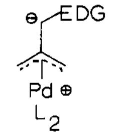

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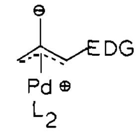

26

such an extraordinary suggestion, detailed MO calculations on such complexes and on those possessing an electron-withdrawing group on the TMM were performed and are reported in the accompanying manuscript.[20] Nevertheless, the remarkable regioselectivity demonstrates the extraordinary control by transition metals in changing the rules of selectivity and reactivity of organic molecules.[21]

Acknowledgment. We thank the National Science Foundation and the National Institutes of Health for their generous support of our programs. We also extend our gratitude for generous supplies of palladium salts to Johnson Matthey and Co. and Englehard Industries. D.M.T.C. acknowledges the receipt of a Standard Oil of Ohio fellowship. Professor Isoe graciously provided comparison spectra for compound **8**.

Supplementary Material Available: Spectral data for both stereoisomers of **6**, **7**, **19**, **21**, **22**, and **24** (3 pages). Ordering information is given on any current masthead page.

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(19) The question of mechanism is clouded by the relative reactivity of **25** vs. **26** and the nature of the bond forming steps. From the protonation results reported herein and our previous studies,[1] this interpretation represents a reasonable working hypothesis.

(20) Gordon, D.; Nanninga, T.; Fenske, R. F.; Trost, B. M. *J. Am. Chem. Soc.*, following paper in this issue.

(21) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385.

A Molecular Orbital Study of Substituted Trimethylenemethane-Bis(phosphine)palladium Complexes

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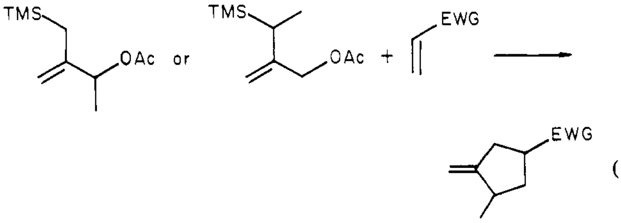
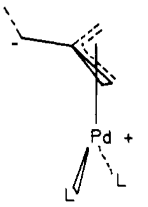
Received May 11, 1981

The chemistry of substituted trimethylenemethane-metal complexes remains almost unexplored from both an experimental and a theoretical point of view. In the preceding paper, a most striking regiochemistry in the cycloaddition reaction was observed for the methyl substituted derivative of η^3-trimethylenemethane-bis(triphenylphosphine)palladium (reaction 1). If one



(1)

considers possible rationales for this most unexpected observation, the question of the relative stabilities of the three isomers of this complex **1**–**3** arises. While intuitively one might think that **2** or **3** would be more stable since they place the electron-releasing substituent on the least electron-rich carbon, the product would most easily be rationalized to arise from **1**. In this communication, this question as well as the question of the effect of electron-withdrawing groups is probed— a study which reveals the extraordinary level of control exerted by the transition metal.



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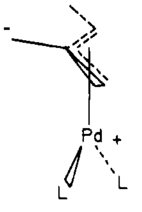

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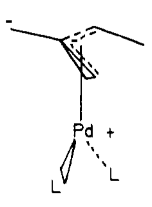
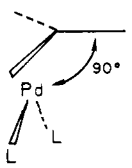


3

Albright[1] has recently undertaken a theoretical investigation of the most stable geometry of d^{10} trimethylenemethane-metal bis(phosphine) complexes, and concluded that the preferred structure is **4**, in which the trimethylenemethane (TMM) is coordinated to the metal in an allylic fashion. We have previously



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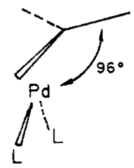

5

reported results of Fenske-Hall calculations, a nonparametrized approximate molecular orbital method,[2] on TMM-Pd$(PH_3)_2$,[3] using structure **5** where the dihedral angle between the P-Pd-P and TMM planes is not 90° as in **4**, but 96°, chosen by analogy to known π-allyl complexes.[4,5] Since it appeared that Albright failed to consider a geometry of type **5**, we undertook a systematic reinvestigation of the preferred geometry for TMM-Pd$(PH_3)_2$ using the Fenske-Hall method. The results of our calculations do indeed lead us to predict that **5** is more stable than **4**.

We have performed molecular orbital calculations on methyl substituted trimethylenemethane complexes **1**–**3** using the tipped geometry calculated to be the most stable. Figure 1 presents molecular orbital diagrams for these three isomers. The highest occupied molecular orbital (HOMO) is indicated by two arrows representing a pair of electrons. The symmetry labels for the metal fragment basis orbitals in the left column are taken from the C_{2v} point group, while those of the Me-TMM fragment orbitals in the right column are from the D_{3h} symmetry of the unsubstituted trimethylenemethane.[6] The orbitals involved in the metal-trimethylenemethane bonding level are the $4b_2$ on the metal (composed of a combination of palladium 4d and 5p orbitals pointing toward the end carbons in the allylic portion of the TMM) and an appropriate combination of $1e_{y''}$ and $1e_{x''}$ on the Me-TMM which is localized on those end carbons. The $2a_2$, $2b_1$, $4a_1$, and

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(1) Albright, T. A. *J. Organomet. Chem.* **1980**, *198*, 159-168.

(2) Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768-775.

(3) Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1980**, *102*, 6359-6361.

(4) (a) Smith, A. E. *Acta Crystallogr.* **1965**, *18*, 331-340. (b) Oberhansli, W. F.; Dahl, L. F. *J. Organomet. Chem.* **1965**, *3*, 43-54. (c) Mason, R.; Wheeler, A. G. *J. Chem. Soc. A* **1968**, 2543-2549, 2549-2554. (d) Kuli-Zade, T. S.; Kukina, G. A.; Poraj-Košic, M. A. *Z. Struckt. Khim.* **1969**, *10*, 149-151 (*J. Struct. Chem.* **1969**, *10*, 141-143). (e) Broadbent, T. A.; Pringle, G. E. *J. Inorg. Nucl. Chem.* **1971**, *33*, 2009-2014. (f) Mason, R.; Whimp, P. O. *J. Chem. Soc. A* **1969**, 2709-2717. (g) Hendriks, P.; Olie, K.; Vrieze, K. *Cryst. Struct. Commun.* **1975**, *4*, 611-616.

(5) The possibility that the dihedral angle in the TMM-Pd$(PH_3)_2$ complex should be different from 90° was suggested by the dihedral angles in ref 4. The value of 96° used in the present calculations is not the result of a rigorous geometry optimization, but rather it comes from the geometric constraints of a planar TMM, fixed Pd-C bond distances, and the PdL_2 unit being situated very near the axis formed by the two methylene carbons. We have performed other calculations on TMM-Pd$(PH_3)_2$ in which the Pd-C bond distances were fixed, but the dihedral angle was as large as 110° and the PdL_2 unit was much closer to the central carbon than to the line connecting the methylene carbons. The geometry used in the calculations presented here was the lowest in energy of all of those considered and the geometry in which the dihedral angle was 90° was the highest in energy.

(6) The energies of the metal and Me-TMM fragment orbitals before mixing are not identical in Figure 1a-c because these values reflect the energies of the orbitals in the changing molecular environment, as derived from the diagonal elements of the approximate Fock matrix.

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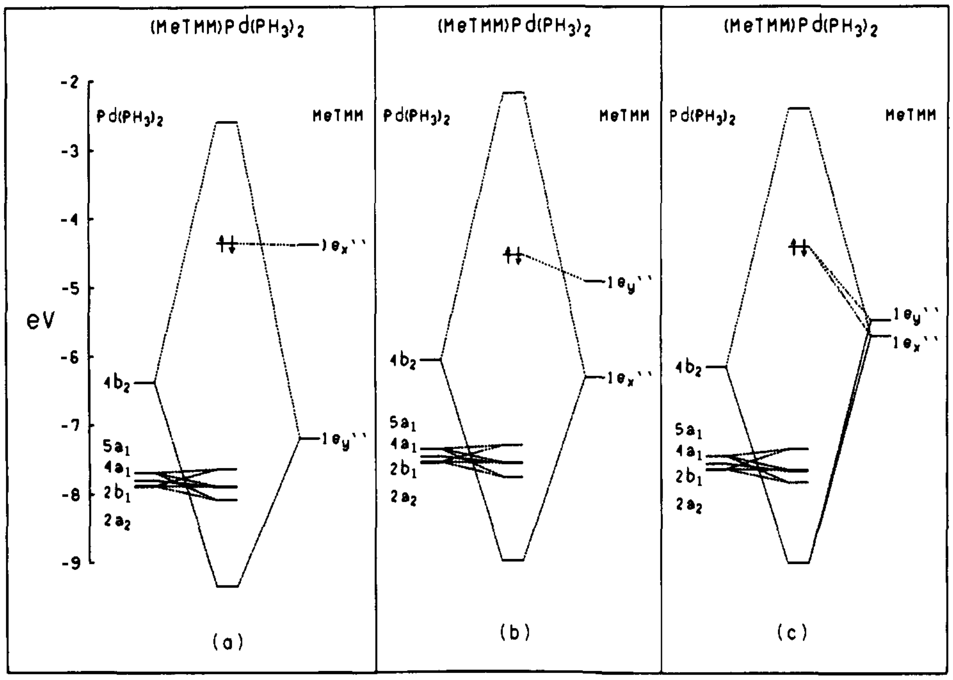
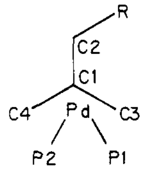
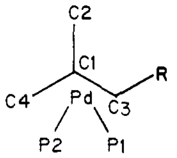
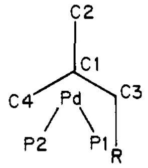


Figure 1. Molecular orbital diagrams for methyl substituted trimethylenemethane–disphosphine palladium isomers (a) **1**, (b) **2**, and (c) **3**. The highest occupied molecular orbital is indicated by two arrows representing a pair of electrons. For an explanation of basis orbital energies, see ref 6.

Table I. Atomic Charges

										
	R = H	R = CH_3	R = CF_3	R = CN	R = CH_3	R = CF_3	R = CN	R = CH_3	R = CF_3	R = CN
C1	+0.157	-0.021	+0.069	+0.026	-0.023	+0.056	+0.009	-0.023	+0.054	+0.005
C2	-0.696	-0.581	-0.853	-0.563	-0.696	-0.724	-0.662	-0.689	-0.712	-0.641
C3	-0.468	-0.300	-0.506	-0.452	-0.381	-0.695	-0.469	-0.385	-0.706	-0.427
C4	-0.468	-0.320	-0.483	-0.462	-0.472	-0.463	-0.446	-0.485	-0.488	-0.438
Pd	+1.134	+1.133	+1.145	+1.146	+1.116	+1.159	+1.148	+1.121	+1.163	+1.159
P1	+0.345	+0.336	+0.293	+0.299	+0.327	+0.287	+0.294	+0.328	+0.291	+0.301
P2	+0.345	+0.336	+0.290	+0.294	+0.326	+0.297	+0.296	+0.330	+0.302	+0.302

$5a_1$ levels are all nonbonding combinations of palladium 4d orbitals. Surprisingly, the HOMO is not localized on the palladium but rather is a Me–TMM nonbonding level, localized on the carbon farthest removed from the metal. A consideration of the total energy of the system, obtained from a sum of orbital energies,[7] yields the following order of stability: **1** > **3** ~ **2**. This difference in stability is a result of a subtle combination of several factors including bonding effects, charge redistribution, and near-neighbor charge effects.

Table I presents the atomic charges obtained from our calculations using a Mulliken population analysis.[8] In all cases the carbon atom farthest from palladium, C2 carries the largest negative charge. On going from **1** to **2** to **3**, it can be seen that there is a redistribution of charge. This charge redistribution causes changes in the relative energies of the levels that are involved in the bonding interactions, which is apparent from the shifts in the bonding levels in Figure 1. Because of changes in the charges carried by near neighbors, the eigenvalues of the nonbonding metal and ligand levels also shift.

We have also considered the effects of substituting electron-withdrawing groups on TMM—the trifluoromethyl (σ interaction only) and cyanide (π interaction also). Geometries employed were analogous to **1**–**3**. Table I summarizes the charge distribution in these complexes. For the CF_3–TMM, the results indicate no clear preference for the CF_3 group being bound to the methylene carbon atom farthest from or nearest to the metal because of a combination of opposing effects. In the case of the CN–TMM, there is again a preference for the cyanide to be bonded to the carbon atom farthest from the metal, with a geometry analogous to **1** being more stable than one analogous to **3**. The chemistry of these systems is unknown but is being actively pursued. Given the similarity between the most stable form of the methyl and cyanide substituted TMM complexes, we would expect to see a product similar to that in eq 1 for the cyanide substituted TMM.

We have presented the results of approximate molecular orbital calculations that indicate the most stable geometry of TMM–$Pd(PH_3)_2$ is **5**. Most importantly, of the three isomers **1**–**3** for Me–TMM–$Pd(PH_3)_2$, the calculations indicate the most stable to be that isomer which places the methyl group on the most electron-rich carbon, i.e., 1. (This violation of usual chemical intuition arises from the bonding of the TMM fragment with the transition metal, i.e., the transition metal reverses normal selectivity patterns.) The regioselectivity of the cycloaddition reactions of **1** may be most easily rationalized as nucleophilic attack by the most negatively charged carbon in **1** on the electron-deficient

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(7) These sums are obtained by adding only those eigenvalues of occupied molecular orbitals directly involved in the bonding interaction between the TMM and metal fragments. In doing so it is assumed that the eigenvalues of the σ bonding framework and lone pairs are frozen and hence are unaffected by the changes in geometry considered here.

(8) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1841.

olefin. On the other hand, the TMM complexes bearing electron-withdrawing groups are more ambiguous. No clear preferences exist for the trifluoromethyl substituent, but the cyanide appears analogous to the methyl substituent in its positional selectivity. These latter predictions await experimental scrutiny.

Acknowledgment. We thank the National Science Foundation for their generous support of our program—Grant CHE-7824882 to R.F.F. and CHE-7913266 to B.M.T.

Novel Reaction Course of Oxosulfonium Ylides to Sulfurane Oxides

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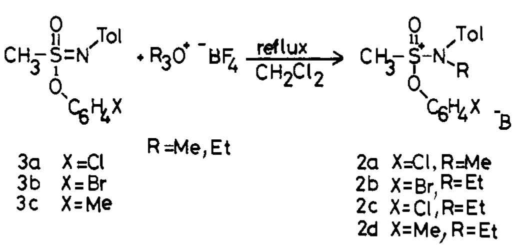
Five-membered dialkoxyspirosulfurane oxides have been prepared by oxidation of the corresponding sulfuranes.[1] Since the original work of Corey and Chaykovsky,[2] many reactions of oxosulfonium ylides have been reported. But no attempt to synthesize sulfurane oxides from oxosulfonium ylides has yet been made. In this communication we report the synthesis of aminodioxysulfurane oxides **1**, which are the first reported four-membered cyclic sulfurane oxides, by the reaction of oxosulfonium ylides with benzaldehyde.

Aminoaryloxyoxosulfonium salts **2** as starting materials were prepared by refluxing (2 h) a dichloromethane solution of the corresponding sulfoximines **3**[3] with 1.2 equiv of Meerwein reagent.[4] Isolation of **2** was carried out by gel chromatography over Sephadex LH-20 (80% crude yield). Recrystallization from methanol gave colorless crystals, identified as **2** by ^{1}H NMR spectra.



To a refluxing THF solution of **2a** (10 mmol) was added dropwise a *n*-hexane solution of *n*-BuLi (10 mmol). After 15 min, a THF solution of benzaldehyde (10 mmol) was added to the above solution at 50 °C in 10 min, and the resulting dark red solution was washed with water and extracted with ether; the ethereal solution was dried over $MgSO_4$. After evaporation of ether, sulfurane oxide **1a** was obtained by SiO_2 chromatography in 20% yield (solvent and eluant; dichloromethane–*n*-hexane).

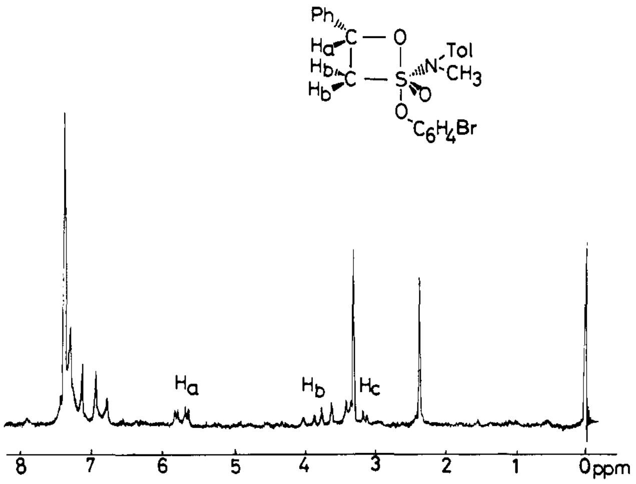
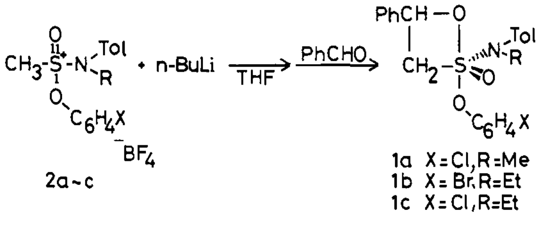


Figure 1. 60-MHz ^{1}H NMR spectrum of compound **1a**.

Recrystallization from methanol gave colorless crystals, mp 118–119 °C. Sulfurane oxides **1b** and **1c** were also obtained by the above method, mp 131–132 °C and 125–126 °C, respectively.[5,6]



The three quartet peaks of **1a** at 3.10, 3.68, and 5.66 ppm show a typical AMX pattern assigned to four-membered cyclic structure (Figure 1). But the peaks of **1b** to be assigned to the ring methylene and N–Et methylene are slightly different; this difference may be caused by the nonequivalence of the diastereotopic methylene protons of the N–Et group (Figure 2). The nonequivalence of geminal proton groups seen in the ^{1}H NMR spectra of **1** is consistent with a four-membered structure. Four-membered cyclic dioxyphosphoranes also show similar spectral patterns.[7] Since all known sulfurane oxides have trigonal-bipyramidal geometries, compounds **1** may also have the same ones.[1]

The reaction can be rationalized by an intramolecular mechanism; the ylides **4** obtained by treatment of **2** with *n*-BuLi attacked benzaldehyde to give betaines **5** in which the negatively charged O entered into bonding with the positively charged S,

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(1) J. C. Martin and R. Arhart, *J. Am. Chem. Soc.*, **93**, 2341 (1971). G. W. Astrologes and J. C. Martin, *ibid.*, **99**, 4390 (1977). P. H. W. Lau and J. C. Martin, *ibid.*, **99**, 5490 (1977). Recently, a certain sulfurane oxide was also prepared by acid-catalyzed hydrolysis of a difluorosulfurane. R. S. Michalak and J. C. Martin, *ibid.*, **103**, 214 (1981).

(2) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **87**, 1353 (1965).

(3) E. U. Johnson and C. R. Johnson, *J. Am. Chem. Soc.*, **93**, 5308 (1971). C. R. Johnson and A. Wambsgans, *J. Org. Chem.*, **44**, 2278 (1979).

(4) **2a**: ^{1}H NMR ($CDCl_3$) δ 2.30 (s, 3, tol–Me), 3.63 (s, 3, N–Me), 4.11 (s, 3, S^+–Me), 7.15 (s, 4, tol), 7.50 (s, 4, OC_6H_4Cl). **2b**: ^{1}H NMR ($CDCl_3$) δ 1.15 (t, 3, J = 8.0 Hz, N–CH_2CH_3), 2.37 (s, 3, N–tol–Me), 3.83–4.37 (m, 2, N–CH_2CH_3), 4.09 (s, 3, S^+–Me), 7.20 (s, 4, N–tol), 7.51 (q, 4, OC_6H_4Br). **2c**: ^{1}H NMR ($CDCl_3$) δ 1.15 (t, 3, J = 7.0 Hz, N–CH_2CH_3), 2.40 (s, 3, N–tol–Me), 3.87–4.33 (m, 2, N–CH_2CH_3), 4.09 (s, 3, S^+–Me), 7.20 (s, 4, N–tol), 7.46 (s, 4, OC_6H_4Cl). **2d**: ^{1}H NMR ($CDCl_3$) δ 1.11 (t, 3, J = 7.0 Hz, N–CH_2CH_3), 2.33 (s, 3, N–tol–Me), 2.38 (O–tol–Me), 3.83–4.20 (m, 2, N–CH_2CH_3), 4.02 (s, 3, S^+–Me), 7.20 (s, 4, N–tol), 7.30 (s, 4, O–tol).

(5) **1a**: ^{1}H NMR ($CDCl_3$) δ 2.40 (s, 3, tol–Me), 3.24 (dd, 1, J_{ac} = 14.3 Hz, J_{bc} = 3.1 Hz, H_c), 3.27 (s, 3, N–Me), 3.68 (dd, 1, J_{ab} = 8.8 Hz, J_{bc} = 14.3 Hz, H_b), 5.66 (dd, 1, J_{ab} = 8.8 Hz, J_{ac} = 3.1 Hz, H_a), 6.83–7.33 (m, 13, aromatic); ^{13}C NMR, ($CDCl_3$) δ 20.97 (tol–Me), 38.87 (N–Me), 57.14 (S–CH_2–), 76.34 (Ph*C*H–), 117.96, 126.13, 126.74, 128.25, 129.12, 129.44, 130.02, 137.49, 138.68, 155.71 (aromatic). M_r (vapor pressure osmometer), calcd 415.5; obsd 384 (solvent; benzene, at 45 °C). This result implies that the structure of sulfurane oxide is monomeric. **1b**: ^{1}H NMR ($CDCl_3$) δ 1.07 (t, 3, J = 7.3 Hz, N–CH_2CH_3), 2.36 (s, 3, tol–Me), 3.26 (dd, 1, J_{bc} = 14.7 Hz, J_{ac} = 1.5 Hz, H_c), 3.55, 3.79 (d, 2, J = 13.7 Hz, H_α and H_β), 3.75 (dd, 1, J_{bc} = 14.7 Hz, J_{ab} = 8.3 Hz, H_b), 5.71 (dd, 1, J_{ab} = 8.3 Hz, J_{ac} = 1.5 Hz, H_a), 6.80–7.35 (m, 13, aromatic). ^{13}C NMR ($CDCl_3$) δ 14.72 (N–CH_2CH_3), 21.02 (tol–Me), 46.80 (N-CH_2CH_3), 57.97 (S–CH_2–), 76.41 (Ph*C*H–), 117.88, 126.10, 126.83, 128.68, 129.12, 129.41, 130.07, 136.08, 138.75, 155.71 (aromatic). **3c**: ^{1}H NMR ($CDCl_3$) δ 1.07 (t, 3, J = 7.1 Hz, N–CH_2CH_3), 2.36 (s, 3, tol–Me), 3.27 (dd, 1, J_{bc} = 15.0 Hz, J_{ac} = 2.4 Hz), 3.55, 3.78 (d, 2, J = 13.7 Hz, H_α and H_β), 3.74 (dd, 1, J_{bc} = 15.0 Hz, J_{ab} = 8.3 Hz, H_b), 5.70 (dd, 1, J_{ab} = 8.3 Hz, J_{ac} = 2.4 Hz, H_a), 6.81–7.34 (m, 13, aromatic). ^{13}C NMR ($CDCl_3$) δ 14.74 (CH_2CH_3), 21.04 (tol-Me), 46.83 (CH_2CH_3), 57.99 (S-CH_2–), 76.48 (Ph*C*H–), 117.90, 126.13, 126.83, 128.92, 129.12, 129.44, 130.09, 136.12, 138.12, 138.78, 155.76 (aromatic).

(6) A new chiral center with the possible formation of two diastereoisomers of **1** will be generated by these reactions. But only one isomer was obtained, and the other was not observed in the ^{1}H NMR spectra of crude reaction mixtures.

(7) M. -U. Haque, C. N. Caughlan, F. Ramirez, J. F. Pirot, and C. P. Smith, *J. Am. Chem. Soc.*, **93**, 5229 (1971). D. Z. Denney, D. W. White, and D. B. Denney, *J. Am. Chem. Soc.*, **93**, 2066 (1971).

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