remarkable tendency for inversion of the alkyl group.[5c,10,11] We therefore investigated the steric course of the present reaction using an optically active alcohol.

When (S)-(+)-2-octanol,[12] [α]D +14.3° (101% optical purity,[13] 6.99 mg/1 ml of n-heptane), was allowed to react with **1**, **2**, and **3c** in THF at room temperature, followed by column chromatography (Wakogel B-5, eluate, benzene), N-2-octylphthalimide was obtained in a 79% yield. The product was then treated with hydrazine hydrate (80%) in ethanol and (R)-(−)-2-octylamine was obtained in a 48% yield (based on (S)-(+)-2-octanol) by distillation (bp 70–72° (31 mm)).[14] The 2-octylamine showed [α]D −7.13° (in benzene, 0.01206 g/1 ml), and this value corresponded to 108% optical purity.[15]

The results described above and in the preceding paper[5c] indicated that, at least in the cases studied, the alkylation by means of alkoxyphosphonium salts proceeded stereospecifically with (nearly) complete inversion of the configuration of the alkyl group.

HO—C◄CH₃   1. 1 + 2 + 3c   CH₃►C—NH₂
                2. hydrazinolysis

(S)-(+)   (R)-(−)
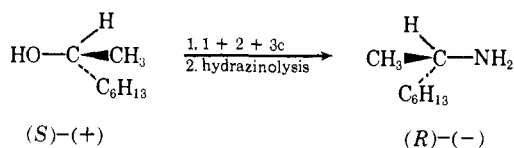
This reaction may possibly be used to infer the absolute configuration of either an alcohol or its homologous amine when that of only one of them is known. Analogous studies of the reactions of alkoxyphosphonium salts with various nucleophiles are now under investigation.

(10) W. Gerrard and W. J. Green, J. Chem. Soc., 2550 (1951).

(11) R. G. Weiss and E. I. Snyder, J. Org. Chem., 35, 1627 (1970); and references therein.

(12) A. W. Ingersoll, "Organic Reactions," Vol. 2, R. Adams, Ed., Wiley, New York, N. Y., 1960, p 376. Optical rotations were measured with a JASCO ORD/UV-5.

(13) M. K. Hargreaves has reported that (+)-2-octanol showed optical activities (in n-heptane) of [α]D +13.1° (l = 2, 10.817 g/100 cm³) and +14.1° (l = 2, 4.973 g/100 cm³). The specific rotatory power increases with dilution until a concentration of about 3% is reached, where it becomes constant. Thus, our (S)-(+)-2-octanol was about 100% optical purity (J. Chem. Soc., 2953 (1953)).

(14) It has been demonstrated that (+)-2-octanol was converted to (−)-2-octylamine with >97% inversion of configuration,[2] the absolute configuration of the (−)-2-octylamine being the R configuration.

(15) The recorded molecular rotation of (+)-2-octylamine is [M]D 8.50° (in 5.953% benzene solution) which corresponds to [α]D + 6.59°: F. G. Mann and J. W. G. Porter, J. Chem. Soc., 456 (1944).

Oyo Mitsunobu,* Makoto Wada, Takashi Sano

Department of Chemistry, College of Science and Engineering
Aoyamagakuin University
Megurisawa-cho, Setagaya-ku, Tokyo, Japan

Three Homobullvalenones. Synthesis and Cope Rearrangements[1,2]

Sir:

Theoretical speculation has been stimulated anew by the fluxional properties of bridged homotropilidenes

(1) Presented in part at the International Symposium on the Chemistry of Nonbenzenoid Aromatic Compounds, Sendai, Japan, Aug 1970.

(2) Chemical Abstract names: **5a**, tricyclo[4.3.2.0²·⁹]undeca-4,7,10-trien-3-one; **5b**, tricyclo[4.3.2.0²·⁹]undeca-3,7,10-trien-5-one; **5c**, tricyclo[4.3.2.0³·⁹]undeca-4,7,10-trien-2-one; **2**, 4-bromo-, 4,4-dibromo-, 5-methoxy-4-bromo-, and 5-methoxy-4,4-dibromotetracyclo[4.3.2.0²·⁹,-0³·⁶]undeca-7,10-diene.

(1).[3–5] We report here the first extension of this series

1   2

beyond its third member (bullvalene) and indicate some theoretical problems and opportunities which then ensue.

In an initial synthetic approach, the dibromocyclopropane (**2**, y = H, n = x = Br, 42%, mp 116°),[6] appropriately obtained from bullvalene,[7,8] was transformed by n-Bu₃SnH[9] into its epimeric monobromides (**2**, y = H, x = Br, n = H, 35%, mp 59°, nmr τH-4 (CCl₄) 6.82 (t, J = 3.2 Hz) and **2**, x = y = H, n = Br, 30%, mp 79°, nmr τH-4 (CCl₄) 7.19 (t, J = 7.9 Hz).[10] Subsequent and varied attempts at solvolytic cleavage,[13] however, proved to be fruitless.

To the degree that such difficulties might indirectly reflect the structural proximity of **3** (y = H) to the

3   4
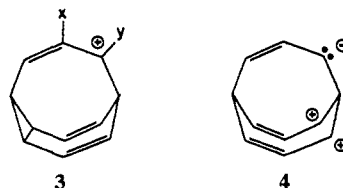
electronically uncomfortable **4**,[14] relief should be accessible via an appropriately electron-donating y. However accurate this diagnosis, analogous transfor-

(3) W. v. E. Doering and W. R. Roth, Angew. Chem., 75, 27 (1963); Angew. Chem., Int. Ed. Engl., 2, 115 (1963); G. Schröder, J. F. M. Oth, and R. Merényi, Angew. Chem., 77, 774 (1965); Angew. Chem., Int. Ed. Engl., 4, 752 (1965); G. Schröder and J. F. M. Oth, Angew. Chem., 79, 458 (1967); Angew. Chem., Int. Ed. Engl., 6, 414 (1967).

(4) (a) R. Hoffmann, Tetrahedron Lett., 2907 (1970); H. Günther, ibid., 5173 (1970); (b) R. Hoffmann and W.-D. Stohrer, J. Amer. Chem. Soc., 93, 6941 (1971); (c) A. Brown, M. J. S. Dewar, and W. Schoeller, ibid., 92, 5516 (1970); M. J. S. Dewar and W. W. Schoeller, ibid., 93, 1481 (1971); M. J. S. Dewar and D. H. Lo, ibid., 93, 7201 (1971); M. J. S. Dewar, Pure Appl. Chem., in press.

(5) (a) M. J. Goldstein, J. Amer. Chem. Soc., 89, 6357 (1967); (b) M. J. Goldstein and R. Hoffmann, ibid., 93, 6193 (1971).

(6) C, H, and Br analyses of all isolated compounds agreed with expectation to within ±0.3%.

(7) D. Seyferth, et al., J. Amer. Chem. Soc., 87, 4259 (1965).

(8) W. v. E. Doering and A. K. Hoffmann, ibid., 76, 6162 (1954); L. Skattebøl, Org. Syn., 49, 35 (1969).

(9) H. G. Kuivila, Accounts Chem. Res., 1, 299 (1968); D. Seyferth, H. Yamazaki, and D. L. Alleston, J. Org. Chem., 28, 703 (1963).

(10) The temperature-dependent pmr spectra resemble those of the dichloride (y = H, x = n = Cl)[11a] and parent hydrocarbon (y = x = n = H).[12]

(11) (a) R. Merényi, J. F. M. Oth, and G. Schröder, Chem. Ber., 97, 3150 (1964); (b) J. F. M. Oth, R. Merényi, J. Nielsen, and G. Schröder, Chem. Ber., 98, 3358 (1965); (c) J. F. M. Oth, R. Merényi, H. Röttele, and G. Schröder, Tetrahedron Lett., 3941 (1968); (d) J. F. M. Oth, E. Machens, H. Röttele, and G. Schröder, Justus Liebigs Ann. Chem., 745, 112 (1971).

(12) A. de Meijere and C. Weitemeyer, Angew. Chem., 82, 359 (1970); Angew. Chem., Int. Ed. Engl., 9, 376 (1970).

(13) (a) U. Schöllkopf, Angew. Chem., 80, 603 (1968); Angew. Chem., Int. Ed. Engl., 7, 588 (1968); W. E. Parham, et al., J. Amer. Chem. Soc., 87, 321 (1965); G. Stork, M. Nussim, and B. August, Tetrahedron, Suppl., No. 8, 105 (1966); (b) A. J. Birch, J. M. Brown, and F. Stansfield, J. Chem. Soc., 5343 (1964); C. D. Gutsche and D. Redman, "Carbocyclic Ring Expansion Reactions," Academic Press, New York, N. Y., 1968.

(14) Like the cyclopentadienyl cation, **4** requires a half-filled (if stabilized) doubly degenerate MO.[5b] The D₃ₕ barbaralyl cation provides an informative contrast. Cf. R. Hoffmann, W.-D. Stohrer, and M. J. Goldstein, Bull. Chem. Soc. Jap., submitted for publication; S. Yoneda, S. Winstein, and Z. Yoshida, ibid., submitted for publication.

mation of methoxybullvalene[11b,15] did afford a more tractable endo monobromide (2, y = OMe, x = H, n = Br), smoothly transformed by ethanolic silver nitrate into an apparently homogeneous ketone.[16]

Augmenting other data,[16] its pmr spectrum (Table I) serves to exclude all structural hypotheses except 5a and 5b[17–19] but with a different proton-connectivity

5a   **5b**
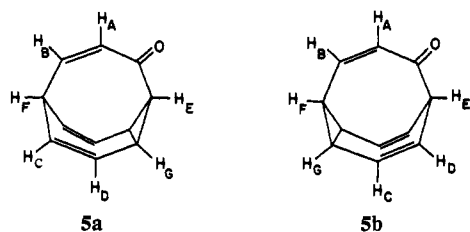
sequence assigned to each. Complete spin decoupling then selects 5b as the only Cope-related isomer detected within the accessible temperature range (−60 to +120°).

Nevertheless, the persistence through repeated purification of a weak, but characteristically sharp ir band at 1782 cm⁻¹ suggested the possibility of contamination by 5c, the third remaining homobullvalenone. Unrecognizable in pmr spectra, yet rapidly equilibrating with 5b, this isomer could be characterized only by its unique plane of symmetry. In practice, solvolytic cleavage of α-deuterated precursor 2 (y = OCH₃, n = Br, x = D) provided a sample of 5b whose pmr-normalized areas at H_A and H_E had fallen to 0.45 and 0.46 proton. The absence of any other area changes is then most simply satisfied by the single equilibration path

5b-1-d   **5c-1-d**   **5b-6-d**
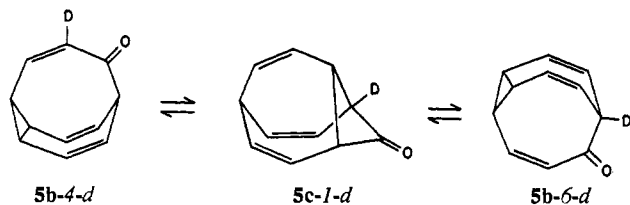
A reasonable extrapolation, as well as analogy to the bullvalene series,[11,19] then suggests a similar description for 5a: in equilibrium with 5b, it is significantly the less stable isomer.

This last conclusion is not easily reconciled with theoretical prediction[4b] nor with those examples cited in its behalf.[4b,20] Electron-withdrawing groups, (e.g., C=O) are expected to be found at C-1 of a bridged homotropilidene (1) rather than at C-5. The more extensive data of Table II now reveal a much more complicated pattern. At the bullvalene level of homologation, both electron-accepting and electron-donating substituents prefer C-5 to C-1.[21] At the homobull-

(15) (a) y = OMe, n = x = Br, 40%, mp 110°; (b) y = OMe, x = Br, n = H, 31%, mp 76°, nmr τ_{H-4} (CDCl₃) 6.84 (d, J = 5.0 Hz); (c) y = OMe, n = Br, x = H, 20%, mp 80°, nmr τ_{H-4} (CDCl₃) 7.06 (d, J = 9.7 Hz). The temperature-independent pmr spectra of all three (−80 to +120°) presumably reflect the thermodynamic instability of their Cope-related isomers. No other isomers were expected.[13b]

(16) The following was observed: 72% isolated; mp 47°; m/e 158, 129 (base peak), 115; ir (CCl₄) 3025, 2939, 1677, 1661, 1647 cm⁻¹; uv max (isooctane) and ε 207 (12,000), 264 (4,370), 320 (124), 331 (160), 344 (171), 360 (127), 381 (44) nm.

(17) N. Heap and G. H. Whitham, J. Chem. Soc. B, 164 (1966).

(18) S. Sternhell, Quart. Rev., Chem. Soc., 23, 236 (1969).

(19) H. Günther, H. Klose, and D. Wendisch, Tetrahedron, 25, 1531 (1969); H. Klose and H. Günther, Chem. Ber., 102, 2230 (1969).

(20) G. R. Krow and K. C. Ramey, Tetrahedron Lett., 3141 (1971).

Table I. Pmr Spectrum of **5**

Assignment	A^a	τ	s^b	Appearance^c
H_A	0.95^d	3.50	−282	dd (J = 14.0, 1.0)^d
H_B	0.99^d	3.57	−78	dd (J = 14.0, 8.1)^d
H_C	2.09	4.13	−66	ddd (J = 12.0, 4.8, 2.5)
H_D	2.09	4.65	−99	dd (J = 12.0, 8.0)
H_E	0.99	6.58	−262	td (J = 8.0, 1.0)
H_F		7.39	−50	dd (J = 8.2, 8.1)^d
	2.96			
H_G		7.53	−56	m

^{a} Areas normalized to ten protons. ^{b} Slope (l./mol) of τ vs. [Eu(fod)₃]; cf. R. E. Rondeau and R. E. Sievers, J. Amer. Chem. Soc., 93, 1524 (1971). ^{c} Reported J are observed first-order splittings and are in hertz. ^{d} Discernible upon Eu(fod)₃ shifting.

Table II. Preferred Orientation of Bridged Homotropilidenes

C-1 terminus	C-5 terminus	Ref

with structures and references: a, a, b,f, c,g, d,h, i, e

^{a} This report. ^{b} R = Me, Et, i-Pr; t-OBu exhibits no marked preference, presumably for steric reasons. ^{c} R = H, Me. ^{d} R = Me, Et; L. A. Paquette, J. R. Malpass, G. R. Krow, and T. J. Barton, J. Amer. Chem. Soc., 91, 5296 (1969). ^{e} L. A. Paquette, S. Kirschner, and J. R. Malpass, ibid., 91, 3970 (1969). ^{f} Reference 11b. ^{g} Reference 11d. ^{h} Reference 19. ^{i} Reference 20.

valene level, the more plausibly electron-accepting terminus (C=O) clearly prefers C-5.

Since the prediction derives largely from theoretical analyses of substituted semibullvalenes, it is obvious that the larger longicyclic frameworks[5b] must alter the consequences of polar substitution. How they do so, a more difficult question, is currently the object of theoretical and experimental effort.

(21) Such weakly donating and accepting substituents as Me,[11d] Cl,[11c] Br,[11b] and I[11c] hardly discriminate at all. Methyl prefers C-1 and deuterium C-5 of barbaralone; K = 3.28, 0.80.[22]

(22) J. C. Barborak, S. Chari, and P. v. R. Schleyer, J. Amer. Chem. Soc., 93, 5275 (1971).

provided by H. S. Hair, and preparative assistance was provided by J. Nunberg.

M. J. Goldstein,* R. C. Krauss, S.-H. Dai

*Department of Chemistry, Cornell University
Ithaca, New York 14850*

Anionic σ Complexes between Amide Ions and the Diazines in Liquid Ammonia

Sir:

We wish to report the first direct evidence for the existence of anionic σ complexes of the type long postulated[1] to occur in the Chichibabin amination reaction of heterocyclic compounds.[2] The nmr spectra of the amide ion–diazine complexes I–III in liquid ammonia were obtained.[3,4]
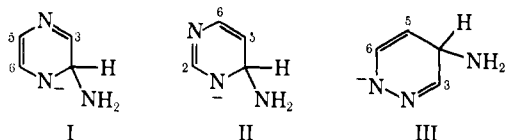
Complexes were formed by the addition of a diazine to $NaNH_2$ or KNH_2 in ammonia. Nmr spectra of the deeply colored solutions obtained at -40 to $0°$ about 30 min after mixing showed no free diazine when excess amide ion was employed. Adduct formation is characterized by the usual upfield shifts[5] (2.2–4.5 ppm). In the presence of a deficiency of amide ion, the spectra of both free and complexed diazine are seen and no noticeable signal averaging is found. Also, spin coupling of the amine protons with a ring proton of the adduct results. With excess amide ion, however, hydrogen exchange occurs and this spin coupling is not found. This change in coupling serves as a useful way to identify the signal of the tetrahedral center of the adduct. Adducts are stable in solution for days at $-70°$, but solutions at room temperature give new signals in what appear to be irreversible reactions.[6,7]

The adduct of pyrazine and amide ion showed the following chemical shifts and coupling constants: τ 3.40 (H-6), 4.18 (H-5), 4.39 (H-3), 5.78 (H-2), $J_{2,3} = 3.0$ Hz, $J_{3,6} \sim 0.5$ Hz, $J_{5,6} = 3.0$ Hz, and $J_{NH_2,H} = 7.7$ Hz. No signals were found for the amino group of this or any other complex, probably because they are included in that for the main solvent peak. This spec-

trum is consistent with the structure 2-amino-1,2-dihydropyrazinide ion (I) and provides direct evidence for it. Free pyrazine in ammonia shows a signal at τ 1.2; note the large changes in chemical shift on complex formation.

Three adducts are possible in the case of pyrimidine. Addition of amide ion to C-2 or C-5 is expected to give anions in which H-4 and H-6 are equivalent, owing to symmetry. However, addition to C-4 should give rise to an anion with four nonequivalent protons. The observed spectrum shows four nonequivalent protons at τ 2.93 (H-2), 3.73 (H-6), 5.37 (H-4), 5.68 (H-5), $J_{2,4} = J_{2,6} = 0.5$ Hz, $J_{2,5} = 1.5$ Hz, $J_{4,5} = 3.5$ Hz, $J_{5,6} = 6.5$ Hz, and $J_{NH_2,H} = 7.0$ Hz. Hence the major adduct is 4-amino-1(or 3),4-dihydropyrimidinide ion (II). Signals of a minor component were not characterized, owing to low intensity and overlap.

Two different adducts are possible for pyridazine, resulting from addition of amide ion to C-3 or C-4. The assignment of a 4-amino-1,4-dihydropyridazinide ion structure (III) follows from the spectra of the pyridazine and pyridazine-3,6-d_2[8] adducts. The proteo adduct is characterized as follows: τ 3.30 (H-6), 3.45 (H-3), 5.73 (H-5), 6.27 (H-4), $J_{3,4} = 3.5$ Hz, $J_{3,5} = 3.0$ Hz, $J_{3,6} = 0.5$ Hz, $J_{4,5} = 4.5$ Hz, $J_{5,6} = 7.0$ Hz, and $J_{NH_2,H} = 7.0$ Hz. (These coupling constants have a larger uncertainty than those for the other adducts, because there is signal overlap.) The dideuterio adduct did not show the low-field multiplets, and the upfield spectrum consisted of a pair of doublets for H-4 and H-5. Because there is decoupling, another pair of doublets at τ 4.20 ($J = 8.0$ Hz) and 5.49 now could clearly be seen above the noise level. These may represent H-4 and H-5 of a small amount of the other adduct.

In the absence of adduct formation, pyridazine-3,6-d_2 is expected to undergo significant H–D exchange in ammonia.[9] But little, if any, dedeuteration took place after 19 hr at $-78°$ or after 0.5 hr at $0°$, owing to adduct formation. The spectrum of the deuterated pyridazine could be regenerated by the addition of ammonium ions to a reaction mixture. It is interesting to consider earlier reports[10] in the light of our results.

An upper limit to the dissociation constants, $K = [C_4H_4N_2][NH_2^-]/[complex]$, for the diazine complexes may be estimated. When both complex and free diazine are present in similar amounts in solution, coupling between a ring proton and the amino group of the adduct is found and the solvent peak is a triplet. This means amide ion-catalyzed hydrogen exchange is slow.[11] Hence, an upper limit to the amide ion concentration may be estimated from the coupling constant ($J = 44$ Hz) and the rate constant (1.5×10^7 M^{-1} sec^{-1} at $25°$)[12] for hydrogen exchange of ammonia. When NH coupling is present, $[NH_2^-] \leqslant 44\pi/(\sqrt{2} \times 10^7)$ and

(1) K. Ziegler and H. Zeiser, *Chem. Ber.*, 63, 1847 (1930).

(2) M. T. Leffler, *Org. React.*, 1, 91 (1942); R. N. Shreve and L. Berg, *J. Amer. Chem. Soc.*, 69, 2116 (1947); M. L. Crossley and J. P. English, U. S. Patent 2394963 (1946); *Chem. Abstr.*, 40, 3143⁷ (1946).

(3) The nmr spectra of the complexes between the diazines and amide ions will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(4) Trimethylamine, τ 7.87, is the shift standard. Spectra were obtained with a Varian A-60A spectrometer equipped with a V-6040 variable-temperature controller.

(5) M. J. Strauss, *Chem. Rev.*, 70, 667 (1970).

(6) Solids which were assumed to be adducts between an alkali amide and isoquinoline or several quinolines have been isolated.⁷ They are too unstable to be characterized. In view of these reports, we have not attempted to isolate the diazine complexes.

(7) F. W. Bergstrom, *Justus Liebigs Ann. Chem.*, 515, 34 (1934); *J. Org. Chem.*, 2, 411 (1937); 3, 424 (1938).

(8) Prepared by hydrogen–deuterium exchange using the method reported by J. A. Zoltewicz and C. L. Smith, *J. Amer. Chem. Soc.*, 89, 3358 (1967).

(9) J. A. Zoltewicz, G. Grahe, and C. L. Smith, *ibid.*, 91, 5501 (1969); I. F. Tupitsyn and N. K. Seminova, *Tr. Gos. Inst. Prikl. Khim.*, 49, 120 (1962); *Chem. Abstr.*, 60, 6721c (1964).

(10) H. J. den Hertog and H. C. van der Plas in "Chemistry of Acetylenes," H. G. Viehe, Ed., Marcel Dekker, New York, N. Y., 1969, Chapter 17.

(11) R. A. Ogg, Jr., *Discuss. Faraday Soc.*, 17, 215 (1954); J. D. Roberts, "Nuclear Magnetic Resonance Applications to Organic Chemistry," McGraw-Hill, New York, N. Y., 1959, Chapter 4.

(12) T. J. Swift, S. B. Marks, and W. G. Sayre, *J. Chem. Phys.*, 44, 2797 (1966).