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An Aza Cyclopropylcarbinyl-Homoallyl Radical Rearrangement−Radical Cyclization Cascade. Synthesis of Dibenzoimidazoazepine and Oxazepine Derivatives

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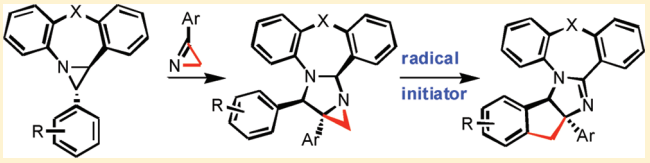
Supporting Information

ABSTRACT: The cycloaddition of the dibenzoxazepinium W-ylides, generated by heating of *trans*-1-aryl-7,11b-dihydro-1*H*-azirino[1,2-*a*]dibenzo[*c*,*f*]azepines, to the C═N double bond of 3-aryl-2*H*-azirines proceeds *endo*-stereoselectively giving regioisomeric cycloadducts in ca. 1:1 ratio, in good overall yields. In contrast to the dibenzoxazepinium ylides, the cycloaddition of the dibenzazepinium W-ylide proceeds regioselectively but without *exo*-*endo*-stereoselectivity. The reasons for this selectivity of the cycloaddition theoretically were studied at the DFT B3LYP/6-31G(d) level. Heating adducts, (2a*RS*,13*SR*,13a*RS*)-13,13a-diaryl-13,13a-dihydro-1*H*,2a*H*-azireno[1′,2′:3,4]imidazo[1,2-*d*]dibenzo[*b*,*f*][1,4]oxazepines and (2a*RS*,13*SR*,13a*RS*)-13,13a-diphenyl-2a,7,13,13a-tetrahydro-1*H*-azireno[1′,2′:3,4]imidazo[1,2-*a*]dibenzo[*c*,*f*]azepine, with an excess of AIBN in toluene gave new polyheterocyclic systems via a novel aza cyclopropylcarbinyl-homoallyl radical rearrangement−radical cyclization cascade. The energy profile of the cascade was studied at the DFT UB3LYP/6-31G(d) level. The transient imidazolinylmethyl radical was trapped by the use of other radical initiators as the corresponding peroxide or alcohol.



INTRODUCTION

Compounds with nitrogen heterocycles *ortho*-fused to dibenzo[*b*,*e*]azepine and dibenz[*b*,*f*][1,4]oxazepine demonstrate various bioactivity. In particular, derivatives of dibenzo[*c*,*f*]-imidazo[1,5-*a*]azepine have specific binding to histamine-1 and histamine-2 receptors[1] and can be used as antiallergics and antithrombotics[2] and sedative and antiulcer agents,[3] and derivatives of dibenz[*b*,*f*]imidazo[1,5-*d*][1,4]oxazepine are useful in pharmaceutical compositions for treating bronchial asthma and allergic bronchitis.[4] The known methods of synthesis of the mentioned heterocyclic system involve the formation of a imidazolidine ring via cyclization of precursors with preformed dibenzo[*b*,*e*]azepine[2−4] or dibenz[*b*,*f*][1,4]oxazepine moieties.[2,4] Approaches to potentially bioactive compounds with dibenzo[*c*,*f*]-imidazo[1,2-*a*]azepine and dibenzo[*b*,*f*]imidazo[1,2-*d*][1,4]-oxazepine skeletons are, to the best of our knowledge, unknown to date.

In the framework of our research concerning the synthesis of heterocycles via N-ylide reactions,[5] we have recently presented an effective approach to *trans*-1-aryl-1,11b-dihydroazirino[1,2-*d*]dibenz[*b*,*f*][1,4]oxazepines[6a,b] and *trans*-1-aryl-7,11b-dihydro-1*H*-azirino[1,2-*a*]dibenzo[*c*,*f*]azepines,[6c] which are excellent precursors of corresponding azomethine ylides and easily undergo stereospecific and stereoselective 1,3-dipolar cycloaddition to C═C dipolarophiles with the formation of a great variety of dibenzo[*b*,*f*]pyrrolo[1,2-*d*][1,4]oxazepine and dibenzo[*c*,*f*]pyrrolo-[1,2-*a*]azepine derivatives. In this study we have extended our investigations to the replacement of the pyrrole moiety in cycloadducts with an imidazole, via cycloaddition of the heterocyclic azomethine ylides to C═N double bond of azirines, and also disclosed a novel aza cyclopropylcarbinyl-homoallyl radical rearrangement−radical cyclization cascade leading to new heterocyclic systems.

Cycloadditions of iminium ylides to the C═N bond are quite rare due to low dipolarophilic activity of imines.[7] The C═N bond of azirines is a more active dipolarophile toward iminium ylides;[7b,g,8] nevertheless cycloadditions to the multiple bond of this strained ring are practically unexplored. According to published works the cycloadditions proceeded regioselectively but usually nonstereoselectively, with conservation of the three-membered ring.[7b,g,8a−c] *exo*-Selectivity was found for cycloaddition of imidazolinium ylides to 2-aryl-3-alkoxycarbonyl-2*H*-azirines.[8b,c]

RESULTS AND DISCUSSION

Heating aziridines **1a**−**c** led to aziridine ring opening with formation of ylides **2a**−**c**, which in the presence of azirines **3a**−**e** give rise to mixtures of the isomeric 1,3-dipolar adducts **4** and **5** in good overall yields (Table 1). When the reactions of **1a** are performed under solvent-free conditions, they proceed much faster than in toluene, yielding the same products. The reaction condition of choice is heating at 90 °C for 3−4 h without solvent. Reactions at higher temperatures, although they proceeded faster, led to a little bit more tarring.

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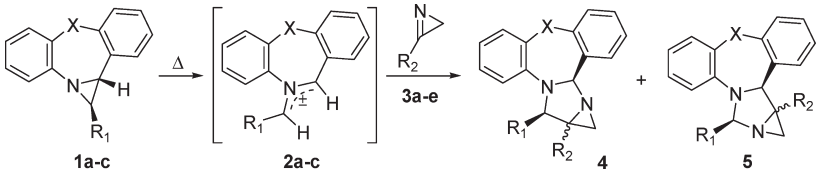
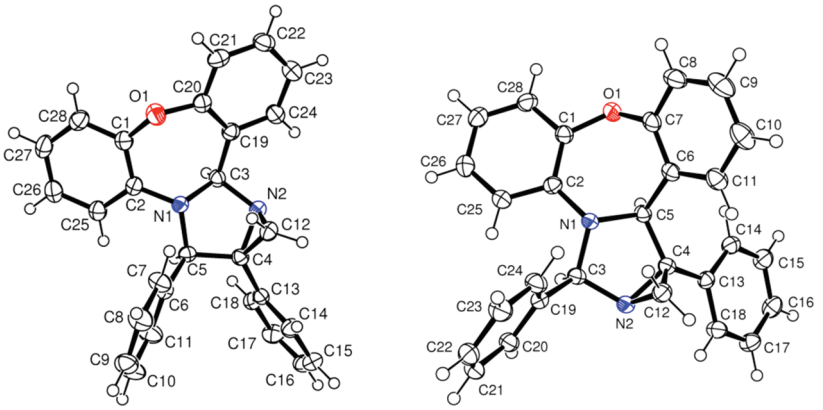
Table 1. Reaction of Aziridines 1a−c with Azirines 3a−e



aziridine/azirine	X	R^1	R^2	solvent/temp (°C)/time (h)	products, ratio[a]	yield (%)[b]
1a/3a	O	Ph	Ph	neat/90/3	*trans*-**4a**/*trans*-**5a**, 1/1.1	40/44
1a/3a	O	Ph	Ph	neat/120/0.67	*trans*-**4a**/*trans*-**5a**, 1/1.1	39/44
1a/3a	O	Ph	Ph	neat/140/0.25	*trans*-**4a**/*trans*-**5a**, 1/1.1	39/39
1a/3a	O	Ph	Ph	MePh/90/8	*trans*-**4a**/*trans*-**5a**, 1/1.1	44/43
1a/3a	O	Ph	Ph	MePh/110/6	*trans*-**4a**/*trans*-**5a**, 1/1.1	44/43
1a/3b	O	Ph	$4\text{-NO}_2C_6H_4$	neat/90/3	*trans*-**4b**/*trans*-**5b**, 1/1.1	34/41[c]
1a/3c	O	Ph	4-MeC_6H_4	MePh/90/10	*trans*-**4c**/*trans*-**5c**, 1/1.1	46/50
1a/3d	O	Ph	4-MeOC_6H_4	neat/90/3	*trans*-**4d**/*trans*-**5d**, 1/1.1	38/49
1b/3e	O	2-BrC_6H_4	2-BrC_6H_4	neat/90/3	*trans*-**4e**/*trans*-**5e**, 1/1	29/33
1c/3a	CH_2	Ph	Ph	neat/90/4	*trans*-**4f**/*cis*-**4f**, 2.5/1	52/21

[a] According to ^{1}H NMR of the reaction mixtures. [b] Isolated yield. [c] As a mixture with *trans*-**4**



trans-**4a**, *trans*-**5a**

Figure 1. X-ray crystal structures of *trans*-**4a** and *trans*-**5a**.

The structures of compounds **4** and **5** were verified by ^{1}H, ^{13}C, ^{1}H 2D NOESY NMR, IR spectroscopy, and elemental analysis. Structures of *trans*-**4a** and *trans*-**5a** were confirmed by X-ray analysis (Figure 1).

According to calculations perfomed earlier,[6b,c] under the thermal conditions the ring opening of aziridines **1a,c** occurs conrotatory with the formation of either the U-ylides or W-ylides,[9] but the barrier to formation of the first are 9−13 kcal·mol^{-1} higher than that of the latter, and the W-ylides are more stable than the U-ylides by 16−18 kcal·mol^{-1}. W-Ylides can be transformed to the even more stable S-ylides by rotating the PhCH group around the ylide C−N bond through a ca. 30 kcal·mol^{-1} activation barrier. The feature of products of the cycloaddition **4** and **5** is *cis*-configuration of hydrogens at the imidazolidine ring. This means that, as in the case of the reactions of aziridines **1a−c** with ethylenic and acetylenic dipolarophiles, the ylides **2** that cycloadd to the C=N double bond of azirines have W-configuration. The structure of the cycloadducts of the dibenzoxazepinium ylides **2a,b** with azirines implies that cycloaddition of these ylides proceeds *endo*-stereoselectively unlike other cyclic dipolarophiles and like maleic anhydride and *N*-arylmaleimides, which cycloadd to ylides **2** *exo*-streoselectively.[6] In contrast to the dibenzoxazepinium ylides, the dibenzazepinium ylide **2c** gives products that imply that cycloaddition proceeds regioselectively but without *exo*-*endo*-stereoselectivity. To understand this difference in reactivity of the ylides, calculations of cycloaddition of ylides **2a,c** to azirine **3a** were performed at the DFT B3LYP/6-31G(d) level (Figures 2 and 3).

According to the calculations (Figure 2) the barriers for *exo*-approach of azirine **3a** to ylide **2a** are higher than those for *endo*-approach by 1.8 and 3.0 kcal·mol^{-1}, for transition states leading to regioisomers **4a** and **5a**, respectively. As a result we obtained only the *endo*-adducts, *trans*-**4a** and *trans*-**5a**. Unfavorable repulsion of unshared electron pairs of azirine nitrogen and oxazepine oxygen in *exo*-transition states *exo*-TS-*cis*-**4a** and *exo*-TS-*cis*-**5a** may at least partly be responsible for the preference of the *endo*-

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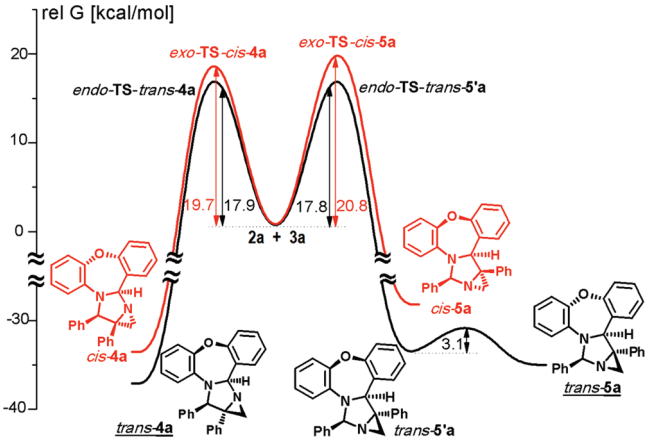


Figure 2. Energy profiles for the cycloaddition of ylide **2a** to azirine **3a**. Relative free energies [kcal·mol^{-1}, 298 K] were computed at the B3LYP/6-31G(d) level.

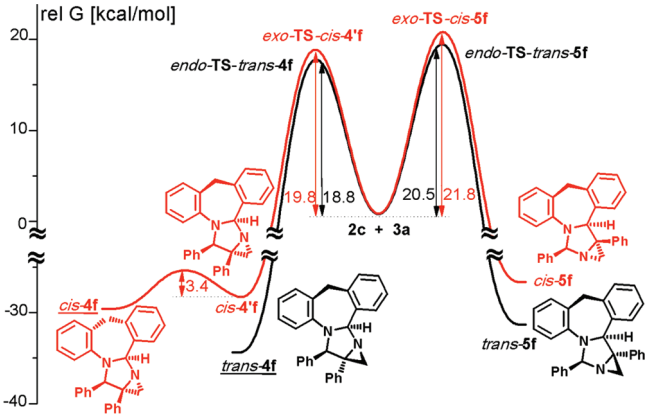


Figure 3. Energy profiles for the cycloaddition of ylide **2c** to azirine **3a**. Relative free energies [kcal·mol^{-1}, 298 K] were computed at the B3LYP/6-31G(d) level.

approach of azirine. Actual equality of energies of *endo*-TS-*trans*-**4a** and *endo*-TS-*trans*-**5′a** transition states explains equal yields of regioisomers *trans*-**4a** and *trans*-**5a**. *endo*-TS-*trans*-**5′a** transition state leads to isomer *trans*-**5′a**, which transforms to the more stable *trans*-**5a** via inversion of the oxazepine ring with a low barrier.

When passing from the dibenzoxazepinium ylides to the dibenzazepinium ylide the selectivity of cycloaddition changed. The main product of the cycloaddition is compound *trans*-**4f** to which corresponds the lowest barrier to cycloaddition (Figure 3) of ylide **2a** to azirine **3a**. The minor product *cis*-**4f** is formed via a higher energy transition state *exo*-TS-*cis*-**4′f** that leads to isomer *cis*-**4′f** and transforms to the more stable *cis*-**4f** via inversion of the azepine ring with a low barrier.

Compounds **4** and **5** are potential sources of iminium ylides via ring opening of aziridine rings, but heating aziridines *trans*-**4a** and *trans*-**5a** with DMAD or dimethyl maleate led only to tarring of reaction mixtures. One more possibility to create new complex heterocyclic systems is the well-known[10] intramolecular radical cyclization of *o*-bromophenyl-substituted compounds such as *trans*-**4e** and *trans*-**5e**. To realize radical cyclization initiated by a radical bromine abstraction, compound *trans*-**4e** was heated in toluene with Bu_3SnH and α,α′-azoisobutyronitrile (AIBN); however, compound **6a** was isolated instead of the expected radical

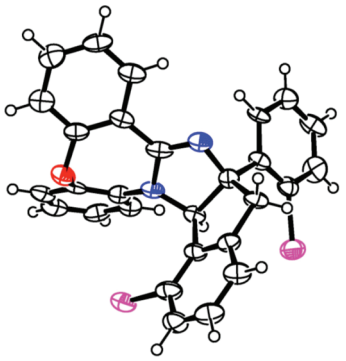
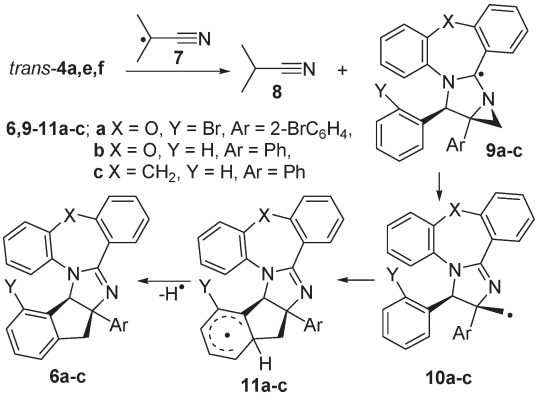


Figure 4. X-ray crystal structure of **6a**; one of the three independent molecules of **6a** (color code: violet Br; blue N; red O).

Scheme 1. Reaction of Compounds *trans*-4 with Isobutyronitrile Radical



cyclization product. Under the same conditions compound *trans*-**5e** gave no isolable products. The structure of **6a** was confirmed by X-ray analysis (Figure 4). It crystallizes with three independent molecules per asymmetric unit (see the Suporting Information).

Further experiments showed that **6a** can be obtained from *trans*-**4e** without addition of Bu_3SnH, and thus heating *trans*-**4e** with an excess of AIBN in toluene gave **6a** in 64% yield. The most probable path of formation of compound **6a** involves abstraction of H-2 by the isobutyronitrile radical **7** from the imidazolidine ring of *trans*-**4e** with formation of radical **9a** and isobutyronitrile **8**. This is followed by aziridine ring opening in **9** with formation of imidazolinylmethyl radical **10a**, which further undergoes radical cyclization on the *ortho*-position of the *cis*-arranged aryl ring (Scheme 1). That is, the reaction is a cascade of a new variant of aza cyclopropylcarbinyl-homoallyl radical rearrangement[11] followed by radical cyclization.

Heating compounds *trans*-**4a,f** with an excess of AIBN in toluene gave **6b,c** in 74% and 59% isolated yield, respectively (Table 2). The isomeric compounds *trans*-**5a,e** and *cis*-**4f** under the same condtions are much less reactive, and longer heating gave complex reaction mixtures with no isolable products. To verify a mechanism of the reaction and to understand the observed reactivity and selectivity, calculations of the energy profiles of the reactions of radical **7** with compounds *trans*-**4a** and -**5a** and transformations of radical **9b** were performed at the DFT UB3LYP/6-31G(d) level (Figures 5 and 6).

An amino substituent is the most effective heteroatomic stabilizer of free radicals.[12] A comparison of the calculated

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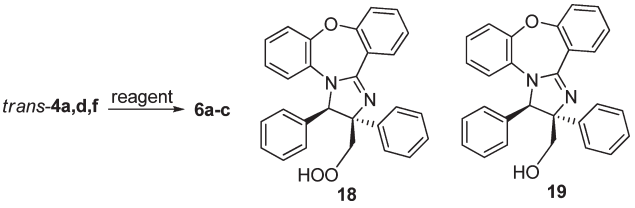
Table 2. Reaction of Aziridines *trans*-4a,e,f under Free-Radical Initiation Conditions



trans-4	reagent	solvent	temp (°C)	yield of 6 (%)[a]	yield of 18 (%)[a]	yield of 19 (%)[a]
a	AIBN, Ar	toluene	100	74	0	0
a	AIBN, Ar	toluene	80	69	0	0
a	DTBP	toluene	110	67	0	19
a	TBHP	benzene	60	17	53	5
a	$h\nu$, O_2	MeCN	25	5	67	25
a	$Mn(OAc)_3$	toluene	110	31	0	53
a	$Mn(OAc)_3$	AcOH	50	13	0	68
e	AIBN, Ar	toluene	80−90	64	0	0
f	AIBN, Ar	toluene	80−90	59	0	0

[a] Isolated yield.

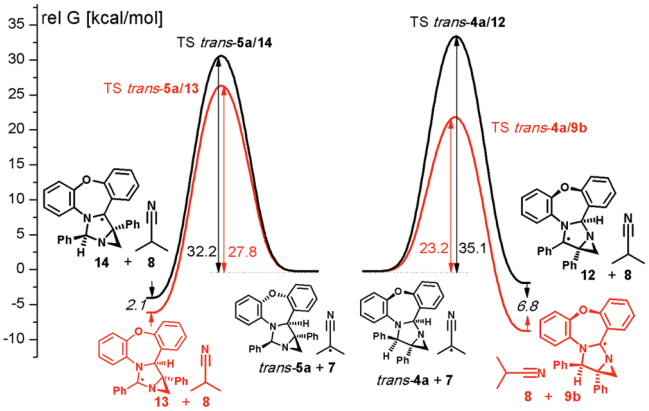


Figure 5. Energy profiles for the reaction of compounds *trans*-**4a** and -**5a** with radical **7**. Relative free energies [kcal·mol^{-1}, 298 K] computed at the UB3LYP/6-31G(d) level.

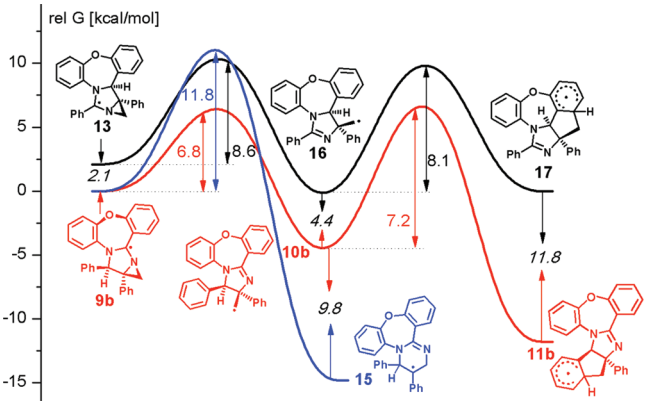


Figure 6. Energy profiles for the transformation of radicals **9b** and **13**. Relative free energies [kcal·mol^{-1}, 298 K] computed at the UB3LYP/6-31G(d) level.

relative stability ($\Delta\Delta G$ kcal·mol^{-1}) of radicals **9b** (0), **13** (4.68), **12** (6.84), and **14** (6.80) shows that stabilization of the radical by two amino substituents is greater than by one. Radical stabilization that involves the resonant delocalization of the unpaired spin into an adjacent π system is more effective for the substituted benzene ring of the benzoxazepine system in comparison with an unsubstituted Ph-ring (corresponding C$^{\bullet}$—Ar bond lengths change in parallel with the stability of the radicals: **9b** 1.415 Å, **13** 1.423 Å, **14** 1.432, **12** 1.439 Å).

According to DFT UB3LYP/6-31G(d) calculations (Figure 5) abstraction of hydrogen from the imidazolidine 2-C, with formation of the more stable imidazol-2-yl radical (**9b**, **13**), proceeds through a much lower barrier than abstraction of hydrogen from the imidazolidine 4-C with formation of the imidazol-4-yl radical (**12**, **14**), in both *trans*-**4a** and *trans*-**5a**. However, the formation of radical **9b** by the reaction of radical **7** with *trans*-**4a** proceeds through a much lower activation barrier (by ca. 5 kcal·mol^{-1}) than the formation of radical **13** by the reaction of radical **7** with *trans*-**5a**, possibly due to steric hindrances. Probably the higher barrier of formation of the corresponding radical is the cause of less reactivity toward the radical initiators of *trans*-**5** in comparison with *trans*-**4**.

The transformation of radical **9b** to radical **10b** proceeds through a very low activation barrier due to the liberation of the strain energy of the three-membered ring (Figure 6). Potentially, radical **9b** could open to a far more stable radical **15** (by 9.8 kcal·mol^{-1} comparing with **10b**) by cleaving the other three-membered ring C—N bond to give a benzylic radical and a six-membered ring. However, this route has a much higher activation barrier (by 5.0 kcal·mol^{-1}), which makes it noncompetitive. The cyclization of radical **10b** onto the vicinal *cis*-phenyl ring proceeds through a 12.2 kcal·mol^{-1} barrier, giving a much more stable radical **11b**, which is the precursor of the product **6b**. According to calculations (Figure 6) a similar transformation of radical **13** to **16** should proceed through a higher activation barrier than the transformation **9b** → **10b**, and cyclization of radical **16** onto the fused benzene ring would led to radical **17**, which is even a little less stable than the starting radical **16** due to the angle strain in the polycyclic system. This is probably the reason of the nonselective reactivity of compounds *trans*-**5**

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toward radical initiators and for the absence of the corresponding cyclization product.

To evaluate the synthetic possibilities of the radical aziridine ring opening, we studied the reactions of **4a** under various free-radical initiation conditions (Table 2). It was found that under oxidation conditions, along with the compounds **6**, the products of oxidation of transient imidazolinylmethyl radical, compounds **18** and **19** are formed. Structures of compounds **6**,**18**, and **19** were verified by ^{1}H, ^{13}C, IR spectroscopy, and elemental analysis. Structures of **6b,c** and **18** were confirmed by X-ray analysis (see the Supporting Information). The use of di-*tert*-butyl peroxide (DTBP) instead of AIBN led to compound **6b** (67%), which was isolated along with alcohol **19** (19%). The latter is probably the result of oxidation of radical **10b**. On changing the initiator from peroxide (DTBP) to hydroperoxide (*tert*-butyl hydroperoxide (TBHP)) the reaction of *trans*-**4a** gave quite different results. Under these conditions compound **6b** was isolated in only 17% yield and the main product was hydroperoxide **18** (53%), along with a small amount of **19** (5%). The formation of hydroperoxide **18** as a main product is due to the reaction of radical **10b** with oxygen, the source of which is TBHP,[13] and the lower temperature used, which prevents decomposition of **18** to **19**. A similar result was obtained under UV irradiation of *trans*-**4a** in the presence of atmospheric oxygen (Table 2). We also tried using $Mn(OAc)_3$ as a mediator of free radical reactions[14] and as an oxidizing agent[15] to improve the yields of hydroxymethyl-derivatives of the new dibenzo[*b*,*f*]imidazo[1,2-*d*][1,4]oxazepine heterocyclic system. In fact, boiling of aziridine *trans*-**4a** in toluene with 2 molar equiv of $Mn(OAc)_3$ for 16 h led to alcohol **19** in 53% yield along with compound **6b** (31%). In AcOH at 50 °C for 0.5 h the same compounds were obtained in 68% and 13% yield, respectively.

CONCLUSIONS

The cycloaddition of the dibenzoxazepinium W-ylides **2a,b**, generated by heating of the corresponding aziridines, to the C═N double bond of azirines **3** proceeds *endo*-stereoselectively unlike other cyclic dipolarophiles, giving regioisomeric cycloadducts in ca. 1:1 ratio, in good overall yields. In contrast to the dibenzoxazepinium ylides, the cycloaddition of the dibenzazepinium W-ylide **2c** proceeds regioselectively but without *exo*-*endo*-stereoselectivity. The reasons for this selectivity of the cycloaddition were theoretically studied at the DFT B3LYP/6-31G(d) level. Heating aziridinoimidazolidines *trans*-**4** with an excess of AIBN in toluene gave a new heterocyclic system **6**, via a novel aza cyclopropylcarbinyl-homoallyl radical rearrangement−radical cyclization cascade. The energy profile of formation of compoud **6a**, involving abstraction of H-2 by the isobutyronitrile radical from the imidazolidine ring of *trans*-**4e** and aziridine ring opening in the primary radical leading to the imidazolinylmethyl radical, which further undergoes radical cyclization on the *ortho*-position of the *cis*-arranged aryl ring, was computed at the DFT UB3LYP/6-31G(d) level. Use of other radical initiators gives a possibility to trap the transient imidazolinylmethyl radical as the corresponding peroxide or alcohol.

EXPERIMENTAL SECTION

General Methods. Melting points were determined on a hot stage microscope and are uncorrected. ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were determined in $CDCl_3$ or DMSO-d_6. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane. The X-ray intensity data were collected at 173 K on a diffraction system equipped with a two-circle goniometer and using Mo Kα graphite monochromated radiation. The structures were solved by direct methods and were refined by full-matrix least-squares on F^2 for all data.[16] The H-atoms were included in calculated positions and treated as riding atoms using SHELXL[17] default parameters. Compound **6a** crystallized with three independent molecules in the asymmetric unit. Compounds **1a**−**c**[6] and **3a**−**e**[18] were prepared by the reported procedures.

3-(2-Bromophenyl)-2*H*-azirine 3e. White solid; mp 57−58 °C (hexane); yield 48%; ^{1}H NMR ($CDCl_3$) δ 1.88 s (2H, CH_2), 7.26−7.53 m (2H, arom), 7.72−7.75 m (1H, arom), 7.83−7.86 m (1H, arom); ^{13}C NMR ($CDCl_3$) δ 21.0 (CH_2), 125.1, 125.5, 127.7, 132.6, 133.6, 133.9, 166.3; IR ($CHCl_3$, cm^{-1}) ν 3056, 3004, 2900, 1746, 1588, 1458, 1434, 1304, 1256, 1112, 1044, 992. Anal. Calcd for C_8H_6BrN: C 49.01, H 3.08, N 7.14. Found: C 49.15, H 3.27, N 7.12.

General Procedures for Cycloaddition of Ylides from *trans*-1-Aryl-1,11b-dihydroazirino[1,2-*d*]dibenz[*b*,*f*][1,4]oxazepines 1a,b and *trans*-1-Phenyl-7,11b-dihydro-1*H*-azirino[1,2-*a*]-dibenzo[*c*,*f*]azepine 2c to Azirines 3a−e. A mixture of compound **1a**−**c** (0.2 mmol) and azirine **3a**−**e** (0.4 mmol) without solvent or in anhyd toluene (3 mL) was heated at the reaction temperature and reaction time indicated in Table 1. The reaction was monitored by TLC. The solvent was removed in vacuum, and the residue was purified by flash chromatography on silica (eluent hexane/ethyl acetate, 40:1).

(2a*RS*,13*SR*,13a*RS*)-13,13a-Diphenyl-13,13a-dihydro-1*H*,2a*H*-azireno[1′,2′:3,4]imidazo[1,2-*d*]dibenzo[*b*,*f*][1,4]oxazepine, *trans*-4a. White solid; mp 102−103 °C (hexane); yield 39−44%; ^{1}H NMR ($CDCl_3$) δ 1.83 s (1H, CH_2), 2.73 s (1H, CH_2), 5.04 s (1H, CH), 5.52 s (1H, CH), 6.76−6.81 m (1H, arom), 6.88−6.96 m (2H, arom), 7.13−7.24 m (7H, arom), 7.29−7.39 m (7H, arom), 7.88 dd (1H, J = 7.9, 1.5 Hz, arom); ^{13}C NMR ($CDCl_3$) δ 29.5 (CH_2), 55.8 (CH), 68.1 (CH), 81.7 (C), 119.7, 120.5, 121.1, 123.0, 123.3, 124.8, 125.8, 127.4, 127.8, 127.9, 128.35, 128.41, 129.0, 129.1, 130.2, 136.4, 136.8, 137.9, 150.6, 154.2; IR ($CHCl_3$, cm^{-1}) ν 3072, 2840, 1604, 1500, 1452, 1316, 1140. Anal. Calcd for $C_{28}H_{22}N_2O$: C 83.56, H 5.51, N 6.96. Found: C 83.76, H 5.62, N 6.92. Crystal data:. $C_{28}H_{22}N_2O\cdot CH_3O$, M = 434.52, monoclinic, a = 12.4719(7), b = 11.9181(9), c = 15.2769(10) Å, β = 94.271(7)°, U = 2264.5(3) Å^3, T = 173(2) K, space group $P2_1/n$ (No. 14), Z = 4, 16666 reflections measured, 4405 unique (R_{int} = 0.048) which were used in all calculations, 2316 observed reflections [$I > 2\sigma(I)$]. The final $R1$ (obs data) was 0.0336. The final $wR(F^2)$ was 0.0748 (all data)

(1a*RS*,1b*SR*,12*RS*)-1a,12-Diphenyl-1a,1b-dihydro-1*H*-azireno-[1′,2′:3,4]imidazo[1,5-*d*]dibenzo[*b*,*f*][1,4]oxazepine, *trans*-5a. White solid; 153−154 °C (hexane; needles), 191−192 °C (MeOH, cubes)); yield 39−44%; ^{1}H NMR ($CDCl_3$) δ 2.10 s (1H, CH_2), 2.56 s (1H, CH_2), 5.71 s (1H, CH), 5.96 s (1H, CH), 6.28 dd (1H, J = 7.9, 1.5 Hz, arom), 6.70−6.82 m (2H, arom), 7.08−7.14 m (1H, arom), 7.19 dd (1H, J = 7.9, 1.5 Hz, arom), 7.28−7.48 m (13H, arom); ^{13}C NMR ($CDCl_3$) δ 34.9 (CH_2), 51.6 (CH), 64.4 (CH), 83.9 (C), 118.4, 120.70, 120.72, 121.3, 123.66, 123.71, 126.9, 127.3, 127.4, 127.6, 128.4, 128.5, 128.7, 129.3, 130.7, 137.81, 137.84, 138.7, 145.6, 156.7; IR ($CHCl_3$, cm^{-1}) ν 3068, 2856, 1604, 1496, 1454, 1304, 1136. Anal. Calcd for $C_{28}H_{22}N_2O$: C 83.56, H 5.51, N 6.96. Found: C 83.68, H 5.71, N 6.84. Crystal data: $C_{28}H_{22}N_2O$, M = 402.48, monoclinic, a = 8.6754(6), b = 18.9368(12), c = 12.4873(9) Å, β = 98.820(8)°, U = 2027.2(2) Å^3, T = 173(2) K, space group $P2_1/n$ (No. 14), Z = 4, 15979 reflections measured, 3881 unique (R_{int} = 0.039) which were used in all calculations, 2355 observed reflections [$I > 2\sigma(I)$]. The final $R1$ (obs data) was 0.0598. The final $wR(F^2)$ was 0.0650 (all data).

(2a*RS*,13*SR*,13a*RS*)-13a-(4-Nitrophenyl)-13-phenyl-13,13a-dihydro-1*H*,2a*H*-azireno[1′,2′:3,4]imidazo[1,2-*d*]dibenzo[*b*,*f*]-[1,4]oxazepine, *trans*-4b. Yelowish solid; mp 227−229 °C (MeOH); yield 34%; ^{1}H NMR ($CDCl_3$) δ 1.78 s (1H, CH_2), 2.89 s (1H, CH_2), 4.98 s (1H, CH), 5.47 s (1H, CH), 6.77−6.80 m (1H, arom), 6.92−6.95

m (2H, arom), 7.16−7.39 m (9 H, arom), 7.49 d (2H, J = 8.7 Hz, arom), 7.85 dd (1H, J = 7.9, 1.5 Hz, arom), 8.22 d (2H, J = 8.7 Hz, arom); ^{13}C NMR ($CDCl_3$) δ 30.0 (CH_2), 54.9 (CH), 67.6 (CH), 81.6 (C), 119.8, 120.7, 121.2, 123.2, 123.5, 123.7, 124.9, 125.2, 127.6, 128.4, 128.8, 129.3, 129.9, 130.2, 135.7, 136.3, 145.6, 147.6, 150.9, 154.2; IR ($CHCl_3$, cm^{-1}) ν 3068, 3032, 2980, 1604, 1500, 1488, 1448, 1350, 1316, 1272, 1140, 1108. Anal. Calcd for $C_{28}H_{21}N_3O_3$: C 75.15, H 4.73, N 9.39. Found: C 75.25, H 4.80, N 9.30.

(1a*RS*,1b*SR*,12*RS*)-1a-(4-Nitrophenyl)-12-phenyl-1a,1b-dihydro-1*H*-azireno[1′,2′:3,4]imidazo[1,5-*d*]dibenzo[*b*,*f*][1,4]-oxazepine, *trans*-5b. ^{1}H NMR ($CDCl_3$) (from isomer mixture with *trans*-**4b**) δ 2.09 s (1H, CH_2), 2.67 s (1H, CH_2), 5.69 s (1H, CH), 5.99 s (1H, CH), 6.27 dd (1H, J = 7.9, 1.5 Hz, arom), 6.69−6.83 m (2H, arom), 7.13−7.50 m (8H, arom), 7.88 d (2H, J = 8.7 Hz, arom), 8.19 d (2H, J = 8.7 Hz, arom), 8.35 d (2H, J = 8.7 Hz, arom).

(2a*RS*,13*SR*,13a*RS*)-13a-(4-Methylphenyl)-13-phenyl-13,13a-dihydro-1*H*,2a*H*-azireno[1′,2′:3,4]imidazo[1,2-*d*]dibenzo[*b*,*f*]-[1,4]oxazepine, *trans*-4c. White solid; mp 176−177 °C (MeOH); yield 46%; ^{1}H NMR ($CDCl_3$) δ 1.82 s (1H, CH_2), 2.41 s (3H, CH_3), 2.71 s (1H, CH_2), 5.04 s (1H, CH), 5.53 s (1H, CH), 6.78−6.81 m (1H, arom), 6.91−6.94 m (2H, arom), 7.14−7.49 m (13H, arom), 7.90 dd (1H, J = 7.9, 1.5 Hz, arom); ^{13}C NMR ($CDCl_3$) δ 21.2 (CH_3), 29.5 (CH_2), 55.5 (CH), 68.1 (CH), 81.7 (C), 119.6, 120.4, 121.1, 122.9, 123.2, 124.8, 125.9, 127.4, 127.7, 128.4, 128.92, 128.98, 129.0, 130.2, 134.9, 136.5, 136.9, 137.6, 150.6, 154.2; IR ($CHCl_3$, cm^{-1}) ν 3068, 2832, 1602, 1500, 1450, 1308, 1272, 1136, 1042. Anal. Calcd for $C_{29}H_{24}N_2O$: C 83.63, H 5.81, N 6.73. Found: C 83.86, H 5.97, N 6.67.

(1a*RS*,1b*SR*,12*RS*)-1a-(4-Methylphenyl)-12-phenyl-1a,1b-dihydro-1*H*-azireno[1′,2′:3,4]imidazo[1,5-*d*]dibenzo[*b*,*f*][1,4]-oxazepine, *trans*-5c. White solid; mp 195−196 °C (MeOH); yield 50%; ^{1}H NMR ($CDCl_3$) δ 2.09 s (1H, CH_2), 2.36 s (3H, CH_3), 2.55 s (1H, CH_2), 5.71 s (1H, CH), 5.95 s (1H, CH), 6.30 dd (1H, J = 7.9, 1.5 Hz, arom), 6.71−6.83 m (2H, arom), 7.08−7.48 m (14H, arom); ^{13}C NMR ($CDCl_3$) δ 21.1 (CH_3), 34.6 (CH_2), 51.5 (CH), 64.4 (CH), 83.8 (C), 118.4, 120.7, 121.2, 123.6, 123.7, 126.8, 127.2, 127.5, 128.3, 128.6, 129.2, 129.3, 130.6, 135.6, 137.3, 137.8, 137.9, 145.7, 156.7; IR ($CHCl_3$, cm^{-1}) ν 3064, 2860, 1602, 1520, 1498, 1304, 1272, 1136, 1026. Anal. Calcd for $C_{29}H_{24}N_2O$: C 83.63, H 5.81, N 6.73. Found: C 83.64, H 5.82, N 6.60.

(2a*RS*,13*SR*,13a*RS*)-13a-(4-Methoxyphenyl)-13-phenyl-13,13a-dihydro-1*H*,2a*H*-azireno[1′,2′:3,4]imidazo[1,2-*d*]dibenzo[*b*,*f*]-[1,4]oxazepine, *trans*-4d. White solid; mp 178−179 °C (MeOH); yield 38%; ^{1}H NMR ($CDCl_3$) δ 1.79 s (1H, CH_2), 2.67 s (1H, CH_2), 3.85 s (3H, CH_3), 4.99 s (1H, CH), 5.51 s (1H, CH), 6.78 dd (1H, J = 7.9, 1.5 Hz, arom), 6.88−6.93 m (4H, arom), 7.12−7.37 m (11H, arom), 7.87 dd (1H, J = 7.9, 1.5 Hz, arom); ^{13}C NMR ($CDCl_3$) δ 31.6 (CH_2), 55.27 (CH_3), 55.29 (CH), 68.2 (CH), 81.7 (C), 113.8, 119.6, 120.5, 121.1, 123.0, 123.3, 124.8, 125.9, 127.4, 127.7, 128.4, 128.9, 130.0, 130.2, 130.3, 136.5, 136.9, 150.6, 154.2, 159.3; IR ($CHCl_3$, cm^{-1}) ν 3068, 2964, 2838, 1612, 1500, 1482, 1300, 1240, 1108. Anal. Calcd for $C_{29}H_{24}N_2O_2$: C 80.53, H 5.59, N 6.48. Found: 80.55, H 5.54, N 6.44.

(1a*RS*,1b*SR*,12*RS*)-1a-(4-Methoxyphenyl)-12-phenyl-1a,1b-dihydro-1*H*-azireno[1′,2′:3,4]imidazo[1,5-*d*]dibenzo[*b*,*f*][1,4]-oxazepine, *trans*-5d. 173−174 °C (ether-hexane) yield 49%; ^{1}H NMR ($CDCl_3$) δ 2.06 s (1H, CH_2), 2.52 s (1H, CH_2), 3.81 s (3H, CH_3), 5.70 s (1H, CH), 5.89 s (1H, CH), 6.30 dd (1H, J = 7.9, 1.5 Hz, arom), 6.70−6.82 m (2H, arom), 6.87−6.97 m (3H, arom), 7.05−7.12 m (2H, arom), 7.17−7.20 m (2H, arom), 7.30−7.48 m (7H, arom). ^{13}C NMR ($CDCl_3$) δ 29.7, 51.5, 55.3, 64.6, 83.8, 114.0, 114.5, 118.5, 120.7, 120.8, 121.3, 123.6, 123.7, 127.3, 127.5, 128.0, 128.2, 128.3, 128.6, 129.3, 130.5, 130.7, 137.8, 137.9, 145.8, 156.7, 159.1; HRMS-ESI calcd for $C_{29}H_{25}N_2O_2^+$ $[M + H]^+$, 433.1911, found 433.1917.

(2a*RS*,13*SR*,13a*RS*)-13,13a-Di(2-bromophenyl)-13,13a-dihydro-1*H*,2a*H*-azireno[1′,2′:3,4]imidazo[1,2-*d*]dibenzo[*b*,*f*]-[1,4]oxazepine, *trans*-4e. White solid; mp 207−209 °C (MeOH); yield 29%; ^{1}H NMR ($CDCl_3$) δ 1.88 s (1H, CH_2), 2.84 s (1H, CH_2), 5.79 s (2H, br, CH), 6.79 dd (1H, 7.9, 1.5, arom), 6.92−7.42 m (12H, arom), 7.54−7.62 m (2H, arom), 7.87 dd (1H, J = 7.9, 1.5 Hz, arom); ^{13}C NMR ($CDCl_3$) δ 30.0 (br), 81.1(br), 119.6, 120.5, 121.1, 123.0, 123.6, 124.4, 125.1, 125.4, 127.4, 128.0, 129.0, 129.3, 129.8, 130.3, 132.5, 132.8, 136.5, 150.7, 154.2; IR ($CHCl_3$, cm^{-1}) ν 3072, 3000, 1604, 1500, 1488, 1448, 1318, 1300, 1140, 1076. Anal. Calcd for $C_{28}H_{20}Br_2N_2O$: C 60.02, H 3.60, N 5.00. Found: C 59.66, H 3.73, N 4.70.

(1a*RS*,1b*SR*,12*RS*)-1a,12-Di(2-bromophenyl)-1a,1b-dihydro-1*H*-azireno[1′,2′:3,4]imidazo[1,5-*d*]dibenzo[*b*,*f*][1,4]oxazepine, *trans*-5e. White solid; mp 257−258 °C (MeOH); yield 33%; ^{1}H NMR ($CDCl_3$) δ 2.05 s (1H, CH_2), 2.72 s (1H, CH_2), 5.73 s (1H, CH), 6.48−6.52 m (1H, arom), 6.55 s (1H, CH), 6.86−6.89 m (2H, arom), 7.00−7.06 m (1H, arom), 7.18−7.41 m (10H, arom), 7.65−7.71 m (2H, arom); ^{13}C NMR ($CDCl_3$) δ 30.1 (CH_2), 54.5 (CH), 64.3 (CH), 80.3 (C), 119.3, 121.1, 121.4, 122.4, 123.3, 124.4, 124.6, 125.3, 127.2, 127.6, 127.8, 128.3, 128.8, 128.9, 129.8, 129.9, 133.1, 133.2, 133.9, 135.8, 137.1, 137.4, 148.9, 155.7; IR ($CHCl_3$, cm^{-1}) ν 3068, 2968, 1604, 1500, 1492, 1448, 1336, 1318, 1302, 1272, 1142, 1040, 1026. Anal. Calcd for $C_{28}H_{20}Br_2N_2O$: C 60.02, H 3.60, N 5.00. Found: C 59.63, H 3.85, N 4.91.

(2a*RS*,13*SR*,13a*RS*)-13,13a-Diphenyl-2a,7,13,13a-tetrahydro-1*H*-azireno[1′,2′:3,4]imidazo[1,2-*a*]dibenzo[*c*,*f*]azepine, *trans*-4f. White solid; mp 86−88 °C (hexane); yield 52%; ^{1}H NMR ($CDCl_3$) δ 1.74 s (1H, CH_2), 3.02 s (1H, CH_2), 3.60 d (1H, J = 13.0 Hz, CH_2), 4.98 d (1H, J = 13.0 Hz, CH_2), 5.05 s (1H, CH), 5.42 s (1H, CH), 6.89−6.94 m (2H, arom), 7.03−7.35 m (15H, arom), 7.82 dd (1H, J = 7.9, 1.5 Hz, arom); ^{13}C NMR ($CDCl_3$) δ 28.7 (CH_2), 40.2 (CH_2), 54.3 (CH), 68.1 (CH), 83.9 (C), 119.6, 123.5, 126.5, 126.8, 127.3, 127.66, 127.69, 127.7, 127.8, 128.2, 128.3, 128.3, 129.0, 129.3, 130.6, 135.4, 136.5, 136.8, 137.1; IR ($CHCl_3$, cm^{-1}) ν 3064, 3004, 2992, 1602, 1500, 1494, 1448, 1344, 1310, 1272, 1136, 1028. Anal. Calcd for $C_{29}H_{24}N_2$: C 86.97, H 6.04, N 6.99. Found: C 87.15, H 6.21, N 6.82.

(2a*RS*,13*SR*,13a*SR*)-13,13a-Diphenyl-2a,7,13,13a-tetrahydro-1*H*-azireno[1′,2′:3,4]imidazo[1,2-*a*]dibenzo[*c*,*f*]azepine, *cis*-4f. Colorless oil; yield 21%; ^{1}H NMR ($CDCl_3$) δ 2.31 s (1H, CH_2), 2.48 s (1H, CH_2), 3.61 d (1H, J = 13.0 Hz, CH_2), 5.14 d (1H, J = 13.0 Hz, CH_2), 5.59 s (1H, CH), 6.28 dd (1H, J = 7.9, 1.5 Hz, arom), 6.51 s (1H, CH), 6.51−6.58 m (3H, arom), 6.78−6.88 m (4H, arom), 7.06−7.48 m (9H, arom), 8.10 dd (1H, J = 7.9, 1.5 Hz, arom); ^{13}C NMR ($CDCl_3$) δ 39.6 (CH_2), 41.1 (CH_2), 56.7 (CH), 67.1 (CH), 81.0 (C), 115.5, 117.0, 119.6, 121.4, 123.5, 126.7, 127.0, 127.2, 127.6, 127.6, 127.7, 128.2, 128.4, 128.4, 129.2, 130.7, 131.1, 136.8, 137.6, 138.3, 140.2, 143.3; IR ($CHCl_3$, cm^{-1}) ν 3068, 3008, 2956, 1596, 1492, 1450, 1344, 1328, 1292, 1152, 1028; HRMS-ESI calcd for $C_{29}H_{25}N_2^+$ $[M + H]^+$, 401.2012, found 401.2028.

Synthesis of Compounds 6 by Reaction of Compounds *trans*-4a,e,f with AIBN. As a representative example, the synthesis of 10a-Phenyl-11,15b-dihydro-10a*H*-dibenzo[*b*,*f*]indeno[2′,1′:4,5]imidazo-[1,2-*d*][1,4]oxazepine **6b** is described here. A degassed solution of aziridine *trans*-**4a** (0.050 g, 0.124 mmol) and AIBN (0. 041 g, 0. 248 mmol) in toluene (2 mL) was heated under Ar at 100 °C for 1 h. The reaction mixture was cooled and AIBN (0.020 g, 0.122 mmol) was added and the mixture was additionally heated under Ar at 100 °C for 2 h. The solvent was removed in vacuum and the residue was purified by flash chromatography on silica (eluent hexane-ethyl acetate, 20:1) to give compound **6b** (37 mg, 74%).

(10a*RS*,15b*RS*)-15-Bromo-10a-(2-bromophenyl)-11,15b-dihydro-10a*H*-dibenzo[*b*,*f*]indeno[2′,1′:4,5]imidazo[1,2-*d*][1,4]-oxazepine, 6a. White solid; mp 157−258 °C (MeOH); ^{1}H NMR ($CDCl_3$) δ 3.85 d (1H, J = 17.1 Hz, CH_2), 4.12 d (1H, J = 17.1 Hz, CH_2), 6.51 s (1H, CH), 6.97−7.49 m (12H, arom), 7.69 dd (1H, J = 7.9, 1.5 Hz, arom), 8.00 dd (1H, J = 7.9, 1.5 Hz, arom), 8.40 dd (1H, J = 7.9, 1.5 Hz, arom); ^{13}C NMR ($CDCl_3$) δ 46.8 (CH_2), 75.3 (CH), 78.7 (C), 120.0, 120.9, 121.0, 121.2, 121.4, 121.6, 123.9, 124.4, 124.9, 125.3, 127.4,

128.9, 129.8, 130.3, 131.39, 131.43, 133.4, 134.3, 135.2, 141.2, 143.5, 145.0, 152.1, 157.1, 158.9; IR ($CHCl_3$, cm^{-1}) ν 3068, 2996, 1604, 1500, 1462, 1452, 1300, 1268, 1220, 1126, 1112; HRMS-ESI calcd for $C_{28}H_{19}Br_2N_2O^+$ $[M + H]^+$, 556.9859, found 556.9855. Crystal data: $C_{28}H_{18}Br_2N_2O$, M = 558.26, monoclinic, a = 13.3684(6), b = 15.8505(8), c = 32.3270(19) Å, β = 90.052(4)°, U = 6850.0(6) Å^3, T = 173(2) K, space group P 2$_1$/c (no. 14), Z = 12, 56776 reflections measured, 12892 unique (R_{int} = 0.209) which were used in all calculations, 5934 observed reflections [I > 2σ(I)]. The final R1 (obs data) was 0.0804.The final $wR(F^2)$ was 0.2016 (all data).

(10a*RS*,15b*RS*)-10a-Phenyl-11,15b-dihydro-10a*H*-dibenzo-[*b*,*f*]indeno[2′,1′:4,5]imidazo[1,2-*d*][1,4]oxazepine, 6b. White solid; mp 129−130 °C (MeOH); ^{1}H NMR ($CDCl_3$) δ 3.80 d (1H, J = 17.6 Hz, CH_2), 3.86 d (1H, J = 17.6 Hz, CH_2), 5.98 s (1H, CH), 7.02−7.07 m (1H, arom), 7.12−7.48 m (13H, arom), 7.59−7.61 m (2H, arom), 8.17 dd (1H, J = 7.9, 1.5 Hz, arom); ^{13}C NMR ($CDCl_3$) δ 50.1 (CH_2), 77.0 (C), 79.7 (CH), 119.9, 120.7, 122.3, 122.7, 123.9, 124.8, 125.0, 125.2, 125.6, 126.9, 127.0, 128.6, 129.1, 131.4, 132.8, 132.9, 140.4, 142.8, 148.0, 151.3, 156.4, 158.3; IR ($CHCl_3$, cm^{-1}) ν 3072, 2948, 1604, 1500, 1486, 1464, 139, 1300, 1140, 1078; HRMS-ESI calcd for $C_{28}H_{21}N_2O^+$ $[M + H]^+$, 401.1648, found 401.1657. Anal. Calcd for $C_{28}H_{20}N_2O$: C 83.98, H 5.03, N 7.00. Found: C 83.73, H 5.05, N 6.94. Crystal data: $C_{28}H_{20}N_2O$, M = 400.48, triclinic, a = 8.7677(6), b = 9.8535(8), c = 13.3542(11) Å, α = 94.163(7), β = 100.662(6), γ = 103.469(6)°, U = 1094.49(15) Å^3, T = 173(2) K, space group P-1 (No. 2), Z = 2, 9419 reflections measured, 4066 unique (R_{int} = 0.065) which were used in all calculations. The final $wR(F^2)$ was 0.1062 (all data).

(10a*RS*,15b*RS*)-10a-Phenyl-5,10a,11,15b-tetrahydrodibenzo-[*c*,*f*]indeno[2′,1′:4,5]imidazo[1,2-*a*]azepine, 6c. White solid; mp 117−118 °C (MeOH); ^{1}H NMR ($CDCl_3$) δ 3.43 d (1H, J = 12.7 Hz, CH_2), 3.83 s (2H, CH_2), 3.95 d (1H, J = 12.7 Hz, CH_2), 6.99−7.46 m (15H, arom), 7.65 d (2H, J = 7.5 Hz, arom), 8.05 dd (1H, J = 7.9, 1.5 Hz, arom); ^{13}C NMR ($CDCl_3$) δ 39.2 (CH_2), 49.8 (CH_2), 77.7 (CH), 79.1 (C), 120.7, 124.1, 124.3, 125.2, 125.3, 126.8, 126.97, 126.99, 127.3, 128.6, 128.7, 128.8, 130.6, 131.3, 135.2, 138.2, 140.8, 141.3, 142.6, 147.9, 158.8; IR ($CHCl_3$, cm^{-1}) ν 3064, 2998, 1604, 1500, 1492, 1388, 1302, 1274, 1136, 1042; HRMS-ESI calcd for $C_{29}H_{23}N_2^+$ $[M + H]^+$, 399.1856, found 399.1861. Crystal data: $C_{29}H_{22}N_2 \cdot 0.9CH_3OH.0.25(H_2O)$, M = 430.54, triclinic, a = 9.0496(9), b = 10.2588(11), c = 13.4558(14) Å, α = 91.748(8), β = 97.676(8), γ = 107.654(8)°, U = 1176.4(2) Å^3, T = 173(2) K, space group P-1 (No. 2), Z = 2, 10922 reflections measured, 4142 unique (R_{int} = 0.109) which were used in all calculations, 2968 observed reflections [$I > 2\sigma(I)$]. The final R1 (obs data) was 0.078, $R(F^2)$ was 0.1861 (all data).

Reaction of Compound *trans*-4a with DTBP. A solution of aziridine *trans*-**4a** (0.020 g, 0.0497 mmol) and DTBP (0.010 g, 0.0684 mmol) in toluene (1 mL) was refluxed in dark for 3 h. The reaction mixture was cooled, DTBP (0.020 g, 0.137 mmol) was added, and the mixture was additionally refluxed for 4 h. The solvent was removed in vacuum, and the residue was purified by flash chromatography on silica (eluent hexane/ethyl acetate, 20:1) to give compound **6b** (13 mg, 67%) and **19** (4 mg, 19%).

((2*RS*,3*RS*)-2,3-Diphenyl-2,3-dihydrodibenzo[*b*,*f*]imidazo-[1,2-*d*][1,4]oxazepin-2-yl)methanol, 19. White solid; mp 95−96 °C (MeOH); ^{1}H NMR ($CDCl_3$) δ 2.49 br s (1H, OH), 3.59 d (1H, J = 11.3 Hz, CH_2), 3.67 d (1H, J = 11.3 Hz, CH_2), 5.59 s (1H, CH), 6.61 dd (1H, J = 7.9, 1.5 Hz, arom), 6.82−6.93 m (2H, arom), 7.23−7.64 m (14H, arom), 8.27 dd (1H, J = 7.9, 1.5 Hz, arom); ^{13}C NMR ($CDCl_3$) δ 67.0 (CH_2), 75.1 (CH), 76.2 (C), 119.1, 120,8, 121.6, 122.4, 123.8, 125.3, 125.4, 126.2, 127.3, 128.2, 128.59, 128.60, 128.8, 131.6, 132.3, 133.4, 134.6, 145.9, 150.8, 158.5, 159.1; IR ($CHCl_3$, cm^{-1}) ν 3576, 3064, 2988, 2964, 1604, 1500, 1464, 1384, 1240, 1160, 1112, 1092; HRMS-ESI calcd for $C_{28}H_{23}N_2O_2^+$ $[M + H]^+$, 419.1754, found 419.1754.

Reaction of Compound *trans*-4a with TBHP. A solution of aziridine *trans*-**4a** (0.050 g, 0.124 mmol) and TBHP (0.012 g, 0.133 mmol) in benzene (2 mL) was heated at 60 °C with stirring for 3 h. The solvent was removed in vacuum, and the residue was purified by flash chromatography on silica (eluent hexane-ethyl acetate, 20:1) to give compounds **6b** (8 mg, 17%), **18** (29 mg, 53%), and **19** (3 mg, 5%).

(2*RS*,3*RS*)-2-(Hydroperoxymethyl)-2,3-diphenyl-2,3-dihydrodibenzo[*b*,*f*]imidazo[1,2-*d*][1,4]oxazepine, 18. White solid; mp 122−125 °C (dec) (MeOH); ^{1}H NMR ($CDCl_3$) δ 4.07 d (1H, J = 13.8 Hz, CH_2), 4.20 d (1H, J = 13.8 Hz, CH_2), 5.69 s (1H, CH), 6.69 dd (1H, J = 7.9, 1.5 Hz, arom), 6.86−6.97 m (2H, arom), 7.24−7.63 m (15H, arom), 8.25 dd (1H, J = 7.9, 1.5 Hz, arom); ^{13}C NMR ($CDCl_3$) δ 75.6 (CH), 76.3 (C), 81.1 (CH_2), 119.5, 120,96, 121.8, 124.5, 125.4, 125.6, 125.9, 127.5, 128.6, 128.87, 128.92, 128.97, 128.99, 129.0, 131.6, 131.8, 133.9, 134.3, 145.9, 151.0, 158.6, 159.2; IR ($CHCl_3$, cm^{-1}) ν 3044, 2968, 1602, 1500, 1464, 1384, 1240, 1152, 1112, 1100. Anal. Calcd for $C_{28}H_{22}N_2O_3$: C 77.40, H 5.10, N 6.45. Found: C 77.68, H 5.38, N 6.44. Crystal data: $C_{28}H_{22}N_2O_3$, M = 434.48, triclinic, a = 9.0578(7), b = 10.9639(11), c = 12.370(1) Å, α = 100.617(8), β = 92.289(6), γ = 113.747(6)°, U = 1096.26(16) Å^3, T = 173(2) K, space group P-1 (No. 2), Z = 2, 13971 reflections measured, 4118 unique (R_{int} = 0.035) which were used in all calculations. The final $wR(F^2)$ was 0.0893 (all data).

Reaction of Compound *trans*-4a with Oxygen from Air under UV Irradiation. A solution of aziridine *trans*-**4a** (0.050 g, 0.124 mmol) in acetonitrile (3 mL) was irradiated with UV light (a medium-pressure mercury lamp) in Pyrex flask at 20−25 °C with stirring and slow bubbling of air for 3 h. The solvent was removed in vacuum, and the residue was purified by flash chromatography on silica (eluent hexane/ethyl acetate, 20:1) to give compounds **6b** (8 mg, 5%), **18** (29 mg, 67%), and **19** (3 mg, 25%).

Reaction of Compound *trans*-4a with Mn(OAc)$_3$. (a) A mixture of aziridine *trans*-**4a** (0.050 g, 0.124 mmol) and $Mn(OAc)_3$ (0.058 g, 0.249 mmol) in toluene (2 mL) was refluxed for 16 h. The solvent was removed in vacuum, and the residue was purified by flash chromatography on silica (eluent hexane/ethyl acetate, 20:1) to give compound **6b** (15 mg, 31%) and **19** (27 mg, 53%).

(b) A mixture of aziridine *trans*-**4a** (0.050 g, 0.124 mmol) and $Mn(OAc)_3$ (0.058 g, 0.249 mmol) in AcOH (2 mL) was heated for 0.5 h at 50 °C. The reaction mixture was cooled, poured into water (10 mL), and extracted with CH_2Cl_2. The extract was dried over Na_2SO_4, the solvent was removed in vacuum, and the residue was purified by flash chromatography on silica (eluent hexane/ethyl acetate, 20:1) to give compound **6b** (6 mg, 13%) and **19** (35 mg, 68%).

Computational Details. All calculations were performed with the B3LYP density functional method[19] by using the Gaussian suite of quantum chemical programs. Geometry optimizations of intermediates, transition states, reactants, and products in the gas phase were performed at the RB3LYP/6-31G(d) or UB3LYP/6-31G(d) level using Gaussian 03.[20] Stationary points on the respective potential-energy surfaces were characterized at the same level of theory by evaluating the corresponding Hessian indices. Careful verification of the unique imaginary frequencies for transition states was carried out to check whether the frequency indeed pertains to the desired reaction coordinate. Intrinsic reaction coordinates (IRC) were calculated to authenticate all transition states.[21]

■ ASSOCIATED CONTENT

Supporting Information. ^{1}H and ^{13}C NMR spectra for all new compounds, 2D ^{1}H-NOESY spectra for compounds *trans*-**5e**, *trans*- and *cis*-**4f**, and crystallographic data for compounds *trans*-**4a**, *trans*-**5a**, **6a**−**c**, **18** (CIF format). Figures with ball and stick representation of the calculated molecules.

Computation details: energies of the reactants, transition states, their Cartesian coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

(1) Walther, G.; Daniel, H.; Bechtel, W. D.; Brandt, K. *Arzneim.-Forsch.* **1990**, *40*, 440.

(2) Walther, G.; Schneider, C.; Weber, K. H.; Fuegner, A. DE 3134672; *Chem. Abstr.* **1983**, *98*, 198233.

(3) Van der Burg, W. J. DE 2248477; *Chem. Abstr.* **1973**, *79*, 5339.

(4) Walther, G.; Schneider, C. S.; Weber, K. H.; Fuegner, A. DE 3008944; *Chem. Abstr.* **1982**, *96*, 6777.

(5) (a) Khlebnikov, A. F.; Novikov, M. S.; Kostikov, R. R. *Russ. Chem. Rev.* **2005**, *74*, 171. (b) Khlebnikov, A. F.; Novikov, M. S.; Kostikov, R. R.; Kopf, J. *Russ. J. Org. Chem.* **2005**, *41*, 1341. (c) Voznyi, I. V.; Novikov, M. S.; Khlebnikov, A. F. *Synlett* **2005**, 1006. (d) Konev, A. S.; Novikov, M. S.; Khlebnikov, A. F. *Tetrahedron Lett.* **2005**, *46*, 8337. (e) Khlebnikov, A. F.; Novikov, M. S.; Amer, A. A.; Kostikov, R. R.; Magull, J.; Vidovic, D. *Russ. J. Org. Chem.* **2006**, *42*, 515. (f) Voznyi, I. V.; Novikov, M. S.; Khlebnikov, A. F.; Kostikov, R. R. *Russ. J. Org. Chem.* **2006**, *42*, 689. (g) Novikov, M. S.; Amer, A. A.; Khlebnikov, A. F. *Tetrahedron Lett.* **2006**, *47*, 639. (i) Shinkevich, E. Yu.; Novikov, M. S.; Khlebnikov, A. F. *Synthesis* **2007**, *2*, 225. (j) Konev, A. S.; Novikov, M. S.; Khlebnikov, A. F. *Russ. J. Org. Chem.* **2007**, *43*, 286. (k) Kadina, A. P.; Novikov, M. S.; Khlebnikov, A. F.; Magull, J. *Chem. Heterocycl. Compd.* **2008**, *44*, 576. (l) Khlebnikov, A. F.; Novikov, M. S.; Dolgikh, S. A.; Magull, J. *ARKIVOC* **2008**, 94. (m) Konev, A. S.; Khlebnikov, A. F. *Collect. Czech. Chem. Commun.* **2008**, 1553. (n) Shinkevich, E. Yu.; Abbaspour Tehrani, K.; Khlebnikov, A. F.; Novikov, M. S. *Tetrahedron* **2008**, *64*, 7524. (o) Khistiaev, K. A.; Novikov, M. S.; Khlebnikov, A. F.; Magull *Tetrahedron Lett.* **2008**, *49*, 1237. (p) Khlebnikov, V. A.; Novikov, M. S.; Khlebnikov, A. F.; Rostovskii, N. V. *Tetrahedron Lett.* **2009**, *50*, 6509. (q) Khlebnikov, A. F.; Novikov, M. S. *Russ. J. Gen. Chem.* **2010**, *80*, 1652. (r) Kobylianskii, I. J.; Novikov, M. S.; Khlebnikov, A. F. *J. Fluor. Chem.* **2011**, *132*, 175.

(6) (a) Khlebnikov, A. F.; Novikov, M. S.; Petrovskii, P. P.; Magull, J.; Ringe, A. *Org. Lett.* **2009**, *11*, 979. (b) Khlebnikov, A. F.; Novikov, M. S.; Petrovskii, P. P.; Konev, A. S.; Yufit, D. S.; Selivanov, S. I.; Frauendorf, H. *J. Org. Chem.* **2010**, *75*, 5211. (c) Khlebnikov, A. F.; Novikov, M. S.; Golovkina, M. V.; Petrovskii, P. P.; Konev, A. S.; Yufit, D. S.; Stoeckli-Evans, H. *Org. Biomol. Chem.* **2011**, *9*, 3886.

(7) (a) Bende, Z.; Simon, K.; Tóth, G.; Töke, L.; Weber, L. *Liebigs Ann. Chem.* **1982**, 924. (b) Bende, Z.; Bitter, I.; Töke, L.; Weber, L.; Tóth, G.; Janke, F. *Liebigs Ann. Chem.* **1982**, 2146. (c) Bartnik, R.; Mloston, G. *Tetrahedron* **1984**, *40*, 2569. (d) Khlebnikov, A. F.; Novikov, M. S.; Kostikov, R. R. *Russ. J. Org. Chem.* **1990**, *26*, 1638. (e) Boruah, A.; Baruah, B.; Prajapati, D.; Sandhu, J. S.; Ghosh, A. C. *Tetrahedron Lett.* **1996**, *37*, 4203. (f) Szollösy, A.; Tischer, T.; Kadas, I.; Töke, L.; Tóth, G. *Tetrahedron* **1999**, *55*, 7279. (g) Brown, D.; Brown, G. A.; Andrews, M.; Large, J. M.; Urban, D.; Butts, C. P.; Hales, N. J.; Gallagher, T. *J. Chem. Soc., Perkin Trans. 1* **2002**, 2014. (h) Novikov, M. S.; Khlebnikov, A. F.; Egarmin, M. A.; Kopf, J.; Kostikov, R. R. *Russ. J. Org. Chem.* **2004**, *40*, 1493.

(8) (a) Matsumoto, K.; Maruyama, K. *Chem. Lett.* **1973**, 759. (b) Hickey, D. M. B.; Moody, C. J.; Rees, C. W. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1119. (c) Meth-Cohn, O.; Williams, N. J. R.; MacKinnon, A.; Howard, J. A. K. *Tetrahedron* **1998**, *54*, 9837. (d) Pinho e Melo, T. M. V. D.; Cardoso, A. L.; Gomes, C. S. B.; d'A Rocha Gonsalves, A. M. *Tetrahedron Lett.* **2003**, *44*, 6313.

(9) Tsuge, O.; Kanemasa, S. *Adv. Heterocycl. Chem.* **1989**, *45*, 231.

(10) Togo, H. *Advanced Free Radical Reactions for Organic Synthesis*; Elsevier: Amsterdam, 2004.

(11) Werry, J.; Stamm, H.; Lin, P.-Y.; Falkenstein, R.; Gries, S.; Irngartinger, H. *Tetrahedron* **1989**, *45*, 5015.

(12) Zipse, H. *Top. Curr. Chem.* **2006**, *263*, 163.

(13) *The Chemistry of Peroxides*;Rappoport, Z., Ed.; John Wiley & Sons Ltd: Chichester, 2006; Vol. 2, Pt 0.1.

(14) Demir, A. S.; Emrullahoglu, M. *Curr. Org. Synth.* **2007**, *4*, 321–351.

(15) De Klein, W. J. *Organic Syntheses by Oxidation with Metal Compounds*; Mijs, W. J., de Jonge, C. R. H. I., Eds.; Plenum Press: New York, 1986.

(16) Jones, G. P.; Cornell, B. A.; Horn, E.; Tiekink, E. R. T. *J. Crystallogr. Spectr. Res.* **1989**, *19*, 715.

(17) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.

(18) Hortmann, G.; Robertson, D. A.; Gillard, B. K. *J. Org. Chem.* **1972**, *37*, 322.

(19) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Becke, A. D. *Phys. Rev. A* **1998**, *38*, 3098. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1998**, *37*, 785.

(20) Frisch, M. J.; Trucks, G. W. Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A. Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision B.05*; Gaussian, Inc.: Pittsburgh, PA, 2003.

(21) (a) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154. (b) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.