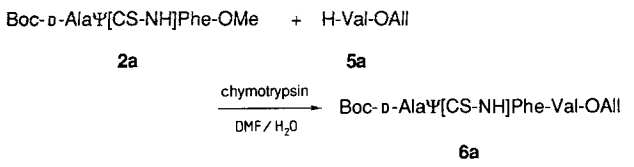
Table 1. Thiopeptides **6a–g** synthesized with chymotrypsin.

Starting materials [a]	Thiopeptides	Yield [%]
2a + **5a**	Boc-D-AlaΨ[CS-NH]Phe-Val-OAll **6a**	70
2a + **5b**	Boc-D-AlaΨ[CS-NH]Phe-Val-OMe **6b**	49
2a + **5c**	Boc-D-AlaΨ[CS-NH]Phe-Leu-NH_2 **6c**	48
2a + **5e**	Boc-D-AlaΨ[CS-NH]Phe-PheΨ[CS-NH]Gly-OMe **6d**	63
	+ Boc-D-AlaΨ[CS-NH]Phe-(PheΨ[CS-NH]Gly)$_2$-OMe **6e**	8 [b]
2b + **5d**	Boc-LeuΨ[CS-NH]Leu-Phe-NH_2 **6f**	66
2b + **5e**	Boc-LeuΨ[CS-NH]Leu-PheΨ[CS-NH]Gly-OMe **6g**	26

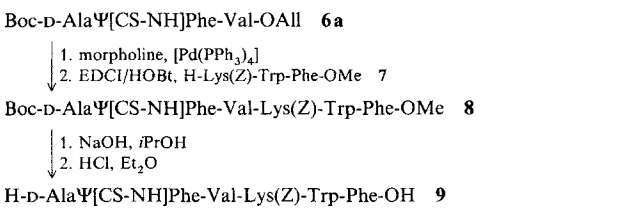
[a] **5a** = H-Val-OAll, **5b** = H-Val-OMe, **5c** = H-Leu-NH_2, **5d** = H-Phe-NH_2, **5e** = H-PheΨ[CS-NH]Gly-OMe. [b] Byproduct in the synthesis of **6d**.

or peptide elongation. Exceptions are the reactions of **2a** + **5c** and **2b** + **5e** in which 46 and 30% of the respective starting peptides were recovered. The results of the enzymatic reactions (Table 1) are not optimized, and yields may be increased by variation of cosolvent, substrate, and enzyme.

When thiopeptides such as **5e** are used as the amino component in peptide couplings, tetrapeptides with alternating thioamide bonds (**6d, g**) are formed. The hexapeptide **6e** containing three thioamide groups was isolated as a byproduct (8%) in the synthesis of **6d**. Apparently some of the amine **5e** dimerized to the tetrapeptide H-PheΨ[CS-NH]Gly-PheΨ[CS-NH]Gly-OMe, which was then preferentially elongated by chymotrypsin to **6e**.



Chymotrypsin cleaves peptides after aromatic amino acids and leucine with high specifity,[8] but does not attack valine esters.[9] Hence, the reaction of thiopeptide **2a** with valine allyl and methyl esters **5a, b** proceeds to thiotripeptides esters. It is remarkable that the slightly larger and more lipophilic allyl ester group in the nucleophile increases the yield by more than 20%. The resulting tripeptides **6a** (70% yield) and **6b** (49% yield) can be deprotected and incorporated into larger fragments. Removal of the allyl ester protecting group in thiotripeptide **6a** under Pd^0 catalysis was not affected by the nucleophilic thioamide sulfur atom (Scheme 1).[10, 11] Subsequent coupling with **7** in the presence of *N'*-(3-dimethylaminopropyl)-*N*-ethylcarbodiimide hydrochloride/1-hydroxybenzotriazole (EDCI/HOBt) gave thiohexapeptide **8** in 85% yield. Deprotection yielded **9** which is presently under investigation in cyclization reactions.



Scheme 1. Reactions sequence starting from thiopeptide **6a**.

The method described here for the enzymatic elongation of thiodipeptides can certainly be applied for the elongation of a number of other amino acids at the *C* terminus. The choice of suitable enzymes and appropriate protecting groups should allow the selective introduction of thioamide bonds in a variety of peptide linkages.

Experimental Precedure

N-tert-Butyloxycarbonyl-D-thioalanyl-L-phenylalanyl-L-valine allyl ester (**6a**): A 500 mg portion (1.37 mmol) of **2a** and 860 mg (5.48 mmol) of **5a** were dissolved in 21.2 mL of DMF/H_2O (1/1) in a plastic vessel. 250 mg of chymotrypsin was added, and the solution was stirred for 48 h. The mixture was concentrated in high vacuum and chromatographed on 30 g silica gel eluting with CH_2Cl_2/MeOH (100/1). Yield 472 mg (70%) **6a**. $[\alpha]_D^{22} = -4.0$ ($c = 1$, MeOH).

Received: March 13, 1992 [Z 5238IE]
German version: *Angew. Chem.* **1992**, *104*, 1231

CAS Registry numbers:
2a, 142765-11-5; **2b**, 128421-81-8; **5a**, 88224-01-5; **5b**, 4070-48-8; **5c**, 687-51-4; **5d**, 5241-58-7; **5e**, 142765-12-6; **6a**, 142765-13-7; **6b**, 142765-14-8; **6c**, 142765-15-9; **6d**, 142765-16-0; **6e**, 142765-17-1; **6f**, 142765-18-2; **6g**, 142765-19-3; **7**, 142765-20-6; **8**, 142765-21-7; **9**, 142765-22-8; chymotrypsin, 9004-07-3; protease, 9001-92-7.

[1] A. F. Spatola in *Chemistry and Biochemistry of Amino Acids, Peptides and Proteins, Vol. 7* (Ed.: B. Weinstein), Marcel Dekker, New York, **1983**, pp. 267–357.
[2] R. E. Beattie, D. T. Elmore, C. H. Williams, D. J. S. Guthrie, *Biochem. J.* **1987**, *245*, 285–288, and references therein.
[3] D. Seebach, S. Y. Ko, H. Kessler, M. Köck, M. Reggelin, P. Schmieder, M. D. Walkinshaw, J. J. Bölsterli, D. Bevec, *Helv. Chim. Acta* **1991**, *74*, 1953–1990; H. Kessler, H. Matter, A. Geyer, H.-J. Diehl, M. Köck, G. Kurz, F. R. Opperdoes, M. Callens, R. K. Wierenga, *Angew. Chem.* **1992**, *104*, 343–345; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 328–330.
[4] K. Clausen, M. Thorsen, S.-O. Lawesson, *Tetrahedron* **1981**, *37*, 3635–3639.
[5] a) M. Yokoyama, Y. Hasegawa, H. Hatanaka, Y. Kawazoe, T. Imamoto, *Synthesis* **1984**, 827–829; b) G. Lajoie, F. Lepine, B. Belleau, *Tetrahedron Lett.* **1983**, *24*, 3815–3818; c) H. Davy, *J. Chem. Soc. Chem. Commun.* **1982**, 457–458.
[6] a) O. E. Jensen, A. Senning, *Tetrahedron* **1986**, *42*, 6555–6564; b) D. B. Sherman, A. F. Spatola, *J. Am. Chem. Soc.* **1990**, *112*, 433–441; c) D. W. Brown, M. M. Campbell, M. S. Chambers, C. V. Walker, *Tetrahedron Lett.* **1987**, *28*, 2171–2174.
[7] C. F. Barbas III, J. R. Matos, J. B. West, C. H. Wong, *J. Am. Chem. Soc.* **1988**, *110*, 5162–5166.
[8] H. D. Jakubke in *The Peptides, Vol. 9* (Eds.: S. Udenfriend, J. Meienhofer), Academic Press, London, **1987**, pp. 103–165.
[9] G. Kloss, G. Schroeder, *Hoppe-Seyler's Z. Physiol. Chem.* **1964**, *336*, 248–256.
[10] H. Waldmann, H. Kunz, *Liebigs Ann. Chem.* **1983**, 1712–1725.
[11] H. Kunz, C. Unverzagt, *Angew. Chem.* **1984**, *96*, 426–427; *Angew. Chem. Int. Ed. Engl.* **1984**, *27*, 1697–1699.

2,4-Didehydrophenol—First Proof of a *meta*-Aryne by IR Spectroscopy**

By *Götz Bucher, Wolfram Sander,* Elfi Kraka,* and *Dieter Cremer**

Dedicated to Professor Günther Maier on the occasion of his 60th birthday

Since the pioneering work of Wittig et al.[1] arynes have enjoyed a special status in mechanistic and preparative organic chemistry.[2] This area has received added impetus re-

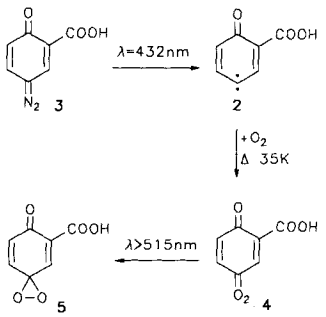
[*] Prof. W. Sander, Dipl.-Chem. G. Bucher
Institut für Organische Chemie der Technischen Universität
Hagenring 30, D-W-3300 Braunschweig (FRG)

Prof. D. Cremer, Prof. E. Kraka
Department of Theoretical Chemistry, University of Göteborg
Kemigården 3, S-41296 Göteborg (Sweden)

[**] This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the Swedish Natural Science Research Council, and the Nationellt Superdatorcentrum (Linköping, Sweden).

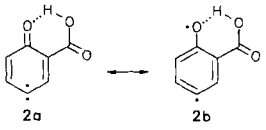
cently from the discovery that derivatives of *p*-dehydrobenzene play an important role in the mechanism of action of the enediyne anticancer agents.[3] Although *o*-dehydrobenzene has been well characterized,[4] unequivocal spectroscopic evidence for *m*- and *p*-dehydrobenzene is lacking. 9,10-Dehydroanthracene is the only derivative of *p*-dehydrobenzene to be characterized by spectroscopy.[5] Both *m*- and *p*-dehydrobenzene have already been investigated by mass spectrometry and UV spectroscopy,[6a, b] but the methods employed did not allow a definite assignment of the UV spectra. Recently, the heats of formation of *o*-, *m*-, and *p*-dehydrobenzene determined by mass spectrometry by measurement of the collision-induced dissociation (CID) were shown to be 106 ± 3, 116 ± 3, and 128 ± 3 kcal mol^{-1}, respectively.[7] According to these results *m*- and *p*-dehydrobenzene should be isolable in a matrix. Ab initio investigations of the dehydrobenzenes have not thoroughly treated *m*- and *p*-dehydrobenzene.[8] The *ortho* isomer has received more attention; its harmonic oscillation frequencies have been determined on the GVB,[9] MP2, and TCSCF levels.[10] Here we report on the first direct IR spectroscopic proof of 2,4-didehydrophenol (**1**), an *m*-dehydrobenzene, by means of matrix isolation.[11, 12]

In connection with our work on the vinylcarbene–cyclopropene rearrangement[13, 14] we also examined 3-carboxy-4-oxo-2,5-cyclohexadienylidene (**2**) and the isotopomer deuterated at the carboxyl group, [D$_1$]**2**. Irradiation of quinone diazide **3**[11] in a matrix with visible light (argon, 10 K, $\lambda > 470$ nm) did not lead to the expected carbene **2**, but rather by cleavage of CO_2 to a new compound, which we identified as aryne **1** (see below). Carbene **2** may be obtained from **3** by narrow-band irradiation ($\lambda = 432 \pm 10$ nm, 90 min) and subsequently investigated by IR and UV/VIS spectroscopy.[15] Proof of the existence of **2** in the matrix was provided by the very characteristic formation of carbonyl oxide **4**[16] in the diffusion-controlled reaction with molecular oxygen.[17] Carbonyl oxide **4** rearranges upon long-wavelength irradiation ($\lambda > 515$ nm) into dioxirane **5**,[18] which is transformed in turn into a lactone[19] when irradiated with blue light ($\lambda > 400$ nm; Scheme 1).

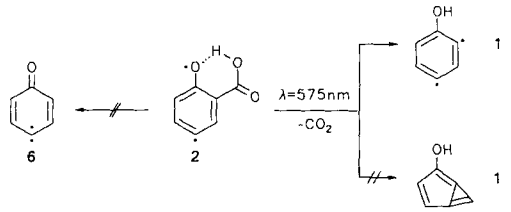


Scheme 1.

A notable feature in the IR spectrum of **2** is the low vibrational frequency of the C4 carbonyl group, which at 1415 cm^{-1} is red-shifted by 82 cm^{-1} relative to the parent compound **6**. This is evidence of the increased importance of the phenoxyl structure **2b** in describing the ground state of **2**. Structure **2b** is presumably stabilized by an intramolecular hydrogen bond. In the UV/VIS spectrum an absorption with a broad and very weak maximum at approximately 600 nm is observed as well as a narrow band with an absorption maximum at 390 nm , both characteristic for a 4-oxo-cyclohexadienylidene structure.[14, 20]



Irradiation of the long-wavelength absorption band of **2** ($\lambda = 575 \pm 10$ nm, 20 min) causes a rapid decarboxylation (intense absorption of CO_2 at 2347 cm^{-1}) and formation of a new compound, **1** (Scheme 2), with intense IR bands at



Scheme 2.

3612.0, 1516.3, 641.2, and 518.8 cm^{-1} (Fig. 1, Table 1). The IR bands assigned to **1** disappear upon irradiation with $\lambda > 420$ nm (see below).

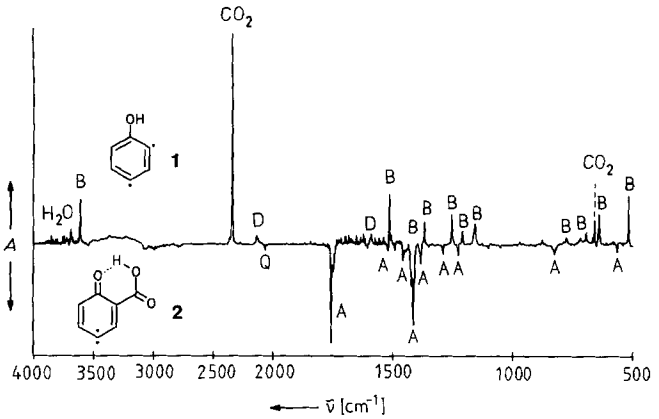


Fig. 1. Difference IR spectrum showing the photochemistry of carbene **2** ($\lambda = 575$ nm, Ar, 10 K). Bottom : bands that disappear upon irradiation; top: bands that arise. A: Carbene **2**, B: dehydrophenol **1**, D: unknown side product, Q: diazide.

The decarboxylation can also be observed in the UV/VIS spectrum: The bands assigned to carbene **2** disappear upon irradiation with $\lambda = 575 \pm 10$ nm, and a new band with a maximum at 344 nm and a shoulder at 356 nm arise.

Under the same conditions other 4-oxo-2,5-cyclohexadienylidenes undergo vinylcarbene–cyclopropene rearrangement to 1,3-bridged cyclopropenes;[13, 14] in our case this is of at most minor importance.[21] Irradiation of [D$_1$]**3**, the derivative of **3** deuterated on the carboxy group, provides a product with absorption bands at 3612.0 and 1157.6 cm^{-1} which are red-shifted relative to the non-deuterated product by 944 and 215 cm^{-1}, respectively. This allows the corresponding assignment of the O–H stretching and the C–O–H deformation vibrations. All the other IR bands show only small deuterium shifts. Analogous bands were observed for phenol at 3623 (− 973) cm^{-1} and 1180 (− 270) cm^{-1}, respectively, indicating the similarity of the hydroxyl groups in the decarboxylated product **1** and in phenol.

Table 1. IR spectroscopic data for 1.

Experiment $\tilde{\nu}$[cm^{-1}]	I [a]	$\tilde{\nu}_i/\tilde{\nu}$ [b]	GVB/6-31G(d,p) $\tilde{\nu}$[cm^{-1}] [c]	I [a]	$\tilde{\nu}_i/\tilde{\nu}$ [b]	Assignment [d]
3612.0	s	0.738	3776	0.85	0.728	ν_{27} (O-H, str.)
			1623	0.26	0.998	ν_{23}
1516.3	s	0.997	1551	0.64	0.998	ν_{22}
1429.0	w	0.982	1409	0.3	0.999	ν_{21}
1368.2	m	0.987	1386	0.46	0.981	ν_{20}
1290.1	w	0.979	1280	0.16	0.990	ν_{19}
1254.9	m	– [e]	1243	1.0	0.982	ν_{18}
1209.1	m	– [e]	1183	0.31	0.979	ν_{17}
1157.6	m	0.814	1117	0.55	0.815	ν_{16} (O-H, def.)
1128.6	vw	– [e]	1074	0.11	1.0	ν_{15}
971.0	w	1.008	979	0.1	1.0	ν_{14}
877.0	w	0.997	905	0.06	1.0	ν_{12}
–			819	0.76	1.0	ν_{10}
–			757	0.32	0.988	ν_9
694.7	m	0.981	–			
641.2	s	1.0	–			
518.8	s	0.984				
–			257	0.43	0.738	ν_1 (O-H, tors.)

[a] Relative intensities. [b] Ratio of the vibration frequencies $\tilde{\nu}_i/\tilde{\nu}$ upon deuteration. [c] Scaling factor 0.9. [d] Approximate assignment based on the positions and the relative intensities of the bands. [e] Because of the large changes in intensities upon deuteration, $\tilde{\nu}_i/\tilde{\nu}$ cannot be determined reliably.

This unequivocal proof of the presence of a hydroxyl group and the absence of a carbonyl group greatly reduces the number of possible structures for **1** with the molecular formula C_6H_4O. Because of the very mild conditions in the synthesis of **1** (irradiation with $\lambda = 575$ nm, 10 K), a rearrangement of the carbon framework or a ring opening can be ruled out. (These would also cause a loss of phenol character.) The remaining reasonable structures are 2,4-didehydrophenol (**1**) and its bicyclic isomer, bicyclo[3.1.0]hexa-1,3,5-trien-1-ol (**1'**) (Scheme 2).

According to calculations (GVB/6-31G(d,p)//HF/6-31G(d,p)), in the singlet ground state the monocyclic biradical structure **1** is 17 kcal mol^{-1} more stable than the bicyclic structure **1'**.[23] In the geometry optimizations with GVB/6-31G(d,p) as well as with MP2/6-31G(d,p), **1'** is converted to **1**, indicating that **1'** most likely does not exist. In the GVB equilibrium geometry of **1** the C_{2v}-symmetric carbon framework of 1,3-didehydrobenzene is only slightly perturbed by the OH substituent (which is also indicated by the small dipole moment of 0.7 D). Thus **1** offers a realistic insight into the bonding relationships in 1,3-didehydrobenzene. **1** is planar, and the OH group points in the direction of the neighboring radical center (Fig. 2). Examination of the calculated electron-density distribution shows that the OH group is held in the plane of the ring by the electrostatic attraction between the partially positively charged H atom and the neighboring radical center.

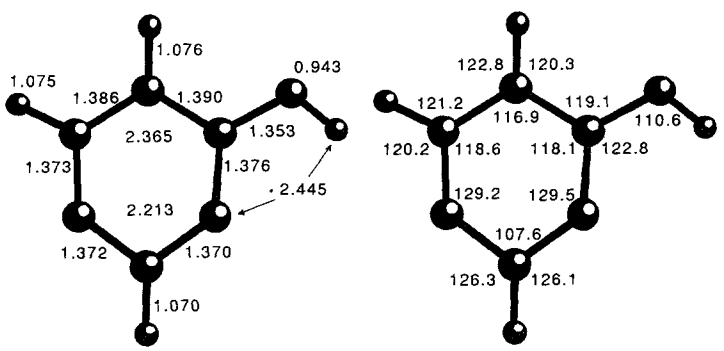


Fig. 2. Structure of 2,4-didehydrophenol (**1**) optimized by GVB/6-31G(d,p). Left, bond lengths [Å], right, bond angles [°].

An assignment of the experimental spectra to **1** or **1'** is possible by comparison with the calculated vibration spectra (Fig. 3). The calculated IR spectrum of **1** (GVB/6-31G(d,p,)) is in full agreement with the measured IR spectrum between 3600 and 800 cm^{-1}; only the bands at 641 and 519 cm^{-1} were not reproduced very well in the calculation. For [D_1]**1** the calculated isotopic shifts of 1027 and 207 cm^{-1} for the O–D stretching and the C–O–D deformation vibrations agree well with the corresponding experimental values (see Table 1).

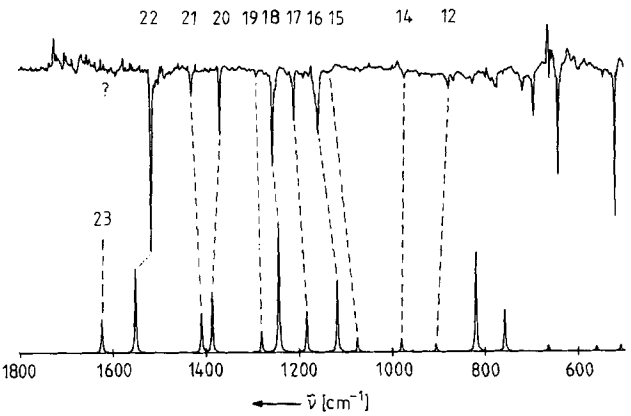


Fig. 3. Correlation between the experimental IR spectrum (top) and that calculated (GVB/6-31G(d,p); bottom). The assignment is only approximate and is based on the comparison of the positions and intensities of the bands. The calculated spectrum has been scaled by a factor of 0.9.

The alternative isomer, bicycle **1'**, can be ruled out by comparison of the experimental and theoretical spectra and by the fact that calculations with neither GVB nor with MP2 indicated its existence. The observed, intense long-wavelength absorption in the UV/VIS spectrum, which is about 80 nm red-shifted relative to the longest wavelength band for phenol, also supports to the diradical structure **1**.[25]

Dehydrophenol **1** is stable to irradiation with $\lambda > 570$ nm, but short-wavelength light ($\lambda > 420$ nm) will convert it into a ketene (IR, Ar, 10 K: $\tilde{\nu}$ = 2138.2 (s), 1419.4 (w), 1046.7 (w), 963.3 (w) cm^{-1}). Upon warming to 30 K in an O_2-doped matrix **1** reacts at a rate comparable to that of carbene **2** to give an oxidation product of unknown composition. Because of the small amount of **3** that could be sublimed into the matrix,[11] the ketene and the oxidation product of **1** could not be characterized further. However, the fast reaction with O_2 is further support for the diradical character of **1**. All experimental and theoretical findings can be explained only with the diradical structure **1**.

Received: March 10, 1992 [Z 5234 IE]
German version: *Angew. Chem.* **1992**, *104*, 1225

CAS Registry numbers:
1, 142746-79-0; **2**, 142746-80-3; **3**, 121-13-1; **4**, 142746-81-4; **5**, 142746-82-5.

[1] G. Wittig, *Naturwiss.* **1942**, 696.
[2] a) C. Grundmann, *Methoden Org. Chem. (Houben-Weyl)*, 4th ed. 1952-, Vol. 5, [Arene und Arine (Ed.: C. Grundmann)], pp. 613–648; b) R. W. Hoffmann, *Dehydrobenzene and Cycloalkynes* in *Organic Chemistry, Vol. 11* (Ed.: A. T. Blomquist), Academic Press, New York, **1967**.
[3] K. C. Nicolaou, W. M. Dai, *Angew. Chem.* **1991**, *103*, 1453; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1387.

[4] a) O. L. Chapman, K. Mattes, C. L. McIntosh, J. Pacansky, G. V. Calder, G. Orr, *J. Am. Chem. Soc.* **1973**, *95*, 6134; b) O. L. Chapman, C. C. Chang, J. Kolc, N. R. Rosenquist, H. Tomioka, *ibid.* **1975**, *97*, 6586; c) C. Wentrup, R. Blanch, H. Briehl, G. Gross, *ibid.* **1988**, *110*, 1874; d) J. G. G. Simon, N. Muenzel, A. Schweig, *Chem. Phys. Lett.* **1990**, *170*, 187; e) J. G. Radziszewski, B. A. Hess, Jr., R. Zahradnik, *J. Am. Chem. Soc.* **1992**, *114*, 52.

[5] O. L. Chapman, C. C. Chang, J. Kolc, *J. Am. Chem. Soc.* **1976**, *98*, 5703.

[6] a) R. S. Berry, J. Clardy, M. E. Schafer, *Tetrahedron Lett.* **1965**, *15*, 1011; b) *ibid.* **1965**, *15*, 1003.

[7] P. G. Wenthold, J. A. Paulino, R. R. Squires, *J. Am. Chem. Soc.* **1991**, *113*, 7414.

[8] J. O. Noell, M. D. Newton, *J. Am. Chem. Soc.* **1979**, *101*, 51.

[9] K. Rigby, I. H. Hillier, M. Vincent, *J. Chem. Soc. Perkin Trans.* **1987**, *2*, 117.

[10] A. C. Scheiner, H. F. Schaefer III, B. Liu, *J. Am. Chem. Soc.* **1989**, *111*, 3118.

[11] An APD closed-cycle helium cryostat was used in the matrix experiments (see ref.[12]). IR spectra were recorded with a Bruker IFS 66 spectrometer between 4000 and 500 cm^{-1} with a resolution of 1 cm^{-1}, UV/VIS spectra with an HP 8452A diode array spectrometer with a resolution of 2 nm. **3** was deposited in the matrix at 25–30 K, the photolyses and the recording of spectra were conducted at 10 K. Because of the low volatility and the low thermal stability of **3** (ref.[24]) only small amounts could be sublimed onto the matrix window. **3:** IR (Ar, 10 K): $\tilde{\nu}$ 2113.6 (s), 2092.9 (w), 2057.2 (vw), 1740.9 (w), 1595.8 (vs), 1564.0 (vw), 1535.1 (w), 1481.1 (m), 1473.3 (s), 1458.4 (w), 1379.3(m), 1335.0 (vw), 1260.3 (vw), 1204.3 (w), 1164.8 (s), 1127.2 (w), 838.9 (vw), 528.9 (vw) cm^{-1} (rel. intensity).

[12] For a description of the apparatus see W. Sander, *J. Org. Chem.* **1989**, *54*, 333.

[13] W. Sander, G. Bucher, F. Reichel, D. Cremer, *J. Am. Chem. Soc.* **1991**, *113*, 5311.

[14] a) G. Bucher, W. Sander, *J. Org. Chem.* **1992**, *57*, 1346; b) G. Bucher, W. Sander, *Chem. Ber.* **1992**, *125*, in press.

[15] **2:** IR (Ar, 10 K): $\tilde{\nu}$ = 1758.3 (vs, 0.994), 1750.1 (m, –), 1523.5 (w, –), 1495.0 (m, 0.998), 1458.9 (w, 0.999), 1422.2 (s, –), 1415.0 (vs, 1.000), 1383.7 (w, 1.000), 1291.6 (w, 1.001), 1228.9 (w, –), 1053.9 (vw, –), 982.6 (vw, –), 826.3 (w, –), 565.0 (vw, 1.000), 542.9 (vw, –) cm^{-1} (rel. intensity, $\tilde{\nu}/\tilde{\nu}_i$); UV/VIS (Ar, 10 K): ca. 600 (vw, br), 390 (m), 316 (s), 306 (s), 236 (vs) nm (rel. intensity).

[16] **4:** IR (Ar, 10 K): $\tilde{\nu}$ = 1772.7 (s), 1766.0 (s), 1607.9 (m), 1601.6 (s), 1598.7 (s), 1583.3 (m), 1578.0 (m), 1573.1 (m), 1406.8 (vs), 1219.3 (m), 1082.4 (s), 888.5 (w), 849.0 (m), 844.2 (m), 658.6 (m), 655.2 (m) cm^{-1} (rel. intensity).

[17] W. Sander, *Angew. Chem.* **1990**, *102*, 362; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 344.

[18] **5:** IR (Ar, 10 K): $\tilde{\nu}$ = 1778 (vs), 1674.9 (s), 1657.0 (s), 1633.4 (w), 1405.9 (vs), 1395.2 (vs), 1391.9 (vs), 1321.5 (m), 1271.3 (vw), 1105.0 (m), 1039.0 (m), 1034.1 (m), 989.3 (vw), 953.1 (vw), 864.0 (w), 853.3 (m), 847.6 (m), 804.2 (w), 793.1 (w), 654.2 (m) cm^{-1} (rel. intensity).

[19] Because of the low concentration of **2** and the products of its subsequent reactions in the matrix, it was not possible to characterize unequivocally the isomeric lactones that formed. In the frequency range for carbonyl groups, absorptions were observed at 1783.8 (s, COOH), 1740.4 (s), 1724.5 (s), 1713.4 (s), 1672.9 (m), and 1623.8 (s) cm^{-1}. However, in analogy to the chemistry of *p*-benzoquinone-*O*-oxide, the formation of a 2,5-oxepinedione is expected (for the parent compound: $\tilde{\nu}$(C=O at 1753 and 1660 cm^{-1}, ref.[13,14,20]).

[20] W. Sander, *J. Org. Chem.* **1988**, *53*, 2091.

[21] In the very slow decarboxylation with red light ($\lambda > 600$ nm) small amounts of an extremely photolabile compound also form with absorption bands between 1700 and 1800 cm^{-1}; this could be the cyclopropene.

[22] a) J. Gebicki, A. Krantz, *J. Am. Chem. Soc.* **1984**, *106*, 8093; b) J. H. S. Green, *J. Chem. Soc.* **1961**, 2236; c) G. T. Reedy, S. Bourne, P. T. Cunningham, *Anal. Chem.* **1979**, *51*, 1535; H. D. Bist, J. C. D. Brand, D. R. Williams, *J. Mol. Spectrosc.* **1967**, *24*, 402.

[23] GVB(1)/6-31G(d,p)//HF/6-31G(d,p) energies [Hartree]: −304.27655 (**1**), −304.248998 (**1'**); GVB(1)/6-31G(d,p): −304.27809 (**1**); RMP2/6-31G(D,p): −305.24500 (**1**). RMP2 and GVB geometries differ only slightly. Thus, the geometry does not depend on the calculational method. This does not hold for the reliable determination of relative energies and the vibration spectrum. In these cases an HF wave-function with corrections for dynamic correlation effects (estimated e.g. with MP2) is not sufficient. The GVB approximation is the simplest multiconfiguration (MC) method that provides a usable description of **1**. More exact data, especially for the low-frequency end of the IR spectrum, could be obtained with a larger MC formulation preferentially along with MP2 in order to account for both statistical and dynamic correlation effects.

[24] A. Rugeddi, *Gazz. Chim. Ital.* **1929**, 13.

[25] According to CNDO/S calculations the UV/VIS band of phenol with the longest wavelength λ_{max} lies at 282 nm, of **1a** at 362 nm. Another band calculated for **1** at λ_{max} = 476 nm is too weak in intensity to be observable under experimental conditions.

Hydride Transfer by Hydrido Transition-Metal Complexes. Ionic Hydrogenation of Aldehydes and Ketones, and Structural Characterization of an Alcohol Complex**

By *Jeong-Sup Song, David J. Szalda, R. Morris Bullock,* Christophe J. C. Lawrie, Mikhail A. Rodkin,* and *Jack R. Norton**

Transfer of hydrogen as a proton (H^+), hydrogen atom ($H^\cdot$), or hydride (H^-) is a decisive step in numerous catalytic and stoichiometric reactions utilizing metal hydrides.[1] The kinetics of proton transfer from metal hydrides[2] to metal-,[3] carbon-,[4] and nitrogen-centered[3] bases have been examined. Quantitative studies of the relative ability of carbonylhydridometal complexes to donate a hydrogen atom to olefins[5] or carbon-centered radicals[5, 6] have recently been reported. However, the little that is known about hydride transfer largely concerns substrates already coordinated to the metal atom.[7–9]

Direct hydride transfer to an uncoordinated substrate appears to be involved in the hydrogenation of sterically hindered olefins by transition-metal hydrides and triflic acid (CF_3SO_3H).[10] Such ionic hydrogenations (the addition to a double bond of H^+ from one source and H^- from another) are common in biological systems,[11] and probably occur in other organometallic reactions, e.g., the hydrogenation of aldehydes and/or ketones by acids and $[Mo_2(CO)_{10}(\mu\text{-H})]^-$,[12] $[Cr(CO)_5H]^-$,[13] $[Ru(bpy)_2(CO)H]^+$ (bpy = 2,2'-bipyridine),[14] $[Cp_2MoH_2]$,[15] or $[Cp_2Ta(CO)H]$.[16] These reactions offer a remarkable instance of kinetic selectivity: the H^+ and H^- are transferred to the same substrate more rapidly than they react with each other to form hydrogen gas.[17–19] In this communication we report on the scope and mechanism of the ionic hydrogenation of aldehydes and ketones by transition-metal hydrides and acids, and on the structure of the hydrogen-bonded alcohol complex that is formed upon hydrogenation of acetone with CF_3SO_3H and the hydrido tungsten complex **1a**.

When a pale yellow CD_2Cl_2 solution of acetone (0.10 M) and **1a** (1.5 equiv.) is treated with CF_3SO_3H (2 equiv.) at room temperature, the color changes to burgundy-red in less than 5 minutes, and the tungsten complex **2** is formed in quantitative (^1H NMR) yield [Eq. (a)]. The proton of the hydroxyl group of **2** gives rise to a doublet (J_{HH} = 7.6 Hz) at δ = 6.29 (^1H NMR in CD_3NO_2), significantly downfield from the position reported for the signal of the hydroxyl proton in the analogous complex with SbF_6 as counterion (δ = 4.90 in CD_3NO_2).[20] This shift suggests formation of hydrogen bond between the triflate anion and the alcohol ligand. A single-crystal X-ray diffraction study[21, 25] of **2** has verified that such a hydrogen bond is present in the solid state (Fig. 1). Especially informative in this connection is the short O···O distance of 2.63(1) Å, similar to the O–H···O distances found in other organometallic complexes that exhibit hydrogen bonding.[22] Only a few other alcohol com-

[*] Dr. R. M. Bullock, Dr. J.-S. Song, Dr. D. J. Szalda[+]
Department of Chemistry, Brookhaven National Laboratory
Upton, NY 11973 (USA)
Prof. J. R. Norton, Dr. C. J. C. Lawrie, Dr. M. A. Rodkin
Department of Chemistry, Colorado State University
Fort Collins, CO 80523 (USA)
[+] Permanent address: Baruch College
New York, NY 10010 (USA)

[**] This work was supported by the U.S. Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences (DE-AC02-76CH00016, Brookhaven National Laboratory) and by the National Science Foundation (Grant CHE-9120454, Colorado State University).