trum of the AB type: $\delta_A = 2.98$, $\delta_B = 3.26$ ppm; $J_{AB} = 14.0$ Hz; remaining protons at 7.2-7.7 ppm (10H, m). IR spectrum: 3160 cm^{-1} (OH). Found: N 3.7%; M^+ 385. $C_{28}H_{19}NO$. Calculated: N 3.7%; M 385.

3'-Phenylethynylspiro[4-azafluorene-9,1'-indene] (VII). A 1.4-g (3.6 mmole) sample of acetylenic alcohol VI was heated in 80 ml of 25% sulfuric acid on a boiling-water bath for 4 h, after which the mixture was cooled and neutralized with sodium carbonate, and the reaction products were extracted with ether. The extract was dried with magnesium sulfate, and the ether was removed by distillation to give 0.78 g of an oily reddish-yellowish substance that solidified upon trituration in heptane to give 0.7 g (53.8%) of spiran VII with the same color and mp 160-161°C. PMR spectrum: 8.5 (1H, q, 3-H), 8.33 (1H, 3 d, 5-H), 6.45 (1H, 3 d 8-H), 6.3 ppm (1H, s, 2'-H); $J_{23} = 4.9$, $J_{13} = 1.6$, $J_{56} = 7.6$, $J_{57} = 1.2$, $J_{58} = 0.7$, $J_{78} = 7.5$, $J_{68} = 1.1$ Hz; the remaining protons were found at 6.5-7.8 ppm (3H, m). Found: C 91.5; H 4.4; N 4.0%; M^+ 367. $C_{28}H_{17}N$. Calculated: C 91.5; H 4.6; N 3.8%; M 367.

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DIAZO CARBONYL DERIVATIVES OF HETEROCYCLES.

3.* ALTERNATIVE 1,3-DIPOLAR ADDITION TO AZIDOALKYL α-DIAZO KETONES AND SYNTHESIS OF FIVE-MEMBERED HETEROCYCLES BASED ON THEM

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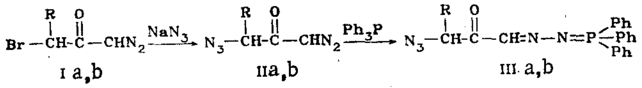
07:543.422.540.14.5

It is shown that the cycloaddition of dimethylacetylenedicarboxylate and N-phenylmaleinimide to azidoalkyl diazomethyl ketones leads to the corresponding 1,2,3-triazole and 2-pyrazoline derivatives. The electronic structure of one of the bisdipoles was determined.

Both diazo ketones [2, 3] and azides [4-6] react readily with various dipolarophiles to give five-membered heterocycles. When an azido grouping is present in the diazo ketone molecule, one cannot a priori predict the direction of 1,3-dipolar addition of dipolarophiles.

It is known that 2-furyl diazomethyl ketone reacts with acetylenedicarboxylic acid ester only at the diazomethine fragment to give pyrazoles and pyrazolines; the diene system of furan does not participate in cycloaddition [7]. In the case of azidoalkyl diazomethyl ketones, which contain two 1,3-dipoles, the reaction may take place at both the azido group and at the diazomethine fragment. A triazole system (VIa, b) or a triazoline system (Xa, b) should be formed in the first case, whereas a pyrazole system (VIIIa, b) or a pyrazoline system (XIIa, b) should be formed in the second case.

To study competitive 1,3-dipolar cycloaddition we synthesized azidoalkyl diazomethyl ketones IIa, b by the reaction of the corresponding bromoalkyl diazomethyl ketones Ia, b with sodium azide:



$$Br-\overset{R}{\underset{\text{I a,b}}{CH}}-\overset{O}{\overset{\|}{C}}-CHN_2 \xrightarrow{NaN_3} N_3-\overset{R}{\underset{\text{II a,b}}{CH}}-\overset{O}{\overset{\|}{C}}-CHN_2 \xrightarrow{Ph_3P} N_3-\overset{R}{CH}-\overset{O}{\overset{\|}{C}}-\underset{\text{III a,b}}{CH{=}N-N{=}P(Ph)_3}$$

I—III a R=H, b R=CH_3

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*See [1] for communication 2.

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TABLE 1. Characteristics of the Compounds Obtained

Compound	mp, °C	N found, %	Empirical formula	N calc., %	Yield, %
IIa	102[a]	55,9	$C_3H_3N_5O$	56,0	98
IIb	84[a]	50,2	$C_4H_5N_5O$	50,4	98
VIa	112	26,3	$C_9H_9N_5O_5$	26,2	40
VIb	88	25,1	$C_{10}H_{11}N_5O_5$	24,9	36
VIIIa	80	26,1	$C_9H_9N_5O_5$	26,2	6
VIIIb	72	24,8	$C_{10}H_{11}N_5O_5$	24,9	Traces
IXa	204	16,9	$C_{15}H_{15}N_5O_9$	17,1	36
IXb	198	16,4	$C_{16}H_{17}N_5O_9$	16,5	29
Xa	128[b]	28,1	$C_{13}H_{10}N_6O_3$	28,2	35
Xb	82	26,9	$C_{14}H_{12}N_6O_3$	26,9	30
XIIa	144[b]	28,1	$C_{13}H_{10}N_6O_3$	28,2	Traces
XIIb	125[b]	26,8	$C_{14}H_{12}N_6O_3$	26,9	Traces
XIIIa	195[b]	20,3	$C_{23}H_{27}N_7O_5$	20,4	39
XIIIb	188[b]	19,9	$C_{24}H_{29}N_7O_5$	19,8	42
XIVa	89	9,1	$C_9H_9BrN_5O_5$	9,2	97
XIVb	72	8,7	$C_{10}H_{11}BrN_2O_6$	8,8	98
XVa	128	12,3	$C_{13}H_{10}BrN_3O_3$	12,5	96
XVb	120	11,9	$C_{14}H_{12}BrN_3O_3$	12,0	95

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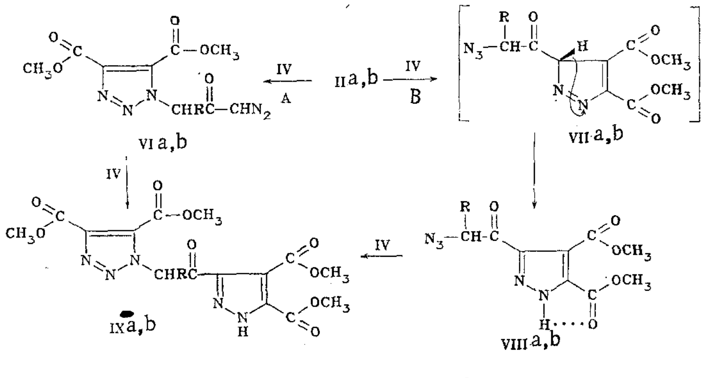
[a] In the form of a phosphazine with triphenylphosphine.
[b] With decomposition.

The reaction proceeds at room temperature and gives the azides in high yields (up to 98%). Information regarding azidoalkyl diazomethyl ketones is not available in the literature. These compounds are yellow oily substances that readily form crystalline phosphazines IIIa, b.

Dimethyl acetylenedicarboxylate (IV) and N-phenylmaleinimide (V) were selected as the dipolarophiles. We found that products of 1,3-dipolar cycloaddition to both the azido (VIa, b) and the diazo carbonyl (VIIIa, b) groups, as well as diadducts IXa, b, are formed in the reaction of diazoketones IIa, b with dipolarophiles IV and V in ether at room temperature.

Pyrazoles VIIIa, b are formed from nonaromatic intermediates VIIa, b with a 1,3-sigmatropic shift of hydrogen [8], and diadducts IXa, b may be formed through the addition of a second molecule of dipolarophile IV both to triazoles VIa, b and to pyrazoles VIIIa, b; the reaction proceeds primarily via pathway A at the more reactive azido group, and the yields of VIIIa, b (pathway B) do not exceed 6%.



VI—IX a R=H, b R=CH_3

Intense absorption bands of ester and ketone carbonyl groups at 1710-1730 and 1620-1630 cm^{-1}, respectively, are observed in the IR spectra of VI-IXa, b. The characteristic absorption band of an azido group at 2100-2210 cm^{-1} is absent in the spectra of VIa, b, but the absorption band of a CHN_2 group is retained. The IR spectra of VIIIa, b correspond to structures with retention of the azido group; the characteristic absorption of a diazomethine fragment (2060-2080 cm^{-1}) is absent (see Table 2). A broad absorption band of an NH group at 3180-3450 cm^{-1} is observed in the IR spectra of VIIIa, b and IXa, b.

Only traces of a product of cycloaddition to the CHN_2 group (XIIa, b) with retention of the azide fragment are formed on passing to the less reactive dipolarophile, viz., N-phenylmaleinimide, and cycloadducts Xa, b and diadducts XIIIa, b are formed in high yields.

TABLE 2. Spectral Characteristics of the Compounds Obtained

Compound	PMR spectrum, δ, ppm (J, Hz)	UV spectrum, λ_{max}, nm (log ε)	IR spectrum, ν, cm^{-1}
IIa	3,94 (2H, s, CH_2); 5,64 (1H, s, CHN_2)	250 (3,94), 272 (3,92)	1625 (C=O), 2150 (N_3), 2070 (CHN_2)
IIb	1,4 (3H, d, J=7, $CHCH_3$); 4,0 (1H, q, J=7, $CHCH_3$); 5,9 (1H, s, CHN_2)	250 (4,12), 268 (3,97)	1625 (C=O), 2210 (N_3), 2080 (CHN_2)
VIa	4,15 (6H, s, 2-OCH_3); 5,75 (2H, s, CH_2); 6,1 (1H, s, CHN_2)	250 (438), 265 (4,36)	1610 (C=O), 1710 (C=O), 2080 (CHN_2)
VIb	1,94 (3H, d, J=7, $CHCH_3$); 5,82 (1H, q, J=7, $CHCH_3$); 3,95 (3H, s, OCH_3); 3,97 (3H, s, OCH_3); 5,96 (1H, s, CHN_2)	252 (4,16), 272 (4,11)	1620 (C=O), 1715 (C=O), 2060 (CHN_2)
VIIIa	3,92 (3H, s, OCH_3); 3,94 (3H, s, OCH_3); 4,74 (2H, s, CH_2); 7,33 (1H, s, NH)	235 (4,22), 282 (4,11)	1690 (C=O), 1730 (C=O), 2120 (N_3), 3180 (NH)
VIIIb	1,7 (3H, d, J=7, $CHCH_3$); 4,9 (1H, q, J=7, $CHCH_3$); 4,12 (6H, s, 2-OCH_3)	232 (4,58)	1700, 1730, 1750 (C=O), 2100 (N_3), 3225 (NH)
IXa[a]	—	255 (4,12), 278 (4,28)	1725, 1730 (C=O), 3450 (NH)
IXb[a]	—	258 (4,01), 280 (4,15)	1720, 1725, 1730 (C=O), 3400 (NH)
Xa	4,75 and 4,78 (2H, s, CH_2); 4,6 and 5,81 (2H, dd, J=13, 5-H+4-H); 5,82 (1H, s, CHN_2); 7,22—7,55 (5H, m, Ar)	250 (4,13), 275 (4,10)	1620 (C=O), 1710 (C=O), 2080 (CHN_2)
Xb	1,78 (3H, d, J=7, $CHCH_3$); 4,1 (1H, q, J=7, $CHCH_3$); 4,8 and 5,3 (2H, dd, J=13, 5-H+4-H); 5,8 (1H, s, CHN_2); 7,15—7,75, 5H, m, Ar)	255 (4,2), 270 (4,0)	1620 (C=O), 1710 (C=O), 2080 (CHN_2)
XIIa	4,43 and 4,47 (2H, s and s, CH_2); 4,83 (1H, d, J=13, 8-H); 5,3 (1H, q, J=13, 7-H); 7,23—7,52 (5H, m, Ar); 9,33 (1H, s, NH)	242 (4,37)	1670, 1710 (C=O), 2100 (N_3), 3250 (NH)
XIIb	1,78 (3H, d, J=7, $CHCH_3$); 4,3 (1H, q, J=7, $CHCH_3$); 4,81 (1H, d, J=13, 8-H); 5,37 (1H, q, J=2,13, 7-H); 7,2—7,6 (5H, m, Ar); 9,4 (1H, s, NH)	245 (4,30), 282 (4,22)	1670, 1710 (C=O), 2100 (N_3), 3250 (NH)
XIIIa[a]	—	256 (4,10), 280 (4,21)	1720, 1725 (C=O), 3350 (NH)
XIIIb[a]	—	250 (4,25), 275 (4,15)	1720, 1730 (C=O), 3350 (NH)
XIVa	3,94 (3H, s, OCH_3); 3,96 (3H, s, OCH_3); 4,56 (2H, s, CH_2); 7,35 (1H, s, NH)	232 (4,44), 285 (4,24)	1710, 1740 (C=O), 3210 (NH)
XIVb	1,87 (3H, d, J=7, $CHCH_3$); 5,48 (1H, q, J=7, $CHCH_3$); 3,96 (3H, s, OCH_3); 4,0 (3H, s, OCH_3); 7,33 (1H, s, NH)	235 (4,41), 282 (4,19)	1690, 1700 (C=O), 3240 (NH)
XVa	4,45 (2H, s, CH_2); 4,81 (1H, d, J=13, 8-H); 5,32 (1H, q, J=2,13, 7-H); 7,2—7,6 (5H, m, Ar); 9,3 (1H, s, NH)	242 (4,4), 282 (4,19)	1690, 1710 (C=O), 3250 (NH)
XVb	1,94 (3H, d, J=7, $CHCH_3$); 5,48 (1H, q, J=7, $CHCH_3$); 4,86 (1H, d, J=13, 8-H); 5,32 (1H, q, J=2,13, 7-H); 7,2—7,6 (5H, m, Ar); 9,32 (1H, s, NH)	245 (4,30), 282 (4,22)	1680, 1700 (C=O), 3240 (NH)

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[a] We were unable to record the PMR spectra of these compounds because of their low solubilities.

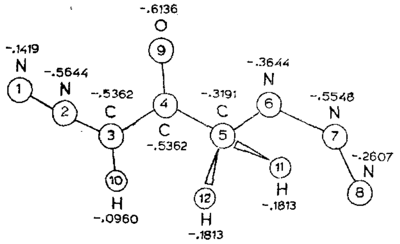
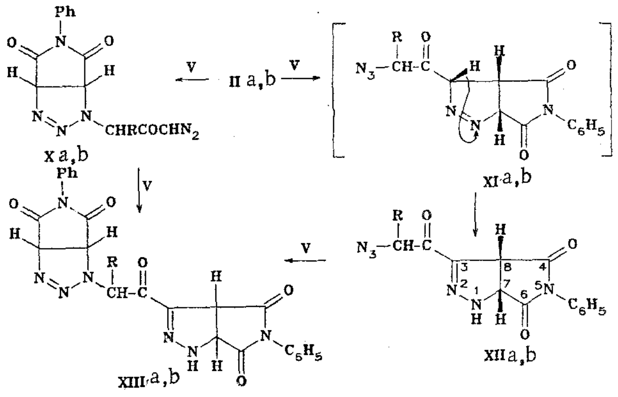


Fig. 1. Distribution of the charges on the atoms in diazo ketone IIa.

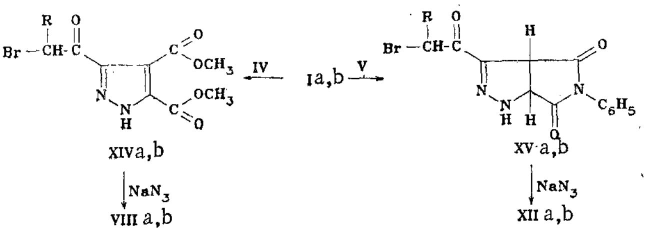
TABLE 3. Coefficients of the Atomic Orbitals in the Highest Occupied (HOMO) and Lowest Unoccupied (LUMO) Molecular Orbitals in Diazo Ketone IIa

Atom	HOMO	LUMO
$N_{(1)}$	0,1499	0,13608
$C_{(3)}$	0,2367	0,21033
$N_{(6)}$	0,6375	0,65636
$N_{(8)}$	0,4829	0,47723



X, XI, XII, XIII a R=H, b $R=CH_3$

The structures of X-XIIIa, b were proved by means of physicochemical methods (see Tables 1 and 2). In addition, VIIIa, b and XIIa, b were obtained by alternative synthesis via the scheme



One's attention is directed to the fact that the protons of the methylene groups are nonequivalent in the PMR spectra of Xa and XIIa (see Table 2). This may be associated with the presence of two asymmetric centers in these compounds, as previously noted in [9]. The signals of the 7-H protons in the PMR spectra of XIIa, b are observed in the form of quartets due to spin–spin coupling with the 8-H and NH protons, while the signal of the 8-H proton appears in the form of a doublet with J = 13 Hz, which constitutes evidence for endo addition of the dipolarophile; 1-pyrazolines XIa, b also undergo rearrangement with the migration of hydrogen and the formation of 2-pyrazolines XIIa, b.

The semiempirical MINDO/3 quantum-chemical method [10] was used to obtain the electronic structure of diazo ketone IIa. The distribution of the charges on the atoms in the molecule is presented in Fig. 1. The geometry of azidomethyl diazomethyl ketone (IIa) was optimized completely. In conformity with the data in [11-13], we examined the contribution of the atomic orbitals to the boundary molecular orbitals of diazo ketone IIa. It is apparent from Table 3 that the contribution of the orbitals of the $N_{(6)}$ and $N_{(8)}$ atoms to the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) is appreciably higher than that of the $N_{(1)}$ and $C_{(3)}$ atoms. On the basis of these data it may be assumed that bonding of the dipolarophiles with the IIa dipole at the $N_{(6)}$ and $N_{(8)}$ atoms is more effective than at the $N_{(1)}$ and $C_{(3)}$ atoms and that the formation of 1-pyrazoline systems is more likely; this is in agreement with the experimental results.

Thus of the alternative pathways of [2 + 3]-cycloaddition to azidoalkyl diazomethyl ketones, addition to the azido group is preferable; the selectivity of cycloaddition increases and is virtually independent of the steric effect of substituent R as the reactivity of the dipolarophile decreases (see Table 1).

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a Specord IR-75 spectrometer. The UV spectra of solutions in methanol were recorded with a Specord UV-vis spectrophotometer. The PMR spectra of solutions in d_6-deuteroacetone and deuterochloroform were obtained with a Tesla BS-497 spectrometer with tetramethylsilane as the internal standard. The purity of the substances was monitored by thin-layer chromatography (TLC) in ethyl acetate—benzene and benzene—acetonitrile systems on Silufol UV-254 plates. The calculations of the electronic structure were performed by the MINDO/3 semiempirical quantum-chemical self-consistent field (SCF) molecular orbitals (MO) linear combination of atomic orbitals (LCAO) method with a BÉSM-6/2 computer.

The physicochemical properties of the compounds are presented in Tables 1 and 2.

Haloalkyl diazomethyl ketones Ia, b were synthesized by the method in [14].

Azidoalkyl Diazomethyl Ketones IIa, b. A solution of 0.2 mole of sodium azide in 2 ml of water was added to a solution of 0.01 mole of the haloalkyl diazomethyl ketone (Ia, b) in 15 ml of tetrahydrofuran (THF), and the mixture was stirred at room temperature until the diazo ketone vanished completely (24 h). The THF was removed by vacuum distillation, the product (IIa, b) was extracted with ether, and the extract was dried. The azidoalkyl diazomethyl ketones were dangerously explosive and were stored in solution in ether in the cold.

Reaction of Azidoalkyl Diazomethyl Ketones with Triphenylphosphine. A solution of 0.01 mole of the azidoalkyl diazomethyl ketone (IIa, b) in 10 ml of ether was added dropwise to a solution of 0.01 mole of triphenylphosphine in 10 ml of ether, and the precipitated crystals were removed by filtration and recrystallized from ether. Compounds IIIa, b were obtained in quantitative yields.

Reaction of Azidoalkyl Diazomethyl Ketones IIa, b with Dimethyl Acetylenedicarboxylate. A solution of 0.005 mole of dimethyl acetylenedicarboxylate in 10 ml of ether was added with stirring to solutions of 0.005 mole of IIa, b in 10 ml of dry ether. After 3-5 days, the precipitate were removed by filtration and washed with boiling chloroform. The precipitates were identified as diadducts IXa, b. Monoadducts VIa, b and VIIIa, b were isolated from the filtrates with a column packed with silica gel [elution with benzene—ethyl acetate (1:2)] by collection of the fractions with R_f 0.52, 0.55 and 0.48, 0.65, respectively.

Reaction of Azidoalkyl Diazomethyl Ketones IIa, b with N-Phenylmaleinimide. This reaction was carried out similarly. After 5 h, the precipitates were removed by filtration and washed with boiling chloroform. The precipitates were identified as diadducts XIIIa, b. Monoadducts Xa, b and XIIa, b, were isolated from the filtrates with a column packed with silica gel [elution with benzene—ethyl acetate (1:2)] by collection of the fractions with R_f 0.42, 0.45 and 0.30, 0.38, respectively.

Reaction of Haloalkyl Diazomethyl Ketones Ia, b with Dimethyl Acetylenedicarboxylate. A 0.002-mole sample of dimethyl acetylenedicarboxylate was added to solutions of 0.002 mole of diazo ketones I in 10 ml of dry ether. After 2 days, the precipitates were removed by filtration and recrystallized from benzene to give XIVa, b.

Reaction of Haloalkyl Diazomethyl Ketones Ia, b with N-Phenylmaleinimide. The reaction was carried out similarly. After 5 h, the precipitates were removed by filtration and recrystallized from benzene to give XVa, b.

Reaction of α-Bromo Ketones XIVa, b and XVa, b with Sodium Azide (General Method). A 0.02-mole sample of sodium azide in 2 ml of water was added to 0.01 mole of the α-bromo ketones in 10 ml of ether. After 24 h, the ether layers were separated from the aqueous layers, and the substances were extracted repeatedly from the aqueous layers with 20-ml portions of ether. The combined ether extracts were dried with Na_2SO_4 and evaporated to give VIIIa, b and XIIa, b in quantitative yields.

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