,0), 91 (64,7), 78 (24,1), 77 (66,1), 76 (16,2), 65 (30,8), 51 (45,4), 50 (22,8) |
| Ic | 171 (65,3), 132 (64,3), 123 (20,3), 107 (39,6), 92 (22,1), 78 (27,5), 77 (100), 76 (24,0), 51 (48,2), 50 (30,3) |
| Id | 287 (12,9), 147 (14,5), 146 (100), 91 (38,0), 90 (13,3), 78 (26,9), 77 (49,9), 65 (32,9), 51 (51,5), 50 (19,5) |
| If | 147 (13,9), 146 (100), 92 (12,6), 91 (67,4), 90 (15,7), 89 (14,5), 65 (43,7), 63 (13,2), 51 (12,4), 41 (12,6) |
| Ie | 163 (18,1), 162 (100), 92 (17,9), 78 (18,3), 77 (67,4), 65 (19,8), 64 (25,3), 63 (22,8), 51 (51,3), 50 (18,5) |
| Ig | 163 (15,1), 162 (100), 106 (17,5), 92 (26,7), 91 (39,7), 77 (23,3), 65 (36,4), 64 (13,2), 62 (28,6), 51 (13,5) |
| Ih | 162 (100), 106 (15,3), 79 (11,7), 78 (23,0), 77 (26,8), 75 (18,3), 64 (13,6), 63 (22,2), 51 (17,6), 50 (17,0) |
| Ii | 171 (100), 123 (29,0), 111 (26,4), 107 (65,4), 92 (34,8), 77 (64,7), 75 (45,5), 64 (32,9), 63 (31,1), 50 (25,1) |
| Ij | 171 (100), 123 (25,4), 107 (57,0), 91 (31,8), 77 (62,4), 76 (36,2), 75 (37,5), 64 (29,7), 63 (29,5), 50 (27,0) |
| IIa | 273 (16,4), 133 (12,6), 132 (100), 105 (10,0), 104 (11,2), 91 (12,0), 77 (84,3), 76 (15,2), 51 (74,2), 50 (16,2) |
| IIb | 287 (18,2), 155 (13,1), 133 (12,8), 132 (100), 104 (10,3), 91 (50,0), 77 (60,1), 76 (14,3), 65 (20,9), 51 (35,4) |
| IIc | 303 (22,6), 171 (70,0), 132 (63,8), 123 (18,5), 107 (43,0), 92 (17,6), 77 (100), 76 (21,3), 51 (44,3), 50 (26,0) |
| IId | 287 (18,9), 147 (13,2), 146 (100), 91 (40,3), 89 (9,3), 78 (9,2), 77 (21,6), 65 (34,9), 51 (28,2), 50 (9,1) |
| IIf | 301 (18,8), 147 (17,0), 146 (100), 91 (69,2), 90 (11,7), 89 (12,6), 65 (47,7), 63 (12,4), 51 (10,7), 41 (12,9) |
| IIe | 303 (13,0), 163 (13,4), 162 (100), 92 (11,9), 79 (11,2), 77 (38,1), 65 (10,3), 64 (12,7), 63 (15,0), 51 (22,8) |
| IIg | 317 (13,1), 163 (12,7), 162 (100), 92 (13,2), 91 (17,2), 79 (9,9), 71 (21,0), 65 (20,3), 64 (11,8), 63 (16,0) |
| IIh | 163 (12,0), 162 (100), 77 (35,6), 69 (19,5), 63 (23,3), 57 (28,8), 55 (24,3), 51 (19,3), 43 (52,4), 41 (34,0) |
| IIi | 171 (100), 166 (24,6), 123 (26,8), 111 (24,4), 107 (55,3), 92 (23,7), 77 (49,4), 75 (41,6), 64 (22,5), 50 (20,2) |
| IIj | 171 (100), 123 (24,9), 107 (55,9), 92 (22,7), 77 (57,0), 76 (32,9), 75 (45,3), 64 (23,2), 63 (20,8), 50 (24,6) |
| IIk | 212 (30,4), 210 (29,7), 155 (45,6), 91 (100), 76 (39,5), 75 (46,3), 65 (43,7), 63 (20,5), 51 (21,7), 50 (25,9) |
| | 2. Chemical ionization |
| Ia | 276 (9,2), 275 (18,5), 274 (100), 273 (7,6), 251 (4,7), 144 (3,5), 143 (38,4), 134 (23,8), 132 (4,0), 127 (3,4) |
| Ib | 316 (14,5), 288 (43,4), 157 (22,4), 141 (32,0), 134 (100), 133 (18,9), 132 (32,9), 71 (48,2), 70 (14,5), 61 (22,8) |
| Ic | 333 (15,8), 332 (100), 331 (13,8), 304 (13,0), 263 (10,8), 173 (38,6), 156 (9,6), 155 (10,0), 134 (27,4), 132 (26,0) |
| Id | 288 (35,0), 149 (12,5), 148 (100), 147 (18,2), 146 (16,4), 143 (17,2), 127 (11,3), 126 (8,4), 71 (22,0), 61 (8,8) |
| Ie | 306 (6,9), 305 (8,6), 304 (100), 303 (8,0), 164 (8,8), 143 (28,1), 142 (4,4), 127 (14,3), 126 (8,8), 71 (8,0) |
| If | 302 (49,9), 279 (12,4), 158 (10,8), 157 (100), 149 (10,3), 148 (86,3), 147 (13,0), 141 (27,4), 140 (23,1), 139 (26,5) |
| Ig | 319 (20,2), 318 (100), 317 (19,5), 164 (76,7), 163 (31,7), 162 (46,9), 157 (21,4), 141 (35,5), 140 (25,2), 71 (42,0) |
| Ih | 341 (6,8), 340 (40,2), 339 (26,1), 338 (100), 337 (68,7), 177 (8,3), 164 (25,3), 163 (20,8), 162 (32,1), 71 (9,8) |
| Ii | 338 (20,3), 305 (21,7), 304 (50,0), 212 (18,4), 168 (100), 167 (43,5), 166 (60,4), 71 (60,9), 70 (20,3), 69 (22,2) |
| Ij | 384 (80,0), 382 (77,0), 304 (20,6), 212 (22,4), 173 (100), 157 (37,6), 156 (44,6), 155 (53,1), 141 (22,2), 139 (20,3) |
| IIa | 276 (6,6), 275 (18,8), 274 (100), 273 (7,3), 143 (1,7), 134 (8,7), 133 (1,3), |

(continued)

TABLE 3 (continued)

| | |
|---|---|
| | 132 (3,2), 71 (1,7), 61 (1,5) |
| IIb | 290 (6,3), 289 (18,4), 288 (100), 287 (6,4), 157 (3,2), 141 (4,2), 140 (4,1), 134 (13,5), 132 (11,6), 71 (7,9) |
| IIc | 306 (7,5), 305 (22,3), 304 (100), 303 (6,2), 156 (5,2), 134 (15,2), 133 (3,9), 132 (16,1), 71 (10,8), 69 (4,9) |
| IId | 290 (6,0), 289 (21,0), 288 (100), 287 (5,7), 149 (4,4), 148 (36,1), 147 (7,7), 146 (16,1), 143 (5,1), 71 (9,0) |
| IIe | 306 (7,1), 305 (20,4), 304 (100), 303 (6,0), 165 (5,2), 164 (46,1), 163 (16,4), 162 (23,7), 143 (8,5), 71 (7,0) |
| IIf | 302 (23,1), 148 (69,2), 146 (48,7), 81 (20,5), 73 (23,1), 71 (100), 70 (24,4), 69 (30,8), 67 (19,2), 61 (46,2) |
| IIg | 320 (6,3), 319 (21,2), 318 (100), 317 (8,1), 164 (12,5), 163 (7,0), 162 (15,2), 157 (4,5), 141 (3,9), 71 (5,3) |
| IIh | 341 (7,6), 340 (41,3), 339 (23,2), 338 (100), 337 (6,2), 164 (23,4), 163 (19,0), 162 (51,9), 161 (6,1), 71 (14,2) |
| IIi | 338 (25,6), 173 (23,1), 168 (38,5), 166 (64,1), 157 (25,6), 156 (87,2), 71 (100), 69 (41,0), 67 (26,6), 61 (23,1) |
| IIj | 385 (18,7), 384 (100), 383 (26,3), 382 (95,0), 381 (8,5), 214 (8,8), 212 (16,1), 173 (24,7), 156 (13,3) ,155 (22,2) |
| IIk | 369 (16,7), 368 (100), 367 (28,6), 366 (97,1), 365 (10,6), 214 (8,7), 212 (13,6), 157 (22,4), 141 (10,3), 71 (9,1) |

The formation of $F_3$ ions from $F_1$ ions confirms the indoxylyl cation structure assigned to the $F_1$ ions and repudiates the alternative oxindolyl cation structure [12], the formation of which should have been expected in the case of the Wolff rearrangement. This fact constitutes convincing evidence that diazo ketones I do not undergo the Wolff rearrangement but rather undergo cyclization to indoxyl derivatives II after the elimination of a molecule of nitrogen.

The $F_3$ and $F_4$ ions undergo subsequent fragmentation to the $F_6$ ion, the peak of which is intense in the EI mass spectra of all of the investigated compounds, while the $F_2$ ion eliminates a molecule of $SO_2$ to give the $F_8$ ion, the peak of which is no less intense. Ejection of a molecule of HHal to give ions with m/z 75, the intensity of the peaks of which is ~2% in the total ion current, is observed when there is a halogen atom in the $F_6$ and $F_8$ ions.

It is apparent from Tables 1 and 3 that I and II are characterized not only by a common fragmentation pathway but also by approximately equal relative intensities of the peaks of the corresponding characteristic ions. Thus the mass-spectral fragmentations of I and II under the influence of electron impact (EI) are identical. The certain deviations in the relative intensities of the peaks of analogous ions are not systematic in character and can be ascribed to measurement errors in working with the apparatus. The complete analogy in the fragmentation confirms the conclusion that under the influence of electron impact the o-(p-phenylsulfamoyl)-ω-diazoacetophenones eliminate a molecule of nitrogen and undergo cyclization to N-(p-phenylsulfonyl)indoxyls.

The principal pathways of fragmentation of I and II under conditions of chemical ionization (with isobutane as the gas reactant) remain the same as in the case of electron impact; however, significant changes are observed in the intensities of the peaks of the characteristic ions. Thus the relative intensities of the peaks of the protonated molecular ions ($MH^+$) of indoxyls II and the peaks of the $[MH - N_2]^+$ ions of diazoacetophenones I are very high. The peaks of these ions are the maximum peaks in the spectra of virtually all cases. Peaks of $MH^+$ ions with intensities of 1.5, 26.2, and 0.9%, respectively, in the total ion current are observed only in the spectra of Ib, c, f. The intensity of the $MH^+$ peak for Ic depends very markedly on the temperature, decreasing as the temperature is increased. The intensity of the peak of $[MH - N_2]^+$ ions increases markedly at the same time. The temperature factor evidently plays a certain role also in the fragmentation of the other compounds; however, it does not seem possible to exclude it, since the compounds do not give spectra when the temperature is lowered, and the mass spectrum obtained at the minimally possible temperature does not contain $MH^+$ peaks. Nevertheless, it should be noted that thermal decomposition does not distort the pattern of fragmentation of the investigated compounds, which is demonstrated by a comparison of the mass spectra of Ic recorded at various temperatures and the mass spectra of this compound and the other compounds. It is apparent from Tables 2 and 3 that the general characteristics of the fragment ions remain the same.

A substantial difference between the CI mass spectra of I and II and their EI mass spectra is the complete absence of peaks of ions that are due to profound fragmentation steps. At the same time, the low-intensity peaks of the $F_{10}$-$F_{13}$ ions due to rearrangements of the sulfo group in the EI mass spectra are extremely intense in the CI mass spectra.

The possibility in the case of chemical ionization of the occurrence of ion-molecular reactions with the participation of a molecule of the gas reactant has been noted by Harrison [13-16]. The data that we obtained in [1, 2] confirm this fact; we examined in detail the possibility of not only replacement of the halogen atom by a hydrogen atom in the benzene ring [the peak of this ion is intense in the spectra of the investigated compounds (1-4% in the total ion current)] but also the formation of a series of ions with m/z values that were 2 amu greater than those for the characteristic ions. The presence in the CI mass spectra of I and II of peaks of such ions ($F''_n$, see Table 2) proves the occurrence of ion-molecular reactions in this case also. These reactions, as previously noted in [1, 2], are random in character, as evidenced by the fact that the relative intensities of the peaks of $F''_n$ ions in the mass spectra of the same substance obtained under virtually identical conditions change very markedly (5-6% in the total ion current), and these changes are chaotic.

In examining the problem of the site of protonation of these compounds attention should be directed to the fact that the $F_1$ and $F_{10}$ ions are accompanied not only by heavier (by 2 amu) ions but also by $F'_1$ and $F'_{10}$ ions that are 1 amu heavier, the peaks of which are quite intense (see Table 2). This fact may constitute evidence in favor of protonation at the oxygen atoms of the sulfo group or at the nitrogen atom or the oxygen atom of the carbonyl group. The $I_{F'_n}/I_{F_n}$ ratio for the $F_{10}$ ions is much greater than for the $F_1$ ions. Probably precisely one of the oxygen atoms of the sulfo group also adds a proton to give $MH^+$; however, the possibility of the development of $F_{10}$ ions as a result of migration of a hydrogen atom from the indoxyl ring is not excluded. Judging from the fact that there are low-intensity peaks of such rearranged ions (less than 0.1% in the total ion current) in the EI mass spectra of only Ie, g, h, it may be assumed that the contribution of such migration to the formation of $F_{10}$ ions is very insignificant.

It should be noted that not a single peak that differs from those in the mass spectra of indoxyls II is present in the CI mass spectra of diazo ketones I. This identical character of the spectra makes it possible to state that in both cases we are dealing with the same original structure, i.e., with N-(p-phenylsulfonyl)indoxyls. The certain chaotic character in the numerical data is evidently associated with the impossibility of complete stabilization of the parameters under CI conditions.

Thus an analysis of the CI mass spectra of I and II makes it possible to conclude that the $[MH - N_2]^+$ ions of diazo ketones I undergo cyclization to N-substituted derivatives of indoxyl, i.e., they do not undergo the Wolff rearrangement. A comparison of the intensities of the peaks of the analogous ions of I and II confirms that cyclization proceeds almost completely; the slight differences in fragmentation that occurred during the study of the mass-spectral behavior of other series of diazo ketones [1, 2] are not observed here.

## EXPERIMENTAL

The mass spectra were obtained with a Varian MAT-44S spectrometer. The electron-impact mass spectra were recorded at 70-200°C and an ionizing-electron energy of 75 eV (the emisson current was 0.4-0.6 mA). The chemical-ionization mass spectra were recorded at an ionization-chamber pressure of 33.3 Pa and an ionizing-electron energy of 160 eV (the emission current was 0.1 mA) at 50-240°C.

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# SYNTHESIS OF 5H-PYRIDAZO[4,5-b]INDOLES BY CONDENSATION OF 2-ACYLINDOLE-3-CARBOXYLIC ACIDS WITH HYDRAZINE

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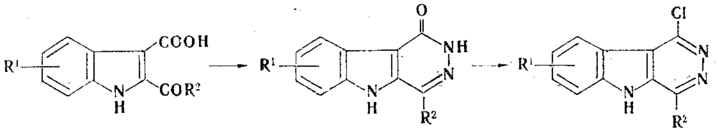
UDC 547.852.9+547.852.2

5H-Pyridazo[4,5-b]indol-1-ones were obtained by heating 2-acetylindole-3- or 2-aroylindole-3-carboxylic acids with hydrazine hydrate in ethylene glycol or alcohol. 1-Chloro-5H-pyridazo[4,5-b]indoles are formed by treatment of 5H-pyridazo[4,5-b]indol-1-ones with phosphorus oxychloride.

Some pyridazine derivatives have found practical application as medicinals. In particular, this is true of Apressin and Nepressol, which have strong hypotensive action. In our search for new compounds of this type we turned to condensed indole and pyridazone systems; such compounds can be regarded as aza analogs of carbolines, the ring system of which lies at the foundation of many substances with high physiological activity.

Only a few methods are known for the synthesis of condensed indole and pyridazine systems; a small number of papers in which 2,3- or 2-carbonyl derivatives of indole are used as the starting compounds have been published [1-8]. Up until now, 5H-pyridazo[4,5-b]indol-1-ones (I-XII) have remained undescribed; this is evidently explained by the lack of convenient methods for the synthesis of the starting compounds. We have found that I-XII can be obtained by condensation of the recently described 2-acylindole-3-carboxylic acids [9-11] with hydrazine hydrate. Their structures were confirmed by reaction with phosphorus oxychloride, as a result of which 1-chloro-5H-pyridazo[4,5-b]indoles (XIII-XVII) are formed, and also by data from their IR spectra.



I–XII XIII–XVII

I, XIII $R^1$=H, $R^2$=$C_6H_5$; II, XIV $R^1$=H, $R^2$=$C_6H_4Cl$-*p*; III, XV $R^1$=H, $R^2$=$C_6H_4Br$-*p*; IV, XVI $R^1$=8-Br, $R^2$=$C_6H_5$; V, XVII $R^1$=6-$CH_3$, $R^2$=$C_6H_5$; VI $R^1$=8-Br, $R^2$=$C_6H_5Cl$-*p*; VII $R^1$=8-$OCH_3$, $R^2$=$C_6H_5$; VIII $R^1$=H, $R^2$=$CH_3$; IX $R^1$=8-$CH_3$, $R^2$=$CH_3$; X $R^1$=6-$CH_3$, $R^2$=$CH_3$; XI $R^1$=8-Br, $R^2$=$CH_3$; XII $R^1$=8-Cl, $R^2$=$CH_3$

The IR spectra of I-XII contain intense peaks of an amide carbonyl group at 1635-1645 $cm^{-1}$. The intensities of the bands in the indicated region are weak in the spectra of the products of treatment of I-VII with phosphorus oxychloride (these bands are evidently due to absorption of the pyridazine ring C=N bond); this is due to disappearance of the absorption of the carbonyl group and makes it possible to conlude that I-XII have lactam (rather than lactim) structures. The stretching vibrations of the NH group of the indole ring of I-IX, XI, and XII are found at 3130-3170 $cm^{-1}$, which corresponds to the intervals presented for the absorption of the NH group of 3-acylindoles [12]. The methyl group attached to the $C_6$ atom

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1064-1066, August, 1982. Original article submitted September 29, 1981; revision submitted January 25, 1982.

0009-3122/82/1808-0811$07.50