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Stable but chimeric antiaromatic 1*H*-azirines? A threefold reinvestigation

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Dedicated to Professor Holger Butenschön on the occasion of his 60th birthday

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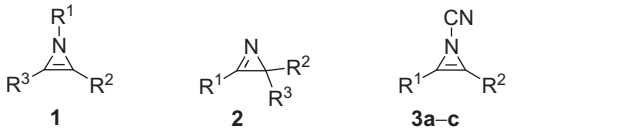
ABSTRACT

Three different reports on the syntheses of isolable 1*H*-azirines **6**, **15**, and **21** were reinvestigated. Instead of the claimed heterocyclic product **6**, the isomeric thiazole derivative **7** has been isolated now with nearly identical yield. In the case of the asserted bicyclic 1*H*-azirine **15**, the corrected structure includes the isomeric 3-aminomaleimide moiety of **18**. A mechanism to explain the formation of this substance is suggested. The isolation of the antiaromatic compound **21** has also to be rejected. Thus, 1*H*-azirines keep their classification as very elusive high-energy intermediates.

Introduction

Strained compounds are of special interest because of their increased energy content and enhanced reactivity, which frequently results from this. For 1*H*-azirines **1** and 2*H*-azirines **2**, it is obvious that both types of heterocycles include a considerable ring strain (Scheme 1). However, the properties of **1** and **2** are quite different.[1] A great number of 2*H*-azirines **2**, especially those with $R^1 \neq H$, were isolated and characterized by spectroscopic methods in solution or even by X-ray crystallographic structure determination. Although compounds of type **2** are highly reactive, the 2*H*-azirine unit has been found in a few natural products.[2] On the other hand, only six examples of short-lived 1*H*-azirines **3a–c** were photochemically generated and detected at very low temperatures by IR and UV spectroscopy.[3] Most probably, the electron-withdrawing property of the cyano group diminishes the antiaromatic character of the 1*H*-azirine structure and increases the relative stability of **3a–c**. Thus, attempts to isolate or observe the parent compound (**1** with $R^1 = R^2 = R^3 = H$) by cycloaddition[4] or cyclorevision[5] approaches and by using argon-matrix isolation technique were unsuccessful and yielded unsubstituted **2** and other isomeric species. Elusive 1*H*-azirine intermediates were merely postulated in several other reactions, which finally led to 2*H*-azirines,[6] pyrroles,[7] indoles,[8] oxazoles,[9] isoquinolines,[10] ketenimines,[11] nitriles,[12] or anilines.[13] Furthermore, many quantum chemical calculations, that analyzed the energy content,[14] the molecular geometry,[15] the nitrogen inversion barrier,[16] the basicity,[17] and the vibrational frequencies and IR intensities[18] of the parent 1*H*-azirine **1**, have been published. All experimental and theoretical results emphasize the properties of the antiaromatic heterocycles **1** as short-lived intermediates, which cannot be isolated at room temperature.

Nevertheless, three quite different studies to generate and isolate 1*H*-azirines were reported.[19–21] We have reinvestigated the corresponding reactions and present our results.



a $R^1 = R^2 = H$
b $R^1 = NPh_2$, $R^2 = P(O)Ph_2$
c R^1 = OMe, O*i*Pr, OCHMeEt, $OCHEt_2$, $R^2 = H$

Scheme 1. Structures of 1*H*-azirines and 2*H*-azirines.

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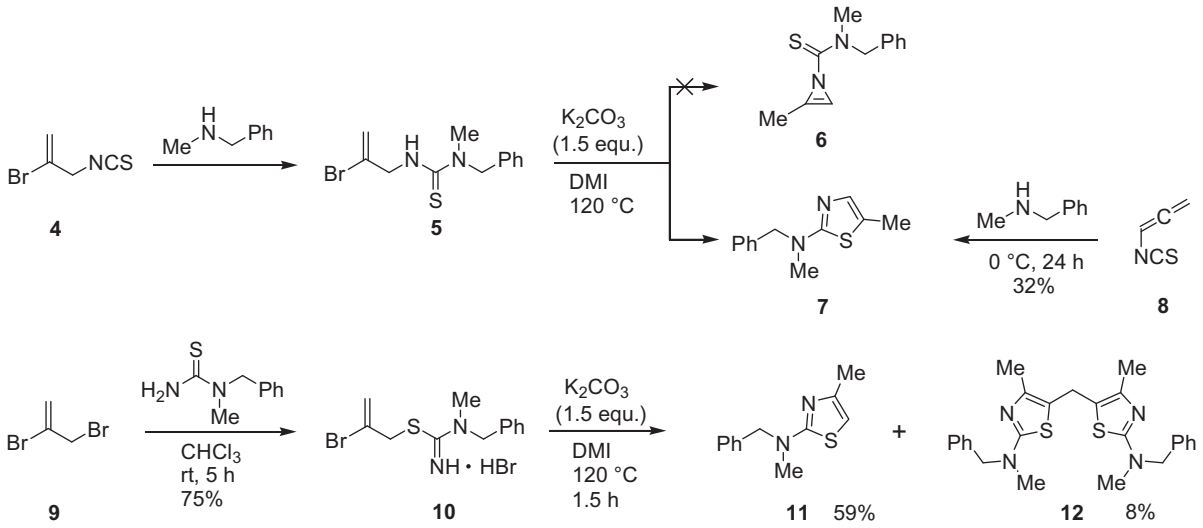


Scheme 2. Cylization products of thiourea **5** and isothiourea **10**.

Results and discussion

Recently, Narasaka and co-workers described the formation of 1*H*-azirine **6** in 28% yield, besides trace amounts of thiazole **7**, by treating thiourea **5** with potassium carbonate in 1,3-dimethyl-2-imidazolidinone (DMI) at 120 °C (Scheme 2).[19] Unfortunately, no information on the spectroscopic data or the properties of the antiaromatic heterocycle **6** was given. Moreover, hints to the synthesis of the new compound **5** are also missing completely. Thus, we subjected the known[22] isothiocyanate **4** to *N*-benzylmethylamine, which led to the desired thiourea **5** in good yield.[23] After treating **5** with potassium carbonate in DMI at 120 °C, we obtained the aromatic heterocycle **7** with 27.5% yield. But no other side products that might have a 1*H*-azirine structure like **6** were detected. The thiazole **7** could be conveniently prepared for comparison when allenyl isothiocyanate (**8**)[24] was reacted with *N*-benzylmethylamine. Alkylation of known[25] *N*-benzyl-*N*-methylthiourea with the help of dibromide **9** did not produce **5**, however, the hydrogen bromide salt of isothiourea **10** was formed instead. This outcome is not surprising because *S*-alkylation of thioureas is well known.[26] Treatment of **10** with potassium carbonate in DMI at 120 °C led to thiazoles **11** and **12**. The formation of the side product **12** might tentatively be explained by the decay of DMI and the condensation of the resulting formaldehyde with **11**.[27] For comparison, the known[28] thiazole **11** was also prepared by Hantzsch synthesis from chloroacetone and *N*-benzyl-*N*-methylthiourea in 92% yield.[23]

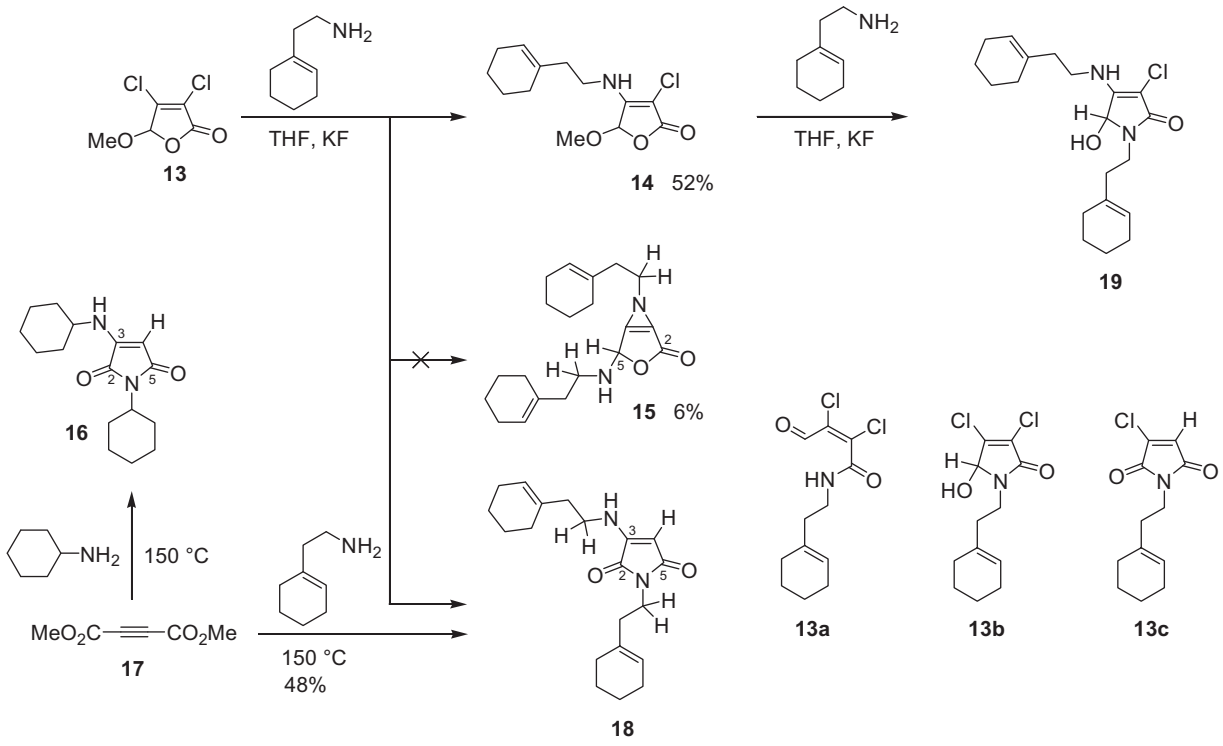
We assume that Narasaka and co-workers[19] erroneously assigned the structure of the antiaromatic compound **6** to the isomeric substance **7** (see the comparable yields) or perhaps to the thiazole **11**.

Quite recently, Chen, Wang, and coworkers reported on the reaction of the 2(5*H*)-furanone **13** with 2-(cyclohex-1-enyl)ethylamine in the presence of potassium fluoride, which afforded the simple substitution product **14** and the 1*H*-azirine **15** after separation by chromatography (Scheme 3).[20] Both products were characterized by melting points, elemental analysis, and UV, IR, MS, ^{1}H NMR, and ^{13}C NMR spectroscopic data. In the case of **15**, a mechanism was offered to explain the formation of this unique nitrogen heterocycle.

We suppose that the bicyclic structure of **15** combines unfavorable antiaromatic electronic properties with extraordinary ring strain, which significantly exceeds that of monocyclic azirines. Thus, the high energy content of the molecule should exclude the isolation of **15**.

When we repeated the reaction of **13** with 2-(cyclohex-1-enyl)ethylamine as described,[20] we obtained two substances, which indicated ^{1}H NMR and ^{13}C NMR spectroscopic data that were identical with those reported for **14** and **15**. However, some additional NMR experiments showed that the structure of **15** has to be excluded. The ^{1}H NMR spectrum of this minor product exhibits a vicinal coupling within the CH_2–NH moiety, which allows to distinguish between both CH_2–N units. But another vicinal coupling between NH and the ring proton 5-H cannot be found even when the measurement is performed in d_6-DMSO instead of $CDCl_3$. Moreover, the minor product shows three quarternary ^{13}C NMR signals at low field (δ = 172.5, 167.3, 149.0), which indicated long-range correlations to CH_2–N protons that are incompatible with the reported structure of **15**. Our HMBC experiments, optimized for $J(^{13}C,^{1}H)$ = 8 Hz, detected coupling between the protons of the CH_2–N unit and the carbon atoms with δ = 167.3 and 172.5, as well as correlation between the CH_2 protons of the CH_2–NH moiety and the carbon atom with δ = 149.0. These and other results from 2D NMR spectroscopy[23] led to the idea that the assigned structure of **15** has to be corrected by the isomeric 3-aminomaleimide structure **18**. Furthermore, we noticed that the UV and IR spectroscopic data, which were reported for **15**,[20] are similar to those published[29a] for compound **16**. The later heterocycle is easily accessible by heating the alkyne **17** with an excess of cyclohexylamine.[29] Thus, we measured the ^{13}C NMR spectrum of **16**, and especially the δ values assigned to the four carbon signals of the maleimide ring (δ = 172.8, 167.6, 147.7, 83.3) bear resemblance to the data, which were reported for the butenolide unit of **15**. Finally, we treated **17** with 2-(cyclohex-1-enyl)ethylamine to synthesize the heterocycle **18**. In every respect,[23] this compound was identical with the product claimed to possess the structure of **15**.

Subjection of halo-substituted butenolides of type **13** to amines is well known to give not only trivial mono-substitution[30] compounds, such as **14**, but also several other products,[30d,31] for example, maleic acid monoamide monoesters[32] or isomaleimides.[33] To the best of our knowledge, however, maleimides like **18** were never reported as a result of these transformations.[34] A simple mechanism to explain the genesis of **18** might include substitution of the methoxy group in **13** by the attack of the primary amine at the carbonyl group and formation of a *cis*-3-aminocarbonyl-acrolein



Scheme 3. Reaction of butenolide **13** with a primary amine.

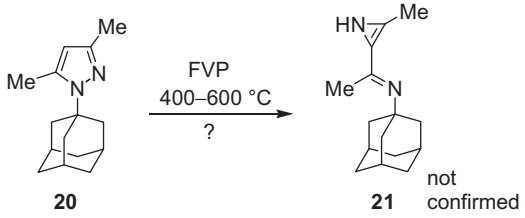
13a, which can cyclize to generate the corresponding 5-hydroxypyrrolin-2-one **13b**. Subsequent shift of the C=C bond within the five-membered ring[33] and elimination of hydrogen chloride to produce **13c** followed by the substitution of the last chlorine atom by a second molecule of the primary amine can lead to maleimide **18**.[29a] Other orders of these steps or alternative reaction mechanisms[32] are also possible.

When we treated **13** with a great excess of 2-(cyclohex-1-enyl)ethylamine (molar ratio 1:11), the yield of **14** significantly diminished, while the proportion of **18** (12%–26% isolated yield) increased and the new product **19**[23] (22%–29% yield) was also formed. Control experiments showed that **19** but no **18** is produced from pure **14** in the presence of 2-(cyclohex-1-enyl)ethylamine and potassium fluoride in THF, whereas pure **19** did not lead to **18** under the same conditions.

Elguero and co-workers described flash vacuum pyrolysis (FVP) of pyrazole derivative **20**, which was claimed to yield the exclusive product **21** at 600 °C (Scheme 4).[21] Unfortunately, no yields or properties of **21** were reported, and characterization by IR, ^{1}H NMR, and ^{13}C NMR spectroscopic data was inadequate. Thus, besides six signals at high field (δ = 13–43), only two additional low-field signals (δ = 128.0, 110.2) were found in the ^{13}C NMR spectrum.[21] This outcome is not compatible with the structure of **21**. Furthermore, a reaction mechanism via an N–N bond cleavage and intermediate generation of a (2*H*-azirin-2-yl)methyleneamine and a aminomethylene-2*H*-azirine[35] was suggested to explain the formation of 1*H*-azirine **21**.[21] However, the following question arises: Why should the stable aromatic compound **20** undergo a multistep rearrangement reaction to produce the strained and antiaromatic isomer **21**, which includes a high energy content.

When we repeated flash vacuum pyrolysis of pure 20[36] at 500–620 °C, we quantitatively obtained the starting compound.[23] Even at 700 °C, we got 84% recovery of 20 without detection of any new product. At 730 °C, we observed unchanged 20 (31%) and a similar amount of a very complicated mixture of products (39%), whereas FVP at 775 °C and also at 850 °C led to complete decay of 20 and formation of the multi-product mixture in low yield. Heating of neat 20 in sealed tubes (150–410 °C for several days) did not give any hint for the generation of 21 as well, while degradation of 20 started at 410 °C.

In summary, it has been demonstrated now that not even a single example of a stable 1H-azirine can be confirmed. In cases of the claimed structures of 6 and 15, the corresponding isomeric compounds 7 and 18 were isolated instead, whereas no antiaromatic heterocyclic product 21 and no other product could be assigned after thermolysis of the aromatic pyrazole 20. Thus, 1H-azirines keep their classification as very short lived intermediates, which can be detected only at very low temperature with the help of the noble gas matrix isolation technique.[37]



Scheme 4. Postulated isomerization of pyrazole **20.**

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.08.122.

References and notes

1. Reviews on 1*H*-azirines and 2*H*-azirines: (a) Backes, J. In *Houben-Weyl*; Klamann, D., Ed.; Thieme: Stuttgart, 1992; Vol. E16c, pp 321–369; (b) Nair, V. In *The Chemistry of Heterocyclic Compounds Small-Ring Heterocycles*; Hassner, A., Ed.; Wiley: New York, 1983; Vol. 42, pp 215–332; (c) Pearson, W. H.; Lian, B. W.; Bergmeier, S. C. In *Comprehensive Heterocyclic Chemistry II*; Padwa, A., Ed.; Pergamon: New York, 1996; Vol. 1A, pp 1–60; (d) Palacios, F.; Ochoa de Retana, A. N.; Martinez de Marigorta, E.; de Los Santos, J. M. *Eur. J. Org. Chem.* **2001**, 2401–2414; (e) Gilchrist, T. L. *Aldrichim. Acta* **2001**, *34*, 51–55; (f) Rai, K. M. L.; Hassner, A. In *Advances in Strained and Interesting Organic Molecules*; Halton, B., Ed.; Jai Press: Greenwich, 2000; Vol. 8, pp 187–257; (g) Fowler, F. W. *Adv. Heterocycl. Chem.* **1971**, *13*, 45–76; (h) Wentrup, C. *Adv. Heterocycl. Chem.* **1981**, *28*, 231–361; (i) Khlebnikov, A. F.; Novikov, M. S. *Tetrahedron* **2013**, *69*, 3363–3401; (j) Padwa, A. *Adv. Heterocycl. Chem.* **2010**, *99*, 1–31.
2. (a) Miller, T. W.; Tristram, E. W.; Wolf, F. J. *J. Antibiot.* **1971**, *24*, 48–50; (b) Molinski, T. F.; Ireland, C. M. *J. Org. Chem.* **1988**, *53*, 2103–2105; (c) Salomon, C. E.; Williams, D. H.; Faulkner, D. J. *J. Nat. Prod.* **1995**, *58*, 1463–1466; (d) Stapley, E. O.; Hendlin, D.; Jackson, M.; Miller, A. K.; Hernandez, S.; Mata, J. M. *J. Antibiot.* **1971**, *24*, 42–47; (e) Davis, F. A.; Reddy, G. V.; Liu, H. *J. Am. Chem. Soc.* **1995**, *117*, 3651–3652; (f) Davis, F. A.; Liu, H.; Liang, C.-H.; Reddy, G. V.; Zhang, Y.; Fang, T.; Titus, D. D. *J. Org. Chem.* **1999**, *64*, 8929–8935; (g) Skepper, C. K.; Molinski, T. F. *J. Org. Chem.* **2008**, *73*, 2592–2597.
3. (a) Maier, G.; Endres, J. *Chem. Eur. J.* **1999**, *5*, 1590–1597; (b) Regitz, M.; Arnold, B.; Danion, D.; Schubert, H.; Fusser, G. *Bull. Soc. Chim. Belg.* **1981**, *90*, 615–631.
4. (a) Jacox, M. E.; Milligan, D. E. *J. Am. Chem. Soc.* **1963**, *85*, 278–282; (b) Kodama, S. *J. Phys. Chem.* **1988**, *92*, 5019–5024.
5. Maier, G.; Schmidt, C.; Reisenauer, H. P.; Endlein, E.; Becker, D.; Eckwert, J.; Hess, B. A.; Schaad, L. J. *Chem. Ber.* **1993**, *126*, 2337–2352.
6. (a) Fowler, F. W.; Hassner, A. *J. Am. Chem. Soc.* **1968**, *90*, 2875–2881; (b) Anderson, D. J.; Gilchrist, T. L.; Rees, C. W. *Chem. Commun.* **1969**, 147; (c) Gilchrist, T. L.; Gymer, G. E.; Rees, C. W. *Chem. Commun.* **1971**, 1519–1520; (d) Anderson, D. J.; Gilchrist, T. L.; Gymer, G. E.; Rees, C. W. *J. Chem. Soc., Perkin Trans. 1* **1973**, 550–555; (e) Gilchrist, T. L.; Gymer, G. E.; Rees, C. W. *J. Chem. Soc., Perkin Trans. 1* **1973**, 555–561; (f) Atkinson, R. S.; Grimshire, M. J. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1215–1224.
7. Gilchrist, T. L.; Gymer, G. E.; Rees, C. W. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1–8.
8. (a) Mitchell, G.; Rees, C. W. *J. Chem. Soc., Perkin Trans. 1* **1986**, 399–401; (b) Mitchell, G.; Rees, C. W. *J. Chem. Soc., Perkin Trans. 1* **1987**, 413–422.
9. (a) Huisgen, R.; Blaschke, H. *Chem. Ber.* **1965**, *98*, 2985–2997; (b) Meinwald, J.; Aue, D. H. *J. Am. Chem. Soc.* **1966**, *88*, 2849–2850.
10. Gilchrist, T. L.; Gymer, G. E.; Rees, C. W. *J. Chem. Soc., Chem. Commun.* **1973**, 835–836.
11. Gilchrist, T. L.; Rees, C. W.; Thomas, C. *J. Chem. Soc., Perkin Trans. 1* **1975**, 8–11.
12. (a) Wentrup, C.; Crow, W. D. *Tetrahedron* **1970**, *26*, 3965–3981; (b) Thétaz, C.; Wentrup, C. *J. Am. Chem. Soc.* **1976**, *98*, 1258–1259.
13. Wentrup, C. *Helv. Chim. Acta* **1972**, *55*, 1613–1617.
14. (a) Clark, D. T. *Theoret. Chim. Acta (Berl.)* **1969**, *15*, 225–234; (b) Hopkinson, A. C.; Lien, M. H.; Yates, K.; Csizmadia, I. G. *Int. J. Quantum Chem.* **1977**, *12*, 355–368; (c) Bock, H.; Dammel, R. *Chem. Ber.* **1987**, *120*, 1971–1985; (d) Alcami, M.; Mó, O.; Yáñez, M. *J. Am. Chem. Soc.* **1993**, *115*, 11074–11083; (e) Lathan, W. A.; Radom, L.; Hariharan, P. C.; Hehre, W. J.; Pople, J. A. *Top. Curr. Chem.* **1973**, *40*, 1–45; (f) Rosi, M.; Falcinelli, S.; Balucani, N.; Casavecchia, P.; Leonori, F.; Skouteris, D. *Lecture Notes in Computer Science (Proceedings)* **2012**, *7333*, 331–344.
15. (a) Mó, O.; Yáñez, M.; Elguero, J. *J. Mol. Struct. (Theochem)* **1989**, *201*, 17–37; (b) Byun, Y.-G.; Saebo, S.; Pittman, C. U. *J. Am. Chem. Soc.* **1991**, *113*, 3689–3696; (c) Malar, E. J. P. *Tetrahedron* **1996**, *52*, 4709–4718; (d) Tavakol, H. *Theochem* **2010**, *956*, 97–102.
16. (a) Budzelaar, P. H. M.; Cremer, D.; Wallasch, M.; Würthwein, E.-U.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1987**, *109*, 6290–6299; (b) Alcami, M.; de Paz, J. L. G.; Yáñez, M. *J. Comput. Chem.* **1989**, *10*, 468–478.
17. (a) Würthwein, E.-U. *J. Org. Chem.* **1984**, *49*, 2971–2978; (b) Mó, O.; de Paz, J. L. G.; Yáñez, M. *J. Phys. Chem.* **1987**, *91*, 6484–6490.
18. Čársky, P.; Hess, B. A.; Schaad, L. J. *J. Am. Chem. Soc.* **1983**, *105*, 396–402.
19. Shen, S.-S.; Lei, M.-Y.; Wong, Y.-X.; Tong, M.-L.; Teo, P. L.-Y.; Chiba, S.; Narasaka, K. *Tetrahedron Lett.* **2009**, *50*, 3161–3163.
20. Chen, R.; Fu, J.; Li, G.; Tan, Y.; Wang, Z.; Yuan, P. *Chin. J. Org. Chem.* **2012**, *32*, 95–103.
21. Yranzo, G. I.; Pérez, J. D.; Ferraris, M. A.; Claramunt, R. M.; Cabildo, P.; Sanz, D.; Elguero, J. *Ann. Quim. Int. Ed.* **1996**, *92*, 3–6.
22. Schmidt, E.; Striewsky, W.; Hitzler, F. *Justus Liebigs Ann. Chem.* **1948**, *560*, 222–231.
23. For details, see the Supplementary data.
24. (a) Banert, K.; Hückstädt, H.; Vrobel, K. *Angew. Chem.* **1992**, *104*, 72–74. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 90–92; (b) Banert, K.; Groth, S.; Hückstädt, H.; Lehmann, J.; Schlott, J.; Vrobel, K. *Synthesis* **2002**, 1423–1433; (c) Banert, K.; Jawabrah Al-Hourani, B.; Groth, S.; Vrobel, K. *Synthesis* **2005**, 2920–2926; (d) Jawabrah. Al-Hourani, B.; Banert, K.; Gomaa, N.; Vrobel, K. *Tetrahedron* **2008**, *64*, 5590–5597.
25. Finnegan, W. G.; Henry, R. A.; Lieber, E. *J. Org. Chem.* **1953**, *18*, 779–791.
26. (a) Spitzner, R.; Mielke, D.; Scholz, D.; Schroth, W.; Preiss, A. *Tetrahedron* **1982**, *38*, 927–936; (b) Kühle, E. In *Houben-Weyl*; Hagemann, H., Ed.; Thieme: Stuttgart, 1983; Vol. E4, pp 522–624; (c) Bögemann, M.; Petersen, S.; Schultz, O.-E.; Söll, H. In *Houben-Weyl*; Müller, E., Ed.; Thieme: Stuttgart, 1955; Vol. 9, pp 773–915.
27. (a) Lässig, W. *Chem. Ber.* **1962**, *95*, 2792–2795; (b) de Groot, A. C.; Flyvholm, M.-A.; Lensen, G.; Menné, T.; Coenraads, P.-J. *Contact Dermatitis* **2009**, *61*, 63–85; (c) Trask-Morrell, B. J.; Franklin, W. E.; Liu, R. H. *Text. Chem. Color.* **1988**, *20*, 21–26.
28. Gillon, D. W.; Forrest, I. J.; Meakins, G. D.; Tirel, M. D.; Wallis, J. D. *J. Chem. Soc. Perkin Trans. 1* **1983**, 341–347.
29. (a) Winterfeldt, E.; Nelke, J. M. *Chem. Ber.* **1968**, *101*, 3163–3171; (b) Chepyshev, S. V.; Chepysheva, Yu. N.; Ryabitskii, A. B.; Prosyanik, A. V. *Chem. Heterocycl. Compd.* **2008**, *44*, 523–529.
30. (a) Tan, Y.; Wang, Z.; Hao, Z.; Li, J. *Chin. J. Org. Chem.* **2011**, *31*, 1222–1229; (b) Song, X.; Tan, Y.; Li, J.; Wang, Z. *Chin. J. Org. Chem.* **2010**, *30*, 1890–1897; (c) Mo, Y.; Wang, Z.; Li, J.; Hong, W. *Chin. J. Org. Chem.* **2010**, *30*, 1051–1058; (d) Fu, J.; Wang, Z.; Hao, Z.; Huo, J. *Chin. J. Org. Chem.* **2011**, *31*, 1460–1467; (e) Song, X.; Wang, Z.; Li, J.; Fu, J. *Chin. J. Org. Chem.* **2009**, *29*, 1804–1810.
31. (a) Li, S.-L.; Guo, J.-B.; Yu, Z.-L.; Chen, Q.-H. *Chin. J. Chem.* **2004**, *22*, 384–389; (b) Wang, J.-P.; Cheng, X.-X.; Chen, Q.-H. *Acta Chim. Sinica* **2006**, *64*, 686–690; (c) Song, X.; Li, J.; Wang, Z.; Mo, Y. *Chin. J. Org. Chem.* **2010**, *30*, 648–654; (d) Blazecka, P. G.; Belmont, D.; Curran, T.; Pflum, D.; Zhang, J. *Org. Lett.* **2003**, *5*, 5015–5017.
32. (a) Mo, Y.-Q.; Wang, Z.-Y.; Mei, W.-J.; Fu, J.-H.; Tan, Y.-H.; Luo, S.-H. *Monatsh. Chem.* **2012**, *143*, 443–453; (b) Fu, J.; Wang, Z.; Huo, J.; Tan, Y.; Zeng, R. *Chin. J. Org. Chem.* **2012**, *32*, 104–112.
33. Karklina, A.; Gudriniece, E.; Petrova, M. V. *Latv. Kim. Z.* **1997**, 44–49.
34. However, the transformation of 3,4,5-trichlorobutenolide into an 3-aminomaleimide via two steps was reported, see Ref. 29a.
35. Methylene-2*H*-azirines are well known as very unstable compounds, which do not isomerize to produce 1*H*-azirines, see (a) Banert, K.; Hagedorn, M. *Angew. Chem.* **1990**, *102*, 90–92. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 103–105; (b) Banert, K.; Hagedorn, M.; Knözinger, E.; Becker, A.; Würthwein, E.-U. *J. Am. Chem. Soc.* **1994**, *116*, 60–62; (c) Fotsing, J. R.; Banert, K. *Eur. J. Org. Chem.* **2006**, 3617–3625.
36. Cabildo, P.; Claramunt, R. M.; Forfar, I.; Elguero, J. *Tetrahedron Lett.* **1994**, *35*, 183–184.
37. For other reinvestigated compounds, which were erroneously claimed to be 1*H*-azirines, see Ref. 6b and: (a) Banert, K.; Hagedorn, M.; Peisker, H. *Synlett* **2012**, 2943–2946; (b) Banert, K. *Tetrahedron Lett.* **2012**, *53*, 6443–6445; (c) Januar, L. A.; Molinski, T. F. *Org. Lett.* **2013**, *15*, 2370–2373; (d) Kornev, M. Yu.; Moshkin, V. S.; El'tsov, O. S.; Sosnovskikh, V.; Ya *Chem. Heterocycl. Compd.* **2013**, *48*, 1565–1567.