11672 *J. Phys. Chem. A* **2002,** *106,* 11672−11675

Bridged and Open Carbocation Structures as a Function of the Correlation Level in ab Initio Calculations: The 4-Methyl-2-pentyl Cation

Dan Fărcaşiu* and Povilas Lukinskas

Department of Chemical and Petroleum Engineering, University of Pittsburgh, 1249 Benedum Hall, Pittsburgh, Pennsylvania 15261

Sudhakar V. Pamidighantam

National Center for Supercomputing Applications, Urbana, Illinois

Received: August 28, 2002

An investigation of the alkylation reaction of propene with the 2-propyl cation by ab initio density functional methods at the B3LYP/6-31G** level found a distorted trimethyl-1-protonated cyclopropane as an energy minimum along the reaction coordinate (intermediate) and an open ion, the 4-methyl-2-pentyl cation (**1**), as another energy minimum (product). In contrast, the open ion **1** was not an energy minimum in MP2/6-31G** calculations. Attempts at geometry optimizations of **1** at that level led invariably to the protonated cyclopropane structure (more symmetrical than in the previous case). The ion **1** was in fact a transition structure in the MP2/6-31G** optimizations. A coupled cluster (CCSD/6-31G**) geometry optimization showed, however, the open ion **1** as a true energy minimum. This result brings a note of caution concerning MP2 geometry optimizations of carbocations. In particular, when these calculations find small energy differences between bridged and open structures, but find only the bridged structures as energy minima, the results might be in error. What the level of calculation is at which the predicted carbocation structures can be considered definitive remains an open question.

1. Introduction

Ab initio molecular orbital calculations[1] have been used with ever-increasing frequency for the determination of structures of molecules and, especially, transient (unstable) reaction intermediates. The description of transition structures and reaction pathways involving these structures, that is, determination of reaction mechanisms, has also been an important subject of investigation. The study of carbocations and carbocationic reaction mechanisms has been one of the first such applications.[2] The treatment of electron correlation by the Møller−Plesset approximation[3] at the MP2 level,[1c,3] with the use of basis sets with *d* functions at second-row atoms and *p* functions at hydrogen (6-31G**) has been considered to give correct carbocation structures.[4] The differences from MP2/6-31G* structures were found, however, to be inconsequential.[4,5] The determination of whether species correspond to energy minima or transition structures has been routinely based on frequency analyses on structures obtained by geometry optimization at the MP2/6-31G** (or even MP2/6-31G*) level.[4,6] Single-point calculations on such structures at the higher MP4 level with larger basis sets provided values for the energies that are considered highly accurate.[7] We have, therefore, always used MP2/6-31G** as the minimum level of theory in our calculations.[8]

More recently, the alternative density functional theory (DFT)[9] has begun to be used more extensively. When electron correlation is handled with the B3LYP method,[10] the results are normally considered to be comparable to those of the standard ab initio calculation with the MP2 method. The DFT calculations being less resource-demanding, we have used them in the studies of larger molecular or ionic systems.[11] On occasions, we used the DFT method to calculate spectral properties of MP2-derived structures.[12] In the investigations where the DFT-B3LYP method was used, we examined at least some of the structures by standard ab initio calculations at the MP2 level, to check the two methods against each other.[11] The agreement was generally good, but there were instances in which the disposition of ions in ion pairs,[11f] or of partners in ion−molecule aggregates,[11d] differed significantly and small differences in the geometries of individual molecules or ions were also recorded. Other investigators have also noticed differences in the results of MP2 and B3LYP optimizations.[13] Nevertheless, in none of those cases was the difference between the results provided by the two methods such as could lead to different conclusions.

We found, however, that for the 4-methyl-2-pentyl cation (**1**), MP2 and B3LYP optimizations gave results that were *qualitatively* different. Whereas our first inclination was to accept the MP2 results as the basis for our conclusions, some literature reports suggested caution. Thus, MP2 gave geometries closer to experiment for alkylalane dimers (hydrogen and alkyl-bridged),[14] but B3LYP predicted better the geometries of metal carbonyls, hydrides, and organometallics.[15] Likewise, overestimation of binding/complexation energies and the relative stabilization of bridged structures and structures with shorter bonds in MP2/6-31G** optimizations was noted.[4,16] It was found, however, that the increase in the correlation level achieved in coupled cluster calculations[17] provided the optimum structures when comparisons with MP2 and B3LYP calculations were made.[15] We decided, therefore, to test our results on cation

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* Corresponding author. Telephone:. 412-624-7449. Fax: 412-624-9639. E-mail: dfarca@pitt.edu.

10.1021/jp0219707 CCC: $22.00

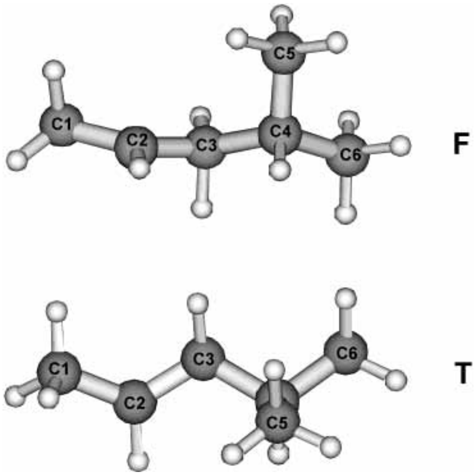


Figure 1. CCSD/6-31G** structure of the 3-methyl-2-pentyl cation (**1**). F, front view; T, top view.

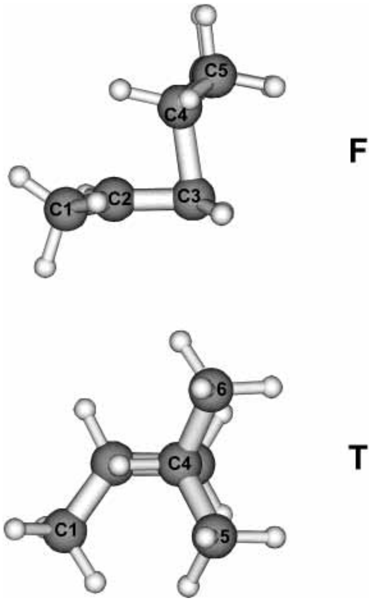


Figure 2. CCSD/6-31G** structure of the 1,1,2-trimethyl-1-protonated cyclopropane (**2**). F, front view; T, top view.

1 by undertaking a coupled cluster calculation (CCSD/6-31G**) on this system. We report our results here.

2. Methods

The MP2(FC)/6-31G** and B3LYP/6-31G** geometry optimizations were conducted with the Gaussian 98 suite of programs.[18] The nature of the stationary points was established by frequency analyses.[1c] The CCSD/6-31G** geometry optimizations were at first attempted by using the same program, but limitations in terms of methods and efficiency precluded a rapid turn-around for the results. ACES II[19] was then employed to perform the same optimization with a quick turn-around time and the calculation also included a quasi-NR (BFGS method[20]) Hessian along with the geometry optimization. This Hessian is constructed from two gradients and a previous Hessian and is an approximation to the correct Hessian. It should give a good indication of the stationary point examined.

The examination of geometrical parameters and generation of projections of the molecular geometry used for the interpretation of results and for Figures 1 and 2 were accomplished with the computer program MOLDEN.[21]

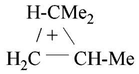
3. Results and Discussion

To test some basic postulates of the shape selectivity model of alkane reactivity on zeolites,[22] we examined computationally the detailed reaction pathway of the alkylation of propene by the propyl cation.[11d] Two ion−molecule complexes of near-equal energy, 10−11 kcal/mol more stable than the isolated reactants, were identified by both the MP2 and the B3LYP calculations. Strong hydrogen bonding between the double bond and one of the methyl hydrogens of the cation was noted; the C−H bond involved was stretched to 1.185−1.223 Å. The reactants in the complex combine to form 1,1,3-trimethyl-1-protonated cyclopropane (**2**) as the first product of a chemical reaction, over a small barrier, 2.5 kcal/mol by MP2/6-31G**.[11d] The MP2 calculations predicted a stronger bridging in **2** than the B3LYP calculations, as evidenced by the smaller difference in length between the bonds to the bridging carbon in the MP2-derived structure.[11d] Noteworthy for the B3LYP/6-31G** structure of **2** were the planarity of the monosubstituted ring carbon and the lengthening of one C−H in the adjacent methyl group, which would interact by hyperconjugation with the open cation (1.106 Å). Additionally, in the B3LYP-derived structure, the secondary atom was more pyramidalized and the $Me_2C-CHMe$ distance was 2.151 Å, suggesting a strong ion−molecule complex rather than a bonded species. Whether such a species is legitimately a bridged ion might be debated. We had set, however, an arbitrary limit of 90° for the largest ring angle for protonated cyclopropanes,[23] and the value for **2**, $\theta(Me_2C-CHMe-CH_2) = 87.60°$, was below that limit. Ion **2** also satisfied the other criterion for bridging, namely, an eclipsed conformation of the shorter bridging bond.[11d] In addition, the existence of the open isomer **1** makes the description of **2** as a bridged ion meaningful.

The second intermediate of the alkylation reaction should be the 4-methyl-2-pentyl cation, **1**. That cation and other secondary and tertiary hexyl and isohexyl cations had been optimized as energy minima by B3LYP/6-31G* calculations, in a study modeling the acid-catalyzed isomerization of 2-methyl-2-pentene.[24] We found **1** as an energy minimum (no imaginary frequencies) in B3LYP/6-31G** calculations as well.[11d] A more thorough examination by the DFT-B3LYP method showed **1** to be an energy minimum (no imaginary frequency) for basis sets from 6-31G* to 6-311++G**. The geometrical parameters of the structure obtained in the latter calculation are given in Table 1 of the supporting information. Ion **1** was not an energy minimum, however, in MP2/6-31G** calculations; whatever conformation was used as the starting point, geometry optimization led to bridging. Varying the basis set from 6-31G* to 6-311++G** did not change matters. Depending upon the basis set, a carbon-bridged (**2**) or a hydrogen-bridged ion was the most stable form, but no open ion **1** existed. This was in line with the MP2/6-31G** results on the 3-methyl-2-butyl cation, for which two stereoisomeric protonated cyclopropanes and a tertiary cation were energy minima and interconverted via three conformations of the open ion as transition structures.[5a]

$Me\text{-}CH^+\text{-}CH_2\text{-}CHMe_2$

1



$$\begin{array}{c} H\text{-}CMe_2 \\ /+\backslash \\ H_2C — CH\text{-}Me \end{array}$$

2

The difference between the MP2 and the B3LYP calculations on ion **1** was no longer one of stability or geometry differences of small consequences, but it pertained to the nature of that cation, intermediate or transition structure. To probe this discrepancy, we went a step higher with the electron correlation in the standard ab initio calculations, by conducting CCSD/6-31G** geometry optimizations[17,18,19] of **1** and **2**.

It turned out that ion **1** preserved its open structure upon optimization and *was* an energy minimum (Hessian analysis showed no negative eigenvalue). The main geometrical parameters of the structure resulting from the CCSD/6-31G** optimization are given as supporting information, and two projections of it are shown in Figure 1. The geometry of the cationic center is reminiscent of the geometries of the 2-propyl[5b,7,25] and *tert*-butyl cations,[26] predicted in calculations at lower levels of correlation. One hydrogen at C1 and another at C3 were positioned to provide hyperconjugative stabilization to the cation, on opposite sides of the C1,C2,C3 plane ("up" and "down"), in a manner reminiscent of the isolated 2-propyl cation.[7,25] A stronger interaction with the secondary C−H bond (at C-3) is indicated. It was argued that the methyl hyperconjugation is not a function of the relative orientation of an individual C−H bond and the empty orbital,[27] a representation in agreement with the low rotational barrier calculated for the 2-propyl cation[25] but not with the significant dependence of the lengths and angles of the β C−H bonds upon the orientation observed here and in previous studies.[5a,7,25] This discrepancy between two measures of the same interaction deserves notice.

A comparison of geometries of **1** predicted by the two theories and presented in Table 1 (Supporting Information) shows rather minor differences: The B3LYP method predicts slightly shorter C(sp^2)-C(sp^3) bonds and longer C(sp^3)-C(sp^3) bonds than the CCSD method, whereas all the C−H bonds are longer in the B3LYP structure. The presence of hyperconjugating hydrogens at C1 and C3 on opposite sides of the C1,C2,C3 plane is found in both, but the CCSD structure shows a better alignment of the C−H bond with the empty orbital and a slightly greater bond angle distortion of the hyperconjugating C−H bonds.

The geometries for the isomer **2** predicted by the B3LYP and CCSD optimizations (Table 2, supporting information) are also similar. The latter structure is shown in two projections in Figure 2. Isomer **2** is more stable than **1** by 2.6 kcal/mol (B3LYP/6-311++G**) and 4.2 kcal/mol (CCSD/6-31G**).

In conclusion, the CCSD calculations on cation **1** are in better agreement with B3LYP than with MP2 calculations. Our choice of **1** as the model for the study was determined by the discrepancy observed in the previous work,[11d] but it is likely that the conclusion is more generally applicable in cases when bridging can occur, because of the known tendency of the MP2 approximation to overstabilize bridged structures.[13,16] In particular, all the results of MP2 geometry optimizations of carbocations in which only bridged structures were energy minima and the energy differences between those and the open-structure isomers optimized as transition structures were small should be viewed with caution. The CCSD calculations provide a different mechanism (intermediates, transition structures) for the alkylation of propene by the 2-propyl cation and carbocationic interconversion of hexane isomers.

More important, we find that the point at which the calculations can be trusted for any type of structure without further verification had not been reached with MP2 optimizations. In fact, improvements beyond the level employed here are possible. Larger basis sets could be used, for example, in CCSD(T)/6-311G(2d,2p) calculations, if feasible. Tests on carbocations of similar nature with **1**, but smaller in size, are currently under way in our laboratories.

We note also that the discussion refers to isolated carbocations. It has been found that for carbocations in ion pairs, as formed upon ionization in solution or on solid acid catalysts, protonated cyclopropanes (including the parent, $C_3H_7^+$) are not stable even in MP2 optimizations. Instead, the corresponding open ions are the first intermediates,[23,28] in agreement with earlier experimental findings.[29] No anchimeric assistance of the ionization was evidenced in the MP2 studies of the formation of some simple, defining examples of carbocations.[23,28] Instead, the primary and secondary electrostatic interactions with the departing anion determine the structure and the subsequent reactions (recombination, elimination, trapping) of the carbocation.[8a]

Acknowledgment. We are indebted to Professor Kenneth D. Jordan for constant advice. The work at Pittsburgh was supported by a grant (CTS-9812704) from the US National Science Foundation. Grants of supercomputer time to D.F. were obtained from the National Center for Supercomputing Applications (NCSA), in Urbana, IL, and Lexington, KY.

Supporting Information Available: Two tables containing geometrical parameters for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Pople, J. A. *Acc. Chem. Res.* **1970**, *3*, 217. (b) Pople, J. A. *Int. J. Mass Spectrom Ion Phys.* **1976**, *19*, 89. (c) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986.

(2) Radom, L.; Popinger, D.; Haddon, R. C. In *Carbonium Ions*; Olah, G. A.; Schleyer, P. v. R., Eds.; Wiley: New York, 1976; Vol. 5, Chapter 38.

(3) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(4) Carneiro, J. W. de M.; Schleyer, P. v. R.; Koch, W.; Raghavachari, K. *J. Am. Chem. Soc.* **1990**, *112*, 4064.

(5) (a) Fărcaşiu, D.; Norton, S. H. *J. Org. Chem.* **1997**, *62*, 5374. (b) Fărcaşiu, D.; Hâncu, D. *J. Phys. Chem. A* **1997**, *101*, 8695.

(6) Schleyer, P. v. R.; Carneiro, J. W. de M.; Koch, W.; Forsyth, D. A. *J. Am. Chem. Soc.* **1991**, *113*, 3990.

(7) Koch, W.; Liu, B.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1989**, *111*, 3479.

(8) (a) Fărcaşiu, D.; Vinslava, A. *J. Mol. Struct., THEOCHEM* **2001**, *548*, 1. (b) Fărcaşiu, D.; Lukinskas, P. *J. Phys. Chem., A* **2000**, *104*, 1944 and references therein.

(9) (a) Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964**, *136*, B864. (b) Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, *140*, A1133. (c) Parr, R. G.; Yang, W. *Density-functional theory of atoms and molecules*; Oxford University Press: Oxford, U.K., 1989.

(10) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785.

(11) (a) Fărcaşiu, D. Lukinskas, P. *J. Phys. Chem., A* **1998**, *102*, 10436. (b) Fărcaşiu, D.; Lukinskas, P. *J. Phys. Chem., A* **1999**, *103*, 8483. (c) Fărcaşiu, D.; Lukinskas, P.; Hâncu, D. *J. Mol. Modeling* **2000**, *6*, 171. (d) Fărcaşiu, D. Lukinskas, P. *Phys. Chem.- Chem. Phys.* **2000**, *2*, 2373. (e) Fărcaşiu, D.; Lezcano, M.; Lukinskas, P. Waldeck, D. H. *J. Phys. Chem., A* **2000**, *104*, 5190. (f) Fărcaşiu, D. Lukinskas, P. *Phys. Chem.- Chem. Phys*. **2000**, *2*, 4219. (g) Lukinskas, P.; Fărcaşiu, D. *Appl. Catal. A, General* **2001**, *209*, 193. (h) Fărcaşiu, D.; Lukinskas, P. *Chem. Commun.* **2001**, 77. (i) Fărcaşiu, D.; Lukinskas, P. *J. Phys. Chem., A* **2002**, *106*, 1619.

(12) (a) Fărcaşiu, D.; Hâncu, D.; Haw, J. F. *J. Phys. Chem. A.* **1998**, *102*, 2493. (b) Fărcaşiu, D.; Hâncu, D. *J. Phys. Chem., A* **1999**, *103*, 754.

(13) Boronat, M.; Viruela, P.; Corma, A. *J. Phys. Chem, B.* **1997**, *101*, 10 069.

(14) Willis B. G.; Jensen, K. F. *J. Phys. Chem. A* **1998**, *102*, 2613.

(15) Gamess-UK Applications, *The Structure of Transition Metal Complexes.* Available at: http://www.dl.ac.uk/CFS/applications/tm/tm.html.

(16) Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5649.

(17) (a) Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem.* **1978**, *14*, 545. (b) Bartlett, R. J.; Purvis, G. D. *Int. J. Quantum Chem.* **1978**, *14*, 516.

(18) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Daprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.;

Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, P.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98, Revision A.6*; Gaussian, Inc.: Pittsburgh, PA, 1998.

(19) ACES II is a program product of the Quantum Theory Project, University of Florida. Authors: Stanton, J. F.; Gauss, J.; Watts, J. D.; Nooijen, M.; Liphant, N.; Perera, S. A.; Szalay, P. G.; Lauderdale, W. J.; Kucharski, S. A.; Gwaltney, S. R.; Beck, S.; Balkova, A.; Bernholdt, D. E.; Baeck, K. K.; Roziczko, P.; Sekino, H.; Hober, C.; Bartlett, R. J. Integral packages included are VMOL (Almlöf, J.; Taylor, P. R.), VPROPS (Taylor, P.), ABACUS (Helgaker, T.; Jensen, H. J. Aa.; Jørgensen, P.; Olsen, J.; Taylor, P. R.).

(20) (a) Broyden, C. G. *J. Inst. Math. Appl.* **1970**, *6*, 76. (b) Fletcher, R. *Comput. J.* **1970**, *13*, 317. (c) Goldfarb, D. *Math. Comput.* **1970**, *24*, 23. (d) Shanno, D. F. *Math. Comput.* **1970**, *24*, 647.

(21) G. Schaftenaar, *MOLDEN. A Portable Electron Density Program*. Available at: ftp ftp.caos.kun.nl Name: anonymous.

(22) (a) Weisz, P. B.; Frillette, V. J. *J. Phys. Chem.* **1960,** *64*, 382. (b) Csicsery, S. M. *J. Catal.* **1971**, *23*, 124. (c) Chen, N. Y.; Garwood., W. E. *J. Catal.* **1978**, *52*, 453. (d) Walsh, D. E.; Rollman, L. D. *J. Catal.* **1979**, *56*, 195. (e) Frillette, V. J.; Haag, W. O.; Lago, R. M. *J. Catal.* **1981**, *67*, 218. (f) Haag, W. O.; Lago, R. M.; Weisz, P. B. *Faraday Discuss. Chem. Soc.* **1981**, *67*, 218. (g) Haag, W. O.; Lago, R. M.; Weisz, P. B. *Faraday Discuss. Chem. Soc.* **1982**, *72*, 317. (h) Haag, W. O.; Dessau, R. M. *Proc. 8th Intl. Congr. Catal., Berlin 1984*; Dechema: Frankfurt-am Main, 1984; Vol. 2, p 305. (i) Review: Chen, N. Y.; Garwood, W. E. *Catal. Rev.-Sci. Eng.* **1986**, *28*, 185.

(23) Fărcaşiu, D.; Hâncu, D. *J. Am. Chem. Soc*. **1999,** *121*, 7173.

(24) Natal-Santiago, M. A.; Alcalá, R.; Dumesic, J. A. *J. Catal*. **1999**, *181*, 124.

(25) (a) Schleyer, P. v. R.; Koch, W.; Liu, B.; Fleischer, U. *J. Chem. Soc. Chem. Commun.* **1989**, 1098. (b) Koch, W.; Schleyer, P. v. R.; Buzek, P.; Liu, B. *Croat. Chim. Acta* **1992**, *65*, 655.

(26) Sieber, S.; Buzek, P.; Schleyer, P. v. R.; Koch, W.; Carneiro, J. W. de M. *J. Am. Chem. Soc*. **1993**, *115*, 259.

(27) Hoffmann, R.; Radom, L.; Pople, J. A.; Schleyer, P. v. R.; Hehre, W. J.; Salem, L. *J. Am. Chem. Soc.* **1972**, *94*, 6221.

(28) Fărcaşiu, D.; Norton, S. H.; Hâncu, D. *J. Am. Chem. Soc*. **2000**, *122*, 668.

(29) (a) Fărcaşiu, D.; Marino, G.; Harris, J. M.; Hovanes, B. A.; Hsu, C. S. *J. Org. Chem*. **1994**, *59*, 154. (b) Fărcaşiu, D.; Marino, G.; Hsu, C. S. *J. Org. Chem*. **1994**, *59*, 163. (c) Fărcaşiu, D.; Bologa, U. L. *J. Org. Chem.* **1996**, *61*, 8860. (d) Fărcaşiu, D.; Miller, G.; Bologa, U. L.; Katritzky, A. R.; Carpenter, B. K. *J. Chem. Soc., Perkin Trans. 2*, **1998**, 2659, and references therein.