clarified before a convincing rationale for the observed asymmetric induction can be offered.

In conclusion, an encouraging step toward incorporating asymmetry into ester–imine condensations has been achieved. This approach to optically active β-lactam is versatile in design and its utility has been demonstrated with a synthesis of (+)-PS-5 (**17**). Studies with other homochiral esters are in progress.

Acknowledgment. We thank the National Institutes of Health for their generous support (AI-21074) and Richard Weisenberger of The Ohio State University Campus Chemical Instrument Center for mass spectral analyses.

Direct Evidence for Spillover of Hydrogen from Ruthenium to Copper in Supported Cu–Ru/SiO_2 Catalysts: A Study by NMR of Chemisorbed Hydrogen

T. S. King and Xi Wu

Department of Chemical Engineering, Iowa State University
Ames Laboratory, Energy and Minerals Resources
Research Institute,[†] Ames, Iowa 50011

B. C. Gerstein*

Department of Chemistry and Ames Laboratory
Energy and Minerals Resources Research Institute[†]
Iowa State University, Ames, Iowa 50011

Received February 12, 1986

Bimetallic catalysts have received intense attention, both because of their industrial utility for catalytic reforming and the possibility of using them as model systems in fundamental investigations of catalytic phenomena.[1-5] Hydrogen chemisorption has been used to characterize these systems. Specifically, on supported Cu–Ru catalysts, the number of surface Ru atoms has been inferred from titration with hydrogen under the assumption that hydrogen does not dissociatively adsorb on copper. The bases for the use of this experiment lie both in experiment and theory: the activation energy for dissociative chemisorption of hydrogen on Cu has been found experimentally to be about 5 kcal mol^{-1}.[6] The activation energy for dissociative adsorption of hydrogen on Cu is a multivalued function of the orientation and vibrational–translational–rotational state of the hydrogen molecule as it approaches the surface and of the surface plane of the metal involved. Theoretical calculations have led to values both much less and much greater than that quoted above, depending upon the above-mentioned parameters, but having an average value of 5 kcal mol^{-1}.[7] Hydrogen does not dissociatively chemisorb on pure copper at room temperature.[8] Spillover of hydrogen from Ru to Cu would invalidate this method of quantifying surface Ru.[9,10]

Studying the (0001) surface of single-crystal Ru having varying amounts of Cu deposited on the surface, various researchers[11-17] have found that hydrogen does not spill over on Cu at temperatur below 150 K, but Goodman et al.[17] have found evidence f spillover of atomic H onto Cu in such a bimetallic single-cryst system at 230 K.

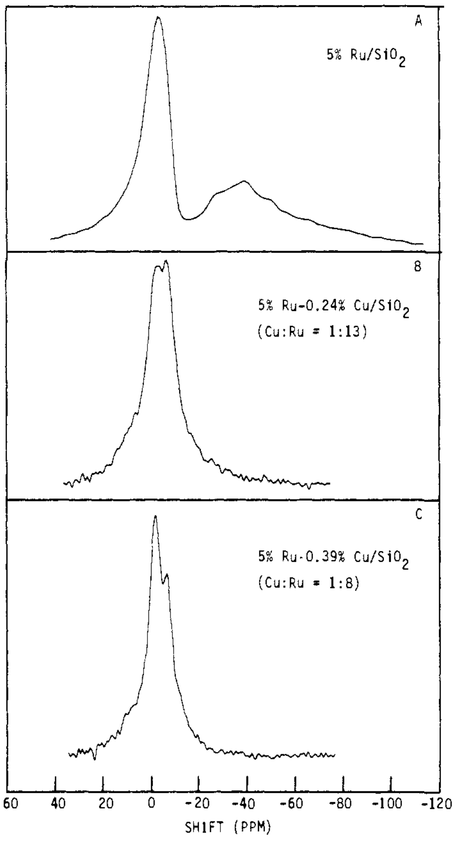


Figure 1. NMR of hydrogen under a single pulse excitation for hydrog on (a) 5% Ru/SiO_2, (b) 5% Ru–0.24% Cu/SiO_2, and (c) 5% Ru–0.39 Cu/SiO_2. Liquid water was used as reference and all spectra we normalized to the height of the highest peak.

Studies of supported Cu–Ru catalysts have not demonstrat spillover of hydrogen from Ru to Cu. The present work mak this demonstration for a number of Cu–Ru catalysts support on SiO_2, using nuclear magnetic resonance (NMR) of hydrog on the substrates. The NMR spectroscopy of chemisorbed h drogen on supported Ru has shown that the chemical shift of t hydrogen does not depend upon coverage and that the isotrop shift of hydrogen on Ru is found to be about 50 ppm upfield fro the proton resonance in Me_4Si.[18]

The home-built NMR spectrometer, similar to one previous described,[19] was operated at 220 MHz for proton resonance. Pro Qs were set between 50 and 200, depending upon the desir experimental response. A Q of 50, corresponding to a pro ringdown time of approximately $21Q/3f_0 = 1.8$ μs and having receiver dead time of 500 ns,[20] was used to determine that no li broader than 20 kHz was present in the samples under study. T 90° broadcast pulse at probe Q of 50 was 2.5 μs long, corr sponding to a broadcast bandwidth of 200 kHz at the 3-dB poi A Biomation 2805 transient recorder was used for digitizati of the NMR signal. The minimum dwell was 0.2 μs, which w used for initial experiments to determine the spectral width of t sample under investigation. A dwell of 5 μs and Q of 200 we used for experiments on hydrogen on the supported bimetall Cu–Ru catalyst, in which the signal-plus-noise to noise ratio w

---

[†] Operated for the U.S. Department of Energy by Iowa State University under Contract W-7405-Eng-82.

(1) Sinfelt, J. H. *Bimetallic Catalysts—Discoveries, Concepts, and Applications*; Wiley: New York, 1983.

(2) Biloen, P.; Heller, J. N.; Verbeek, H.; Dautzenberg, F. M.; Sachtler, W. M. H. *J. Catal.* **1980**, *63*, 112.

(3) Menon, P. G.; Froment, G. F. *J. Mol. Catal.* **1984**, *25*, 59.

(4) Sachtler, W. M. H. *J. Mol. Catal.* **1984**, *25*, 1.

(5) Christmann, K.; Ertl, G. *J. Mol. Catal.* **1984**, *25*, 31.

(6) Balooch, M.; Cardillo, M. J.; Miller, D. R.; Stickney, R. E. *Surf. Sci.* **1974**, *46*, 358.

(7) Lee, C.-Y.; Depristo, A. E. *J. Chem. Phys.* **1986**, *84*, 485.

(8) Greuter, F.; Plummer, E. W. *Solid State Commun.* **1983**, *48*, 37.

(9) Rouco, A. J.; Haller, G. L.; Oliver, O. J.; Kimball, C. *J. Catal.* **1983**, *84*, 297.

(10) Haller, G. L.; Reasasco, D. E.; Wang, J. *J. Catal.* **1983**, *84*, 477.

(11) Christmann, K.; Ertl, G.; Shimizu, H. *J. Catal.* **1980**, *61*, 397.

(12) Shimizu, H.; Christmann, K.; Ertl, G. *J. Catal.* **1980**, *61*, 412.

(13) Vickerman, J. C.; Christmann, K.; Ertl, G. *J. Catal.* **1981**, *71*, 175.

(14) Vickerman, J. C.; Christmann, K. *Surf. Sci.* **1982**, *120*, 1.

(15) Vickerman, J. C.; Christmann, K.; Ertl, G.; Heiman, P.; Himpsel, F. J.; Eastman, D. E. *Surf. Sci.* **1983**, *134*, 367.

(16) Yates, J. T. Jr.; Peden, C. H. F.; Goodman, D. W. *J. Catal.* **19** *94*, 576.

(17) Goodman, D. W.; Peden, C. H. F. *J. Catal.* **1985**, *95*, 321.

(18) Sheng, T.-C.; Gay, I. D. *J. Catal.* **1982**, *77*, 53.

(19) Cheung, T. T. P.; Worthington, L. E.; Murphy, P. D. B.; Gerste B. C. *J. Magn. Reson.* **1980**, *41*, 158.

(20) Stoll, M. E. *A Simple, Fast Recovery, Low-Noise Receiver-Amplifi for Pulsed NMR Experiments*, Sandia Laboratories Report SAND80-87

0002-7863/86/1508-6056$01.50/0

maximized. A dwell of 0.5 μs and a probe Q of 50 was used for measurements of hydrogen on supported pure Ru. The probe was determined to have no observable hydrogen in the absence of a sample after 32 000 scans, which was the number used to obtain the results reported herein.

The supported Ru and Cu–Ru catalysts used in the present study were prepared by the impregnation procedure described by Sinfelt.[21] The support was a Cab-O-Sil HS-5 silica, having a surface area of 300 $M^2\ g^{-1}$. After impregnation, the resulting material was dried at 383 K and then reduced in flowing H_2 at 723 K for 4 h. The samples were stored in air before introduction into a 5-mm quartz NMR tube connected to a standard BET/chemisorption apparatus. Once in the tube, they were again reduced at 93 KPa of H_2 and 673 K for 4–5 h and outgassed to 0.13 Pa at 673 K for 1 h. This cycle was repeated 5 times. The samples were then outgassed at 1.3 mPa at 673 K for 15 h before being sealed at the final pressure of 4 kPa of hydrogen at room temperature.

NMR spectra of hydrogen on Ru/SiO_2 and on two different compositions of $Cu–Ru/SiO_2$ are shown in Figure 1A–C. The peak at about −6 ppm in Figure 1 corresponds to hydroxyl hydrogen. The upfield peak at −38 ppm in Figure 1A, representing hydrogen on supported Ru, forms the basis shift for inferring the meaning of results shown in Figure 1B,C. While the upfield peak shows its highest intensity at −38 ppm, a first moment calculation yields an average chemical shift of −51 ppm, agreeing with previous studies of hydrogen adsorbed on silica-supported ruthenium.[18] Figure 1B,C shows the NMR spectra of hydrogen on Cu–Ru/SiO_2, having 5% Ru in the sample and Cu/Ru atomic ratios of $^1/_{13}$ (Figure 1B) and $^1/_8$ (Figure 1C). Two peaks are also observed for the samples containing both Ru and Cu; one corresponds to the hydroxyl proton, which does not change location with change in concentration of Cu, and the second moves downfield with increasing Cu concentration.

This result indicates that the protons thus observed are exchanging between environments associated with Ru and Cu on a time scale fast compared to the difference in chemical shifts of H on Cu and on Ru. In other words, the protons observed on a bimetallic, supported $Cu–Ru/SiO_2$ catalyst at room temperature are experiencing both Cu and Ru environments. A possible explanation for this observation is that hydrogen is dissociatively chemisorbed on Ru and spills over to the Cu surface atoms. Furthermore, the direction of the shift with increasing Cu concentration indicates, by extrapolation, that the shift for H on pure Cu would appear a few parts per million downfield from the zero shift. With the addition of a small amount of copper, the magnitude of the variation of the chemical shift suggests that most of the copper is at the surface, covering much of the previously available ruthenium. This inference is in agreement with the single-crystal studies cited earlier. Note that at these temperatures and pressures, the available adsorption sites of both copper and ruthenium are completely filed;[17] therefore, the time the proton is in association with either element is only a function of their relative surface concentration. At less than the full coverages, differences in the strength of hydrogen–copper and hydrogen–ruthenium adsorption bonds would cause the hydrogen atom to spend more time on one of the elements.

Another possible explanation for the downfield shift of the proton frequency with increasing concentration of Cu is that while there is no spillover from Ru to Cu, the increasing the number of Cu atoms sufficiently changes the band structure of the Ru to cause the observed effect. This explanation seems unlikely on the basis of the known independence of hydrogen thermal desorpton from the Ru (0001) having various Cu coverages.[12,16] The thermal desorption results suggest that the presence of Cu will not change the electronic structure of Ru to account for the observed shift in proton NMR.

To test whether spillover and exchange or an electronic effect is the reason for the downfield shift of the adsorbed hydrogen upon addition of copper to the catalyst, a pulse spin labeling experiment was performed on hydrogen adsorbed on the 5% Ru–0.39% Cu/SiO_2 catalyst. In this experiment, a soft prepulse was used to selectively invert spins which would be at the frequency associated with protons on Ru. The pulse was 40 μs wide, corresponding to a 3-dB bandwidth of ±6.25 kHz (±28 ppm) and was centered 50 ppm upfield. Consequently, this pulse had a negligible frequency intensity at the frequencies associated with the hydroxyl protons and the H-metal protons observed on the bimetallic catalyst. After a period τ, varying between 50 μs and 60 ms, the magnetization of all protons was placed in the x–y plane of the rotating frame with a hard (pulse width = 2 μs) $90°_x$ pulse, and with the magnetization monitored along the y direction of the rotating frame.

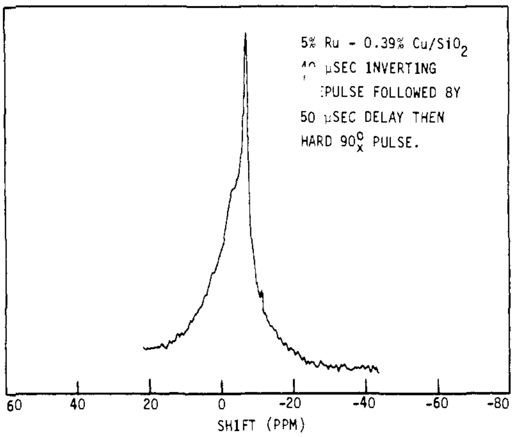


Figure 2. Spectrum resulting from soft inverting prepulse centered at the resonance of hydrogen on ruthenium.

If the downfield shift of the proton on the bimetallic catalyst is due to an electronic effect or susceptibility variation, then the spin labeling prepulse would have no effect on the resultant spectrum and it should be identical with that shown in Figure 1C. This is because the prepulse excites a region excluding any observed resonances. If, on the other hand, the downfield shift of the protons on the bimetallic catalyst is due to a fast exchange of protons on Cu and Ru, the prepulse will alter the observed spectrum. Even though the proton on Ru resonance is not observed on the bimetallic catalyst, protons still resonate at that frequency and the prepulse in that region effects those nuclei.

Furthermore, when there is a fast exchange of the protons on Cu and Ru, there are two possible results of the spin labeling experiment. First, if chemical exchange exists on a time scale which is slow compared to the time of the soft pulse, one would expect inverted spins initially at the center frequency of the soft pulse to exchange with spins out of this frequency range. Also, as τ increases, the intensity of the peak identified as that resulting from fast exchange would initially decrease with τ, and then increase as τ approaches $5T_1$. A second possibility is that the exchange rate is fast compared to that of the time of the soft pulse. In this case, there is a continual exchange between H–Cu and H–Ru during the soft pulse. The effect of the soft pulse in this situation is to disturb the protons associated with the metal surface from equilibrium, such that the initial intensity observed for such protons is reduced after a hard $90°_x$ pulse. The result would be an initial decrease in intensity of the observed fast exchange peak and an increase as τ is increased due to longitudinal relaxation of the protons associated with the metals in the variable time τ between the soft and hard pulses. It is the latter case that is observed, as shown in Figure 2. At a τ = 50 μs, the intensity of the H–metal peak is attenuated to a shoulder downfield of the peak due to hydroxyl protons. At τ = 40 ms, the intensity of the H–metal peak has recovered to its initial value (Figure 1C.). It is notable that the intensity of the hydroxyl peak is not affected by the soft pulse, indicating that both the hydroxyl protons and the species identified as being H–metal on the bimetallic in the fast exchange limit are outside the bandwidth of the soft pulse.

The frequency difference between protons on Ru and protons on Cu is on the order of 11 kHz. In the fast exchange limit, for

---

(21) Sinfelt, J. H. *J. Catal.* **1973**, *29*, 308.

a single sharp peak to be observed intermediate between the two resonances, the exchange rate must be on the order of 10 times this value or about 10^5 Hz. This exchange rate is fast compared with the inverse width of the soft pulse, but must be slow relative to the frequency of the NMR experiment (10^8 Hz). Hence, the exchange frequency of protons on the bimetallic catalyst must be from about 10^5 to 10^7 Hz.

In summary, we have observed that hydrogen will dissociatively adsorb on Cu–Ru/SiO_2 catalysts and populate sites on both Cu and Ru. This direct evidence for hydrogen spillover from Ru onto Cu suggests that hydrogen chemisorption cannot be used to titrate the number of surface Ru atoms in a Cu–Ru bimetallic catalyst.

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Energy Sciences, WPAS-KS-03-02-01. In addition, work of two of the authors (T. S. King and X. Wu) was partially supported by Grant CPE-8307959 of the National Science Foundation.

Facile Net Loss of a Carbon Atom from a Constrained Intermediate

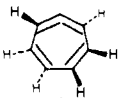
Supanna Tivakornpannarai and Edward E. Waali*

Department of Chemistry, University of Montana
Missoula, Montana 59812

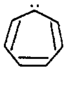
Received March 13, 1986

In a study of physically constrained cycloheptatrienylidenes and cycloheptatetraenes, an anthraceno bridged intermediate has been generated and an unusual reaction resulting in the net loss of a lone *carbon atom* has been discovered.

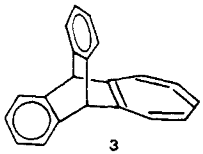
The relationship between cycloheptatetraene (**1**) and cycloheptatrienylidene (**2**) has been the focus of considerable experimental and theoretical effort.[1-4] It now appears that all of the chemistry once attributed to the singlet state of planar **2**[5] should instead be explained in terms of the nonplanar allene **1**.[2-4] Our calculations using both reaction coordinates and vibrational force constants led to the conclusion that planar singlet **2** is a *transition state* for the interconversion of chiral **1** and its enantiomer.[4d]



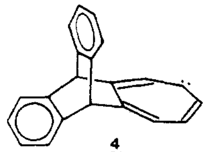
1



2



3



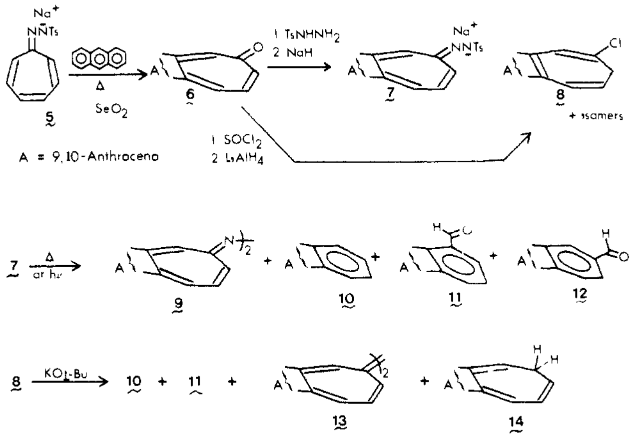
4

The tropone **6** has been prepared.[7] The structure of **6** was indicated by high-field NMR spectroscopy and a high-resolution mass spectroscopy and was verified by X-ray crystallographic structure determination. The ketone **6** was converted to **7** and **8** by known methods.[1a] The decomposition of **7** or the reaction of **8** with strong base should give the allene **3** since this type of constraint (C4–C5 bridging using the numbering of **1**) should only reinforce its stability relative to **4**. Upon thermolysis or photolysis, **7** gave the azine **9** and triptycene (**10**) (Table I). In some experiments, the aldehydes **11** and **12**, the dimer **13**, and the cycloheptatriene **14** were also observed.[7]

Table I. Product Yields from the Decomposition of **7** and **8**

starting material	conditions[b]	yields,[a] %			
		9	**10**	**11**	other
7	$h\nu$, 30 °C, 0.0212 M, THF	30	5		
7	$h\nu$, 30 °C, 0.0124 M, THF	9	37		
7	Δ, 125 °C, 0.0405 M, diglyme	32	2		
7	Δ, 125 °C, 0.0117 M, diglyme	18	19	5	
7	Δ, 125 °C, 0.0124 M, Me_2SO	22	12		2 (Me_2S)
8	KO-*t*-Bu, RT,[d] 0.161 M, THF		12		45 (13)[c]
8	KO-*t*-Bu, RT,[d] 0.085 M, THF		12		4 (13)

[a] Isolated yields after preparative thin-layer chromatography (TLC). The remaining material would not move under the TLC conditions. [b] Nitrogen atmosphere. [c] The dimer 13 was not stable to TLC. This represents a column chromatographic purification. It was probably also formed in the previous reactions but was destroyed under the TLC conditions. [d] RT = room temperature.



Although the formations of **11–14** are in some respects unusual under these conditions, they will be discussed at a later time.[8,9]

The formation of **10** requires the net loss of a carbon atom and is, to our knowledge, unknown in carbene or allene chemistry under such mild conditions in solution. The amounts of **9** and **10** are concentration dependent with more **10** being formed at lower concentrations of **7** and **8**.[10] The loss of carbon atoms from quadricyclanylidene (**15**),[11] norbornadienylidene (**16**),[12] and other strained cyclic carbenes[13] has been observed under the much more vigorous conditions of the vacuum pyrolysis of the tosylhydrazone salts at 250–400 °C. The reverse of this type of reaction (benzene + arc-produced carbon atoms giving, ultimately, heptafulvalene) has been reported.[13,14] Thus, the loss of a carbon atom in rea-

---

(1) (a) Jones, W. M.; Ennis, C. L. *J. Am. Chem. Soc.* **1969**, *91*, 6391. (b) Christensen, L. W.; Waali, E. E.; Jones, W. M. *Ibid.* **1972**, *94*, 2118. (c) Waali, E. E.; Jones, W. M. *Ibid.* **1973**, *95*, 8114. (d) Waali, E. E.; Jones, W. M. *Synthetic Commum.* **1973**, *3*, 49. (e) Waali, E. E.; Jones, W. M. *J. Org. Chem.* **1973**, *38*, 2573. (f) Duell, B. L.; Jones, W. M. *J. Org. Chem.* **1978**, *43*, 4901. (g) Mayor, C.; Jones, W. M. *Tetrahedron Lett.* **1977**, 3855. (h) Reiffen, M.; Hoffmann, R. W. *Ibid.* **1978**, 1107.

(2) Harris, J. W.; Jones, W. M. *J. Am. Chem. Soc.* **1982**, *104*, 7329.

(3) West, P. R.; Chapman, O. L.; LeRoux, J.-P. *Ibid.* **1982**, *104*, 1779.

(4) (a) Tyner, R. L.; Jones, W. M.; Ohrn, Y.; Sabin, J. R. *J. Am. Cvhem. Soc.* **1974**, *96*, 3765. (b) Radom, L.; Schaefer, H. F.; III; Vincent, M. A. *Nouv. J. Chim.* **1980**, *4*, 411. (c) Dewar, M. J. S.; Landman, D. *J. Am. Chem. Soc.* **1977**, *99*, 6719. (d) Kassaee, M. Z.; Nimlos, M. R.; Downie, K. E.; Waali, E. E. *Tetrahedron* **1985**, *41*, 1579.

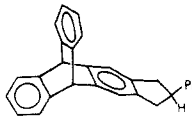
(5) There have been two very recent reports of the matrix isolation ESR spectrum of triplet **2**. (a) Kuzaj, M.; Luerssen, H.; Wentrup, C., private communication from C. Wentrup, 1985. (b) McMahon, R. J.; Chapman, O. L. *J. Am. Chem. Soc.* **1986**, *108*, 1713.

(6) Saito, K.; Omura, Y.; Mukai, T. *Tetrahedron Lett.* **1980**, 349.

(7) New compounds (**6–9** and **11–14**) were identified on the basis of their 270-MHz proton NMR spectra, 22.5-MHz carbon NMR spectra, and their high-resolution mass spectra (or satisfactory elemental analysis). Authentic samples of **10–12** were prepared and compared to the materials isolated in the described reactions.

(8) Rearrangements of the type which ultimately give **11** and **12** are discussed in: (a) Jones, W. M. *Acc. Chem. Res.* **1977**, *10*, 353. (b) Gaspar, P. P.; Hsu, J.-P.; Chari, S.; Jones, M., Jr. *Tetrahedron* **1985**, *41*, 1479.

(9) The generation of **3** in the presence of styrene gave a 17% yield of **i**



i

in addition to the above products. Such an addition and rearrangement has also been observed from **1**.[1c]

(10) Shevlin, P. B.; Wolf, A. P. *Tetrahedron Lett.* **1970**, 3987.

(11) Brown, W. T.; Jones, W. M. *J. Org. Chem.* **1970**, *44*, 3090.

(12) (a) Moss, R. A.; Dolling, U.-H.; Whittle, J. R. *Tetrahedron Lett.* **1971**, 931. (b) Okumura, K.; Murahashi, S.-I. *Ibid.* **1977**, 3281.

(13) Biesida, K. A.; Kooch, C. T.; Shevlin, P. B. *J. Am. Chem. Soc.* **1980**, *102*, 2098.

(14) The loss of carbon has been observed in the oxidation of tropylium ions (Volpin, M. E.; Kursanov, D. N.; Dulova, V. G. *Tetrahedron* **1960**, *8*, 33), but this is probably not related to the reaction described in the present work.

0002-7863/86/1508-6058$01.50/0