1-(3-CHLORO-2-BUTENYL)-3-METHYLPYRAZOLE AND 1-(3-CHLORO-2-BUTENYL)-5-METHYLPYRAZOLE FROM OXIDATION PRODUCTS OF HYDRAZO-3-CHLORO-2-BUTENE

František HRABÁK, Jiří WEBR* and Danica DOSKOČILOVÁ

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6

Received September 12th, 1980

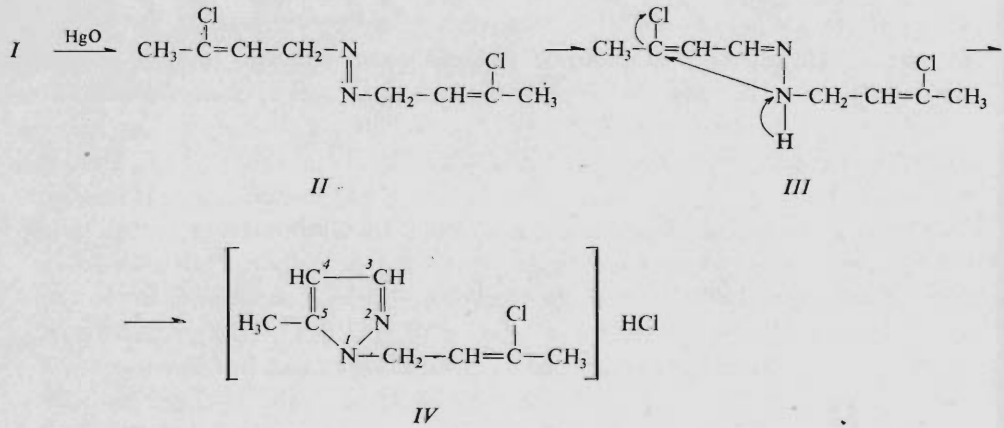
By oxidation of hydrazo-3-chloro-2-butene, (*I*), 1-(3-chloro-2-butenyl)-3-methylpyrazole (*VII*) and 1-(3-chloro-2-butenyl-5-methylpyrazole (*IV*) are formed; the structures of these compounds have been proved by ^{1}H-NMR, UV, IR and mass spectrometry.

Unsaturated azo compounds with an H atom on the α-carbon are isomerized to en--hydrazones in acid medium[1]. The hydrazones of 2- or 3-halogen-2-alkenecarbonyl compounds are unstable and are cyclized to pyrazoles with evolution of hydrogen halide[2-5].

In our previous communication we have described the preparation of *I* by alkylation of N,N'-diformylhydrazine by 3-chloro-2-butenyl-bromide and subsequent hydrolysis of N,N'-bis-(3-chloro-2-butenyl)-N,N'-diformylhydrazine by hydrochloric acid[6]. In attempts to oxidize *I* to the azo-compound in benzene or ether by mercuric or cupric oxides, by air or by iodine, a spontaneous exothermal reaction took place even in the presence of powdered sodium bicarbonate or magnesium oxide. The product was a colorless liquid distilling in the range 57–62°C/40 Pa, of refractive index n_D^{20} 1·508. It was soluble in aqueous hydrochloric acid from which it separated after neutralization; it did not exhibit the absorption of an azo group in UV spectra in the vicinity of 350 nm, it did not decompose even after several hours of heating to 100°C, and its chemical composition corresponded to the compound which would be formed by subtraction of HCl from *I*. By preparative gas chromatography the isolated compound could be resolved into two components, X_1 at the lower and X_2 at the higher elution volume. Based on the described properties chemical composition, NMR and UV spectra it could be assumed that X_1 and X_2 might be the isomeric derivatives of pyrazole 1-(3-chloro-2-butenyl)-5-methylpyrazole (*IV*) and 1-(3-chloro-2-butenyl)-3-methylpyrazole (*VII*). Therefore by alkylation of a mixture of 3- and 5-methylpyrazole by 3-chloro-2-butenyl bromide a mixture of *IV* and *VII* was prepared and separated into its components on a preparative chromatograph.

* Present address: Centre of Scientific, Technical and Economic Information, Central Technical Base, 110 00 Prague 1

By analysis of ^{1}H-NMR and UV spectra the component with the lower elution volume was identified as *VII* and the component with the higher elution volume as *IV*. NMR, UV, IR and mass spectra of the model compounds *IV* and *VII* were compared with the spectra of the compounds X_1 and X_2 isolated from the product of oxidation of *I*. ^{1}H-NMR spectra of the compounds *IV* and X_2 are identical. They exhibit a quartet of the side chain methyl group centered at 2·1δ (J = 1·7 Hz), the methyl band at 2·2δ with an indication of doublet structure (J = 0·6 Hz), multiplets of —N—**CH$_2$**—CH= at 4·65δ and of —CH$_2$—**CH**=C(Cl)— at 5·65δ, a broader multiplet of the proton on $C_{(4)}$ at 5·8δ wih an indication of fine structure (J = 0·6 Hz) and the doublet of the proton on $C_{(3)}$ at 7·1δ (J = 1·8 Hz). An indication of an allyl coupling of the proton on $C_{(4)}$ with the methyl on the ring suggests methyl substitution on $C_{(5)}$. Also the spectra of both compounds *VII* and X_1 are identical. They contain the overlapping quartet of the side chain methyl centered at 2·15δ (J = = 1·7 Hz) and the methyl singlet at 2·18δ, the multiplets of —N—**CH$_2$**—CH= at 4·65δ and —CH$_2$—**CH**=C(Cl)— at 5·7δ, the doublets of the protons on $C_{(4)}$ at 5·8δ and on $C_{(5)}$ at 7·15δ. The methyl singlet at 2·18δ may be assigned to the methyl at position 3 on the ring. This is supported by the same splitting (2·2 Hz) and the same shape of the doublet of the protons on $C_{(4)}$ and $C_{(5)}$ which do not exhibit long-range coupling with methyl.

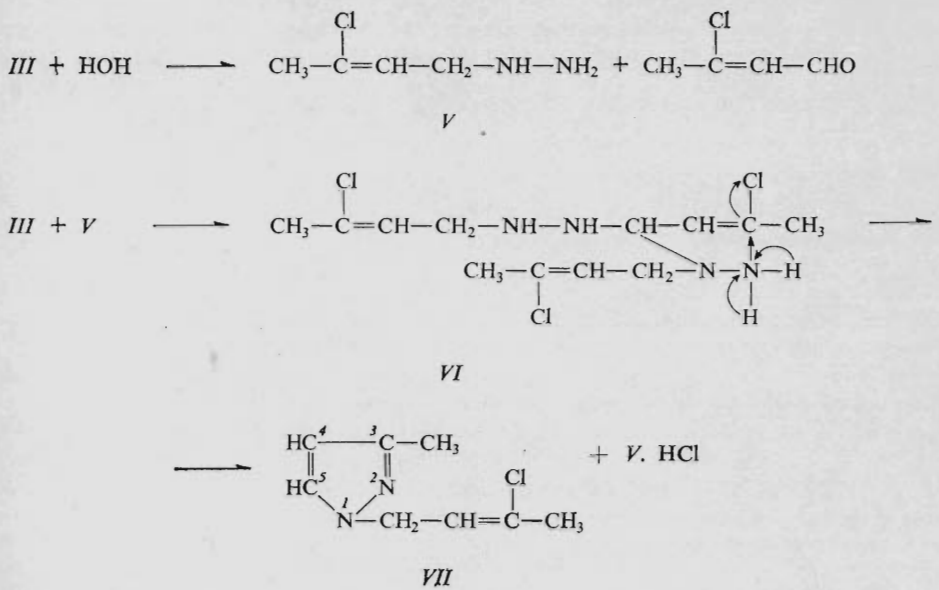


SCHEME 1

UV spectra of *VII* are identical with X_1 and of *IV* with X_2. All exhibit a strong absorption peak in the vicinity of 220 nm. In the spectra of *VII* and X_1 the maximum is shifted slightly towards longer wavelengths. A similar shift of the maximum is evident in the spectrum of 1,3-dimethylpyrazole as compared with 1,5-dimethylpyrazole[15]. A weaker peak is observed in the vicinity of 290 nm. IR spectra of *IV*,

VII, X_1 and X_2 are identical and exhibit characteristic bands of substituted pyrazoles[16]: 3 100 w (CH_{ar}), 2 860–2 980 m (CH_3, CH_2), 1 680 s (C=C), 1 390 s (CH), 1 360 m (pyrazole ring), 1 280 m (N-substituted pyrazole), 1 090 s, 1 045 w, 960 w, 930 s (normal modes of the pyrazole ring), 780 s (CH) cm^{-1}. Fragmentation of *IV*, *VII*, X_1 and X_2 evident in mass spectra was identical: *m/z* 170, 172 (M^+), 169, 171 ($M^+-[H]$), 89, 91 ($CH_2CH=C(Cl)CH_3$), 135 ($M^+-[Cl]$), 120 ($M^+-[Cl]$,—$-[CH_3]$), 108 ($M^+-[C(Cl)CH_3]$), 95 ($M^+-[CH=C(Cl)CH_3]$), 81 ($M^+-[CH_2.CH=C(Cl)CH_3]$).

The spectra of the substances studied confirm that the isolated products of oxidation of *I* in benzene are the compounds *IV* and *VII*. It may be assumed that *IV* is formed similarly as 1,5-dialkylpyrazoles from alkylhydrazines and 3-halogen-2-alkenals[2–5]. The original *I* is probably oxidized to azo-3-chloro-2-butene (*II*) which is rearranged[1] to 3-chloro-2-butenylhydrazone of 3-chloro-2-butenal (*III*); in consequence of intramolecular donor-acceptor transfer of the electron charge, compound *III* is cyclized with subtraction of hydrogen chloride to the resulting 1-(3-chloro-2-butenyl)-5-methylpyrazole (*IV*) or to its hydrochloride according to Scheme 1. The straight arrow indicates the donor-acceptor transfer of the electron charge and the curved arrows the increase of the atomic bond[7]. The formation of *VII* can be explained by anomalous cyclization[8–12] of *III* catalyzed by (3-chloro-2-butenyl) hydrazine (*V*) according to Scheme 2.



SCHEME 2

EXPERIMENTAL

Methods

IR spectra of the samples were measured in a KBr cell of 30 μm thickness using the Zeiss UR 10 spectrometer. ^{1}H-NMR spectra were measured in CCl_4 solution (0·25 mol dm^{-3}) with hexamethyldisiloxane as internal standard using the JEOL PS-100 spectrometer at 100 MHz. UV spectra were measured in ethanol solution on the Cary 14 spectrometer. Mass spectra were measured on the AEI mass spectrometer MS 902 with electron energy 70 eV. The mixture of isomers was separated on 10% XE-60 Chromaton N-AW at 210°C using the Preparative Gas Chromatograph Perkin–Elmer F-21.

Starting and Model Compounds

Hydrazo-3-chloro-2-butene was prepared by alkylation of N,N-diformyl-hydrazine by 3-chloro--2-butenyl bromide and hydrolysis of N,N′-bis(3-chloro-2-butenyl)-N,N′-diformylhydrazine by hydrochloric acid[6]; b.p. 92—93°C/62 Pa, n_D^{20} 1·5080. The mixture of 3- and 5-methylpyrazole was prepared from 2-bromo-2-butenal and hydrazine[13]; b.p. 125°C/5·23 kPa, n_D^{20} 1·4945. For $C_4H_6N_2$ (82·1) calculated: 58·51% C, 7·37% H; found: 59·01% C, 7·56% H. 3-Chloro-2-butenyl bromide was prepared by boiling the mixture of 500 g of hydrobromic acid 48%, 106 g of 3-chloro--2-butenol and 190 g od dry sodium sulfate; yield 103 g (61%), b.p. 52—53°C/3, 3 kPa, n_D^{20} 1·5095.

The mixture *IV* and *VII* was prepared similarly to the allylation of 3-methylpyrazole[14], adding dropwise 77 g (0·227 mol) of 3-chloro-2-butenyl bromide to a methanolic solution of 18·6 g (0·227 mol) of 3- and 5-methylpyrazole and 0·37 mol of sodium methanolate (6·2 g of Na in 250 cm^3 of CH_3OH). After completion of the reaction, the methanol was distilled off and the residue was dissolved in 90 cm^3 of dilute (1 : 1) hydrochloric acid. The acid solution was filtered, neutralized by a solution of sodium bicarbonate and extracted with chloroform. After drying with sodium sulphate the solvent was distilled off and the residue was rectified on a concentric tube column of 13 TP. Main fraction: 16·1 g (41·6% referred to the original mixture of methylpyrazoles), b.p. 105—106°C/3·3 kPa, n_D^{20} 1·5080. For $C_8H_{11}ClN_2$ (170·6) calculated: 56·30% C, 6·50% H, 16·42% N, 20·78% Cl; found: 56·43% C, 6·80% H, 16·69% N, 20·89% Cl. The mixture of *IV* and *VII* was separated on the preparative gas chromatograph. The ratio of the peaks of *IV* and *VII* on the chromatogram was 1·5.

Oxidation of Hydrazo-3-chloro-2-butene (*I*)

The mixture of 7·5 g (0·036 mol) of *I*, 1·95 g (0·1 mol) HgO, 1·5 g of anhydrous Na_2SO_4 and 170 cm^3 of benzene was mixed for 24 h at 6°C in nitrogen atmosphere, filtered and the filtrate heated for 6 h to the b.p. After cooling the solution was extracted by 50 cm^3 of dilute (1 : 1) hydrochloric acid, the acid solution was neutralized by sodium bicarbonate and extracted by ether. After drying by anhydrous sodium sulfate, ether was distilled off from the extract and the residue was rectified on a concentric tube column of 13 TP. Main fraction: 3·12 g (42% with respect to *I*), b.p. 105·5°C/3·32 kPa, n_D^{20} 1·5085, found: 56·50% C, 7·07% H, 16·40% N, 20·60% Cl; chemical composition corresponds to the formula $C_8H_{11}ClN_2$. By separation of the main fraction on a preparative gas chromatograph two components were obtained, X_1 with a lower and X_2 with a higher elution volume.

The authors wish to thank Dr M. Ryska for the measurement of the mass spectra and for help with their interpretation.

REFERENCES

1. Simon H., Brodka S.: Tetrahedron Lett. *1969*, 4991.
2. Viguier P. L.: Ann. Chim. (Paris) [8], *28*, 433 (1913).
3. Auwers K., Hügel R.: J. Prakt. Chem. [2], *143*, 157 (1935).
4. Desmukh G. V., Wheeler T. S.: J. Chem. Soc. *1939*, 96.
5. Ioffe B. V., Zelenina H. L.: Khim. Geterotsikl. Soedin. *1970*, 1414.
6. Hrabák F.: This Journal *34*, 4010 (1969).
7. Gutmann V.: Coord. Chem. Rev. *15*, 207 (1975).
8. Auwers K., Broche H.: Ber. Deut. Chem. Ges. *55*, 3880 (1922).
9. Ioffe B. V., Tsibulskii V. V.: Zh. Org. Khim. *3*, 1903 (1967).
10. Ioffe B. V., Tsibulskii V. V.: Khim. Geterotsikl. Soedin. *1969*, 1061.
11. Ioffe B. V., Tsibulskii V. V.: Khim. Geterotsikl. Soedin. *1970*, 1249.
12. Ioffe B. V., Tsibulskii V. V., Stopskii V. C., Sergeeva Z. I.: Khim. Geterotsikl. Soedin. *1966*, 932.
13. Viguier P. L.: Ann. Chim. (Paris) [8], *28*, 467 (1914).
14. Auwers K., Bähr K.: J. Prakt. Chem. [2], *116*, 97 (1927).
15. Dal Monte D., Mangini A., Passerini R.: Gazz. Chim. Ital. *86*, 797 (1956).
16. Zerbi G., Alberti C.: Spectrochim. Acta *18*, 407 (1962).

Translated by D. Doskočilová.