(18) By infrared spectroscopic comparison with authentically synthesized samples.
(19) This is reduced to 1.30 ± 0.05 if one value is deleted from the set of six. All isotope effects were derived from low-voltage mass spectral analysis of benzene-d_0 and benzene-d_3 obtained after 5–13% pyrolysis of the corresponding isotopic mixture of precursors. Appropriate care was taken to exclude the consequences of mass spectrometric isotopic discrimination.
(20) (a) H. M. Frey and B. M. Pope, *Trans. Faraday Soc.*, **65**, 441 (1969); (b) W. R. Dolbier, Jr., in "Isotopes in Organic Chemistry", Vol. 1, E. Buncel and C. C. Lee, Ed., Elsevier, Amsterdam, 1975, p 27.
(21) (a) Both values assume that ΔH_f(bicyclo[2.2.0]hexadiene) − ΔH_f(bicyclo[2.2.0]hexene) = ΔH_f(bicyclo[2.2.0]hexene) − ΔH_f(bicyclo[2.2.0]hexane) = ΔH_f(cyclobutene) − ΔH_f(cyclobutane) = 30.6 kcal/mol. Neglect of "superstrain" [21b] implies that both are *minimal* estimates of exothermicity. Agreement with the MINDO/3 estimate of Dewar benzene cyclodissociation exothermicity (70 kcal/mol)[21c] is as fortuitous as was the previous agreement of 60 kcal/mol between a different empirical estimate[2c] and the MINDO/2 value[21d] for the same reaction. Experimental data would greatly be preferred. (b) J. F. Liebman and A. Greenberg, *Chem. Rev.*, **76**, 311 (1976). (c) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1294 (1975). (d) N. C. Baird and M. J. S. Dewar, *ibid.*, **91**, 352 (1969). (e) Still more recent MNDO calculations predict −61.6 kcal/mol for the cyclodissociation of Dewar benzene. They also require the trans isomer (**3**) to be less stable than the cis by 85.8 kcal/mol. **3** would therefore be excluded as a potential intermediate unless the latter value were in error by >63 kcal/mol (M. J. S. Dewar, private communication).
(22) The structure of the ($^3B_{1u}$) benzene triplet is most often regarded as that of a D_{2h}-distorted ground state. Distortions in the sense of **2** or **3** have not explicitly been considered. Cf. P. J. Vergragt and J. H. van der Waals, *Chem. Phys. Lett.*, **36**, 283 (1976), and references there cited.
(23) Taken in part from the Ph.D. thesis of R.S.L., Cornell University, 1977; U.S. Public Health Service Trainee, 1973–1976.

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A Partial Optical Resolution of a Hydrocarbon by Free-Radical Kinetic Resolution

Sir:

The optical resolution of racemic hydrocarbons must normally be accomplished via indirect and tedious methods.[1] Because of the chemical inertness of hydrocarbons toward standard resolving agents, the direct formation of separable diastereomers is usually precluded. Hydrocarbons do, however, react with free radicals in hydrogen abstraction reactions. Therefore, if there is a significant difference in energy between the two different diastereotopic transition states formed upon approach of a chiral hydrogen abstracting radical to the two enantiomeric forms of the racemic hydrocarbon, it is hypothetically possible to partially resolve the hydrocarbon. If a limiting amount of the hydrogen abstracting species is used, hydrocarbon remaining unreacted should be enriched in the enantiomer which reacts more slowly with the chiral radical. We report here a direct partial resolution of 2-phenylbutane by taking advantage of the difference in the rates of reaction of the two enantiomers with optically active 2-phenyl-2-butoxy radical. This is the first example, to our knowledge, of kinetic resolution[2] reported for hydrogen abstraction by free radicals.

Alkyl hypochlorites have been extensively studied[3] as reagents for effecting free-radical chlorination and react via the chain reaction shown below.

$$\mathrm{ROCl} \xrightarrow{h\nu} \mathrm{RO\cdot} + \mathrm{Cl\cdot}$$

$$\mathrm{RO\cdot} + \mathrm{R'-H} \rightarrow \mathrm{ROH} + \mathrm{R'\cdot}$$

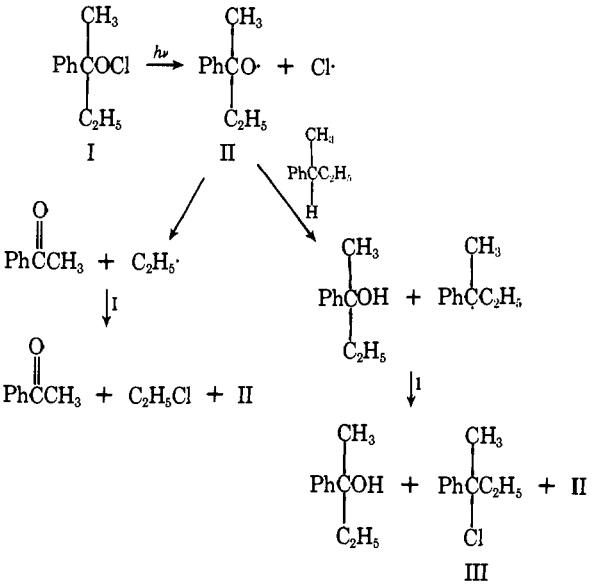
$$\mathrm{R'\cdot} + \mathrm{ROCl} \rightarrow \mathrm{RO\cdot\ R'-Cl}$$

If the alkoxy radical contains moieties which can form relatively stable radicals, extensive fragmentation occurs, forming ketones and free radicals. Thus, when a carbon tetrachloride solution of racemic 2-phenyl-2-butyl hypochlorite (I, 5 M) and 2-phenylbutane (II, 0.5 M) which had been degassed by three freeze–thaw cycles was immersed in a 20 °C water bath and photolyzed with a sun lamp, acetophenone and ethyl chloride are produced predominately (~90% of the original hypochlorite). The 2-phenylbutane was 45.2% consumed, and a 38% yield of 2-chloro-2-phenylbutane (III) was produced.

Table I. Results of Photolysis of (+)-2-Phenyl-2-butyl Hypochlorite with Racemic 2-Phenylbutane

Optical purity of hypochlorite, %	27.2	86.2
Starting weight 2-phenylbutane, g	5.36	2.20
Residual weight 2-phenylbutane, g	2.88	1.10
Recovered from gas chromatograph, g	1.90	0.90
Observed rotation, deg	+0.475[b]	+0.31[c]
Specific rotation, deg	+1.24	+4.29
(+) isomer,[a] %	4.4	15.4

[a] Based on a rotation of optically pure 2-phenylbutane of ±28.0 °C: D. Seyferth and Y. M. Cheng, *J. Am. Chem. Soc.*, **95**, 6763 (1973). [b] 1.90 g/5 mL of CCl_4. [c] 0.65 g/9 mL of CCl_4.



Two samples of 2-phenyl-2-butanol of differing optical purity (A, $[\alpha]_D^{25}$ +4.75° (27.2% optically pure[4]), and B, $[\alpha]_D^{25}$ +15.05° (86.2% optically pure[4])), which were resolved by the method of Davies et al.,[5] were converted into the hypochlorites.[6] Solutions of these partially resolved hypochlorites and 2-phenylbutane (10:1 mole ratio) in carbon tetrachloride were photolyzed under the conditions described above. The experimental results are summarized in Table I. The unreacted hydrocarbon was isolated by spinning-band distillation and samples used for determination of optical rotation were collected by gas chromatography to further ensure their purity. Upon second attempted chromatographic separation, no impurities were detected.

By assuming that an initial rate approximation holds and that the rate constant k_+ for reaction of (+)-2-phenylbutane with (+)-II is identical with that of (−)-2-phenylbutane with (−)-II and that the rate constant k_- for reaction of (−)-2-phenylbutane with (+)-II is identical with that of (+)-2-phenylbutane with (−)-II one can derive the expression

$$\frac{\%\text{ (+)-2-phenylbutane reacted}}{\%\text{ (−)-2-phenylbutane reacted}} = \frac{k_-(R) + k_+}{k_- + k_+(R)}$$

where R is the original ratio of +/− hypochlorite. The approximation of using a constant ratio of optical purity of the hypochlorite should be valid since at least 90% of the alkoxy radicals derived from the hypochlorite reacts via a first-order decomposition to acetophenone and ethyl radical. When our experimental results are treated in this manner, the ratio k_-/k_+ from expt A is 1.42 and that from expt B is 1.41. This allows

calculation of the difference of free energy of activation ($\Delta\Delta G^{\ddagger}$) for the two diastereotopic reactions of 0.20 kcal/mol (20 °C).

These results are of interest both from theoretical and practical viewpoints. Although the degree of resolution achieved in these preliminary experiments is low, the relatively large difference in rate of reaction of the two enantiomers has encouraged further experiments designed to explore the potential and origin of this phenomenon.

Acknowledgment. The authors gratefully acknowledge helpful discussions with Dr. F. A. Johnson.

References and Notes

(1) S. H. Wilen, *Top. Stereochem.*, **6**, 107 (1971).
(2) P. H. Boyle, *Q. Rev. Chem. Soc.*, **25**, 323 (1971).
(3) C. Walling and A. Padwa, *J. Am. Chem. Soc.*, **85**, 1593 (1963).
(4) Based on $[\alpha]_D^{25}$ +17.45° reported by H. H. Zeiss, *J. Am. Chem. Soc.*, **73**, 2391 (1951).
(5) A. G. Davies, J. Kenyon, and L. W. F. Salame, *J. Chem. Soc.*, 3148 (1957).
(6) M. C. Taylor, R. B. MacMullin, and C. A. Gammal, *J. Am. Chem. Soc.*, **47**, 395 (1925).

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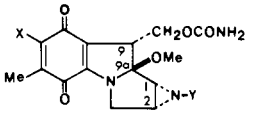
Synthetic Studies toward Mitomycins. 2.[1] Total Synthesis of *dl*-Porfiromycin[2]

Sir:

The mitomycins (**1a–e**) are a class of antibiotics with activity against gram-positive and gram-negative bacteria and also against several kinds of tumors.[3] Since their structures were first elucidated in 1962,[3] numerous synthetic approaches to the mitomycins have been reported.[4] However, the mitomycins themselves have not yet been synthesized. In this communication, we wish to report the first total synthesis of *dl*-porfiromycin (**1d**) by the synthetic route that we recently used for the synthesis of deiminomitomycin A.[1]



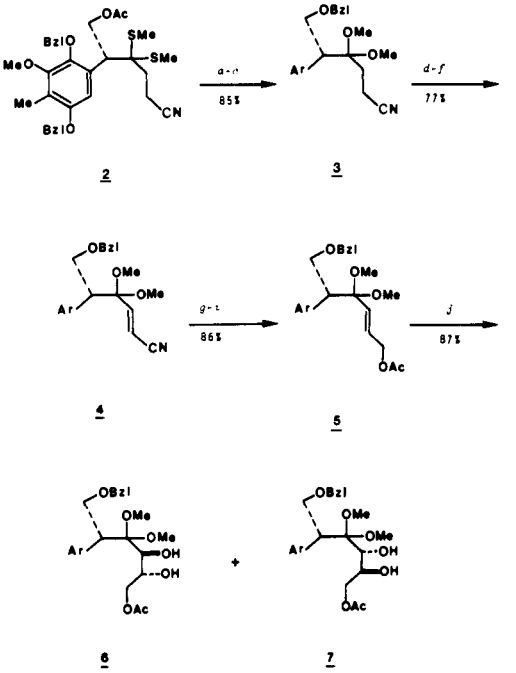
1a, mitomycin A, X = OCH_3, Y = H
b, mitomycin B[5]
c, mitomycin C, X = NH_2, Y = H
d, porfiromycin, X = NH_2, Y = CH_3
e, mitiromycin[6]

Scheme I summarizes the synthesis of diols **6** and **7** from nitrile **2**.[1] The ^{1}HNMR spectra clearly showed that the olefinic bonds of **4** and **5** were exclusively trans. Osmium tetroxide oxidation of **5** yielded about a 1:1 mixture of diastereomeric diols **6**[7] (oil; ^{1}H NMR ($CDCl_3$) δ 1.96 (3 H, s), 2.21 (3 H, s), 2.91 (3 H, s), 3.28 (3 H, s), 3.80 ppm (3 H, s)) and **7**[7] (oil; ^{1}H NMR ($CDCl_3$) δ 1.96 (3 H, s), 2.21 (3 H, s), 3.08 (3 H, s), 3.41 (3 H, s), 3.83 ppm (3 H, s)) which could be separated by silica gel chromatography.[8] The stereochemistry assignments of **6** and **7** were made from the experiments discussed later.

Scheme II summarizes the transformation of **6** into dibenzylamino-*N*-methylaziridine **10**[7] (oil; ^{1}H NMR ($CDCl_3$) δ 2.18 (6 H, s), 3.01 (3 H, s), 3.15 (3 H, s), 3.76 ppm (3 H, s)). The high regio- and stereospecificity realized in this transformation is mainly due to the fact that the C-1 position[9] is sterically hindered by the adjacent dimethyl ketal group.

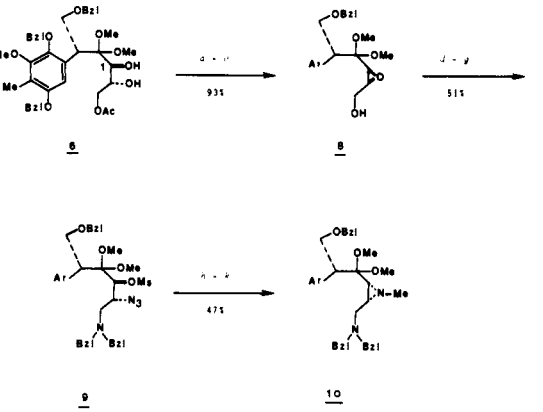
The eight-membered quinone **11**[7] (deep red needles; mp 165–168 °C; M^+ obsd 352.1641, calcd for $C_{17}H_{24}O_6N_2$ 352.1634; ^{1}H NMR ($CDCl_3$) δ 1.85 (3 H, s), 2.41 (3 H, s), 3.13 (3 H, s), 3.36 (3 H, s), 4.01 (3 H, s); UV (CH_3OH) λ_{max} 220 nm (log ϵ 4.37), 305 (4.24), 505 (3.25)) was obtained from **10** in 35–40% yield by the procedure which we had previously developed.[1] An analogous synthetic route starting with the diastereomeric diol **7** resulted in the eight-membered quinone **12**[7] (deep red needles; mp 104–105 °C dec; M^+ obsd 352.1639, calcd for $C_{17}H_{24}O_6N_2$ 352.1634; ^{1}H NMR ($CDCl_3$) δ 1.81 (3 H, s), 2.44 (3 H, s), 3.14 ($^3/_5 \times 3$ H,[10] s), 3.38 (3 H, s), 3.46 ($^2/_5 \times 3$ H,[10] s), 4.01 (3 H, s); UV (CH_3OH) λ_{max} 221 nm (log ϵ 4.44), 306 (4.24), 500 (3.27)). On addition of 1 drop of 0.1 N hydrochloric acid, the UV spectrum (methanol) of **11** changed smoothly to a new spectrum, characteristic of the mitosene (**13** or its degradation products) chromophore.[11] However, under the same conditions, the UV spectrum of **12** was unchanged. This observed reactivity difference suggests a cis relationship between the aziridine ring and the hy-

Scheme I



[a] $NaOCH_3/CH_3OH-CH_2Cl_2/25$ °C. [b] $C_6H_5CH_2Br/KH/DMF/25$ °C. [c] $HgCl_2/CH_3OH/25$ °C. [d] LDA/THF/−78 °C. [e] $C_6H_5SeBr/THF/-78$ °C. [f] $H_2O_2/THF-EtOAc/25$ °C.[20] [g] DIBAL/$CH_2Cl_2-C_6H_5CH_3/0$ °C. [h] $NaBH_4/CH_3OH-CH_2Cl_2/0$ °C. [i] Ac_2O–Py/25 °C. [j] OsO_4/Py–THF/25 °C.

Scheme II



[a] $MsCl/Et_3N/CH_2Cl_2/0$ °C. [b] NaH/DMF/25 °C. [c] $NaOCH_3/CH_3OH-CH_2Cl_2/25$ °C. [d] LiN_3/DMF/150 °C. [e] Ms_2O/Py/25 °C. [f] $C_6H_5CH_2NH_2/150$ °C. [g] $C_6H_5CH_2Br/K_2CO_3$/acetone/reflux. [h] $P(OCH_3)_3$/THF/reflux. [i] NaH/THF/25 °C. [j] $LiAlH_4/Et_2O/0$ °C. [k] CH_3I/K_2CO_3/acetone/reflux.