Table I. Uv–Visible Spectra of Dipyrromethenes, Dipyrromethene Hydrobromides, and Copper Chelates Derived from These Intermediates

Compd	λ_{max}, mμ[c]	ϵ, l. mol^{-1} cm^{-1}
19[a]	369	11,300
	465 sh	
	493	85,000
20[b]	369	8,500
	464 sh	
	493	91,000
18	254	33,400
	262 sh	
	370	17,600
	465 sh	
	493	164,000
17	260	33,000
	330	10,500
	465 sh	
	491	72,600
Cu^{II} chelate derived from **19**	333	9,800
	(398)	12,400
	474 ssh	
	493	49,000
	519 ssh	
Free base derived from **19**	338	4,800
	474	42,900
Cu^{II} chelate derived from **20**	(400)	
	469	s
	495 ssh	
	519	
Free base derived from **20**	344	4,300
	482	38,000
Cu^{II} chelate derived from **18**	264 ssh	
	(402)	
	470	s
	492 sh	
	517	s
Cu^{II} chelate derived from **17**	260	s
	330	w
	470	s
	519	s
Free base derived from **17**	338	w
	481	s

[a] Identified with that reported by H. Fischer, *Justus Liebigs Ann. Chem.*, **475**, 221 (1929). [b] Every step in the synthesis reported here was duplicated in a simple porphyrin synthesis. The compound **20** is an intermediate in a model synthesis. The C, H, N, and Br analyses agree with the structure indicated. [c] s = strong, w = weak, sh = shoulder, ssh = strong shoulder. These symbols are used where concentrations were not determined.

Work-up by repeated chromatography through silica gel gave a pink solution which showed in the uv and visible spectrum typical bands for copper porphyrins, *i.e.*, 562 (ϵ 23,000) (α band), 524 ($\epsilon \cong$ 10,000) (β band), and 399 mμ (ϵ 310,000) (Soret band), and an additional intense absorption around 265 mμ ($\epsilon \cong$ 300,000) (biphenyl). The yield was about 5%. Mass spectrum showed a parent peak at 917, the calculated molecular weight of the copper porphyrin **1**. The increase in extinction coefficient at 265 mμ from 33,000 to 300,000 in going from **17** to the porphyrin **1** is typical of flattening a biphenyl system and supplies further evidence for the cyclophane structure of **1**.

By shaking the chloroform solution of the copper porphyrin with 10 *M* H_2SO_4[19] we obtained the free porphyrin with uv and visible absorption bands at 610 (broad and weak), 562, 528, 496 (strongest in the visible four-band series), 399 (Soret), and 265 mμ. Treatment of this porphyrin by the usual ferrous sulfate procedure[20] gave a violet solution with the uv–visible spectrum expected for Fe(III) porphyrins.

Table II. Nmr Spectra of Some Intermediates[a]

Proton(s) (see structures in Table I)	**19**	**20**	**18**	**8**
N–H	$\left.\begin{matrix}-3.28\\-3.38\end{matrix}\right\}$b	$\left.\begin{matrix}-3.24\\-3.36\end{matrix}\right\}$b	$\left.\begin{matrix}-3.23\\-3.35\end{matrix}\right\}$b	0.58 b
1	2.93 s	2.80 s	2.76 s	
2	7.32 s 7.68 s 7.98 s	7.30 s 7.63 s 7.96 s	7.30 s 7.65 s 7.94 s	7.35 s 7.65 s
3	7.26 q 7.53 q	7.17 t ~7.55	7.16 ~7.5–7.55	
4		7.6–7.7	7.6–7.7	
5		~8.25 m	~8.25 m	
6		~8.55 m	~8.4 m	~8.2 m
7	8.83 t 8.93 t			~7.7
8		9.04 t		
9			≈7.35	~7.5 m
10			2.58 (AB spectrum)	2.58
11 (Et)		5.83 q 8.73 t	5.83 q 8.73 t	5.83 q 8.73 t

[a] All spectra were taken in $CDCl_3$. Chemical shifts are given in τ values (10 − δ). Resonances for which only approximate τ values are listed could not be determined accurately because of superposition with other resonances; b = broad, s = singlet, t = triplet, q = quartet, m = multiplet.

Conversion of **1** to the corresponding histidyl ferroporphyrin and alternate procedures to improve the yields of **1** are underway.

Acknowledgment. We are grateful to the National Institutes of Health for financial support, and to Professors David Mauzerall and David A. Lightner for helpful advice and assistance.

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resulted in severe steric interference with the amine-catalyzed ring closure. No porphyrin could be obtained. Substitution of less-hindered bases, *e.g.*, DABCO and DBN for trimethylamine, gave about 0.1% yield of the copper porphyrin **1**. In model systems, *e.g.*, using **20**, the yield of porphyrin is 15–20%.

(19) Treatment with concentrated H_2SO_4 resulted in decomposition of the cyclophane porphyrin.

(20) J. E. Falk, "Porphyrins and Metalloporphyrins," Elsevier, New York, N. Y., 1964, p 133.

Herbert Diekmann, C. K. Chang, T. G. Traylor*
Chemistry Department, Revelle College
University of California, San Diego
La Jolla, California 92037

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Olefin Inversion by the Phosphorus Betaine Method

Sir:

We wish to describe a stereospecific method for synthesis of phosphorus betaines and application of this method for facile inversion of olefin stereochemistry. Previous examples of betaine generation include the classical Wittig reaction of alkylidenetriphenylphosphoranes with carbonyl compounds,[1] deprotonation of β-hydroxyphosphonium salts,[2] and reaction of epoxides or ethylene carbonates with trisubstituted phosphines.[3]

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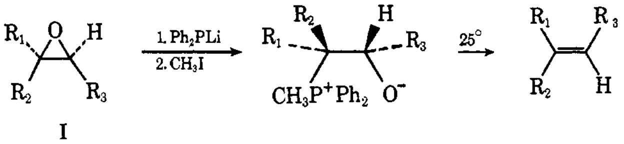
(1) A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966, Chapter 4.

(2) (a) M. E. Jones and S. Trippett, *J. Chem. Soc. C*, 1090 (1966); (b) G. Wittig and U. Schollkopf, *Chem. Ber.*, **87**, 1318 (1954).

(3) (a) G. Wittig and W. Haag, *ibid.*, **88**, 1654 (1955); (b) M. J. Boskin and D. B. Denney, *Chem. Ind.* (*London*), 330 (1959); (c) A. J.

Of these methods, only the Wittig reaction is useful for stereoselective synthesis of olefins.[4]

We have found that lithium diphenylphosphide[5] in tetrahydrofuran (THF) opens epoxides stereospecifically, and that quaternization of the crude product with methyl iodide leads directly to betaines. The betaines generally fragment under the conditions of quaternization (25°) and olefins are formed as well as methyldiphenylphosphine oxide. As expected from the sequence SN2 epoxide opening followed by cis elimination of phosphine oxide, the product olefins are formed with inversion of stereochemistry relative to the starting epoxide. The method is illustrated by stereospecific (>98%) conversion of *cis*- or *trans*-stilbene oxides into *trans*- or *cis*-stilbene, respectively, in 95% yield, and by similar inversion of *cis*- or *trans*-2-octenes (75% yield, >99.5% stereospecific).



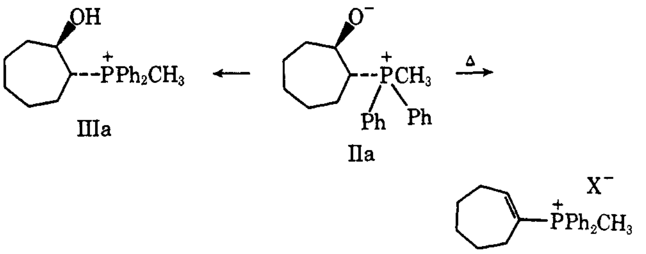
I

a, $R_1 = R_3 = Ph$; $R_2 = H$
b, $R_2 = R_3 = Ph$; $R_1 = H$
c, $R_1 = CH_3$; $R_2 = H$; $R_3 = C_5H_{11}$[a]
d, $R_1 = H$; $R_2 = CH_3$; $R_3 = C_5H_{11}$[a]

[a] Two modes of epoxide opening are observed.

Olefin inversion[6] by the betaine technique is a convenient method for the synthesis of *trans*-cyclooctene derivatives uncontaminated by the cis isomer. *cis*-Cyclooctene oxide is converted to *trans*-cyclooctene in 95% yield, >99.5% trans isomer under typical conditions.[7] Similarly, the monoepoxide of 1,5-cyclooctadiene affords the reactive *cis,trans*-1,5-cyclooctadiene[8] (60% yield, >99.5% trans) although in this case a longer reaction time is necessary to complete betaine fragmentation. The hitherto unknown *cis,trans*-1,4-cyclooctadiene[9] can also be prepared in this manner (40% yield, >99.5% trans). The new diene is characterized by an intense infrared absorption at 10.14 μ (trans olefin), complex olefinic signals in the nmr spectrum (δ 5.4–6.4, 4 H), and quantitative formation of a Diels–Alder adduct, mp 208–209°, with diphenylisobenzofuran at 25°.

Our efforts in the cycloheptene series have so far failed to produce any evidence of *trans*-cycloheptene[6a] generation, but the results do provide valuable information concerning the fate of phosphorus betaines under forcing conditions. Cycloheptene oxide is converted, as before, into the betaine IIa, characterized as the fluoroboric acid salt IIIa[10] in 65% isolated yield. In contrast to the analogous cyclooctene derivatives, IIa is stable at 25° and does not decompose to methyldiphenylphosphine oxide under aprotic conditions. The only reaction observed when IIa is refluxed in THF is elimination to the cycloheptenylmethyldiphenylphosphonium salt IV.[11,12] The structure of IV is proved by independent synthesis from 1-lithiocycloheptene upon treatment with chlorodiphenylphosphine followed by methyl iodide.



IIIa

IIa

IV

cis-Cycloheptene (30–45%) and methyldiphenylphosphine oxide are formed, however, when IIIa is refluxed in THF with the amidine base 1,5-diazabicyclo[5.4.0]-undec-5-ene (DBU). The cycloheptenyl salt IV (~50%) is also formed under these conditions. When the same experiment is performed in the presence of benzaldehyde, the products include styrene (10–15%) and benzylidenecyclohept-2-ene V (20%) instead of IV. Similar treatment of IV ($X^- = I^-$) with DBU and benzaldehyde again affords styrene, V, and methyldiphenylphosphine oxide, but no cycloheptene.[13]

To explain these results, we propose that DBU converts IIIa to IIa, and that IIa is converted to the hydroxy ylide VI in refluxing tetrahydrofuran. In the presence of a good proton donor such as DBU · HBF_4, VI is reprotonated to IIIb which has the correct stereochemistry for eventual fragmentation to *cis*-cycloheptene. In the absence of a proton donor, elimination of hydroxide is the favored pathway and VI is converted to IV.[14] This salt, in turn, equilibrates with the ylide VII as evidenced by the trapping experiment with benzaldehyde.[15] The appearance of styrene in the

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Speziale and D. E. Bissing, *J. Amer. Chem. Soc.*, **85**, 1888, 3878 (1963); (d) D. E. Bissing and A. J. Speziale, *ibid.*, **87**, 2683 (1965); (e) P. T. Keough and M. Grayson, *J. Org. Chem.*, **27**, 1817 (1962).

(4) (a) M. Schlosser and K. F. Christmann, *Justus Liebigs Ann. Chem.*, **708**, 1 (1967); (b) L. D. Bergelson, L. I. Barsukov, and M. M. Shemyakin, *Tetrahedron*, **23**, 2709 (1967); (c) M. Schlosser, K. F. Christmann, and A. Piskala, *Chem. Ber.*, **103**, 2814 (1970); (d) E. J. Corey and H. Yamamoto, *J. Amer. Chem. Soc.*, **92**, 226, 6636, 6637 (1970).

(5) K. C. Hansen, C. H. Wright, A. M. Aguiar, C. J. Morrow, and R. M. Turkel, *J. Org. Chem.*, **35**, 2820 (1970).

(6) Other methods of olefin inversion have been employed for *trans*-cyclooctene synthesis: (a) E. J. Corey, F. A. Carey, and R. Winter, *J. Amer. Chem. Soc.*, **87**, 934 (1965); (b) J. N. Hines, M. J. Peagram, G. H. Whitham, and M. Wright, *Chem. Commun.*, 1593 (1968).

(7) High stereoselectivity is achieved easily in acyclic cases, but synthesis of isomerically pure *trans*-cyclooctene requires scrupulous exclusion of hydroxylic impurities.

(8) A. C. Cope, C. F. Howell, J. Bowers, R. C. Lord, and G. M. Whitesides, *J. Amer. Chem. Soc.*, **89**, 4024 (1967).

(9) Substituted *cis,trans*-1,4-cyclooctadienes have been prepared: M. S. Baird and C. B. Reese, *Chem. Commun.*, 1644 (1970).

(10) IIIa: mp 159–160°; nmr ($CDCl_3$, δ) 1.3–2.1 (10 H, m), 2.53 (3 H, d, J = 13.5 Hz), 3.1–4.0 (3 H, m), 7.55–7.95 (10 H, m). *Anal.* Found: C, 60.06; H, 6.67; F, 18.86; P, 7.81 (within 0.13% of theoretical).

(11) IV: mp 89–90° ($X^- = I^-$); nmr ($CDCl_3$, δ) 1.40–1.95 (6 H, m), 2.20–2.80 (4 H, m), 2.88 (3 H, d, J = 13.5 Hz), 6.86 (1 H, dt, J = 25 Hz, 6.5 Hz), 7.40–8.05 (10 H, m).

(12) Hydroxide elimination to a cyclohexenyltriphenylphosphonium salt, presumably *via* the betaine, is also observed upon attempted deoxygenation of cyclohexene oxide with triphenylphosphine: S. Trippett and B. S. Walker, *J. Chem. Soc. C*, 887 (1966).

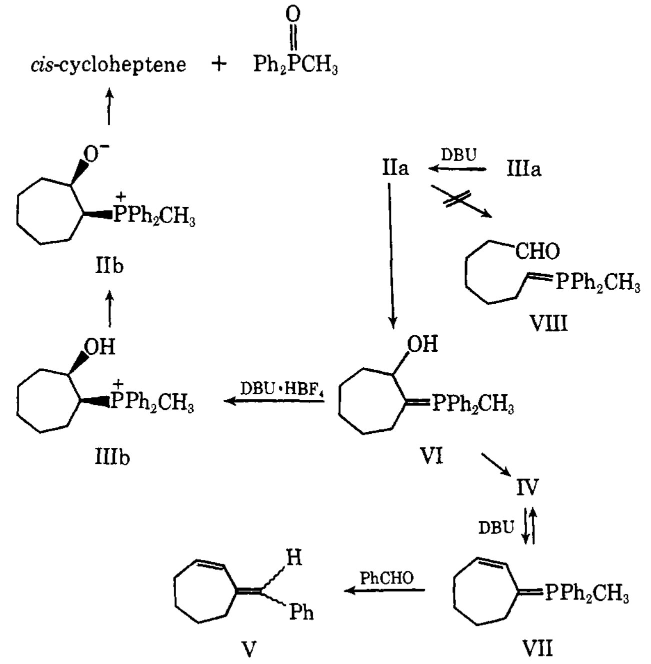
(13) A source of hydroxide would be necessary in order to convert IV to cycloheptene *via* IIb. However, cycloheptene is not formed with or without an added equivalent of water.

(14) Appearance of IV under aprotic conditions is the first conclusive evidence that hydroxy ylides such as VI are readily formed from betaines. In fact, the conversion of IIa to VI and eventually to IV is remarkably facile. The reaction conditions for this process (refluxing THF) are similar to conditions which are often used for preparative Wittig reactions. Clearly, temperatures above 25° should not be used for the Wittig synthesis with reactive ylides since betaine decomposition to olefins occurs readily at room temperature in THF solution.

(15) We have considered the possibility that V is formed by reaction

various experiments indicates equilibration of both IIa and IV with the corresponding methylides.

An alternate pathway for destruction of IIa, the retro-Wittig process leading to the ylide aldehyde VIII, is excluded by our results. Similar cleavage to ylides and carbonyl compounds has been claimed to explain loss of stereochemistry and the appearance of crossover products upon decomposition of phosphorus betaines prepared by other methods.[2a,3b,3d] The ultimate consequence of cleavage of IIa to VIII should be the appearance of *cis*-cycloheptene since VIII is expected to reclose to IIb. Alternately, intermolecular Wittig condensation of VIII would at least afford methyldiphenylphosphine oxide, but neither the oxide nor *cis*-cycloheptene are detected under aprotic conditions. Thus, elimination of hydroxide to form IV is faster than the retro-Wittig reaction. Retro-Wittig cleavage is also excluded for all of the other betaines which we have studied since inverted olefins are formed in good to excellent yield with high isomeric purity.[17]



The convenience of the betaine technique for olefin inversion suggests a variety of synthetic applications. Initial studies indicate that our method is general and can be extended to trisubstituted olefins provided that base-sensitive functional groups are suitably protected. These results will be presented in a full paper.

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of benzaldehyde with VI to yield 2-benzylidenecycloheptanol[16] or 1-cycloheptenylphenylcarbinol,[16] followed by dehydration. However neither alcohol is present in the product mixture, and both alcohols are stable under the reaction conditions.

(16) E. A. Braude, W. F. Forbes, and E. A. Evans, *J. Chem. Soc.*, 2202 (1953).

(17) In response to a referee's comments, we do not imply that betaine reversal is necessarily ruled out in the experiments involving DBU and IIIa. It is conceivable that opening to VIII may be catalyzed in some way by the proton donor DBU·HBF$_4$ to account for some of the cycloheptene, but there is no evidence or analogy to support such a process. The presence or absence of lithium cation is not a factor in cycloheptene formation; the yield of cycloheptene is unaffected when IIIa is treated with DBU and LiBF$_4$.

(18) Alfred P. Sloan Foundation Fellow, 1971–1973.

E. Vedejs,*,[18] P. L. Fuchs
Chemistry Department, University of Wisconsin
Madison, Wisconsin 53706

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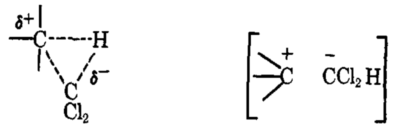
The Stereochemistry of the Insertion of Phenyl(bromodichloromethyl)mercury-Derived Dichlorocarbene into a Benzylic Carbon–Hydrogen Bond

Sir:

Our previous studies of the insertion of PhHgCCl$_2$Br-derived dichlorocarbene into the C–H bonds of alkanes and alkylbenzenes,[1] saturated ethers,[2] and tetraalkyl derivatives of silicon,[3] germanium,[4] and tin[3] showed that these reactions (eq 1) are promoted by substituents,

$$R{-}\overset{|}{\underset{|}{C}}{-}H + PhHgCCl_2Br \longrightarrow R{-}\overset{|}{\underset{|}{C}}{-}CCl_2H + PhHgBr \quad (1)$$

R, which would be expected to stabilize best a partial positive charge on carbon. A concerted process with transition state I or a hydride abstraction process involving a tight ion pair intermediate, II, were considered as being the most likely possibilities for the mechanism of the insertion reaction. The reaction of PhHgCCl$_2$Br with Me$_3$SiCH$_2$CDMe$_2$ occurred with almost complete deuterium retention.[3] The related insertion of dichlorocarbene into optically active bis-(*S*)-methylbutylmercury gave MeEtCHCH$_2$HgCH$_2$CMeEtCCl$_2$H with overall retention of configuration (~23%).[5]



I II

The report by Franzen and Edens[6] that insertion of CCl$_2$ (*via* PhHgCCl$_3$ or CCl$_3$CO$_2$Na) into optically active 2-phenylbutane gave practically inactive or completely inactive PhCMeEtCCl$_2$H, therefore, was rather surprising to us. Since this result was at variance with the picture of CCl$_2$ insertion into C–H bonds which had developed, we have reinvestigated the stereochemical course of dichlorocarbene insertion (*via* PhHgCCl$_2$Br) into optically active 2-phenylbutane.

The reaction of 79.4 mmol of phenyl(bromodichloromethyl)mercury[7] with 35 ml of (+)-2-phenylbutane[8] at

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(1) D. Seyferth, J. M. Burlitch, K. Yamamoto, S. S. Washburne, and C. J. Attridge, *J. Org. Chem.*, **35**, 1989 (1970).

(2) D. Seyferth, V. A. Mai, and M. E. Gordon, *ibid.*, **35**, 1993 (1970).

(3) D. Seyferth, S. S. Washburne, C. J. Attridge, and K. Yamamoto, *J. Amer. Chem. Soc.*, **92**, 4405 (1970).

(4) D. Seyferth, H. Shih, P. Mazerolles, M. Lesbre, and M. Joanny, *J. Organometal. Chem.*, **29**, 371 (1971).

(5) J. A. Landgrebe and D. E. Thurman, *J. Amer. Chem. Soc.*, **91**, 1759 (1969).

(6) V. Franzen and R. Edens, *Justus Liebigs Ann. Chem.*, **729**, 33 (1969).

(7) D. Seyferth and R. L. Lambert, Jr., *J. Organometal. Chem.*, **16**, 21 (1969).

(8) Prepared by the method of Bonner and Greenlee,[9] bp 95–97° (62 mm), $n^{25}D$ 1.4876, $[\alpha]^{25}D$ +24.032° (neat, l = 1 dm); lit.[9] $[\alpha]^{25}D$ +26.6°. The absolute configuration of 2-phenylbutane has been established.[10]