REACTION OF DIPHENYLDIAZOMETHANE WITH PHENYLPROPIOLALDEHYDE

I. N. Domnin, E. F. Zhuravleva,
V. L. Serebrov, and R. R. Bekmukhametov

UDC 547.778.2:542.952.1

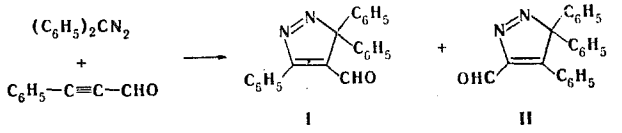
Two isomeric pyrazolenines — 4-formyl-3,3,5-triphenylpyrazolenine and 5-formyl-3,3,4-triphenylpyrazolenine — are formed as a result of the reaction of diphenyldiazomethane with phenylpropiolaldehyde. The experimental data and the calculated values relative to the orientation of the addition of diazoalkanes and unsymmetrically substituted alkynes are discussed. The thermal transformations of the isomeric pyrazolenines were studied, and it is shown that the thermolysis of 5-formyl-3,3,4-pyrazolenine can serve as a method for the synthesis of 1-formyl-2,3,3-triphenylcyclopropene.

The addition of diazoalkanes to the multiple bond of dipolarophiles is one of the numerous 1,3-dipolar cycloaddition reactions [1]. Two orientations of addition, namely, in conformity with and counter to the Auwers rule [2], are possible in the case of unsymmetrically substituted dipolarophiles. It should be noted that, in contrast to alkenes, considerably less study has been devoted to the regioselectivity of 1,3-dipolar cycloaddition to alkynes.

4-Formyl-3,3,5-triphenylpyrazolenine (I) was isolated as the only product of the reaction of phenylpropiolaldehyde with diphenyldiazomethane [3].

Unfortunately, the spectral characteristics of the compounds obtained are completely absent in [3], and it was later shown [4] that Hüttel and co-workers [3] assigned erroneous structures to some of them.

We have shown that the reaction of diphenyldiazomethane with phenylpropiolaldehyde actually leads to the formation of two isomeric pyrazolenines — pyrazolenine I and the previously undescribed 5-formyl-3,3,4-triphenylpyrazolenine (II).



I II

The IR spectra of I and II contain high-intensity absorption bands at 1690 cm^{-1} that indicate the presence in their structures of a formyl carbonyl group; stretching vibrations of the C—H bond of the formyl group appear at 2760 and 2860 cm^{-1}. Absorption bands at 1610-1620 cm^{-1} correspond to the stretching vibrations of the multiple bonds of the pyrazolenine ring [5].

Bands of a π—π^* transition at 300 nm, which correspond to the conjugated system of the pyrazolenine ring [6, 7], are present in the UV spectra of the 3H-pyrazoles obtained in this study. Bands at 350 nm, which correspond to the n—π^* transition of the N=N chromophore in pyrazolenine structures [8, 9], can also be noted in the spectra. However, the establishment of the authentic extinctions for these maxima is extremely difficult because of the substantial superimposition on them of the terminal absorption of the more intense band of π—π^* transitions.

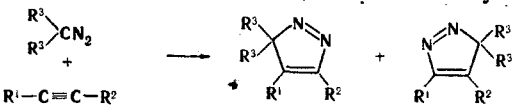
The PMR spectra of the isomeric pyrazolenines are also in agreement with the structures assigned to them.

To estimate the regioselectivity of the reaction we determined the ratio of the isomers in the reaction mixture, which was found to be 1:1 (the data were obtained from five

A. A. Zhdanov Leningrad State University, Leningrad 199164. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1091-1096, August, 1978. Original article submitted February 14, 1978.

0009-3122/78/1408-0879$07.50

TABLE 1. Values of the Relative Change in the Energy of the Perturbations of the Molecular Orbitals (ΔE) and Regioselectivity of the Addition of Diazoalkanes to Alkynes



A B

R^1	R^2	ΔE, kJ/mole		Isomer ratio, A/B		
		$R^3=H$	$R^3=CH_3$	$R^3=H$	$R^3=CH_3$	$R^3=C_6H_5$
H	C_6H_5	5,19	4,85	90/10[a]	100/0[b]	100/0[c]
CH_3	CO_2CH_3	5,90	3,89	80/20[d]	85/15[d]	60/40[e]
C_6H_5	CHO	3,39	2,26	—	—	50/50
C_6H_5	CO_2CH_3	2,22	1,21	52/48[f]	33/67[g]	0/100[h]

[a]According to the data in [16]. [b]According to the data in [17]. [c]According to the data in [18]. [d]According to the data in [15]. [e]According to the data in [9]. [f]According to the data in [19]. [g]According to the data in [5]. [h]According to the data in [20].

mutually independent experiments), by means of PMR spectroscopy from the intensity of the signal of the proton of the formyl group of pyrazolenines I and II.

A satisfactory explanation of the orientation in the addition of diazoalkanes to alkynes was recently obtained by application of molecular orbital perturbation theory to 1,3-dipolar addition processes [10, 11]. Most reactions involving the 1,3-dipolar cycloaddition of diazoalkanes are of the type that involves the reaction of the frontal molecular orbitals, where control is realized by the upper occupied molecular orbitals (UOMO) of the dipole and the lower vacant molecular orbitals (LVMO) of the dipolarophile. Thus the quantum-chemical analysis of the regioselectivity in the addition of diazoalkanes to alkynes can be restricted to the interaction of the UOMO of the diazoalkanes and the LVMO of the alkynes [12], in which case, according to [13, 14], one can estimate the change in the energy of the perturbations of the MO for various orientations in the addition.

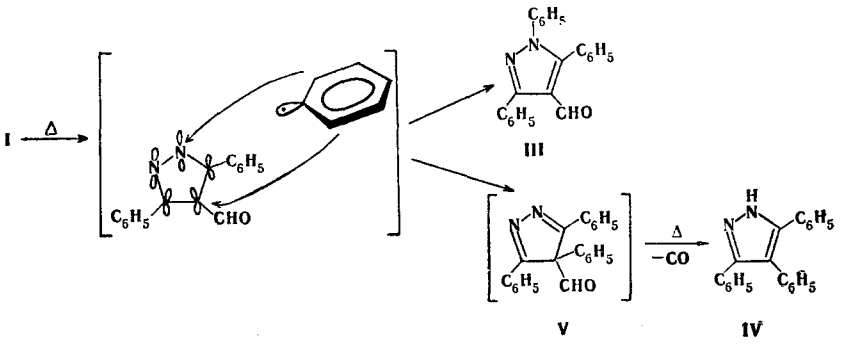
Some experimental data on the regioselectivity of the addition of diazoalkanes to a number of unsymmetrically substituted alkynes and values of the relative change in the energy of the perturbations of the MO (ΔE) corresponding to different orientations in the addition — in conformity with (A) and counter (B) to the Auwers rule — are presented in Table 1. The calculations were performed via an additive scheme by means of the data in [15].

It follows from the data in Table 1 that the regioselectivity of the addition of diazomethane and dimethyldiazomethane to alkynes decreases as the ΔE value decreases. The calculation of ΔE for the addition of a molecule of diphenyldiazomethane is considerably more complicated; however, according to a preliminary estimate, the corresponding ΔE values in this case should be 0.8-2.1 kJ/mole lower than the corresponding values calculated for diazomethane. The character of the orientation in the addition of diazoalkanes also changes as ΔE decreases, and steric factors take on greater significance in the case of diphenyldiazomethane; thus the orientation in the addition of diphenyldiazomethane to phenylacetylene is the opposite of the orientation in the addition to phenylpropiolic ester. It is apparent from the data in Table 1 that the reaction under discussion in the present paper occupies an intermediate position in the series under examination and that the experimental data obtained are in agreement with the theoretical conclusions. According to [21], the observed regioselectivity of the addition of diazoalkanes is explained by the ambident nucleophilicity of the latter.

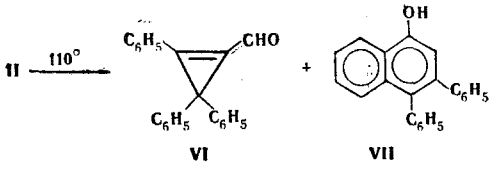
The structures of isomeric pyrazolenines I and II were also confirmed by means of chemical methods. It is known that thermal isomerization of pyrazolenines and pyrazoles to isopyrazoles (which sometimes even hinders their synthesis) is extremely characteristic for compounds of this class [22]. Rather comprehensive literature devoted to the thermal isomerization of pyrazolenines is currently available; however, no comparative study of the thermal transformations of isomeric pyrazolenines that corresponds to the addition of diazolalkanes in conformity with and counter to the Auwers rule has yet been made.

Two compounds, the constants and spectral characteristics of which were in complete agreement with those of the previously described 4-formyl-1,3,5-triphenylpyrazole (III) [23] and 3,4,5-triphenylpyrazole (IV), were obtained in the thermolysis of pyrazolenine I. Compound IV was identified by comparison with an authentic sample synthesized by an independent method [24].

The formation of pyrazole III can be represented as being the result of a 1,5-sigmatropic shift of the phenyl group to the nitrogen atom [22]. The formation of pyrazole IV is associated with migration of the phenyl group to the carbon atom to give intermediate isopyrazole V, which is apparently unstable under the thermolysis conditions and is converted to pyrazole IV.



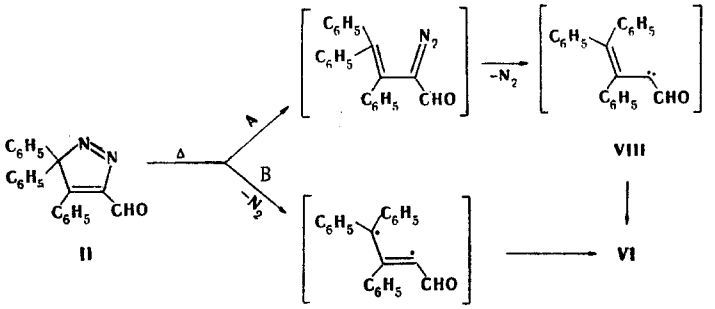
Two isomeric compounds corresponding to products of the elimination of nitrogen were obtained instead of the expected products of isomeric transformations when pyrazolenine II was heated. The 1-formyl-2,3,3-triphenylcyclopropene structure (VI) was assigned to the principal thermolysis product on the basis of spectral data and the results of elementary analysis; the second substance was identified as 1-hydroxy-3,4-diphenylnaphthalene (VII), which was previously described in [25].



We are describing cyclopropene VI for the first time; its synthesis is only mentioned in [26], and no constants or spectral characteristics are presented. The spectral data for cyclopropene VI are in complete agreement with the structure assigned to it. The IR spectrum of this compound is particularly characteristic. It is known that the absorption band of the cyclopropene double bond that is not included in the conjugation system has an extremely low intensity [27]. On the other hand, the intensity of the absorption band of the cyclopropene double bond at 1804 cm^{-1} in the spectrum of cyclopropene VI is comparable to the intensity of the absorption band of the formyl carbonyl group at 1670 cm^{-1} because of the presence of an effective conjugation system.

Reactions involving the thermal elimination of nitrogen are not characteristic for pyrazolenine systems, since the energy necessary for ring opening considerably exceeds the activation barrier for the corresponding isomeric transformations [22]. The formation of cyclopropene VI and the absence of isomeric pyrazoles in the thermolysis of pyrazolenine II is the first example in the 3,3-diphenyl-substituted pyrazolenine series in which the energy necessary for ring opening is lower than the activation barrier for isomeric transformation.

Cyclopropene VI can be obtained by thermolysis of pyrazolenine II via two possible mechanisms:



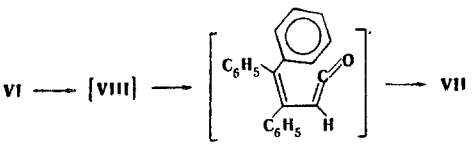
II IX VIII VI

The first mechanism (mechanism A) includes the intermediate formation of a diazo compound and vinylcarbene VIII and is similar to the thoroughly investigated mechanism of the formation of cyclopropenes in the photolytic decomposition of pyrazolenines. In this case the intermediate of vinylcarbenes was proved both by means of ESR spectroscopy and by means of special 1,1-cycloaddition reactions of carbenes (for example, see [28, 29]). We carried out the thermolysis of pyrazolenine II in vinyl butyl ether, but the product of addition of vinylcarbene VIII to it was not detected.

Alternate mechanism B includes the formation of diradical IX and its subsequent cyclization to cyclopropene VI.

Taking into account the data in [30], one might expect that the presence of an electron-acceptor group attached to the $C_{(5)}$ atom of the pyrazolenine ring evidently promotes weakening of the $C_{(5)}$—N bond and subsequent elimination of nitrogen to give intermediate diradical IX in analogy with the decomposition of Δ^1-pyrazoline systems [31, 32].

The formation of naphthol VII in the thermolysis of pyrazolenine II is, in all likelihood, a secondary process, namely, the result of thermal isomerization of cyclopropene VI. In fact, naphthol VII, the mechanism of the formation of which can be represented by the following scheme [26], was obtained in high yield when cyclopropene VI was heated:



X

According to the data in [33-35], the thermal isomerization of cyclopropenes proceeds through the formation of vinylcarbenes. The position of the formyl group in vinylcarbene VIII predetermines the possibility of its conversion to vinylketene X, which is subsequently converted to naphthol VII as a result of intramolecular cycloaddition [36].

EXPERIMENTAL

The PMR spectra of 15% solutions of the compounds in $CDCl_3$ were recorded with a Varian HA-100D-15 spectrometer with tetramethylsilane as the internal standard. The IR spectra of 3% solutions of the compounds in $CHCl_3$ were obtained with a UR-20 spectrometer. The UV spectra of solutions of the compounds in heptane and ethanol were measured by means of a Perkin—Elmer M-402 spectrophotometer. Eastman Kodak Chromagram plates with a fixed layer of silica gel were used for analytical thin-layer chromatography (TLC). The chromatograms were developed with iodine vapors and in UV light.

4-Formyl-3,3,5-triphenylpyrazolenine (I). A solution of 6 g (0.031 mole) of diphenyldiazomethane [38] in 5 ml of absolute ether was added to a solution of 4 g (0.031 mole) of freshly distilled phenylpropiolaldehyde [37] in 5 ml of absolute ether, and the mixture was allowed to stand in the dark at room temperature. After 5 days, the crystalline precipitate was removed by filtration, washed on the filter with a small amount of ether, and recrystallized from alcohol—chloroform (1:1) to give 2.5 g (25%) of a product with mp 152°C and R_f 0.66 (chloroform). IR spectrum (cm^{-1}): 915 w, 980 m, 1010 w, 1030 w, 1040 w, 1090 m, 1290 w, 1343 m, 1404 m, 1460 m, 1507 m, 1623 m, 1688 s, 2765 w, and 2860 w. UV spectrum, λ_{max} (log ε): in alcohol, 297 (3.68) and 218 (4.17); in heptane, 301 (3.88) and 220 nm (4.22). PMR spectrum: 10.11 (1H, s, CH=O) and 7.68 ppm (15H, m, C_6H_5). Found: C 81.5; H 4.9; N 8.5%. $C_{22}H_{16}N_2O$. Calculated: C 81.5; H 4.9; N 8.6%.

5-Formyl-3,3,4-triphenylpyrazolenine (II). The solvent was removed by vacuum distillation from the residue of the reaction mixture after separation of pyrazolenine I, and the residue was chromatographed in 2.5 g portions with a column filled with silica gel (70 g) [elution with hexane–diethyl ether (1:1)]. A total of 2 g (20%) of pale-yellow crystals of pyrazolenine II was isolated. To obtain an analytically pure sample the product was purified by two reprecipitations from chloroform by the addition of diethyl ether, which gave a sample with mp 134°C (dec.) and R_f 0.11 (chloroform). IR spectrum (cm^{-1}): 835 w, 926 w, 950 w, 1017 w, 1050 m, 1080 w, 1095 w, 1205 m, 1250 m, 1355 w, 1400 w, 1455 m, 1479 m, 1502 m, 1605 m, 1695 s, 2760 w, and 2855 w. UV spectrum, λ_{max} (log ε): in alcohol, 296 (3.65), 211 (4.18); in heptane, 304 (3.80) and 225 nm (4.16). PMR spectrum: 10.13 (1H, s, CH=O) and 7.17 ppm (15H, m, C_6H_5). Found: C 81.7; H 5.0; N 8.5%. $C_{22}H_{16}N_2O$. Calculated: C 81.5; H 4.9; N 8.6%.

Thermal Isomerization of 4-Formyl-3,3,5-triphenylpyrazolenine (I). A solution of 1 g of pyrazolenine I in 20 ml of o-xylene was refluxed on a oil bath for 1 h, after which the solvent was removed by vacuum evaporation, and the residue was chromatographed with a column filled with 100 g of silica gel [elution with hexane–ether (1:2)]. Workup of the first fraction of the eluate gave 4-formyl-1,3,5-triphenylpyrazole (III), and the second fraction yielded 3,4,5-triphenylpyrazole (IV). Pyrazole III was identified from its melting point, spectral data, and the results of elementary analysis and was compared with the previously described 4-formyl-1,3,5-triphenylpyrazole. Pyrazole IV was identified from a mixed-melting point determination and comparison of the spectral data for an authentic sample of 3,4,5-triphenylpyrazole obtained by the method in [24].

Thermolysis of 5-Formyl-3,3,4-triphenylpyrazolenine (II). A solution of 1 g of pyrazolenine II in 20 ml of o-xylene was heated on an oil bath at 110°C for 30 min, during which 62 ml (90% of the calculated amount) of nitrogen (at 0°C and 760 mm) was evolved. The solvent was removed by vacuum evaporation, and the residue was chromatographed with a column filled with 100 g of silica gel (elution with chloroform). Workup of the first fraction gave 0.4 g (49%) of 1-formyl-2,3,3-triphenylcyclopropene (VI), and the second fraction yielded 0.17 g (19%) of 1-hydroxy-3,4-diphenylnaphthalene (VII). To obtain an analytically pure sample of cyclopropene VI the crude product was recrystallized from methylene chloride–pentane (1:1) to give a sample with mp 128°C and R_f 0.45 (chloroform). IR spectrum (cm^{-1}): 930 w, 1004 w, 1045 m, 1085 m, 1134 m, 1187 m, 1278 m, 1320 w, 1390 w, 1455 m, 1507 m, 1610 m, 1670 s, 1804 s, 2735 w, 2845 m. UV spectrum, λ_{max} (log ε): in alcohol, 228 (4.08), 266 (3.82), 308 (3.86), and 347 nm (3.18). PMR spectrum: 10.36 (1H, s, CH=O) and 7.50 ppm (15H, s, C_6H_5). Found: C 89.2; H 5.4%. $C_{22}H_{16}O$. Calculated: C 89.2; H 5.4%.

The spectral data, melting points, and results of elementary analysis of naphthol VII were in complete agreement with the literature data.

Thermal Isomerization of 1-Formyl-2,3,3-triphenylcyclopropene (VI). A 0.5-g sample of cyclopropene VI was refluxed in 15 ml of o-xylene on an oil bath for 6 h, after which the solvent was removed, and the residue was chromatographed with a column filled with 50 g of silica gel (elution with chloroform). Removal of the solvent from the principal fraction gave 0.4 g (80%) of hydroxynaphthalene VII.

LITERATURE CITED

1. R. Huisgen, Angew. Chem., 75, 604 (1963).
2. K. Auwers and O. Ungemach, Ber., 66, 1205 (1933).
3. R. Hüttel, J. Riedl, H. Martin, and K. Franke, Chem. Ber., 93, 1425 (1960).
4. M. I. Komendantov and R. R. Bekmukhametov, Khim. Geterotsikl. Soedin., No. 1, 79 (1975).
5. C. Deitrich-Buchecker and M. Franck-Neumann, Tetrahedron, 33, 745 (1977).
6. G. L. Closs and W. A. Böll, J. Am. Chem. Soc., 85, 3904 (1963).
7. A. C. Day and M. C. Whiting, J. Chem. Soc., C, No. 19, 1719 (1966).
8. G. L. Closs, L. E. Closs, and W. A. Böll, J. Am. Chem. Soc., 85, 3796 (1963).
9. V. V. Razin, Zh. Org. Khim., 11, 1457 (1975).
10. K. N. Houk, J. Sims, R. E. Duke, R. W. Strozier, and J. K. George, J. Am. Chem. Soc., 95, 7287 (1973).
11. K. N. Houk, J. Sims, C. R. Watts, and L. J. Luskus, J. Am. Chem. Soc., 95, 7301 (1973).
12. R. Sustmann, Pure and Appl. Chem., 40, 569 (1974).
13. J. Bastide, El Ghandour, and O. Henri-Rousseau, Bull. Soc. Chim. France, Nos. 7-8, 2290 (1973).

14. J. Bastide and O. Henri-Rousseau, Bull. Soc. Chim. Chim. France, Nos. 7-8, 2294 (1973).
15. J. Bastide and O. Henri-Rousseau, Bull. Soc. Chim. France, Nos. 5-6, 1037 (1974).
16. W. Kirmse and L. Horner, Ann., 614, 1 (1958).
17. C. Dumont, J. Naire, M. Vidal, and P. Arnaud, Compt. Rend., C, 268, 348 (1969).
18. G. Rio, A. Ranjon, O. Pouchot, and M. J. Scholl, Bull. Soc. Chim. France, No. 5, 1667 (1969).
19. J. Bastide and J. Lematre, Bull. Soc. Chim. France, No. 10, 3543 (1970).
20. M. I. Komendantov and R. R. Bekmukhametov, in: Fifth All-Union Conference on the Chemistry of Acetylene [in Russian], Tbilisi (1975), p. 374.
21. R. Huisgen, J. Org. Chem., 41, 403 (1976).
22. R. R. Bekmukhametov, in: Modern Problems of Organic Chemistry [in Russian], Vol. 5, LGU (1976), p. 105.
23. I. L. Finar and M. Manning, J. Chem. Soc., No. 7, 2733 (1961).
24. W. E. Parham and W. R. Hasek, J. Am. Chem. Soc., 76, 799 (1954).
25. L. I. Smith and H. H. Hoehn, J. Am. Chem. Soc., 61, 2619 (1939).
26. L. Schrader and W. Hartmann, Tetrahedron Lett., No. 41, 3995 (1973).
27. M. I. Komendantov and R. R. Kostikov, Zh. Org. Khim., 4, 1128 (1968).
28. D. R. Arnold, R. W. Humphreys, W. J. Leigh, and G. E. Palmer, J. Am. Chem. Soc., 98, 6225 (1976).
29. M. Franck-Neumann and I. I. Lohmann, Angew. Chem. Internat. Ed., 16, 334 (1977).
30. H. Reimlinger, Chem. Ber., 100, 3097 (1967).
31. R. I. Crawford and A. Mishra, J. Am. Chem. Soc., 88, 3963 (1966).
32. D. Wendish, in: Houben-Weyl Methoden der Organischen Chemie, IV/3, Georg Thieme Verlag, Stuttgart (1971), p. 76.
33. E. J. York, W. Dittmar, J. R. Stevenson, and R. G. Bergman, J. Am. Chem. Soc., 95, 5680 (1973).
34. R. D. Streeper and P. D. Gardner, Tetrahedron Lett., No. 10, 767 (1973).
35. M. I. Komendantov, R. R. Bekmukhametov, and I. N. Domnin, Zh. Org. Khim., 14, 759 (1978).
36. H. Wittmann, V. Illi, H. Sterk, and E. Ziegler, Monatsh., 99, 1982 (1968).
37. Organic Synthesis [Russian translation], Vol. 3, Inostr. Lit., Moscow (1952), p. 444.
38. J. B. Miller, J. Org. Chem., 24, 560 (1959).