Valence Bond Isomerization of Fused [1,2,3]Triazolium Salts with Bridgehead Nitrogen Atom. Fused Azolium Salts. 19[†,‡]

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[1,2,3]Triazolo[1,5-*a*]quinolinium (**7**), [1,2,3]triazolo[1,5-*b*]isoquinolinium (**8**), and [1,2,3]triazolo-[1,5-*a*]pyrazinium salts (**9**) when heated in trifluoroacetic acid and/or 1,2-dichlorobenzene undergo valence bond isomerization to ring-opened reactive intermediates (e.g., **8** gave **13**) which can participate in (i) electrophilic substitution as nitrenium cations to yield pyrazole- and indazole-fused new heterocycles (e.g., from **13**, **14**, and **15** are formed), (ii) pseudoelectrocyclization (e.g., intermediate **19c** leads to the pyrazolo[3,4-*b*]pyrazine **21**), or (iii) in nucleophilic addition as carbenium cations (e.g., **1** gave the methoxy-substituted adduct **22** when heated in methanol). Comparison of these and some recent results reveals that this ring opening of fused [1,2,3]triazolium salts is a general phenomenon and is closely related to the well-known retro-electrocyclizations (called "1,5-dipolar cyclizations") of neutral fused [1,2,3]triazoles and tetrazoles.

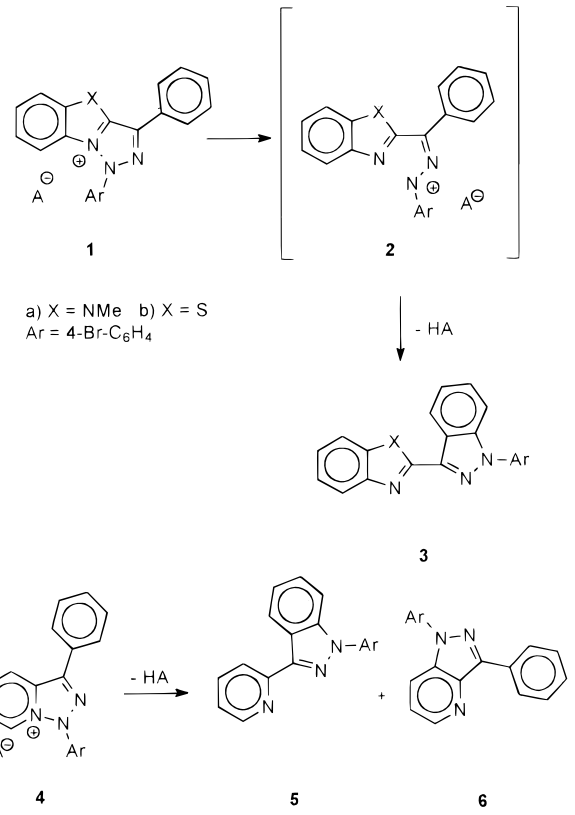
Recently we have reported[1] that some 1,3-diaryl-substituted fused [1,2,3]triazolo[1,5-*a*]benzimidazolium (**1a**) and benzthiazolium salts (**1b**) when heated at 80 °C undergo rearrangement to indazoles (**3**) (Scheme 1). This thermal isomerization was rationalized by formation of a nitrenium cation (**2**) which upon an electrophilic substitution on the neighboring phenyl group afforded the indazolyl product (**3**) in high yield. We have shown, furthermore, that treatment of [1,2,3]triazolo[1,5-*a*]pyridinium salts (**4**) also results in a similar transformation to yield the pyridylindazole compound **5** (58%), but the intermediate nitrenium cation can, simultaneously, attack also the pyridine ring in a side reaction to lead to the pyrazolopyridine derivative (**6**) in traces (4%).

As a continuation of these studies, we decided to extend the study of this rearrangement for novel related ring systems. Thus, in this paper we report on the behavior of three additional fused triazolium systems: two benzologues of **4**, i.e., the angularly fused [1,2,3]triazolo[1,5-*a*]quinolinium salt (**7**) and the linearly fused [1,2,3]-triazolo[1,5-*b*]isoquinolinium salt (**8**) as well as the aza analogue [1,2,3]triazolo[1,5-*a*]pyrazinium salt (**9**), and provide a general interpretation of the experienced phenomena (Scheme 2).

Behavior of the angularly fused [1,2,3]triazolo[1,5-*a*]-quinolinium salt **7** upon heating (7 days, in boiling 1,2-dichlorobenzene) proved to be similar to that of the bicyclic analogue **4**: formation of the intermediate nitrenium cation **10** and a subsequent electrophilic attack at the phenyl substituent afforded the indazolylquinoline **11** as the main product, which was obtained in crystalline form in good yield, whereas a small amount of pyrazoloquinoline **12** as a result of the ring closure on the quinoline ring has also been detected in the reaction mixture (Scheme 3).

The linearly fused triazolium salt **8**, although leading also to products of the same type, reacted entirely differently from the angular analogue. When the reaction was carried out in dichlorobenzene, the pyrazole-fused compound **14** became the main product (83%) and the indazole derivative **15** was formed only in traces (the ratio of **15** to **14** in the crude product was found 2:98). This product ratio changed, however, dramatically when the reaction was carried out in trifluoroacetic acid: in this case the indazolylisoquinoline **15** was formed exclu-

Scheme 1



1 2 3 4 5 6

[†] Cordially dedicated to Prof. van der Plas to the occasion of his 70th birthday.

[‡] For part 18: see ref 16.

(1) Soós, T.; Hajós, G.; Messmer, A. *J. Org. Chem.* **1997**, *62*, 1136.

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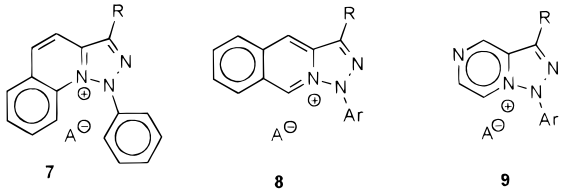
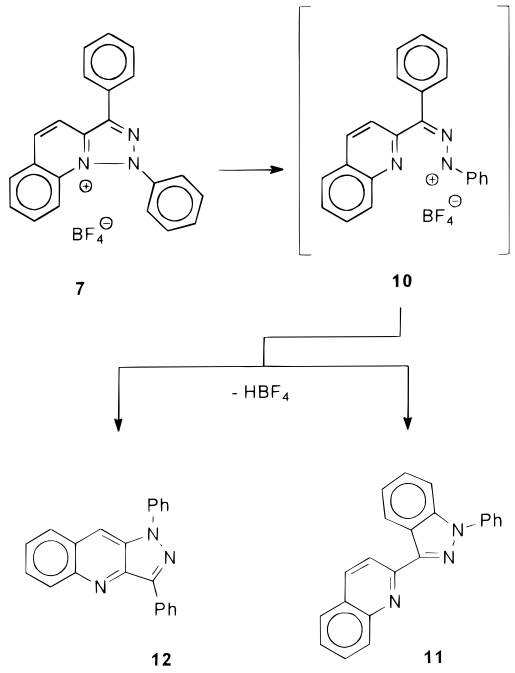
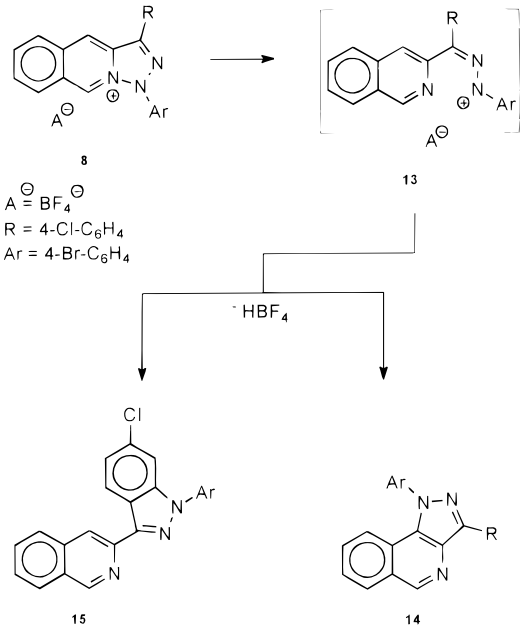
Scheme 2



Scheme 3



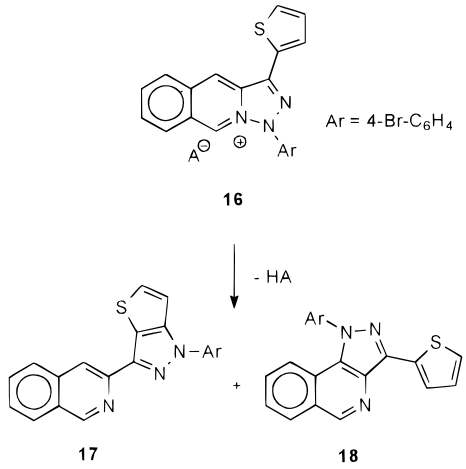
Scheme 4



sively and no ring closure to the isoquinoline ring was observed (Scheme 4).

This essential difference between the product distributions with dichlorobenzene and trifluoroacetic acid seems to be in good accordance with our previously suggested mechanism: the high reactivity of position 4 of the isoquinoline ring toward electrophiles is well-known;[2] therefore under neutral conditions the intermediate **13** attacks obviously this carbon atom. In trifluoroacetic acid, however, the reactivity of the pyridine moiety is totally blocked by the protonation and the electrophilic substitution on the *p*-chlorophenyl substituent will be favored. This experimental finding is, furthermore, of considerable preparative importance: by the choice of an appropriate solvent, products of both types, **14** and **15**, can be synthesized in almost quantitative yield.

Scheme 5



Further support for the electrophilic nature of this thermal isomerization was provided by the ring transformation of **16** to **17** and **18**: these compounds contain a 2-thienyl group in position 3 instead of the *p*-chlorophenyl moiety and, because of the relatively high reactivity of the tiophene ring toward electrophiles, an increase of the amount of **17** in the product compared to **18** could be expected (Scheme 5). While treatment of **16** in TFA afforded exclusively **17** because of the deactivation of the isoquinoline moiety by protonation, the experiments carried out in 1,2-dichlorobenzene by heating proved to be in accordance with the above expectation: the two derivatives **17** and **18** were found in the crude product in a ratio of 7:3, i.e., in comparable amounts (whereas the ratio of the corresponding *p*-chlorophenyl-substituted compounds, i.e., **15**:**14** was 2:98).

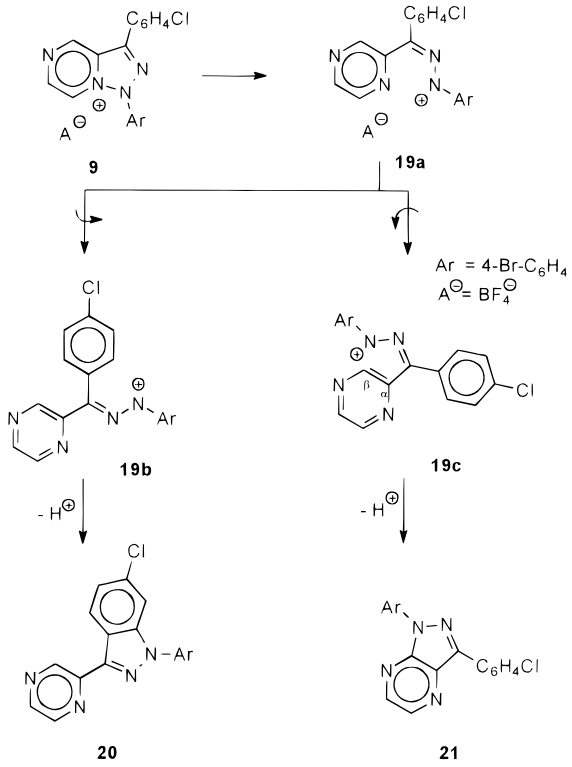
While all of the findings mentioned here previously seemed to support the same course of the reaction mechanism, investigation of the diaza analogue of **4**: the bicyclic [1,2,3]triazolo[1,5-*a*]pyrazinium salt (**9**)—recently synthesized in our laboratory[3]—prompted us to modify our interpretation to a certain extent. This compound (**9**) when subjected to heat treatment (3 h at 180 °C in dichlorobenzene) afforded again two products: the pyrazinyl-substituted indazole compound **20** and the 1,3-diarylpyrazolo[3,4-*b*]pyrazine compound **21** (Scheme 6). The ratio of these two components as shown by the NMR spectrum of the crude product was 7:3, with isolated yields of 20% and 21%, respectively. As a first step of this reaction, formation of the nitrenium intermediate **19a** should be anticipated which, analogous to the previous cases,[1] can attack the 4-chlorophenyl moiety—via formation of the geometric isomer **19b**—in the *ortho* position to yield **20**.

To rationalize the formation of the second product (i.e., **21**), one could assume that the positively charged nitro-

(2) Grethe, G. Isoquinolines. *The Chemistry of Heterocyclic Compounds*; Wiley: London, 1986; Vol. 44, Part 2, p 17.

(3) Béres, M.; Hajós, G.; Riedl, Zs.; Timári, G.; Messmer, A.; Holly, S.; Schantl, J. G. *Tetrahedron* **1997**, *53*, 9393.

Scheme 6



gen atom in the intermediate adopts the rotameric form **19c** and can be orientated into the vicinity of the unsubstituted β-carbon atom of the pyrazine ring; an attack on this atom could result in formation of **21**. This conception is, however, basically contradictory to the general behavior of pyrazine derivatives: it is widely documented[4] that electrophilic attacks on the pyrazine ring can be carried out only under drastic conditions. As our finding revealed that the chance of formation of the pyrazine-coupled product was comparable with that of the phenyl-coupled one and, furthermore, the ratio of product **21** in comparison to **20** (approximately 3:7) was substantially higher than that of the analogous products obtained from the pyridine derivative (**6** and **5**, isolated yields 4:58, respectively), a reinterpretation of the above supposed mechanism seemed necessary.

Figure 1 demonstrates that the nitrenium intermediate **a** formed by the ring opening of fused [1,2,3]triazolium salts can also be represented by its mesomeric carbenium cationic form **b** and, furthermore, this bent form can be, in principle, in equilibrium with the isomeric cumulene 1,2-diazaallenium structure **c**.

It is well-known from the literature[10] that neutral conjugated cumulenes (like iminodiazomethanes[11] or iminoazides[12]) readily undergo ring closure reactions (to

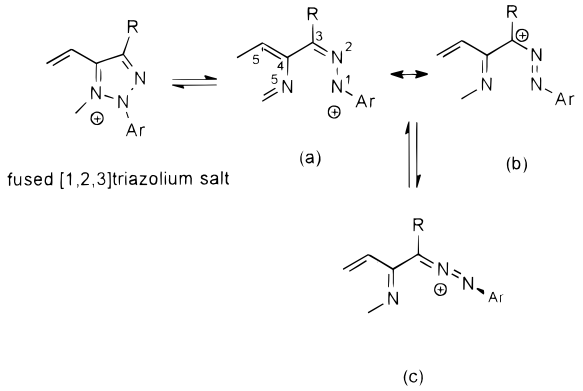


Figure 1.

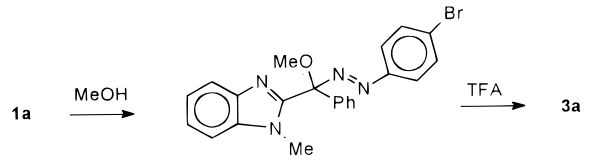
fused [1,2,3]triazoles or tetrazoles, respectively). Transformations of this kind are generally called 1,5-dipolar cyclization[15] or most recently (as more sophisticated theoretical calculation do not support the pericyclic nature of the ring closure) pseudoelectrocyclization.[9] Thus, upon analogy with these cited cases, formation of our intermediate—though bearing a positive charge—could also be considered to proceed in an analogous way, i.e., the reverse ring closure of **a** to the triazolium salt can be interpreted by the pseudoelectrocyclization of the five atomic (1−5) conjugated moieties. Inspection of the structural formula **a**, however, clearly shows that a different conjugated chain of the same molecule, that involving C-4 and C-5′, can also undergo such an electrocyclization[9] to lead to a cyclized product different from the starting [1,2,3]triazolium salt. Consequently, in intermediate **19c** the Cα−Cβ moiety could also fulfill the role of the conjugated double bond necessary for the ring closure to yield the product **21**. Thus, ring transformation of **9** to **21** may well be a manifestation of such a pseudoelectrocyclization rather than electrophilic substitution. Recent results of Jochims et al.[5−7,14] with alkyl- and phenyl-substituted diazaallenium salts (i.e., with close analogues of **c** in Figure 1)—the existence of which was postulated by Huisgen in the 1960s[8]—generated in situ (by oxidation of hydrazones at low temperature) seem to be in good accordance with this suggestion: these authors found that this group of compounds can undergo both pericyclic and multistep cycloadditions with proper dipolarophiles.

Upon this general proposal as shown in Figure 1, one could suggest that reactions of the carbenium form **b** could, in principle, also take place. We have found that triazolium salt **1a** when heated in methanol for several hours undergoes an addition reaction, and the azo compound **22** as a relatively stable yellow crystalline solid (obviously the addition product of the methoxide anion and the carbenium **b** in Figure 1) can be isolated in good yield. This compound, when heated in trifluoroacetic acid, undergoes a reverse transformation and leads to the isomerized indazole (**3a**) (Scheme 7).

A special model compound, a linearly fused [1,2,3]-triazoloisoquinolinium salt having an alkyl group in position 3 (**23**), allowed us to study the reactivity of the reactive intermediate **24** with externally added reagents.

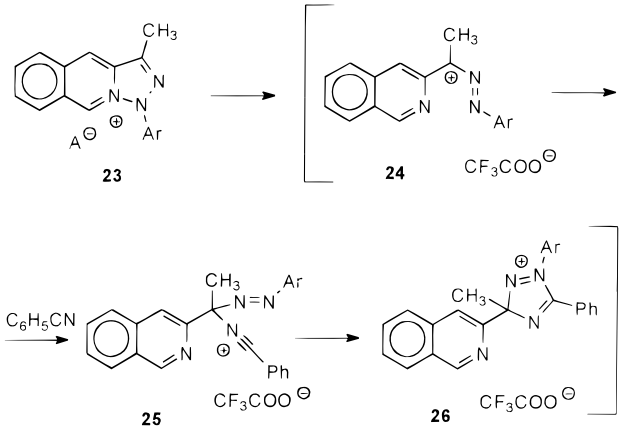
(4) Barlin, G. B. *The Pyrazines. The chemistry of Heterocyclic compounds*; Wiley: London, 1982; Vol.41, p 70.
(5) Wang, Q.; Jochims, J. C.; Köhlbrandt, S.; Dahlenburg, L.; Al-Talib, M.; Hamed, A.; Ismail, E. A. *Synthesis* **1992**, 710.
(6) Guo, Y.; Wang, Q.; Jochims, J. C. *Chem. Ber.* **1994**, *127*, 541.
(7) Al-Soud, Y. A.; Wirschun, W.; Hassan, N. A.; Mayer G.-M.; Jochims, J. C. *Synthesis* **1998**, 721.
(8) Huisgen, R.; Koch, H.-J. *Liebigs Ann. Chem.* **1955**, *591*, 200.
(9) Fabian, W. M. F.; Bakulev, V. A.; Kappe, O. *J. Org. Chem.* **1998**, *63*, 5801.
(10) Taylor, E.; Turchi, I. J. *Chem. Rev.* **1979**, *79*, 181.
(11) Chapman, O. L.; LeRoux, J.-P. *J. Am. Chem. Soc.* **1978**, *100*, 282.
(12) Davies, L. S.; Jones, G. *J. Chem. Soc. C* **1971**, 759.
(13) Tisler, M. *Synthesis* **1973**, 123.
(14) Al-Masoudi, N. A.; Al-Soud, Y. A.; Geyer, A. *Tetrahedron* **1999**, *55*, 751.
(15) Huisgen, R. *J. Org. Chem.* **1976**, *41*, 403.

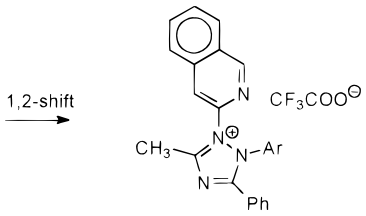
Scheme 7



22

Scheme 8





The suitability of **23** for such investigations is due to the fact that (i) no intramolecular ring closure of **24** to a substituent is possible because of the presence of the methyl group, (ii) when working in trifluoroacetic acid no ring closure to the isoquinoline ring—except the reverse cyclization to **23**—can occur for the reasons mentioned above.

We found indeed that the active intermediate **24** formed from **23** reacted with benzonitrile and a cyclization to **26** followed by a 1,2 shift of the isoquinoline ring afforded the triazolium salt **27** (Scheme 8). This observation seems to be entirely analogous with the case published by Jochims et al.,[5] who suggested that this reaction proceeds by a two-step mechanism starting with the nucleophilic addition of the nitrogen atom of benzonitrile to the carbon atom of the intermediate. Thus, the primary formation of the addition product **25** should occur in our case which is again a manifestation of the carbenium reactivity (Figure 1, **b**) of the reactive intermediate.

Our efforts to carry out cycloadditions of **24** with other "external" multiple bonds, unfortunately, failed probably because of the fairly forced reaction conditions which seemed to be necessary for the generation of this intermediate.

These results lead to the following conclusions:

1. Bridgehead nitrogen atom containing fused [1,2,3]-triazolium salts when heated at higher temperatures undergo valence bond isomerization (Figure 1) involving an N−N bond cleavage to yield a reactive positively charged intermediate. This process seems to be in close analogy with the valence bond isomerizations of neutral fused [1,2,3]triazoles with bridgehead nitrogen atoms.[10−12]

2. This positively charged intermediate can be described by three structural formulas as shown by Figure 1. Two of these (**a** and **b**) are mesomeric bent structures whereas these—in analogy with the pertinent literature data—can be, in principle, in equilibrium with the cumulene structure **c**. At higher temperatures the equilibrium is obviously shifted to the bent form.

3. Intramolecular ring closures of two types of this intermediate have been observed by us: (i) attack of N-1 at an adjacent substituent (e.g., with **13** at R if R = aryl); (ii) attack of N1 at the β position (in compound **19c**) of the heterocycle fused to the [1,2,3]triazole ring in the starting triazolium salt. These reactions can proceed by electrophilic mechanism or as pseudoelectrocyclizations. In special cases, when none of these two reactions can take place, intermolecular nucleophilic additions to the C-3 atom can also be realized.

Our findings reveal that the valence bond isomerization of fused [1,2,3]triazolium salts with bridgehead nitrogen atoms is a general phenomenon: it leads to an active intermediate depicted in Figure 1 which is able to undergo further ring closures or other transformations, thereby providing new synthetic possibilities to some fused N-heterocycles.

Experimental Section

1-(4-Phenyl)-3-(2-quinolyl)-1*H*-indazole (11). A solution of 1,3-diphenyl[1,2,3]triazolo[1,5-*a*]quinolinium tetrafluoroborate (**7**, 500 mg, 1.2 mmol) in 1,2-dichlorobenzene (5 mL) was refluxed for 1 week. The solvent was then removed in vacuo, aqueous sodium hydroxide solution was added, the mixture was extracted by chloroform, and the organic solution was chromatographed on silica. The first and major fraction gave the title compound: 350 mg (89%), mp 140−2 °C: ^{1}H NMR ($CDCl_3$) δ 9.12 (1H, dd, J = 8.1, 1.2 Hz), 8.46 (1H, d, J = 8.7 Hz), 8.26 (1H, dd, J = 8.2, 1.5 Hz), 8.21 (1H, d, J = 8.7 Hz), 7.86 (4H, m), 7.75 (1H, ddd, J = 8.1, 6.9, 1.5 Hz), 7.59 (2H, m), 7,54 (1H, ddd, J = 8.2, 6.9, 1.2 Hz), 7.50 (1H, ddd, J = 8.5, 6.9, 1.3 Hz), 7.42 (2H, m); MS, M_{calcd} 321.1266, M_{found} 321.1242 ± 5 ppm. Collection of the fractions containing the second component afforded a solid in trace amounts (4 mg, 1%) which proved to be 1-(4-phenyl)-3-phenylpyrazolo[4,3-*b*]quinoline (**12**); ^{1}H NMR ($CDCl_3$) δ 8.46 (1H, s), 8.35 (1H, d), 7.95 (1H, d, J = 9 Hz), 7.91 (2H, m), 7.70 (1H, m), 7.56−7.60 (4H, m), 7.50 (2H, m), 7,45 (1H, m), 7.39 (2H, m).

1-(4-Bromophenyl)-3-(4-chlorophenyl)-1*H*-pyrazolo-[4,3-*c*]isoquinoline (14). A mixture of 1-(4-chlorophenyl)-3-(4-bromophenyl)[1,2,3]triazolo[1,5-*b*]isoquinolinium tetrafluoroborate (**8**, 160 mg, 0.29 mmol) and *o*-dichlorobenzene (15 mL) was heated with stirring at 190 °C for 5 h. The solvent was removed in vacuo, and the crude product containing **14** in addition to traces of **15** (in a ratio of 98:2) was triturated with hot acetonitrile and was filtered off to yield the product: 110 mg (82.6%), mp >270 °C (from nitromethane); ^{1}H NMR ($CDCl_3$ + DMSO-d_6) δ 9.18 (1H, s), 8.57−7.50 (4H, AA′−BB′), 8.24 (1H, m), 7.81−7.62 (4H, AA′−BB′), 7.76 (1H, m), 7.68 (2H, m); MS, M_{calcd} 432.9981, M_{found} 432.9959 ± 5 ppm. Anal. Calcd for $C_{22}H_{13}BrClN_3$: C 60.78, H 3.01, N 9.67. Found: C 61.53, H 3.02, N 10.03.

1-(4-Bromophenyl)-6-chloro-3-(3-isoquinolyl)-1*H*-indazole (15). A mixture of 1-(4-chlorophenyl)-3-(4-bromophenyl)-[1,2,3]triazolo[1,5-*b*]isoquinolinium tetrafluoroborate (**8**, 155 mg, 0.29 mmol) and trifluoroacetic acid (5 mL) was heated under reflux for 2.5 h. The reaction mixture was poured onto a mixture of aqueous sodium hydrogencarbonate solution and ice, and the product was extracted by dichloromethane: yield

110 mg (85.3%); mp 207−209 °C (from nitromethane); ^{1}H NMR ($CDCl_3$ + DMSO-d_6) δ 9.40 (1H, s), 8.80 (1H, d, J = 8.5 Hz), 8.61 (1H, s), 8.06 (1H, dd, J = 1, 8 Hz), 7.97 (1H, dd, J = 1, 8 Hz), 7.76−7.74 (4H, AA′-BB′), 7.76 (1H, d, J = 1.8 Hz), 7.76 (1H, ddd, J = 1, 7, 8 Hz), 7.65 (1H, ddd, J = 1, 7, 8 Hz), 7.31 (1H, dd, J = 1.8, 8.5 Hz), MS, M_{calcd} 432.9981, M_{found} 432.9959 ± 5 ppm. Anal. Calcd for $C_{22}H_{13}BrClN_3$: C 60.78, H 3.01, N 9.67. Found: C 61.42, H 3.23, N 10.09.

1-(4-Bromophenyl)-3-(3-isoquinolyl)-1*H*-thieno[3,2-*c*]-pyrazole (17). This compound was prepared from 1-(4-bromophenyl)-3-(2-thienyl)[1,2,3]triazolo[1,5-*b*]isoquinolinium tetrafluoroborate **16**, A = BF_4[16] (60 mg, 0.12 mmol) by the procedure (in TFA) described for compound **15**. **17:** yield 25 mg (50.6%); mp 251−252 °C; ^{1}H NMR ($CDCl_3$) δ 9.45 (1H, s), 8.63 (1H, s), 8.08 (1H, dd, J = 1, 8.5 Hz), 8.01 (1H, dd, J = 1, 8.5 Hz), 7.88−7.73 (4H, AA′−BB′), 7.79 (1H, ddd, J = 1, 6.5, 8.5 Hz), 7.71 (1H, d, J = 5 Hz), 7.68 (1H, ddd, J = 1, 6.5, 8.5 Hz), 7.35 (1H, d, J = 5 Hz), MS, M_{calcd} 404.9935, M_{found} 404.9939 ± 5 ppm.

1-(4-Bromophenyl)-3-(2-thienyl)-1*H*-pyrazolo[4,3-*c*]isoquinoline (18). This compound was prepared from the triazoloisoquinolinium salt **16** (110 mg, 0.22 mmol) according to the procedure (in 1,2-dichlorobenzene) described for **14**. The crude product containing two main components **17** and **18** was purified by preparative layer chromatography (on silica by toluene); the upper spot proved to be identical with **17** whereas separation of the component with a lower R_f yielded colorless needles: 20 mg (22.1%); mp 238−239 °C; ^{1}H NMR ($CDCl_3$) δ 9.16 (1H, s), 8.30 (1H, dd, J = 1.2, 3.5 Hz), 8.26 (1H, m), 7.76−7.57 (4H, AA′−BB′), 7.72−7.62 (3H, m), 7.43 (1H, dd, J = 1.2, 5 Hz), 7.22 (1H, dd, J = 3.5, 5 Hz); MS, M_{calcd} 404.9935, M_{found} 404.9939 ± 5 ppm.

1-(4-Bromophenyl)-6-chloro-3-(2-pyrazinyl)-1*H*-indazole (20) and 1-(4-Bromophenyl)-3-(4-chlorophenyl)-1*H*-pyrazolo[3,4-*b*]pyrazine (21). A mixture of [1,2,4]triazolo-[1,5-*a*]pyrazinium tetrafluoroborate (**9**, A = BF_4, 250 mg, 0.53 mmol) and *o*-dichlorobenzene (25 mL) was heated at 190 °C for 5 h, and the reaction mixture was evaporated under vacuo to give a residue containing two main components (i.e., **20** and **21**) in a ratio of 7:3 which were separated by column chromatography (on silica with chloroform). The first fraction (**21**) was crystallized from nitromethane and obtained as colorless crystals, 43 mg (21%) of product: mp 204 °C; ^{1}H NMR ($CDCl_3$) δ 8.70 (1H, d, J = 2 Hz), 8.57 (1H, d, J = 2 Hz), 8.51−7.49 (4H, AA′−BB′), 8.28−7.66 (4H, AA′−BB′); MS, M_{calcd} 383.9777, M_{found} 383.9772 ± 5 ppm. Anal. Calcd for $C_{17}H_{10}BrClN_4$: C 52.95, H 2.61, N 14.53. Found: C 53.01, H 2.59, N 14.88. The second fraction gave **20**, 40 mg (19.6%): mp 248−250 °C; ^{1}H NMR ($CDCl_3$ + DMSO-d_6) δ 9.43 (1H, d, J = 1.5 Hz), 8.74 (1H, dd, J = 1.5, 2.8 Hz), 8.62 (1H, d, J = 2.8 Hz), 8.59 (1H, d, J = 8.5 Hz), 7.85 (1H, d, J = 1.5 Hz), 7.82−7.76 (4H, AA′−BB′) 7.38 (1H, dd, J = 1.5, 8.5 Hz), MS, M_{calcd} 383.9777, M_{found} 383.9772 ± 5 ppm.

1-Methyl-2-(1′-methoxy-1′-(4-bromophenylazo)benzyl-benzimidazole (22). A solution of **1a** (X = NMe, A = BF_4, 100 mg, 0.2 mmol) in absolute methanol (3 mL) was heated under reflux for 90 min. The mixture was poured to an aqueous sodium hydrogencarbonate solution (50 mL, 10%), and the product was extracted by dichloromethane. Evaporation of the organic solvent afforded a yellow solid which was recrystallized from acetonitrile to yield 60 mg (86%) of product: mp 106 °C (dec); ^{1}H NMR (DMSO-d_6) δ 3.48 (s, 3H), 3.56 (s, 3H), 7.21−7.35 (m, 3H), 7.40 (s, 4H), 7.47−7.78 (m, 6H); MS, $M(cation)_{calcd}$ 435.0819, $M(cation)_{found}$ 435.0820 ± 5 ppm.

2-(4-Bromophenyl)-1-(3-isoquinolyl)-3-phenyl-5-methyl-[1,2,4]triazolium Trifluoroacetate (27). A mixture of 1-(4-bromophenyl)-3-methyl[1,2,3]triazolo[1,5-*b*]isoquinolinium tetrafluoroborate **23**, A = BF_4[16] (150 mg, 0.35 mmol), trifluoroacetic acid (2 mL), and benzonitrile (5 mL) was heated at 110−120 °C for 35 h. The solvent was removed in vacuo, and the residue was subjected to flash vacuum chromatography (silica, 10:1 mixture of chloroform and methanol as an eluent) to yield 100 mg (51.1%) of product: mp 217−219 °C; ^{1}H NMR (CD_3CN) δ 9.22 (1H, s), 8.21 (1H, dd, J = 1.5, 8.5 Hz), 8.17 (1H, s), 8.09 (1H, dd, J = 1.5, 8.5 Hz), 7.96 (1H, ddd, J = 1.5, 7, 8.5 Hz), 7.91 (1H, ddd, J = 1.5, 7, 8.5 Hz), 7.67−7.66 (3H, m), 7.59−7.48 (4H, AA′−BB′), 7.51 (2H, m), 2.71 (3H, s); ^{13}C NMR (CD_3CN) δ (cation) 160.7, 158.9, 155.1, 138.0, 137.0, 134.6, 134.4, 133.8, 132.0, 131.8, 131.1, 130.7, 130.4, 130.3, 129.1, 128.8, 128.0, 124.5, 124.0, 14.0; (anion) 162.0 q, 118.5 q; IR (KBr) 1675 (ν_{as} − CF_3COO^-), 1459 (ν_s − CF_3COO^-); MS, $M(cation)_{calcd}$ 441.0715, $M(cation)_{found}$ 441.0716 ± 5 ppm.

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