the solid state. Rather the simultaneous observation of three signals indicates the presence of two phases, most likely a liquid and a solid phase, in the sample at these temperatures. Further evidence of this is seen in the first set of spinning sidebands in the spectrum at −26 °C; the sidebands corresponding to the solid phase are observed, but a sideband representing the average of axial and equatorial signals is not present.

Clearly it can be concluded from these results that axial–equatorial exchange of carbonyls is not rapid on the NMR time scale in solid $Fe(CO)_5$ at temperatures of −26 °C and lower. This is in contrast to the conclusion reached from broadline NMR.[6] We propose therefore that the motion indicated by broadline NMR in iron pentacarbonyl is best represented by a rotation about the 3-fold axis of the trigonal-bipyramidal and not a pseudorotation. Such a rotation does not exchange axial and equatorial carbonyls.

Further examination of the MAS NMR results for $Fe(CO)_5$ shows that the line widths of both peaks diminish as the temperature is lowered. Although in principle a plot of the log of the line width vs $1/T$ will yield an activation energy for the process responsible for the line narrowing, in the present case the data is not sufficiently good to put a great deal of faith in the result.[11] The line narrowing observed as the temperature is lowered may be due to rotation about the molecular 3-fold axis.

At temperatures above −50 °C the chemical shift anisotropy appears to diminish as judged by the relative intensity of the spinning side bands to the center band. This may be indicative of incipient axial–equatorial exchange but at a rate which is too slow to average signals on the NMR time scale. Work at high field in the slow spinning regime is necessary for the elucidation of the chemical shift parameters which may shed further light on the molecular motions in solid $Fe(CO)_5$.[12]

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(11) From five data points at −38 °C and lower an activation energy of 0.6 kcal mol^{-1} is calculated; however, the correlation coefficient from the least-squares fit is only 0.7.

(12) Walter, T. H.; Reven, L.; Oldfield, E. *J. Phys. Chem.* **1989**, *93*, 1320.

A Novel Intramolecular Cyclopropanation Using Iodonium Ylides

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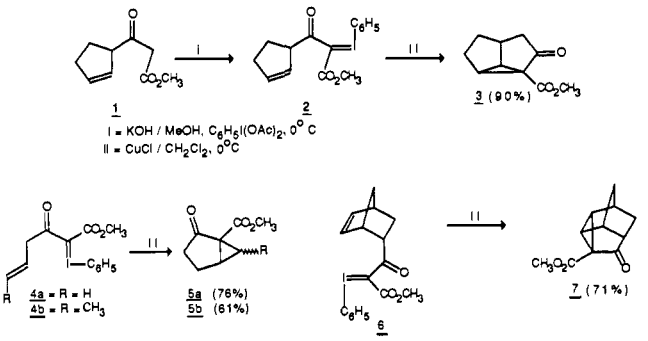
In 1961, Stork and Ficini reported intramolecular cyclopropanation in the Cu bronze decomposition of an unsaturated α-diazo ketone.[1] Since then, this reaction has emerged as a widely useful method in organic synthesis.[2,3] Particularly noteworthy are recent examples by Hudlicky et al.,[4] Taber et al.,[5] Chen,[6] and Kang et al.[7] Reasoning from a formal analogy between β-dicarbonyl iodonium ylides and the β-dicarbonyl α-diazo compound[8] and motivated to find a method that avoids the hazards of diazo compounds (explosive carcinogens)[9] for intramolecular cyclopropanation, we synthesized iodonium ylide **2** and carried out its decomposition in the presence of CuCl.[10] Indeed, a 90% yield of **3** was obtained.[10] Reactions **4a,b** → **5a,b** as well as **6** → **7** suggest the generality of the intramolecular cyclopropanation.



In the transition-metal-catalyzed decomposition of diazo compounds, a metal–carbene complex probably intervenes.[3] In the present reactions, we do not believe carbenoid intermediates are involved for the following reasons. First, iodonium ylides undergo a number of cycloaddition reactions leading to the formation of five-membered heterocycles. These include reactions with CS_2,[11] phenyl isothiocyanate,[11] acetonitrile,[11] alkenes,[11] and diphenylketene.[12] In the reaction of 2,4-dinitro-6-phenyliodonium phenolate with alkenes, alkynes, and aromatics, 2,3-dihydrobenzo[*b*]furans, benzo[*b*]furans, and 6-aryl-2,4-dinitrophenols are formed.[13] Secondly, no Wolff-type rearrangement products were formed in these reactions, although the analogous α-keto carbene

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(1) Stork, G.; Ficini, J. *J. Am. Chem. Soc.* **1961**, *83*, 4678.

(2) Burke, S. D.; Grieco, P. A. *Org. React.* **1987**, *26*, 361.

(3) Maas, G. *Top. Curr. Chem.* **1987**, *137*, 75.

(4) Hudlicky, T.; Rami, B. C. *J. Org. Chem.* **1985**, *50*, 123 and references contained therein.

(5) Taber, D. F.; Krewson, K. R.; Roman, K.; Rheingold, A. L. *Tetrahedron Lett.* **1984**, *25*, 5283.

(6) Chen, E. Y. *J. Org. Chem.* **1984**, *49*, 3245.

(7) Kang, S. H.; Kim, W. J.; Chae, Y. B. *Tetrahedron Lett.* **1988**, *29*, 5169.

(8) Moriarty, R. M.; Bailey, B. R., III; Prakash, O.; Prakash, I. *J. Am. Chem. Soc.* **1985**, *107*, 1375.

(9) Sax, N. I. *Dangerous Properties of Industrial Materials*, 5th ed.; Van Nostrand Reinhold: New York, 1979; pp 544–546. Bretherick, L. *Handbook of Reactive Chemical Hazards*, 2nd ed.; Butterworth: London, Boston, 1979; pp 589–590.

(10) Ylide **2** was synthesized by the reaction of **1** with diacetoxyiodobenzene in KOH/MeOH at 0 °C (yield 80%): mp 113–115 °C (dec); IR ($CHCl_3$) 1726 (C=O stretching), 1655 (C=C stretching) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.46–2.37 (m, 4 H, CH_2CH_2 in cyclopentene), 3.04 (d, 2 H, CH_2CO), 3.12–3.22 (m, 1 H, CH in cyclopentene), 3.65 (s, 3 H, $COOCH_3$), 5.67–5.73 (m, 2 H, CH=CH), 7.33–7.78 (m, 5 H, aromatic protons). Ylide **4a**: mp 54–56 °C (dec); yield 78%; IR ($CHCl_3$) 1734 (C=O stretching), 1653 (C=C stretching) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.5 (t, 2 H, CH_2), 3.75 (s, 3 H, $COOCH_3$), 5.1 (m, 2 H, $CH=CH_2$), 6.0 (m, 1 H, CH), 7.4–7.9 (m, 5 H, aromatic protons). Ylide **4b**: mp 85–86 °C (dec); yield 85%; IR ($CHCl_3$) 1735 (C=O stretching), 1650 (C=C stretching) cm^{-1}; ^1H NMR δ 1.6 (d, 3 H, CH_3), 2.33 (m, 2 H, $CH_2CH=$), 3.03 (t, 2 H, CH_2CO), 3.65 (s, 3 H, $COOCH_3$), 5.45 (m, 2 H, CH=CH), 7.35–7.75 (m, 5 H, aromatic protons). Ylide **6**: mp 94–96 °C (dec); yield 91%; IR ($CHCl_3$) 1730 (C=O stretching), 1653 (C=C stretching) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.3–2.1 (m, 4 H, 2 × CH_2), 2.85 (m, 1 H, CH), 3.2 (m, 1 H, CH), 3.70 (s, 3 H, $COOCH_3$), 4.15 (m, 1 H, CH), 5.8 (m, 2 H, CH=CH), 6.2 (m, 2 H, CH=CH), 7.3–7.90 (m, 5 H, aromatic protons). In a typical experiment, cuprous chloride (10–20 mg) was added to a solution of **2** (3.70 g, 10 mmol) in dichloromethane (20 mL) under nitrogen at 0 °C. The reaction mixture was stirred at 0 °C for 10 min and then at room temperature for 1 h. The mixture was then filtered, evaporated to dryness in vacuo, and chromatographed on silica gel (9:1 (v/v) hexane–ethyl acetate) to remove C_6H_5I and gave pure **3** (1.60 g, 90%). The spectral properties (IR, ^1H NMR, MS) of product **3** were identical with those reported in ref 24. Product **5a**: yield 76%; this product had the same properties as those reported in ref 25. Product **5b**: yield 81%; IR (neat) 1740 (b, C=O stretching of COOMe), 1725 (C=O stretching) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25 (d, 3 H, CH_3), 1.78–2.68 (m, 6 H), 3.78 (s, 3 H, $COOCH_3$) (the ^1H NMR of **5b** shows about a 70:30 mixture of two diastereomers; one diastereomer (30%) is reported[5]). Product **7**: yield 71%; IR ($CHCl_3$) 1754 (C=O stretching of COOMe), 1734 (C=O stretching) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.50 (d, 1 H, CH), 1.70 (m, 2 H, 2 × CH), 2.02 (d, 1 H, CH), 2.40 (dd, 1 H, CH), 2.63 (m, 1 H, CH), 2.75 (m, 1 H, CH), 3.05 (m, CH), 3.70 (s, 3 H, $COOCH_3$), 3.78 (m, CH); MS M^+ = 192 (12.49%), 77 (100%).

(11) Hadjiarapoglou, L. *Tetrahedron Lett.* **1987**, 4449. Papadopoulou, M.; Spyroudis, S.; Varvoglis, A. *J. Org. Chem.* **1985**, *50*, 1509.

(12) Koser, G. F.; Yu, S.-M. *J. Org. Chem.* **1975**, *40*, 1166.

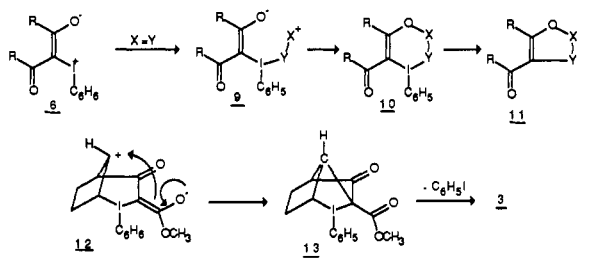
(13) Spyroudis, S. P. *J. Org. Chem.* **1986**, *51*, 3453.

0002-7863/89/1511-6443$01.50/0

from α-diazo ketones has been shown to follow this pathway.[14,15] This suggests that a keto carbene is not involved in the iodonium ylide reactions.

A mechanism that applies to the cyclopropanation reaction, and the cycloadditions of iodonium ylides with unsaturated compounds (dipolarophiles) in general, may involve addition of the unsaturated molecule to the electrophilic iodine center in **8** (**8** → **9**) to give a zwitterionic intermediate that can undergo ring closure (**9** → **10**) followed by reductive elimination of C_6H_5I to yield the heterocyclic product (**10** → **11**). An equivalent expression using radical and diradical intermediates may be drawn; vide infra.

In the case of **2** → **3**, intermediate **12** is analogous to **9** but a six-membered ring as in **9** → **10** cannot occur (Bredt's rule), so the alternative C–C bond formation occurs (**12** → **13**). Reductive elimination of C_6H_5I yields **3**:[16]



As far as intermolecular cyclopropanation using iodonium ylides is concerned, bis(arylsulfonyl)methylide phenyliodonium ylides $[C_6H_5I^+C^-(SO_2Ar)_2]$ react with olefins to yield *gem*-disulfonyl cyclopropyl derivatives.[17,18] Also, a report exists of the reaction of $C_6H_5I^+C^-(CO_2CH_3)_2$ with cyclohexene to yield the *gem*-dicarbomethoxycyclopropane derivative.[19]

Finally, the role of metal catalysis in these reactions remains obscure. It should be noted that although reaction **2** → **3** occurs in the absence of a catalyst (in lower yield), **2** → **3** does not occur photochemically (in contrast to other iodonium ylide cycloadditions).[11] Both Cu(I) and Cu(II) catalyst **2** → **3**. Beringer and co-workers reported that both Cu(I) and Cu(II) catalyze the decomposition of diaryliodonium salts.[20,21] Roberts et al. attribute the catalytic role of Cu(I) to electron transfer to yield the the iodinanyl radical ArİAr as a reactive intermediate.[22a,b] In the case of nucleophilic addition of aniline to diphenyliodonium-2-carboxylate, Cu(II) catalysis is unique.[23]

In summary, the present method is a viable alternative to the diazo ketone route for intramolecular cyclopropanation, and high yields as well as ease of execution reommend its use.

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(14) Stork, G.; Szajewski, R. P. *J. Am. Chem. Soc.* **1974**, *96*, 5787.
(15) Hayasi, Y.; Kawanisi, M. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 2506.
(16) The sequence of steps **8** → **9**; **10** → **11**, namely, addition of a ligand or nucleophile to yield a tricoordinate intermediate, followed by ligand coupling via reductive elimination is a fundamental pathway in hypervalent iodine reactions, and intermediates such as **9** have already been proposed in the reaction of 6-aryl-2,4-dinitroiodonium phenolates with CS_2.[11]
(17) Hatjiarapoglou, L.; Spyroudis, S.; Varvoglis, A. *J. Am. Chem. Soc.* **1985**, *107*, 7178.
(18) Hatjiarapoglou, L.; Varvoglis, A.; Alcock, N. W.; Pike, G. A. *J. Chem. Soc., Perkin Trans. 1* **1988**, 2839.
(19) Nicholas, J.; Hood, C.; Lloyd, D.; MacDonald, W. A.; Shepherd, T. M. *Tetrahedron* **1982**, *38*, 3355.
(20) Beringer, F. M.; Huang, S. J. *J. Org. Chem.* **1964**, *29*, 445.
(21) Beringer, F. M.; Huang, S. J. *J. Org. Chem.* **1964**, *29*, 1637.
(22) (a) Caserio, M. C.; Glusker, D. L.; Roberts, J. D. *J. Am. Chem. Soc.* **1959**, *81*, 336. (b) For an excellent discussion of the radical pathway for diaryliodonium decomposition, see: Galli, C. *Chem. Rev.* **1988**, *88*, 765.
(23) Scherrer, R. A.; Beatty, H. R. *J. Org. Chem.* **1980**, *45*, 2127. Cu(I) and Cu(II) may function in **2** → **3**, **4a,b** → **5a,b**, and **6** → **7** in a chelation.
(24) Callant, P.; Wilde, H. D.; Vandewalle, M. *Tetrahedron* **1981**, *37*, 2079.
(25) Kondo, K.; Hiro, E.; Tunemoto, D. *Tetrahedron Lett.* **1976**, 4489.

A High Precision Structure of a Bacteriochlorophyll Derivative, Methyl Bacteriopheophorbide *a*

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Current X-ray studies of antenna[2,3] and reaction center[4-8] bacteriochlorophyll (BChl) proteins are unveiling the architecture used by photosynthetic bacteria to harvest and transduce light into chemical energy. BChls in antenna complexes funnel incident photons into reaction centers where BChls and bacteriopheophytins (BPheo, demetalated BChls) carry out the primary charge separation that eventually drives the biochemistry of the organisms.[9] Besides the inherent difficulties of refining structures of high molecular weight complexes, X-ray studies of the BChl proteins have been further hampered by a lack of high precision data for BChl derivatives. To date, only three structures of bacteriochlorins have been reported, two synthetic bacteriochlorins[10] and a low precision structure of methyl bacteriopheophorbide *a*,[11] (MeBPheo) in which the phytyl chain of BPheo *a* is replaced by a methyl group (Figure 1a). As a consequence, all BChl protein refinements are based on chlorophyll X-ray data[12] modified to reflect

(1) (a) Brookhaven National Laboratory. (b) Stanford University.
(2) Tronrud, D. E.; Schmid, M. F.; Matthews, B. W. *J. Mol. Biol.* **1986**, *188*, 443.
(3) Cogdell, R. J.; Woolley, K.; MacKenzie, R. C.; Lindsay, J. G.; Michel, H.; Dobler, J.; Zinth, W. *Antennas and Reaction Centers of Photosynthetic Bacteria*; Michel-Beyerle, M. E., Ed.; Springer-Verlag: Berlin, 1985; p 85. Allen, J. P.; Theiler, R.; Feher, G. *Antennas and Reaction Centers of Photosynthetic Bacteria*; p 82. Mantele, W.; Steck, K.; Wacker, T.; Welte, W.; Levoir, B.; Breton, J. *Antennas and Reaction Centers of Photosynthetic Bacteria*; p 88. Papiz, M. Z.; Hawthornthwaite, A. M.; Cogdell, R. J.; Woolley, K. J.; Wightman, P. A.; Ferguson, L. A.; Lindsay, J. G. *J. Mol. Biol.*, in press.
(4) Deisenhofer, J.; Epp, O.; Miki, K.; Huber, R.; Michel, H. *J. Mol. Biol.* **1984**, *180* 385; *Nature (London)* **1985**, *318*, 618. Michel, H.; Epp, O.; Deisenhofer, J. *EMBO J.* **1986**, *5*, 2445.
(5) Chang, C. H.; Tiede, D.; Tang, J.; Smith, U.; Norris, J. R.; Schiffer, M. *FEBS Lett.* **1986**, *205*, 82.
(6) Yeates, T. O.; Komiya, H.; Chirino, A.; Rees, D. C.; Allen, J. P.; Feher, G. *Proc. Nat'l Acad. Sci. U.S.A.* **1988**, *85*, 7993.
(7) Ducruix, A.; Reiss-Husson, F. *J. Mol. Biol.* **1987**, *193*, 419.
(8) Wacker, T.; Gad'On, N.; Becker, A.; Mantele, W.; Kreutz, W.; Drews, G.; Welte, W. *FEBS Lett.* **1986**, *197*, 267. (A reaction center–antenna complex.)
(9) Fajer, J.; Brune, D. C.; Davis, M. S.; Forman, A.; Spaulding, L. D. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 4956. Fajer, J.; Davis, M. S.; Brune, D. C.; Spaulding, L. D.; Borg, D. C.; Forman, A. *Brookhaven Symp. Biol.* **1976**, *28*, 74. Parson, W. W.; Monger, T. G. *Brookhaven Symp. Biol.* **1976**, *28*, 195. Dutton, P. L.; Prince, R. C.; Tiede, D. M.; Petty, K. M.; Kaufmann, K. J.; Netzel, T. L.; Rentzepis, P. M. *Brookhaven Symp. Biol.* **1976**, *28*, 213. Shuvalov, V. A.; Klevanik, A. V.; Sharkov, A. V.; Matveetz, A.; Krukov, P. G. *FEBS Lett.* **1978**, *91*, 135. Holten, D.; Hoganson, C.; Windsor, M. W.; Schenk, C. C.; Parson, W. W.; Migus, A.; Fork, R. L.; Shank, C. V. *Biochim. Biophys. Acta* **1980**, *592*, 461. Breton, J.; Martin, J. L.; Fleming, G. R.; Lambry, J. C. *Biochemistry* **1988**, *27*, 8276. For a recent review, see: Kirmaier, C.; Holten, D. *Photosynthesis Res.* **1987**, *13*, 225.
(10) (a) Barkigia, K. M.; Fajer, J.; Chang, C. K.; Young, R. *J. Am. Chem. Soc.* **1984**, *106*, 6457. (b) Waditschatka, R.; Kratky, C.; Jaun, B.; Heinzer, J.; Eschenmoser, A. *J. Chem. Soc., Chem. Commun.* **1985**, 1604.
(11) Barkigia, K. M.; Fajer, J.; Smith, K. M.; Williams, G. J. B. *J. Am. Chem. Soc.* **1981**, *103*, 5890.
(12) Chow, H. C.; Serlin, R.; Strouse, C. E. *J. Am. Chem. Soc.* **1975**, *97*, 7230. Serlin, R.; Chow, H. C.; Strouse, C. E. *J. Am. Chem. Soc.* **1975**, *97*, 7237. Kratky, C.; Dunitz, J. D. *Acta Crystallogr., Sect. B.* **1975**, *B32*, 1586; **1977**, *B33*, 545. Kratky, C.; Dunitz, J. D. *J. Mol. Biol.* **1977**, *113*, 431. Kratky, C.; Isenring, H. P.; Dunitz, J. D. *Acta Crystallogr., Sect. B* **1977**, *B33*, 547.

0002-7863/89/1511-6444$01.50/0