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OXIDATIVE ADDITION OF N-AMINO-PHTHALIMIDE AND 3-AMINO-2-METHYL-QUINAZOLIN-4(3H)-ONE TO CONJUGATED AZOCYCLOPENTENES AND AZOCYCLOHEXENES

S. M. Buchaka[1], M. A. Kuznetsov[1], and J. G. Schantl[2]

The oxidation of N-aminophthalimide and 3-amino-2-methylquinazolin-4(3H)-one in the presence of conjugated azocyclopentenes, azocyclohexenes, and 3-arylazocyclohexen-2-ones gives adducts at the carbon-carbon double bond corresponding to C-azoaziridines and/or bicyclic 2H-1,2,3-triazoles.

Keywords: C-azoaziridines, 1-azocycloalkenes, 3-azocycloalken-2-ones, 3-amino-2-methylquinazolin-4(3H)-one, N-aminophthalimide, 2H-1,2,3-triazoles, oxidative aminoaziridination.

The oxidation of a series of N-amino heterocycles related to N-aminophthalimide using lead tetraacetate in the presence of a compound with a carbon-carbon double bond gives N-aminoaziridine derivatives or the aminoazimine valence isomers of triaziridines [1, 2] with azo compounds. Non-conjugated γ,δ-unsaturated alkylazoalkenes react with the system N-aminophthalimide – $Pb(OAc)_4$ at the azo group only [3] but with conjugated phenylazoalkenes and 1-isopropylazocycloalkenes to give adducts at the C=C bond (the corresponding C-azoaziridines) and also, quite unexpectedly, 2H-1,2,3-triazoles and 1,2-dicarbonyl compound dihydrazones [3-5]. The formation of the two latter types of compound has not previously been reported in the reactions with olefines or in reactions with azo compounds and is clearly due to the specific conjugated azoalkene system.

In this case the composition of the products of the oxidative addition of N-aminophthalimide to conjugated azocycloalkenes strongly depends, at first glance, on small changes in the structure of the substrate. Whereas in the reaction of the systems N-aminophthalimide – $Pb(OAc)_4$ with 1-isopropylazocyclopentene, 1-isopropylazocyclohexene, and 1-phenylazocyclohexene we have separated only the bicyclic C-azoaziridines, the single product of the reaction with 1-phenylazocyclopentene is 2-phenyl-2,4,5,6-tetrahydrocyclopenta-[*d*][1,2,3]triazole [3-5] in 70% yield.

In order to reveal the factors which determine the course of the oxidative addition of N-amino heterocycles to conjugated azocycloalkenes we have carried out the oxidation of N-aminophthalimide (*Pi*NNH_2) and the related 3-amino-2-methylquinazolin-4(3H)-one (*MeQ*NNH_2) using lead tetraacetate in the presence of a series of conjugated azocyclopentenes **1a,b** and azocyclohexenes **1c-j**, in which we have varied the nature of the substituent on the azo group and the C=C bond.

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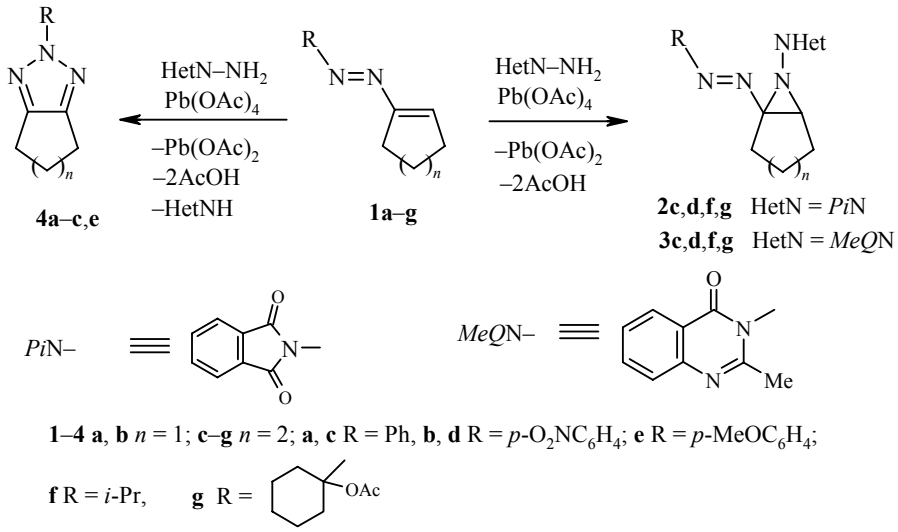
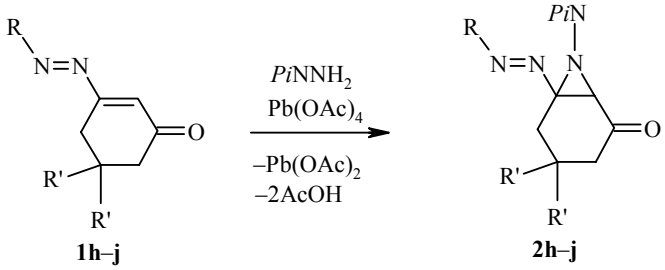
[1] St. Petersburg State University, St. Petersburg 198504, Russia; e-mail: mak@org.chem.lgu.spb.su. [2] Institute for Organic Chemistry, Innsbruck University, Innsbruck A-6020, Austria; e-mail: Joachim.Schantl@uibk.ac.at. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 1043-1051, July, 2004. Original article submitted May 27, 2004.



1–**4** **a**, **b** n = 1; **c**–**g** n = 2; **a**, **c** R = Ph, **b**, **d** R = p-$O_2NC_6H_4$; **e** R = p-$MeOC_6H_4$;

f R = *i*-Pr, **g** R =

In addition to the compounds **1a,c,f** already introduced into the reaction with N-aminophthalimide we have taken arylazocycloalkenes with acceptor **1b,d** and donor **1e** substituents in the aromatic ring. The 1-cyclohexylazocyclohexanol acetate **1g** was selected as a sterically hindered azoalkene. In addition, we considered it useful to introduce an acceptor group at the C=C bond (substrates **1h-j**) since, in the case of the oxidative aminoaziridination of olefines, such a structural modification generally increases the yield of the adduct [1].



1, **2** **h** R = Ph, R' = H; **i** R = p-$O_2NC_6H_4$, R' = H; **j** R = Ph, R' = Me

The reactions were carried out with an equimolar ratio of reagents with the addition, in turn, of small portions of the corresponding N-amino heterocycle and $Pb(OAc)_4$ to a cooled solution (-20 to -30°C) of the azocycloalkene **1** in methylene chloride with a small excess of potassium carbonate. Separation of the reaction mixture was carried out by column chromatography on silica gel. As a result, for both N-amino heterocycles with the majority of 1-azocyclohexenes **1c,d,f,g** and all of the 3-azocyclohexen-2-ones **1h-j**, the bicyclic aziridine adducts **2** and **3** at the carbon-carbon double bond were obtained in yields from 10 to 57%. The separation of the mixture of products with the azocyclopentenes **1a,b** and 4-(cyclohexen-1-ylazo)anisole (**1e**) gave the bicyclic 1,2,3-triazoles **4a,b,e**. In none of the given reactions were there recorded adducts at the azo group or dihydrazones of the 1,2-dicarbonyl compounds.

In addition to the azoaziridines **2, 3** or triazoles **4** there are always present in the reaction mixtures phthalimide or 2-methylquinazolin-4(3H)-one (the desamination products of the starting N-amino heterocycles). Their formation is typical of the oxidative reactions of N-aminophthalimide and related compounds [6, 7] and always accompanies the oxidative addition at the multiple bond or the unsaturated pair of electrons. Hence the yield of these desamination products can serve as a measure of the "inertness" of the substrate. However, the

formation of the 2H-triazoles **4** are considered as an exception since with either mechanism the phthalimide or 2-methylquinazolin-4(3H)-one must separate only after the reaction with the azoalkene and here it is a main and not a side product of the reaction.

The composition of the bicyclic 1,2,3-triazoles **4** and the majority of the azoaziridines **2, 3** were confirmed from elemental analytical data, their structure from ^{1}H and ^{13}C NMR spectroscopy, and in the case of the azoaziridines their mass spectra (in which the molecular ion peaks could be detected). The assignment of signals in the NMR spectra was made on the basis of a spectroscopic comparison of the entire series of compounds prepared and also from literature data with the use of additive schemes [3-5, 8, 9].

Certain azo-7-azabicyclo[4.1.0]heptanes proved to be quite unstable in $CDCl_3$ solution hence to monitor the state of the samples we recorded their ^{1}H NMR spectra both before and after the recording of the ^{13}C NMR spectra. The low stability of the azoaziridines complicates carrying out their elemental analysis and also recording their mass spectra. Hence in the EI mass spectrum of the 6-(4-nitrophenyl)azo-7-phthalimido-7-azabicyclo[4.1.0]heptan-2-one (**2i**) recorded under standard conditions with direct introduction of the sample the molecular ion peak is absent. This is related to the fact that, with a comparatively slow heating of the sample, it decomposes well before its vaporization. The molecular ion peak for the azoaziridine **2i** could be recorded only with rapid heating of the sample above 400°C, however the intensity is low in this case. In both mass spectra the base peaks are signals for the decomposition products of the azoaziridine.

A typical feature of N-aminoaziridine derivatives is the inversion (slow on the NMR time scale) of the endocyclic nitrogen atom [8], which often leads to the appearance of signals for two invertomers in their spectra. In the NMR spectra of the N-phthalimidoaziridines **2** only one set of signals is seen and signs of slow dynamic processes are absent and thus point to their existence in a single, more stable form. The position of the signals of the aziridine protons of the *syn* and *anti* invertomers are usually markedly different [8], but for all of the azo-7-azabicyclo[4.1.0]heptanes **2** they lie in quite a narrow range (3.70-4.25 ppm) hence it can be assumed that all these azoaziridines can be assigned to a single series of stereoisomers. Since the effective bulk of the azo group is less than the tetramethylene chain of the bicyclic system these are more likely the invertomers with a *syn* positioning of the azo group and the phthalimide substitutent (*Z*-invertomers) (cf. [4, 5]).

Confirmation of this comes from the anomalously high field signal for the CH_3COO proton group (1.63 ppm) in the ^{1}H NMR spectrum of the adduct **2g** which lies far from the usual limits for its chemical shift range (1.9-2.2 ppm; in the starting azo compound **1g** it is at 2.11 ppm). Its position can only be explained by the acetoxy group falling in the area of magnetic shielding by the phthalimide group. Optimization of the geometry of the different conformers of the *E*- and *Z*-invertomers of the adduct **2g** by the method of molecular mechanics (AMBER force field) and the semi-empirical methods AM1 and PM3 have shown that this is only possible for a *syn* positioning of the phthalimide substituent and the azo group.

It might be expected that when crossing from the phthalimidoaziridines **2** to the compounds of series **3** with the more sterically demanding 2-methyl-4-oxoquinazolinyl substituent the *Z*-invertomer would also be more thermodynamically stable. However, in the ^{1}H NMR spectra of the adducts **3c,d,f** with 3-amino-2-methylquinazolin-4(3H)-one, there are clear signs of a slowing of the dynamic processes on the NMR time scale and even the appearance of a second form, clearly seen in the spectra of the isopropylazoaziridine **3f**. Thus the signals of the aziridine proton, the methyl group, and the aromatic H-5 proton signal of the heterocyclic fragment are markedly broadened. Moreover, the intensity of the signal for the aziridine proton at ~4 ppm is slightly reduced and along with this there is present an additional broad signal in the range 3.0-3.4 ppm.

The observed picture can be explained by the appearance in the NMR spectra of the aminoaziridines **3** of hindered rotation about the N–N bond. Since the van der Waals radius of the methyl group is significantly larger than the oxygen atom and substituents in the six-membered ring of the oxoquinazolinyl radical is placed markedly closer to the aziridine fragment than the carbonyl groups of the five membered phthalimide ring, the barrier to rotation about the N–N bond of the asymmetric oxoquinazolinyl substituent can be so high that evidence for hindered rotation and even signals for the separate rotamers might be observed.

A notable feature of the ^{1}H NMR spectra of the azoaziridines **2f** [3] and **3f** is the diastereotopism of the methyl groups of the isopropyl fragment and, in the ^{1}H NMR spectra of the phthalimidoaziridine **2g**, a pairwise diastereotopism of the oppositely placed $C_{(2',6')}$ and $C_{(3',5')}$ cyclic substituents is observed.

The number of signals in the NMR spectra of the bicyclic 2H-triazoles **4** and also the nature of the multiplets in the proton spectra point to the magnetic equivalence of the oppositely placed atoms in the molecule. This agrees with the structure **4** proposed by us (local symmetry C_{2v}) and fully excludes their structure as the isomeric 1H-triazoles.

With the exception of the adduct of 1-isopropylazocyclohexene with 3-amino-2-methylquinazolin-4(3H)-one **3f** (which is a pale, greenish oil) the remaining azoaziridines are colored (orange, yellow, or greenish), crystalline materials which are readily soluble in polar organic solvents. Their stability depends strongly on the nature of the substituent on the azo group. Hence the azoaziridines with an acceptor substituent on the azo group decompose slowly, even when they are stored at room temperature. The compounds **2d** and **2i** with a *p*-nitrophenyl substituent are particular unstable and rapidly decompose in $CDCl_3$ solution to a mixture of phthalimide and the bicyclic triazole **4d** or **4i** respectively. At the same time, the C-isopropylazoaziridines **2f, 3f** are unchanged in chloroform solution, even when gently heated over several days.

In this connection, it should be noted that in the ^{1}H NMR spectrum of the mixture of reaction products of 3-amino-2-methylquinazolin-4(3H)-one with 4-(cyclopenten-1-ylazo)-1-nitrobenzene **1b** before its separation on a silica gel column there is seen a broadened triplet at 3.93 ppm which is absent in the spectra of all of the compounds separated on the column. It cannot be ruled out that this signal corresponds to a proton of the azoaziridine **3b** which decomposes on silica gel to the 1,2,3-triazole **4b**. The low stability of the proposed azo-6-azabicyclo[3.1.0]hexane **3b** with a 4-nitrophenyl substituent on the azo group is in good agreement with the dependence noted above. Also in agreement we had previously been able to separate and characterize the corresponding 1-isopropylazo-6-azabicyclo[3.1.0[hexane [3] from the reaction of N-aminophthalimide with 1-isopropylazocyclopentene.

By studying the effect of the structure of the reagents on the course of the oxidative addition of N-aminophthalimide and 3-amino-2-methylquinazolin-4(3H)-one to the conjugated azocycloalkenes **1a-j** it can immediately be seen that both N-amino heterocycles react very similarly, although the yields of the adducts with the N-aminophthalimide are usually a little higher. This is possibly due simply to the greater steric bulk of the 3-amino-2-methylquinazolin-4(3H)-one. The change from the arylazocyclohexenes **1c,d** to the corresponding arylazocyclohexenones **1h-j** has comparatively little effect on the preparative yields of the C-azoaziridines **2**. At the same time, the yield and composition of the reaction products depends on the substituent on the azo group and the size of the carbocycle in the azocycloalkene.

The addition to 4-(cyclohexen-1-ylazo)anisole **1e** clearly occurs poorly since almost all is recovered from the reaction with N-aminophthalimide and with both N-amino heterocycles the 2-(4-methoxyphenyl)triazole **4e** is produced in low yield. A similar low yield of the adduct **2g** occurs with the acetate **1g**, in which a bulky tertiary substituent is found on the azo group. The reason for this seems purely steric. In the reactions with azocyclopentenes we more often separate the 2H-triazoles and with the azocyclohexenes the corresponding C-azoaziridines.

In summary, we have shown that the formation not only of azoaziridines but also of 1,2,3-triazoles occurs generally in the series of conjugated azocyclohexenes and azocyclopentenes. We consider that, independently of the size of the ring olefine fragment, the oxidative addition of the N-amino heterocyclic compound to the conjugated azocycloalkene occurs at the carbon-carbon double bond to give azoaziridines. Formation of the bicyclic 2H-1,2,3-triazoles is the result of secondary reactions. A study of the possible preparation of bicyclic 1,2,3-triazoles by the decomposition of azoaziridines will be the subject of our next paper.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded on Varian Gemini 2000 (200 and 50 MHz) and Bruker DPX-300 (300 and 75 MHz) instruments using $CDCl_3$ solvent. The internal standard was the residual proton signal for the solvent at 7.25 ppm or carbon signal at 77.0 ppm. DEPT Spectra were used for assignment of the carbon atom signals. Mass spectra were obtained on Finnigan MAT 95 and MX-1303 mass spectrometers. Electron impact ionization was used with an ionization energy of 70 eV and FAB (Cs source, 20 kV 0.2 μA) in a 3-nitrobenzyl alcohol matrix. Elemental analysis was carried out on a Hewlett-Packard HP-185B C,H,N automatic analyzer. Melting points were measured on a Boetius type heating stage with a VEB Analytik PHMK 05 direct reading device at an accuracy of 0.2°C. The composition of the reaction mixtures and their separated fractions together with the purity of the individual components were monitored by TLC on Macherey-Nagel Polygram sil G/UV_{254} and Alugram sil G/UV_{254} plates.

The conjugated azocycloalkenes used in this work were synthesized by known methods or on their basis [10-15].

Oxidative Addition of N-Amino Heterocycles to Azocycloalkenes. (General Method). N-Aminophthalimide (162 mg, 1 mmol) [16] (or 175 mg of 3-amino-2-methylquinazolin-4(3H)-one [17]) and lead tetraacetate (520 mg, 1 mmol) (containing ~15% acetic acid) were added alternately and in small portions over 30 min to a suspension of potassium carbonate (966 mg, 7 mmol (690 mg, 5 mmol)) in anhydrous methylene chloride (50 ml) containing the azo compound (1 mmol) with vigorous stirring and cooling to -20 to -30°C. The reaction mixture was held for a further 20 min at -20 to -30°C, then heated to 12-16°C, and filtered through a 1.5-20 cm layer of silica gel. The viscous precipitate of inorganic salts was washed with methylene chloride to a colorless filtrate. Solvent was removed at reduced temperature in vacuo using a water pump and the oily residue was separated on a silica gel column (40-63 μm) using hexane (or petroleum ether)–ether (5:1) as eluent with a gradual increase in the fraction of the latter.

Addition of N-Aminophthalimide to 1-Nitro-4-(cyclohexen-1-ylazo)benzene (1d) (0.5 mmol) to give the starting azo compound **1d** (44 mg, 38%), phthalimide (24 mg, 33%), and 112 mg (57%, 93% based on recovered starting azo compound) of 1-(4-nitrophenyl)azo-7-phthalimido-7-azabicyclo[4.1.0]heptane (**2d**) as bright yellow crystals; mp 109.8-110.3°C, R_f 0.15 (petroleum ether–ether, 5:1). Using TLC and NMR spectroscopy, the aziridine was found to decompose rapidly in $CDCl_3$ solution. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.30-1.75 (4H, m, H-3,4); 2.04-2.28 (2H, m, H-5); 2.49 (1H, m, H-2); 2.93 (1H, m, H-2); 3.91 (1H, dd, *J* = 5.3, *J* = 1.3, H-6); 7.53 (2H, d, *J* = 9.2, Ar); 7.65-7.77 (4H, m, *Pi*N); 8.18 (2H, d, *J* = 9.2, Ar). ^{13}C NMR spectrum, δ, ppm: 19.9 and 20.2 ($C_{(3,4)}$); 23.3 and 23.5 ($C_{(2,5)}$); 52.0 ($C_{(6)}$); 74.1 ($C_{(1)}$); 122.8, 123.0 (PiN, $C_{(3,6)}$ and Ar, $C_{(2,6)}$); 124.6 (Ar, $C_{(3,5)}$); 130.5 (*Pi*N, $C_{(1,2)}$); 134.1 (*Pi*N, $C_{(4,5)}$); 148.5 (Ar, $C_{(1)}$); 155.0 (Ar, $C_{(4)}$); 165.0 (*Pi*N, C=O). Mass spectrum (FAB), *m/z* (*I*, %): 393 (22), 392 (M^++ 1) (54), 391 (M^+) (33), 327 (30), 308 (25), 307 (100), 289 (60), 281 (42), 267 (25), 245 (85), 244 (40), 221 (27), 207 (43).

Addition of N-Aminophthalimide to 4-(Cyclohexen-1-ylazo)anisole (1e) (1.6 mmol) to give the starting azo compound **1e** (191 mg, 55%), phthalimide (206 mg, 89%), and 192 mg of an oily residue which, from NMR spectroscopic data, is a mixture of the starting azo compounds **1e** and 2-(4-methoxyphenyl)-4,5,6,7-tetrahydro-2H-benzo-1,2,3-triazole (**4e**) in the molar ratio 5.4: 1. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): signals for the 4-(cyclohexen-1-ylazo)anisole **1e**: 1.70-1.78 (4H, m, H-4,5); 2.40-2.50 (4H, m, H-3,6); 3.85 (3H, s, CH_3O); 6.88 (1H, t, H-2); 6.95 (2H, d, *J* = 9, Ar, H-3,5); 7.72 (2H, d, *J* = 9, Ar, H-2,6); triazole signals: 1.90-1.95 (4H, m, H-5,6); 2.84-2.88 (4H, m, H-4,7); 3.84 (3H, s, CH_3O); 6.95 (2H, d, *J* = 9, Ar, H-3,5); 7.92 (2H, d, *J* = 9, Ar, H-2,6). ^{13}C NMR spectrum, δ, ppm: azo compound **1e** signals: 22.1 and 22.4 ($C_{(4,5)}$); 22.8 ($C_{(3)}$); 26.3 ($C_{(6)}$); 55.5 (MeO); 114.1 (Ar, $C_{(3,5)}$); 123.9 (Ar, $C_{(2,6)}$); 139.9 ($C_{(2)}$); 147.1 (Ar, $C_{(1)}$); 155.0 (Ar, $C_{(4)}$), 161.1 ($C_{(1)}$): triazole **4a** signals: 21.9 ($C_{(5,6)}$); 23.1 ($C_{(4,7)}$); 55.5 (CH_3O); 114.3 (Ar, $C_{(3,5)}$); 119.7 (Ar, $C_{(2,6)}$); 145.1 ($C_{(3a,7a)}$ and Ar, $C_{(1)}$); 158.7 (Ar, $C_{(4)}$).

Addition of N-Aminophthalimide to 1-(1-Cyclohexenylazo)cyclohexanol Acetate (1g) (3.5 mmol) to give the starting azo compound **1g** (356 mg, 41%) and 1-(1-acetoxycyclohexyl)azo-7-phthalimido-7-azabicyclo[4.1.0]heptane **2g** (146 mg, 10%) as yellow crystals; mp 114-117°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.19-1.82 (m, H-2',3,3',4,4'5',6'); 1.63 (s, MeCOO) and 1.99-2.13 (m, H-2,5) overall 19H; 2.33 (1H, m, H-5); 2.60 (1H, m, H-2); 3.73 (1H, d, *J* = 4.9, H-6); 7.63-7.75 (4H, m, *Pi*N). ^{13}C NMR spectrum, δ, ppm: 19.9 and 20.1 ($C_{(3,4)}$); 21.2 (AcO); 22.9 and 23.3 ($C_{(2,5)}$); 21.8, 21.9, 24.9, 32.6, and 32.8 ($C_{(2',3',4',5',6')}$); 49.5 ($C_{(6)}$); 71.7 ($C_{(1)}$); 102.4 ($C_{(1')}$); 122.6 (*Pi*N, $C_{(3,6)}$); 130.7 (*Pi*N, $C_{(1,2)}$); 133.7 (*Pi*N, $C_{(4,5)}$); 164.9 (*Pi*N, C=O); 168.9 (AcO, C=O). Mass spectrum (EI), *m/z* (*I*, %); 410 [M^+] (12), 368 (16), 350 (4), 325 (35), 299 (17), 267 (17), 264 (14), 248 (100), 222 (99), 207 (39), 179 (33), 167 (31), 154 (96), 10 (89), 109 (86), 104 (20), Found, %: C 64.67; H 6.35; N 13.43. $C_{22}H_{26}N_4O_4$. Calculated, %: C 64.38; H 6.39; N 13.65.

Later fractions contained phthalimide (145 mg, 28%).

Addition of N-Aminophthalimide to 3-Phenylazocyclohexen-2-one (1h) (2.4 mmol) to give the starting compound **1h** (311 mg, 65%), phthalimide (198 mg, 56%), and 268 mg (31%, 88% based on recovered starting material) of 6-phenylazo-7-phthalimido-7-azabicyclo[4.1.0]heptan-2-one (**2h**) as yellow crystals with mp 172°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.86-1.95 (1H, m, H-4); 2.09-2.30 (2H, m, H-3,4); 2.61-2.76 (3H, m, H-3,5); 4.23 (1H, s, H-1); 7.34-7.40 (3H, m, Ph, H-3,4,5); 7.47-7.50 (2H, m, Ph, H-2,6); 7.67-7.79 (4H, m, *Pi*N). ^{13}C NMR spectrum δ, ppm: 17.6 ($C_{(4)}$); 23.2 ($C_{(3)}$); 36.8 ($C_{(5)}$); 54.3 ($C_{(1)}$); 74.5 ($C_{(6)}$); 122.4 and 123.2 (*Pi*N, $C_{(3,6)}$ and Ph, $C_{(2,6)}$); 129.0 (Ph, $C_{(3,5)}$); 130.3 (*Pi*N, $C_{(1,2)}$); 131.4 (Ph, $C_{(4)}$); 134.1 (*Pi*N, $C_{(4,5)}$); 151.6 (Ph, $C_{(1)}$); 164.2 (*Pi*N, C=O); 201.1 ($C_{(2)}$).

Addition of N-Aminophthalimide to 3-(4-Nitrophenyl)azocyclohexen-2-one (1i) (2.3 mmol). Several fractions of the filtrate with change in intensity of the solution color were collected when filtering through a layer of silica gel. The latter colorless fraction contained only phthalimide (77 mg). The remaining fractions were combined and the solvent was distilled off in vacuo. The oily residue (849 mg) was triturated with a minimum amount of ether until a precipitate appeared and this was filtered off (phthalimide 27 mg). The filtrate was evaporated. Repeat of this procedure gave a further 56 mg of phthalimide (overall yield of phthalimide 160 mg (47%)). According to ^{1}H NMR spectroscopic analysis, the oily residue after evaporation of the filtrate (671 mg) was a mixture of the starting azo compound **1i** and the aziridine **2i** in the molar ratio of ~1.8:1 (346 mg (62%) of **1i** and 317 mg (34%, 88% based on the recovered starting azo compound) of **2i** and also contained traces of phthalimide. It was dissolved in a minimum amount of methylene chloride, hexane was added to solution turbidity, and the mixture was left in the cold for several hours. The precipitate was filtered off (starting azo compound **1i**) and the filtrate was evaporated (206 mg, a mixture of the starting azo compounds **1i** and the aziridine **2i** in the molar ratio 1: 4 according to ^{1}H NMR spectroscopy). Repeat of this procedure gave 6-(4-nitrophenyl)azo-7-phthalimido-7-azabicyclo[4.1.0]heptan-2-one **2i** (141 mg, 15%) as orange crystals. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.88-1.93 (1H, m, H-4); 2.14-2.31 (3H, m, H-3,4); 2.64-2.65 (2H, m, H-5); 4.24 (1H, s, H-1); 7.61 (2H, d, *J* = 8.2, Ar, H-2,6); 7.70-7.80 (4H, m, *Pi*N); 8.22 (2H, d, *J* = 9.2, Ar, H-3,5). ^{13}C NMR spectrum, δ, ppm: 17.3 ($C_{(4)}$); 23.1 ($C_{(3)}$); 36.7 ($C_{(5)}$); 54.9 ($C_{(1)}$); 75.3 ($C_{(6)}$); 123.0 and 123.3 (*Pi*N, $C_{(3,6)}$ and Ar, $C_{(2,6)}$); 124.7 (Ar, $C_{(3,5)}$); 130.1 (*Pi*N, $C_{(1,2)}$); 134.4 (*Pi*N, $C_{(4,5)}$); 148.9 (Ar, $C_{(1)}$); 154.6 (Ar, $C_{(4)}$); 164.2 (*Pi*N, C=O); 200.3 ($C_{(2)}$). Mass spectrum (EI) obtained with rapid heating above 400°C, *m/z* (*I*, %): 405 [M^+] (3), 366 (37), 349 (35), 319 (28), 276 (39), 259 (43), 258 (60), 216 (100), 162 (83), 148 (52), 147 (83), 130 (44), 122 (79), 104 (78), 93 (78), 92 (79). In the mass spectrum obtained under the standard conditions of plotting the main peaks were m/z 258 and 147 corresponding to the molecular ion peaks of the triazole **4i** and phthalimide. The molecular ion peak of the azoaziridine **2i** is located only with rapid sample heating above 400°C.

Addition of N-Aminophthalimide to 5,5-Dimethyl-3-phenylazocyclohex-2-enone(1j) (3.5 mmol) to give compound **1j** (437 mg, 55%), phthalimide (167 mg, 33%), and 595 mg (44%, 97% based on recovered starting azo compound) of 4,4-dimethyl-6-phenylazo-7-phthalimido-7-azabicyclo[4.1.0]heptan-2-one (**2j**) as yellow crystals with mp 113°C (decomp.). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.90 (3H, s, CH_3); 1.16 (H, s, CH_3); 2.07 (1H, d, *J* = 13.3, H-3); 2.21 (1H, d, *J* = 14.8, H-5); 2.70 (1H, d, *J* = 13.8, H-3); 3.22 (1H, d,

J = 14.3, H-5); 4.13 (1H, s, H-1); 7.33-7.35 (3H, m, Ph, H-3,4,5); 7.46-7.48 (2H, d, J = 7.2, Ph, H-2,6); 7.67-7.79 (4H, m, *Pi*N). ^{13}C NMR spectrum, δ, ppm: 26.9 (CH_3); 30.4 (CH_3); 35.2 ($C_{(4)}$); 35.9 ($C_{(3)}$); 50.0 ($C_{(5)}$); 54.0 ($C_{(1)}$); 76.1 ($C_{(6)}$); 122.5 and 123.2 (*Pi*N, $C_{(3,6)}$ and Ph, $C_{(2,6)}$); 129.0 (Ph, $C_{(3,5)}$); 130.2 (*Pi*N, $C_{(1,2)}$); 131.4 (Ph, $C_{(4)}$); 134.1 (*Pi*N, $C_{(4,5)}$); 151.3 (Ph, $C_{(1)}$); 164.2 (*Pi*N, C=O); 202.4 ($C_{(2)}$). Found, %: C 67.94; H 4.71; N 13.04. $C_{22}H_{20}N_4O_3$. Calculated, %: C 68.03; H 5.19; N 14.42.

Addition of 3-Amino-2-methylquinazolin-4(3H)-one to Cyclopenten-1-ylazobenzene (1a) (5 mmol). The oily residue (692 mg) was dissolved in a minimum amount of ether and the precipitate formed was filtered off (336 mg (42%) of the quinazolinone). The filtrate was evaporated on a rotary evaporator to give 2-phenyl-2,4,5,6-tetrahydrocyclopenta-1,2,3-triazole **4a** (344 mg, 37%) as white crystals with mp 62°C (lit. mp 62-64°C [4, 5]). The ^{1}H and ^{13}C NMR spectra for the compound obtained agreed with data in [4, 5].

Addition of 3-Amino-2-methylquinazolin-4(3H)-one to 1-Nitro-4-(cyclopenten-1-ylazo)benzene (1b) (0.6 mmol). Several fractions of the filtrate with change in intensity of the solution color were collected when filtering through a layer of silica gel. The latter colorless fraction contained only 2-methylquinazolin-4(3H)-one (53 mg). The remaining fractions were combined and the solvent distilled off in vacuo. The ^{1}H NMR spectrum of the mixture obtained showed a characteristic triplet for the aziridine proton at 3.93 ppm. The oily residue (183 mg) was chromatographed of a silica gel column (20 g) using petroleum ether–methylene chloride (4:1), gradually increasing its polarity to 1: 1 to give the starting azo compound **1b** (20 mg, 15%) and 2-(4-nitrophenyl)-2,4,5,6-tetrahydrocyclopenta-1,2,3-triazole **4b** (120 mg, 87%) as yellowish crystals with mp 227-229°C (decomp.) and R_f 0.63 (ether). ^{1}H NMR spectrum, δ, ppm (J, Hz): 2.58 (2H, q, J = 7.6, H-5); 2.87 (4H, t, J = 7.6, H-4,6); 8.09 (2H, d, J = 9.3, Ar, H-2,6); 8.28 (2H, d, J = 9.3, Ar, H-3,5). ^{13}C NMR spectrum, δ, ppm: 22.1 ($C_{(4,6)}$); 28.7 ($C_{(5)}$); 117.9 (Ar, $C_{(2,6)}$); 125.2 (Ar, $C_{(3,5)}$); 144.6 and 145.3 (Ar, $C_{(1,4)}$), 159.0 ($C_{(3a,6a)}$). Found, %: C 57.61; H 4.48; N 23.39. $C_{11}H_{10}N_4O_2$. Calculated, %: C 57.39; H 4.35; N 24.35.

Later fractions contained 2-methylquinazolin-4(3H)-one (27 mg) (overall yield 80 mg (82%)).

Addition of 3-Amino-2-methylquinazolin-4(3H)-one to Cyclohexen-1-ylazobenzene (1c) (5 mmol) to give the starting azo compound **1c** (200 mg, 22%), 2-phenyl-4,5,6,7-tetrahydro-2H-benzotriazole **4c** (12 mg, 1%) as white crystals with mp 70°C. ^{1}H NMR spectrum, δ, ppm (J, Hz): 1.85-1.90 (4H, m, H-5,6); 2.78-2.82 (4H, m, H-4,7); 7.25 (1H, t, Ph, H-4); 7.42 (2H, t, Ph,, H-3,5); 7.96 (2H, d, Ph, H-2,6). ^{13}C NMR spectrum, δ, ppm: 21.9 ($C_{5,6}$); 23.1 ($C_{4,7}$); 118.3 (Ph, $C_{2,6}$); 126.5 (Ph, C_4); 129.2 (Ph, $C_{3,5}$); 140.1 (Ph, C_1); 145.7 ($C_{3a,7a}$)] together with 1.209 g of a mixture of the aziridine **3c** and 2-methylquinazolin-4(3H)-one. The last fraction was triturated with a small amount of a low polarity mixture of cold petroleum ether and ether. The crystals formed were filtered off, the filtrate was evaporated on a rotary evaporator, and the residue was recrystallized from methanol. The yield of 2-methyl-3-(1-phenylazo-7-azabicyclo[4.1.0]hept-7-yl)quinazolin-4(3H)-one (**3c**) was 653 mg (37%, 47% based on recovered starting azo compound) as yellow needles with mp 98-101°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.50-1.76 (4H, m, H-3,4); 1.97-2.21 (2H, m, H-5); 2.38 (3H, s, CH_3); 2.62-2.70 (1H, m, H-2); 2.94-3.01 (1H, m, H-2); 3.20 broad signal and 3.98 (d, J = 4.1) overall 1H, H-6; 7.26-7.46 (6H, m, Ph and *MeQ*N, H-6); 7.57-7.72 (2H, m, *MeQ*N, H-7,8); 8.24 (1H, d, J = 8, *MeQ*N, H-5). ^{13}C NMR spectrum, δ, ppm: 19.8, 20.5, 23.2, 23.6 ($C_{(2,3,4,5)}$); 22.6 (*MeQ*N, Me); 53.0 ($C_{(6)}$); 76.6 ($C_{(1)}$); 121.4 ($C_{(4a)}$); 122.1 (Ph, $C_{(2,6)}$); 126.0, 126.1, 126.4 (*MeQ*N, $C_{(5,6,8)}$); 128.8 (Ph, $C_{(3,5)}$); 131.2 (Ph, $C_{(4)}$); 133.5 (*MeQ*N, $C_{(7)}$); 145.9 ($C_{(8a)}$); 151.4 (Ph, $C_{(1)}$); 154.0 (*MeQ*N, $C_{(2)}$); 160.1 (*MeQ*N, $C_{(4)}$). Found, %: C 70.24; H 5.96; N 19.91. $C_{21}H_{21}N_5O$. Calculated, %: C 70.20; H 5.85; N 19.50.

The yield of the 2-methylquinazolin-4(3H)-one was 365 mg (45%).

Addition of 3-Amino-2-methylquinazolin-4(3H)-one to 1-Nitro-4-(cyclohexen-1-ylazo)benzene (1d) (2 mmol) to give the starting azo compound **1d** (54 mg, 12%) and 2-methyl-3-(1-(4-nitrophenyl)azo-7-azabicyclo[4.1.0]hept-7-yl)quinazolin-4(3H)-one **3d** (364 mg, 45%, 51% based on recovered starting azo compound) as yellow crystals with mp 180.4-181.1°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.47-1.82 (4H, m, H-3,4); 2.04-2.24 (2H, m, H-5); 2.35 (3H, br. s, *MeQ*N, CH_3); 2.62-2.74 (1H, m, H-2); 3.00 (1H, ddd, J = 14.6, J = 8, J = 6, H-2); 3.39 br. s and 4.15 br. s (1H, H-6); 7.40-7.48 (3H, m, Ar, H-2,6 and *MeQ*N, H-6); 7.60 (1H,

d, J = 8, *MeQ*N, H-8); 7.72 (1H, t, J = 7.8, *MeQ*N, H-7); 8.15-8.18 (3H, m, Ar, H-3,5 and *MeQ*N, H-5). ^{13}C NMR spectrum, δ, ppm: 19.7 and 20.4 ($C_{(3,4)}$); 22.7 (*MeQ*N, CH_3); 23.2 and 23.5 ($C_{(2,5)}$); 54.2 ($C_{(6)}$); 76.0 ($C_{(1)}$); 122.9 ($C_{(4a)}$, Ar, $C_{(2,6)}$); 124.7 br. signal, 126.3 br. signal, 126.4 and 126.7 (Ar, $C_{(3,5)}$ and *MeQ*N, $C_{(5,6,8)}$); 133.9 (*MeQ*N, $C_{(7)}$); 146.0 ($C_{(8a)}$); 148.1 (Ar, $C_{(1)}$); 154.3 and 155.2 (Ar, $C_{(4)}$ and *MeQ*N, $C_{(2)}$); 160.1 (*MeQ*N, $C_{(4)}$). Mass spectrum (FAB), *m/z* (*I*, %): 405 [M^+] (84), 369 (74), 338 (48), 307 (65), 289 (52), 282 (32), 245 (100). Found, %: C 62.47; H 5.20; N 19.86. $C_{21}H_{20}N_6O_3$. Calculated, %: C 62.37; H 4.99; N 20.78.

Later fractions contained 2-methylquinazolin-4(3H)-one (99 mg, 31%).

Addition of 3-Amino-2-methylquinazolin-4(3H)-one to 4-(Cyclohexen-1-ylazo)benzene (1e) (2 mmol) to give the starting azo compound **1e** (42 mg, 10%), 2-(4-methoxyphenyl)-4,5,6,7-tetrahydro-2H-1,2,3-triazole **4e** (30 mg, 7%), 110 mg of a mixture of several compounds with similar retention times using a mixture of petroleum ether–ether (5: 1) (for which the ^{1}H NMR spectrum showed no signals in the range 3-5 ppm), and the quinazolinone (100 mg, 31%).

Compound 4e. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.89 (4H, m, H-5,6); 2.80 (4H, m, H-4,7); 3.84 (3H, s, MeO); 6.95 (2H, d, J = 9, Ar, H=3,5); 7.89 (2H, m J = 9, Ar, H-2,6). ^{13}C NMR spectrum: 21.8 ($C_{(5,6)}$); 23.1 ($C_{(4,7)}$); 55.5 (MeO); 114.3 (Ar, $C_{(3,5)}$); 119.8 (Ar, $C_{(2,6)}$); 145.1 ($C_{(3a,7a)}$ and Ar, $C_{(1)}$); 158.4 (Ar, $C_{(4)}$).

Addition of 3-Amino-2-methylquinazolin-4(3H)-one to 1-Isopropylazocyclohexene (1f) (4 mmol) to give the starting azo compound **1f** (46 mg, 7%) and 3-(1-isopropylazo-7-azabicyclo[4.1.0]hept-7-yl)-2-methylquinazolin-4(3H)-one **3f** (628 mg, 48%, 52% based on recovered starting azo compound) as a greenish oil. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.05 (d, J = 6.8) and 1.06 (d, J = 6.6), 6H, *i*-Pr, $2CH_3$; 1.30-1.60 (4H, m, H-3,4); 1.92-2.09 (2H, m, H-5); 2.34 s and 2.40 s (3H, *MeQ*N, CH_3); 2.43-2.67 (2H, m, H-2); 3.59 (1H, sept, J = 6.6, *i*-Pr, CH); 3.05 br. s and 3.85 (1H, d, J = 4.2, H-6); 7.23 (1H, t, J = 7.2, *MeQ*N, H-6); 7.40-7.55 (2H, m, *MeQ*N, H-7,8); 8.10 (d, J = 7.2) and 8.01-8.06 m (1H, *MeQ*N, H-5). ^{13}C NMR spectrum, δ, ppm: signals for the main rotamer: 19.7 (*i*-Pr, $2CH_3$); 19.6 and 20.2 ($C_{(3,4)}$); 22.6 (*MeQ*N, CH_3); 22.8 ($C_{(5)}$); 23.2 ($C_{(2)}$); 50.9 ($C_{(6)}$); 67.9 (*i*-Pr, CH); 74.5 ($C_{(1)}$); 121.3 ($C_{(4a)}$); 125.7, 125.9, 126.2 (*MeQ*N, $C_{(5,6,8)}$); 133.2 (*MeQ*N, $C_{(7)}$); 145.8 ($C_{(8a)}$); 153.9 (*MeQ*N, $C_{(2)}$); 159.8 (*MeQ*N, $C_{(4)}$): signals for the minor rotamer: 20.9 (*MeQ*N, Me); 126.1, 127.8, 128.1 (*MeQ*N, $C_{(5,6,8)}$); 136.0 (*MeQ*N, $C_{(7)}$); 146.0 ($C_{(8a)}$).

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