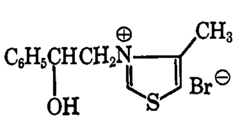
fonate and fractionally crystallized to a constant rotation ($[\alpha]^{25}_{546}$ +82.5° (*c* 1.55, ethanol)).[5] The bromide was regenerated by the use of an ion-exchange column to give (+)-I, $[\alpha]^{25}_{546}$ +76.3° (*c* 1.29, ethanol).

Treatment of (+)-I with cyclohexanecarboxylic acid anhydride and pyridine gave a 77% yield of (+)-N-[2-phenyl-2-(cyclohexanecarboxylate)ethyl]-4-methylthiazolium bromide (II), $[\alpha]^{25}_{546}$ +83.0° (*c* 1.50, ethanol).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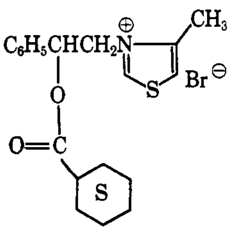
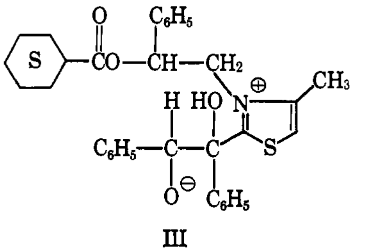

II

Using II as a catalyst in the benzoin condensation[4] with a 10:1 molar ratio of benzaldehyde to catalyst and a 1:1 molar ratio of triethylamine to catalyst, in methanol at ambient temperature, a precipitate of 0.52 g of benzoin (theory, 1.046 g) was obtained. This material was purified by chromatography on silica gel and showed a rotation of $[\alpha]^{25}_{546}$ +2.0° (*c* 2.0, $CHCl_3$) (optical purity 0.77%).[6]

The mother liquors from the reaction mixture were evaporated and purified by chromatography on silica gel to give 98.4 mg of benzoin, mp 123–131°. This material showed the following rotations, $[\alpha]^{25}_{546}$ (optical purity given in parentheses): +34.8° (*c* 0.79, acetone) (23.5%), +56.2° (*c* 1.04, $CHCl_3$) (21.5%), +112.5° (*c* 0.51, CS_2) (22.4%). An ORD curve of this material in *n*-hexane was consistent with that of benzoin with an optical purity of 22%.[7] This material had an infrared spectrum identical with that of authentic benzoin and showed only one spot on tlc.

In a separate experiment in which N-benzyl-4-methylthiazolium chloride was used as a catalyst, a measured amount of (+)-benzoin was added to the reaction mixture. After the aforementioned purification process all of the optically active benzoin was accounted for, principally in the mother liquor fraction.

The observed asymmetric catalysis was predicted on the basis of a "Lapworth-type" mechanism for benzoin condensation. The asymmetry presumably is induced during the formation of species III.


III

Acknowledgment. This work was supported by a grant from the National Institutes of Health.

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(5) Rotations were determined on a Zeiss photoelectric precision polarimeter.

(6) E. G. Rule and J. Crawford, *J. Chem. Soc.*, 138 (1937).

(7) P. Preiswerk, *Helv. Phys. Acta*, 7, 203 (1933).

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The Fate of the 1-([2.2]Paracyclophanyl)methylcarbonium Ion. A Double-Barrelled Ring Expansion Route to the [3.3]Paracyclophane System

Sir:

One of the more interesting questions which arose during our investigation of the bridge chemistry of paracyclophanes was the fate of the carbonium ion derived from solvolysis of the tosylate IV. In particular, rarely observed fragmentation[1] generating the stabilized benzylcarbonium ion I might occur because of the high strain energy[2a,b] (31.3 kcal $mole^{-1}$) of the [2.2]paracyclophane ring. Alternatively, the role of the distorted phenyl ring[2c–e] as a neighboring group[3] is of interest. Furthermore, the rate of ionization of tosylate IV might be predicted to be sterically accelerated[4] to the extent that strain relaxation occurs in the transition state.

The 1-carbomethoxy[2.2]paracyclophane was prepared by chloroformylation of [2.2]paracyclophane with oxalyl chloride in the presence of benzoyl peroxide and subsequent methanolysis of the crude acid chloride (see Chart I).[5] Reduction of the ester and tosylation of the resulting alcohol gave the tosylate IV in high yield.[6] When the tosylate IV was solvolyzed in refluxing acetic acid for 19 hr, a single acetate was obtained in 97% yield which, on the basis of the nmr, has structure Va. Less than 1% of unrearranged acetate or olefin was obtained on the basis of vpc analysis.

Chemical proof of structure was obtained by oxidation of the alcohol Vb derived from the corresponding acetate to give the ketone VI in 80–90% yield. The simplicity of the nmr spectrum for VI which displayed resonances at 6.86–6.33 (multiplet, aromatic), 3.70 (singlet, CH_2–CO), and 2.97 ppm (singlet, $-CH_2CH_2-$) (relative to tetramethylsilane in chloroform-*d*) in an area ratio of 2:1:1 rules out the alternate structure for the acetate which would result from benzyl migration and carbonium ion II. Conversion of ketone VI by Wolff–Kishner reduction to [2.3]paracyclophane (VII) which was identical in all respects with authentic material[7] offers chemical proof for the hydrocarbon skeleton.

Kinetic analysis of the solvolysis in acetic acid by the method of Winstein and Schreiber[3a] generated the rate constants for rearrangement of IV to tosylate Vc (k_r), solvolysis of IV to acetate Va (k_p), and solvolysis of rearranged tosylate Vc to acetate Va (k_s). These data

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(1) (a) J. Meinwald, P. G. Gassmann, and J. J. Hurst, *J. Am. Chem. Soc.*, **84**, 3722 (1962); (b) V. J. Shiner, Jr., and G. F. Meir, *J. Org. Chem.*, 31, 137 (1966).

(2) (a) R. H. Boyd, *Tetrahedron*, **22**, 119 (1966); (b) P. K. Gantzel and K. N. Trueblood, private communication; (c) C. J. Brown, *J. Chem. Soc.*, 3265 (1953); (d) K. Lonsdale, H. J. Milledge, and K. V. K. Rao, *Proc. Roy. Soc.* (London), **A255**, 82 (1960); (e) D. A. Bekoe and K. N. Trueblood, Meeting of American Crystallographic Association, Bozeman, Mont., 1964.

(3) (a) S. Winstein and K. C. Schreiber, *J. Am. Chem. Soc.*, 74, 2165 (1952); (b) R. Huisgen, G. Seidl, and S. Wimmer, *Tetrahedron*, 20, 623 (1964); (c) R. Huisgen and G. Seidl, *Chem. Ber.*, **96**, 2740 (1963); (d) D. J. Cram and L. S. Singer, *J. Am. Chem. Soc.*, **85**, 1084 (1963).

(4) H. C. Brown, Special Publication No. 16, The Chemical Society, London, 1963.

(5) (a) M. S. Kharasch and H. C. Brown, *J. Am. Chem. Soc.*, **64**, 329 (1942); (b) M. S. Kharasch, S. S. Kane, and H. C. Brown, *ibid.*, **64**, 1621 (1942); (c) E. Hedaya and L. M. Kyle, in preparation.

(6) All new compounds had correct elemental analyses along with consistent infrared, ultraviolet, and nmr spectra.

(7) We wish to thank Professor D. J. Cram for sending us an authentic sample.

Chart I

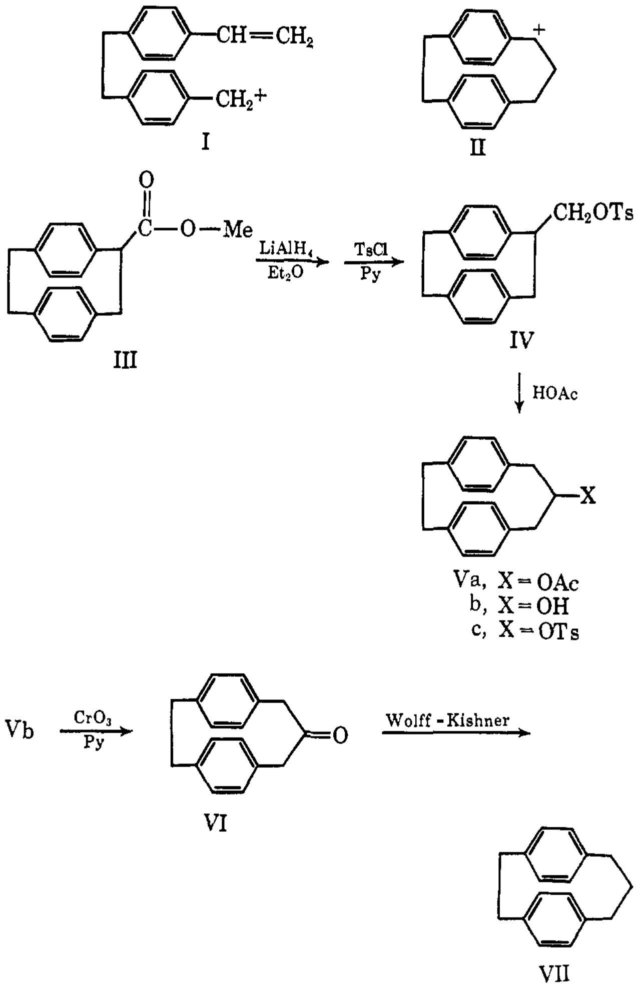
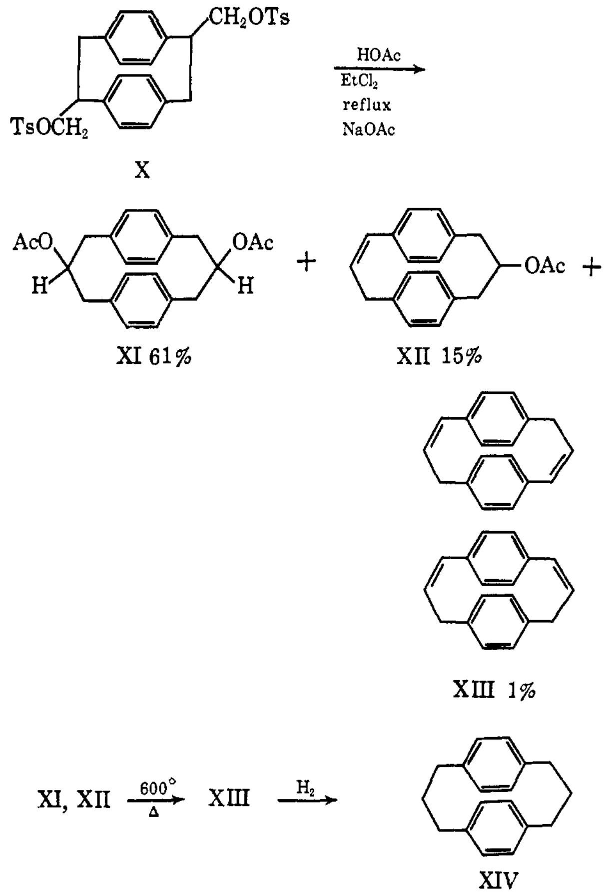


Chart II



are summarized in Table I along with analogous data estimated for the solvolysis of 2-phenyl-1-propyl tosylate (VIII)[3a] and measured for tetralyl-1-methyl tosylate IX.[3b] In our study confirmation of the values of k_r and k_s was obtained by isolation of rearranged tosylate as a function of time for the former and independent solvolysis of the rearranged tosylate Vc for the latter.

Table I. Solvolysis of Tosylates IV, VIII, and IX at 90° in Acetic Acid

Tosylate	$10^5 k_p$, sec^{-1}	$10^5 k_r$, sec^{-1}	$10^5 k_s$, sec^{-1}	$10^5(k_r + k_p)$, sec^{-1}
IV	7.04	38.0	5.12	45.0
VIII[a]	0.5	1.1	6.3	1.6
IX[b]	6.5	5.5	48.0	12.0

[a] Rates were estimated from data at other temperatures for solvolysis of 2-phenyl-1-propyl *p*-bromobenzenesulfonate[3a] using a factor of three to account for the difference in leaving groups. [b] Reference 3b.

These data show that the rate of ionization (k_r + k_p) is only enhanced by factors of about 28 and 3.8 compared to VIII and IX, respectively. Thus, the estimated 15–20-kcal difference in strain energy between the [2.2]- and [2.3]paracyclophane systems[2a,b] is not significantly relieved in the transition state for solvolysis of IV. However, Dreiding models indicate that the preferred phenonium ion geometry may not be attained in the transition state for solvolysis of IV and, consequently, this may counterbalance rate acceleration due to stain relaxation. Another feature revealed by the data is the high degree of internal return (85%) for IV compared to VIII and IX.

Exploitation of this ring expansion reaction for the preparation of the interesting but synthetically very expensive [3.3]paracyclophane system[8] was achieved by the twofold ring expansion of the ditosylate X as shown in Chart II. The ditosylate X was prepared by dichloroformylation of [2.2]paracyclophane,[5] methanolysis of the product to give a diester mixture, reduction of the diester, and tosylation of the diol as above. The ditosylate was solvolyzed in a refluxing mixture of acetic acid, ethylene dichloride (*ca.* 1:1), and sodium acetate (0.2 *M*) because of its insolubility. The structures of the products were initially based on spectra (nmr, ultraviolet, and infrared) and elemental analysis. Chemical proof of structure was obtained by nearly quantitative pyrolytic conversion of the diacetates XI and monoacetate XII to dienes XIII in a 15 × $^1/_2$ in. quartz tube packed with quartz wool at 600° and 1 mm. Subsequent reduction of dienes XIII to [3.3]paracyclophane was readily accomplished using Adams catalyst in ethanol solvent. The infrared spectrum[8] and melting point[8] of our hydrocarbon, as well as the ultraviolet spectra of both the hydrocarbon[8] and tetracyanoethylene complex,[9] corresponded with that previously published. In actual practice this simple six-step synthesis of [3.3]paracyclophane can be carried

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[8] D. J. Cram, N. L. Allinger, and H. Steinberg, *J. Am. Chem. Soc.*, 76, 6432 (1954).

[9] D. J. Cram and R. A. Bauer, *ibid.*, 81, 5971 (1959).

out in about 7% over-all yield based on [2.2]paracyclophane, with the yield in the primary dichloroformylation reaction being only 15%.[6c] The previous preparation[8] of [3.3]paracyclophane required a difficult ten-step synthesis involving a particularly unfavorable acyloin reaction occurring in only about 1% yield (over-all yield was 0.1%). Consequently, the ring expansion route represents a distinct improvement.

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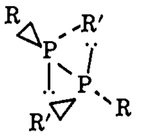
The Inversion of Diphosphines

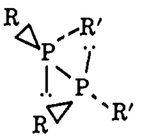
Sir:

The configurational instability of asymmetric tertiary amines has thus far prevented their resolution into optical antipodes, although inversion about nitrogen has been studied by nmr spectroscopy.[1] In the absence of ring constraints or ponderous substitution, inversion is generally too rapid to permit kinetic analysis even by this method. The recently reported isolation of optically active phosphines[2] might imply that inversion about phosphorus, on the other hand, is too slow for detection by nmr spectroscopy. We wish to report that the resonances of diphosphines exhibit reversible, temperature-dependent properties that are the kinetic result of phosphorus inversion. p_π–d_π bonding between the phosphorus atoms in diphosphines[3] apparently decreases the configurational stability with respect to that of monophosphines.[2]

Unsymmetrical diphosphines (I) may exist in two diastereomeric forms, the *meso* (II) and the *dl* (III), which should produce separate and distinct resonances.

RR′P–PRR′
Ia, R = CH_3; R′ = C_6H_5
Ib, R = CH_3; R′ = p-$CH_3C_6H_4$


II


III

Indeed, the ^{31}P spectrum of Ia is reported by Maier to consist of two peaks.[4] We have found that the aromatic region of the proton spectrum[5] of Ia also consists of two distinct multiplets below 130°. The *meso* form (II) may be converted to the *dl* form (III) (and *vice versa*) by a single inversion about phosphorus.[6] If this process becomes fast with respect to the nmr time scale, the effective loss of diastereomeric identity would cause the peaks to coalesce. Between 130 and 180°, the phenyl peaks broaden and coalesce into a single resonance with a line width comparable to that of the resonances at slow exchange. The aromatic methyl group of Ib also gives a doublet resonance that collapses to a sharp singlet at elevated temperatures. The slow-exchange spectra may be reproduced by lowering the temperature. The spectral properties at high temperatures are therefore consistent with rapid and reversible inversion about phosphorus.

Since the ring protons of each diastereomer are not magnetically equivalent, the aromatic resonances of Ia are highly structured. In order to develop an unambiguous kinetic analysis, we have synthesized 1,2-dimethyl-1,2-bis(2,4,6-trideuteriophenyl)diphosphine (Ia-d_3).[7] The unsplit but broad resonances of the *meta* protons have been kinetically analyzed at various temperatures by the Gutowsky–Holm–Borčić method.[8] The equilibrium constant at 32° (1.35) corresponds to a free-energy difference between diastereomers of 180 cal/mole.[9] From an Arrhenius plot of the kinetic data (Table I), the activation energy for inversion was calculated to be 26.0 ± 2 kcal/mole.

Table I. Kinetic Data for the Interconversion of Diastereomeric Diphosphines

T, °C	τ_A, sec[a]	τ_B, sec[a]	$W_{1/2}$, hertz[b]
125	. . .	. . .	3.7
140	0.4	0.3	. . .
146	0.25	0.19	. . .
149	0.195	0.15	. . .
153	0.163	0.125	. . .
160	0.091	0.070	. . .
162	0.071	0.055	. . .
168	0.058	0.045	. . .
200	. . .	. . .	4.5

[a] Mean lifetime. [b] Line width at half-height.

Several alternative explanations have been considered. (1) Since the distance between the two peaks of Ia-d_3

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(1) A. T. Bottini and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 5126 (1956); A. Loewenstein, J. F. Neumer, and J. D. Roberts, *ibid.*, **82**, 3599 (1960); A. T. Bottini, R. L. VanEtten, and A. J. Davidson, *ibid.*, **87**, 755 (1965); D. L. Griffith and J. D. Roberts, *ibid.*, **87**, 4089 (1965); W. N. Speckamp, U. K. Pandit, and H. O. Husiman, *Tetrahedron Letters*, No. **44**, 3279 (1964); V. F. Bystrov, R. G. Kostyanovskii, O. A. Panshin, A. U. Stepanyanta, and O. A. Iuzhakova, *Opt. Spectry.* (*USSR*), **19**, 122 (1965).

(2) L. Horner, H. Winkler, A. Rapp, A. Mentrup, H. Hoffman, and P. Beck, *Tetrahedron Letters*, No. **5**, 161 (1961); L. Horner and H. Winkler, *ibid.*, No. **9**, 461 (1964); D. P. Young, W. E. McEwen, D. C. Velez, J. W. Johnson, and C. A. VanderWerf, *ibid.*, No. **7**, 359 (1964); I. G. M. Campbell and J. K. Way, *J. Chem. Soc.*, 5034 (1960).

(3) For a review of the chemistry and properties of diphosphines, see A. H. Cowley, *Chem. Rev.*, **65**, 617 (1965).

(4) L. Maier, *Ber.*, **94**, 3043 (1961); L. Maier, *J. Inorg. Nucl. Chem.*, **24**, 275 (1962).

(5) Methyldibromophosphine sulfide and the phenyl Grignard reagent were converted to *dl*- and *meso*-1,2-dimethyl-1,2-diphenyldiphosphine disulfide according to the method of Maier.[4] Either isomer gave the same *dl*-/*meso*-diphosphine mixture upon reduction. The methyl resonances of Ia were masked by the solvent, tri-*n*-butylphosphine sulfide. All spectra were taken with a temperature-adaptable Varian A-60 spectrometer. Accurate temperatures were obtained by measurement of the distance between the resonances of ethylene glycol.

(6) The simultaneous inversion of both phosphorus atoms with a planar, alkene-like transition state would introduce statistical factors that only influence the preexponential portion of the rate expression. The essentials of the following discussion would not be altered.

(7) Deuterium was introduced into the *ortho* and *para* positions of aniline hydrochloride by treatment with deuterium oxide at 100°. The free amine was then converted by way of the Sandmeyer reaction to bromobenzene-2,4,6-d_3, which was used in Maier's diphosphine synthesis.[4,5]

(8) J. B. Lambert, W. L. Oliver, and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 5085 (1965).

(9) An equilibrium constant different from unity eliminates the possibility that the distinct resonances are due to *meta* protons that are nonequivalent by hindered rotation about the P–C bond. This conclusion is confirmed by the coalescence of the aromatic methyl resonances of Ib (*vide supra*).