SYNTHESIS AND STRUCTURE OF 6- AND 7-NITRO-1-OXOISOCHROMAN-4-SPIROOXIRANES

S. V. Chapyshev, Z. G. Aliev,
V. G. Kartsev, and L. O. Atovmyan

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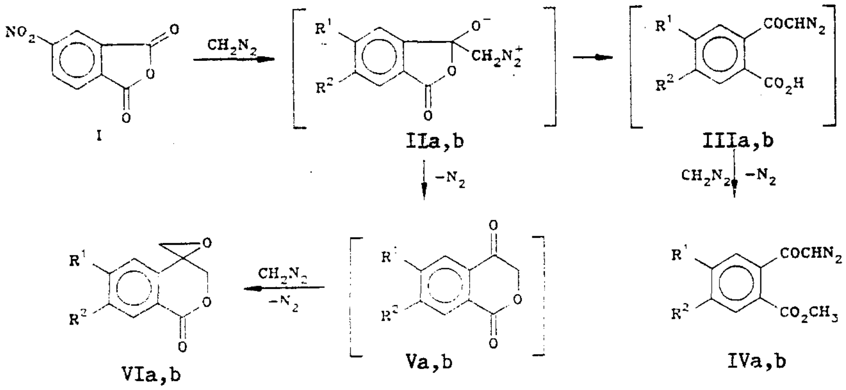
The reaction of diazomethane with 4-nitrophthalic acid anhydride gave 4- and 5-nitro-2-carbomethoxy-ω-diazoacetophenones and 6- and 7-nitro-1-oxoisochroman-4-spirooxiranes. The structure of 7-nitro-1-oxoisochroman-4-spirooxirane was investigated by x-ray diffraction analysis.

In a study of the reactions of diazomethane with quinolinic and acridinic acid anhydrides it was established that one of the pathways of these reactions leads to the formation of new heterocyclic spiro compounds [1].

In the present research we investigated the possibility of obtaining new heterocyclic compounds in the reaction of dizaomethane with 4-nitrophthalic acid anhydride (I); it was established that, in addition to acylation of diazomethane by anhydride I and the formation of the corresponding 4- and 5-nitro-2-carbomethoxy-ω-diazoacetophenone (IVa, b), one also observes intramolecular heterocyclization of the initially formed intermediates IIa,b to isochroman-1,4-diones Va,b, the subsequent reaction of which with excess diazomethane leads to the formation of 6- and 7-nitro-1-oxoisochroman-4-spirooxiranes (VIa, b).



II—VI a $R^1=NO_2$, $R^2=H$; b $R^1=H$, $R^2=NO_2$

The mechanism of this reaction is evidently similar to the mechanism of the reactions of diazomethane with quinolinic and acridinic acid anhydrides [1]. The structures of VIa, b(Fig. 1) are in complete agreement with IR, UV, and PMR spectroscopic and mass-spectrometric data. Thus an intense absorption band at 1730 cm^{-1}, which is characteristic for the vibrations of the C=O group in the ester fragment of a δ lactone [1], and an intense absorption band at 1530 cm^{-1} from an NO_2 group are observed in the IR spectra of VIa, b. Two weak bands at 1605 and 1570 cm^{-1} correspond to the stretching vibrations of C=C bonds of an aromatic ring. In addition to signals of three aromatic protons at 7.47-8.98 ppm, a group of signals of two AB spin-spin coupling systems appears in the PMR spectra of VIa, b. The quartet at 3.17-3.24 ppm and the doublet at 3.38 ppm with geminal constant J_{AB} = 5 Hz are characteristic for the protons of an oxirane ring [1], while the doublet at 4.27-4.3 ppm and the quartet at 4.8 ppm with J_{AB} = 11.8 Hz are characteristic for the protons of the methylene group in δ lactones [1]. The presence of two quartets at 3.17-3.24 and 4.8 ppm is evidently due to the existence of long-range spin-spin coupling between the protons of the oxirane ring and the δ lactone

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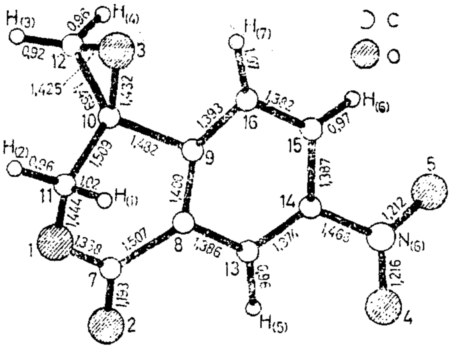

Fig. 1. Structure of the VIb molecule.

with spin-spin coupling constants (SSCC) of 1.5 and 1.8 Hz, respectively, for VIa and VIb. In addition to a molecular-ion peak, intense peaks of $[M - CO]^+$, $[M - CHO]^+$, $[M - CO_2]^+$, and $[M - 2CHO]^+$ ions are observed in the mass spectra of VIa, b, and the maximuim peak corresponds to the $[M - CH_2O]^+$ ion; on the whole this resembles the pattern of the mass-spectral fragmentation of similar spirooxiranes obtained in the reaction of diazomethane with quinolinic and acridinic acid anhydrides [1].

Since the results of spectral investigations presented above do not make it possible to indicate unequivocally the position of the nitro group in the aromatic ring of VI, we carried out the x-ray diffraction analysis of one of these compounds. It was established that the spirooxirane with mp 164-165°C corresponds to the structure of VIb. The conformation of its isochroman ring has a chair form in which the plane of the $O_{(1)}-C_{(11)}-C_{(10)}$ atoms deviates from the plane of the aromatic ring and the $C_{(7)}-C_{(10)}-O_{(1)}$ atoms, forming a dihedral angle of 27°. The plane of the oxirane ring is perpendicular to the plane of the aromatic ring; the protons of the oxirane ring and the δ lactone are situated on different sides of the plane passing through the $O_{(1)}$, $C_{(10)}$, and $C_{(9)}$ atoms. The latter, according to [2, p. 132], provides evidence that the long-range spin-spin coupling between the protons of the oxirane ring and the δ lactone is due to coupling of the $H_{(1)}$ and $H_{(4)}$ protons, the bonds between which comprise the M configuration.

EXPERIMENTAL

The PMR spectra of solutions of the compounds in $CDCl_3$ were recorded with a Bruker WM-250 spectrometer (250 MHz) with tetramethylsilane as the internal standard. The IR spectra of suspensions in mineral oil were obtained with a Specord 75-IR spectrometer. The UV spectra of solutions in methanol were obtained with a Specord UV-Vis spectrophotometer. The mass spectra were recorded with an MKh-1303 spectrometer with direct introduction of the substances into the ion source; the ionizing-electron energy was 70 eV, the emission current was 150 μA, and the temperature was 40-120°C. For column chromatography we used $L_{40/100}$ silica gel with benzene–ethyl acetate (9:1) as the eluent. The purity of the substances was monitored by TLC in a benzene–ethyl acetate system (9:1) on Silufol UV-254 plates.

X-Ray Diffraction Studies. We investigated well-faceted monoclinic crystals of VIb ($C_{10}H_7NO_5$) with the following parameters: a = 12.486(3), b = 10.376(2), c = 7.203(2) Å, V = 931.41 Å^3, d_{calc} = 1.59 g/cm^3, M = 221.17, Z = 4, space group P2/n. The preliminary investigation of the crystals and the set of experimental reflections and the subsequent processing of the results were carried out in Dron-2, DAR-UM, and BESM-6 systems. Copper K_α emission was used. We recorded 1181 independent nonzero reflections. The maximum value of sin θ/λ was 0.60. Absorption was disregarded. The structure was determined by the direct method by means of Rontgen-75 programs [3]. The H atoms were revealed from differential synthesis. Refinement was carried out within an anisotropic (for the nonhydrogen atoms) total-matrix approximation. The final uncertainty factor R was 0.052. The coordinates of the atoms are presented in Table 1. The bond angles are presented in Table 2.

Reaction of 4-Nitrophthalic Anhydride (I) with Diazomethane. A solution of 2.89 g (15 mmole) of anhydride I in 50 ml of dry benzene was added dropwise to a stirred and cooled (to –15°C) solution of diazomethane (from 15 g of nitrosomethylurea) in 150 ml of dry ether, after which the temperature of the reaction mixture was brought up to room temperature, and the excess diazomethane was removed by passing nitrogen through the reaction mixture. The solvent

TABLE 1. Coordinates of the Atoms ($\cdot 10^4$) in the VIb Molecule*

Atom	X	Y	Z
$C_{(1)}$	1545(2)	3808(2)	3352(4)
$O_{(2)}$	2467(2)	2288(2)	4583(4)
$O_{(3)}$	−1175(2)	3728(2)	1264(4)
$O_{(4)}$	1419(2)	−2285(2)	2884(4)
$O_{(5)}$	−258(2)	−2781(2)	2624(5)
$N_{(6)}$	497(3)	−1990(3)	2706(5)
$C_{(7)}$	1708(3)	2568(4)	3699(6)
$C_{(8)}$	866(3)	1574(3)	3022(5)
$C_{(9)}$	−143(3)	1953(4)	2469(5)
$C_{(10)}$	−291(3)	3357(4)	2369(5)
$C_{(11)}$	752(3)	4127(4)	1998(6)
$C_{(12)}$	−1206(4)	3939(5)	3218(7)
$C_{(13)}$	1085(3)	282(3)	3104(5)
$C_{(14)}$	277(3)	−617(3)	2629(5)
$C_{(15)}$	−742(3)	−286(4)	2128(6)
$C_{(16)}$	−946(3)	1007(4)	2041(5)
$H_{(1)}$	1031	3898	712
$H_{(2)}$	709	5050	1953
$H_{(3)}$	−1047	4703	3821
$H_{(4)}$	−1730	3353	3790
$H_{(5)}$	1774	−15	3348
$H_{(6)}$	−1283	−992	2071
$H_{(7)}$	−1698	1422	1836

*The coefficients of the anisotropic thermal vibrations can be obtained from the authors.

TABLE 2. Bond Angles (ω, deg) in the VI Structure

Angle	ω
$C_{(7)}O_{(1)}C_{(11)}$	119,6
$O_{(1)}C_{(7)}C_{(8)}$	117,2
$O_{(1)}C_{(7)}O_{(2)}$	120,3
$C_{(8)}C_{(7)}O_{(2)}$	122,5
$C_{(7)}C_{(8)}C_{(9)}$	120,1
$C_{(7)}C_{(8)}C_{(13)}$	118,5
$C_{(8)}C_{(9)}C_{(10)}$	117,3
$C_{(9)}C_{(10)}C_{(16)}$	123,6
$C_{(9)}C_{(10)}C_{(11)}$	111,9
$C_{(10)}C_{(11)}O_{(1)}$	109,9
$O_{(3)}C_{(10)}C_{(12)}$	59,1
$C_{(10)}C_{(12)}O_{(3)}$	59,5
$C_{(12)}O_{(3)}C_{(10)}$	61,4
$C_{(9)}C_{(10)}O_{(3)}$	115,8
$C_{(9)}C_{(10)}C_{(12)}$	122,3
$C_{(11)}C_{(10)}O_{(3)}$	114,4
$C_{(11)}C_{(10)}C_{(12)}$	121,8
$C_{(8)}C_{(13)}C_{(14)}$	117,8
$C_{(13)}C_{(14)}C_{(15)}$	122,9
$C_{(14)}C_{(15)}C_{(16)}$	118,6
$C_{(15)}C_{(16)}C_{(9)}$	120,4
$C_{(16)}C_{(9)}C_{(8)}$	119,1
$C_{(9)}C_{(8)}C_{(13)}$	121,2
$C_{(15)}C_{(14)}N_{(6)}$	118,6
$C_{(13)}C_{(14)}N_{(6)}$	118,5
$C_{(13)}C_{(14)}N_{(6)}$	118,5
$C_{(14)}N_{(6)}O_{(4)}$	118,9
$C_{(14)}N_{(6)}O_{(5)}$	118,1
$O_{(4)}N_{(6)}O_{(5)}$	122,9

*The error in the determination was 0.3°.

was removed by distillation, and the residue was chromatographed with a column to give VIa and IVb.

6-Nitro-1-oxoisochroman-4-spirooxirane (VIa). This compound was obtained in a yield of 1.07 g (32%) and had R_f 0.57 and mp 153-154°C (benzene—hexane). IR spectrum: 1730 (C═O), 1605, 1570 (C═C), 1530 cm^{-1} (NO_2). UV spectrum, λ_{max} (log ε): 220 (4.30), 262 nm (3.80). PMR spectrum: 8.33 (2H, s, 7-H, 8-H), 8.1 (1H, s, 5-H), 4.80 (1H, q, 4-H, $J_{3,4}$ = 11.9 Hz, $J_{4,1}$ = 1.47 Hz), 4.32 (1H, d, 3-H, $J_{3,4}$ = 11.9 Hz), 3.38 (1H, d, 2-H, $J_{2,1}$ = 4.78 Hz), 3.24 ppm (1H, q, 1-H, $J_{1,2}$ = 4.75 Hz, $J_{1,4}$ = 1.47 Hz). Mass spectrum, m/z (%): 221 (15) M$^+$, 193 (21), 192 (7), 191 (100), 178 (54), 163 (54), 161 (44), 149 (6), 135 (16), 133 (23), 132 (11), 118 (7), 117 (33), 105 (28), 104 (6), 103 (73).

4-Nitro-2-carbomethoxy-ε-diazoacetophenone (IVb). This compound was obtained in a yield of 0.76 g (20%) and had R_f 0.34 and mp 65°C (benzene—hexane). IR spectrum: 2105 (N═N), 1730, 1620 (C═O), 1605, 1570 (C═C), 1530 cm^{-1} (NO_2). UV spectrum, λ_{max} (log ε): 225 (4.31), 257 (4.28), 291 nm (4.06)1. PMR spectrum: 8.62 (1H, s, 3-H), 8.38 (1H, d, 5-H, $J_{5,6}$ = 8.1 Hz), 7.65 (1H, d, 6-H, $J_{6,5}$ = 8.1 Hz), 5.73 (1H, s, CH), 3.95 ppm (3H, s, $COOCH_3$). Mass spectrum, m/z (%): 221 (69) M$^+$, 208 (37), 178 (61), 162 (28), 149 (9), 148 (7), 147 (52), 146 (26), 134 (10), 133 (7), 132 (100), 120 (9), 119 (37), 118 (65), 117 (12), 105 (11), 104 (19), 103 (15).

A mixture of VIb and IVa with R_f 0.45 was washed successively on the filter with methanol and acetone to give 0.67 g (20%) of 7-nitro-1-oxoisochroman-4-spirooxirane (VIb) with mp 164-165°C (benzene—hexane). IR spectrum: 1730 (C═0), 1605, 1570 (C═C), 1530 cm^{-1} (NO_2). UV spectrum, λ_{max} (log ε): 221 (4.31), 263 nm (3.80). PMR spectrum: 8.98 (1H, d, 8-H, $J_{8,6}$ = 2.2 Hz), 7.47 (1H, d, 5-H, $J_{5,6}$ = 8.7 Hz), 4.80 (1H, q, 4-H, $J_{4,3}$ = 11.76, $J_{4,1}$ = 1.84 Hz), 4.27 (1H, q, 3-H, $J_{3,4}$ = 11.78 Hz), 3.38 (1H, d, 2-H, $J_{2,1}$ = 5.15 Hz), 3.17 ppm (1H, q, 1-H, $J_{1,2}$ = 4.97, $J_{1,4}$ = 1.84 Hz). Mass spectrum, m/z (%): 221 (10) M$^+$, 193 (13), 192 (8), 191 (100), 178 (38), 163 (45), 161 (31), 149 (10), 135 (15), 133 (22), 132 (15), 131 (27), 117 (40), 105 (34), 103 (82).

The mother liquor was evaporated, and the residue was recrystallized twice from benzene—hexane to give 0.53 g (14%) of 5-nitro-2-carbomethoxy-ω-diazoacetophenone (IVa) with mp 98°C (benzene—hexane). IR spectrum: 2130 (N═N), 1730, 1620 (C═O), 1605, 1570 (C═C), 1530 cm^{-1}

(NO_2). UV spectrum, λ_{max} (log ε): 225 (4.31), 257 (4.28), 291 nm (4.06). PMR spectrum: 8.45 (1H, q, 4-H, $J_{4,3}$ = 8.3 Hz, $J_{4,6}$ = 2.2 Hz), 8.30 (1H, d, 6-H, $J_{6,4}$ = 2.2 Hz), 7.96 (1H, d, 3-H, $J_{3,4}$ = 8.3 Hz), 5.73 (1H, s, CH), 3.95 ppm (3H, s, $COOCH_3$). Mass spectrum, m/z (%): 221 (69) M^+, 208 (11), 204 (12), 193 (10), 179 (6), 178 (100), 174 (5), 162 (18), 161 (10), 150 (5), 134 (8), 135 (5), 132 (61), 120 (6), 119 (8), 117 (6), 105 (8), 104 (12), 103 (23).

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REACTIONS ON A SURFACE.

1. CONDENSATION OF 3-METHYL-3-BUTEN-1-OL WITH CARBONYL COMPOUNDS ON SiO_2 AND Al_2O_3

U. G. Ibatullin, Yu. V. Pavlov, and M. G. Safarov

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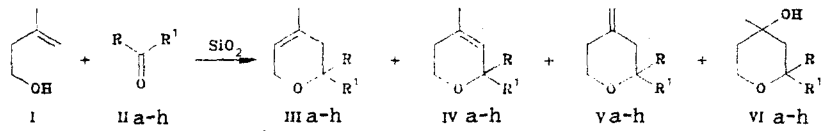
3-Methyl-3-buten-1-ol reacts with various aldehydes and ketones on silica gel and Al_2O_3 surfaces in the absence of solvents and conventional catalysts for this reaction to form derivatives of di- and tetrahydropyrans.

Recently, a series of papers has been published in which silica gel or Al_2O_3 are used in carrying out organic reactions (not in the vapor phase) — for example, for the selective reduction of one of the carbonyl groups in diketones ($LiAlH_4/SiO_2$) [1], with acetalization of ethylene glycol with aldehydes [2], etc. Of particular interest are the nontraditional synthetic methods in which reactions are carried out essentially in the solid phase on a surface of SiO_2 or Al_2O_3. Such a variant was used for the intra- [3] and intermolecular [4] conversion of dicobalthexacarbonyl complexes of enyne derivatives.

Condensation of carbonyl compounds with γ-unsaturated alcohols is a convenient method to obtain six-membered, cyclic ethers. Usually it is carried out by distilling off the forming water as an azeotropic mixture with hydrocarbons [5, 6], on mixing the reactants in an organic solvent [7] or water [8] in the presence of mineral and aromatic sulfonic acids or cation exchange resins. Depending on the conditions, one obtains either isomeric di- and tetrahydropyrans [5, 6] or tetrahydropyranols [8], or a mixture of them [7]. Any information concerning the possibility of carrying out such a condensation on an oxide surface is lacking.

The present work was devoted to studying the reaction of 3-methyl-3-buten-1-ol (I) and carbonyl compounds IIa-h on SiO_2 and Al_2O_3 surfaces in the absence of the catalysts mentioned and of any solvent. It turned out that under these conditions, derivatives of di- (III, IVa-h) and tetrahydropyranones (V, VIa-h) form even at room temperature.



II—VI a R=H, $R^1=C_2H_5$; b R=H, $R^1=C_4H_9$; c R=H, $R^1=i\text{-}C_4H_9$; d R=H, $R^1=C_6H_5$;
e $R=R^1=CH_3$; f $R=CH_3$, $R^1=i\text{-}C_4H_9$; g $R+R^1=(CH_2)_4$; h $R+R^1=(CH_2)_5$

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