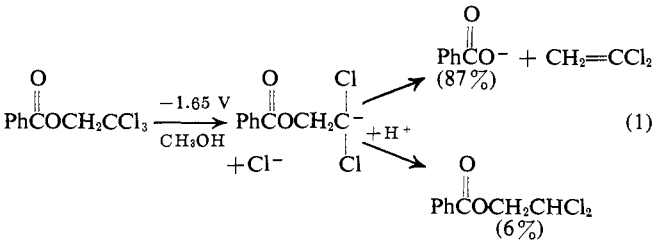
is added 2,2,2-trichloroethyl benzoate (0.50 g, 1.97 mmol) and the mixture is degassed with an argon stream[7] for 15–30 min. Then the potentiostat is engaged to provide a potential difference of −1.65 V between the mercury pool and the reference electrode. The current, initially 145 mA, drops off slowly over 2 hr, reaching a steady value of *ca.* 3 mA. Water cooling is necessary to prevent local heating effects, especially at the glass frit separating the working and counter electrodes. The reaction mixture is separated from the mercury, concentrated at reduced pressure, and after protonation, the usual isolation *via* acidification, aqueous extraction, and one recrystallization, 0.21 g (87%) of benzoic acid is obtained, mp 120–121°.

Several entries in Table II require special mention. In most cases of electroremoval of the 2,2,2-trichloroethoxy unit, small and variable quantities of the corresponding 2,2-dichloroethoxy derivative are isolated. For example, this side reaction leads to 6% of 2,2-dichloroethyl benzoate from the electrolysis of 2,2,2-trichloroethyl benzoate (entry 1, Table II; eq 1). The



(1)

amount of this substitution product is relatively insensitive to changes in solvent (dimethylformamide, acetonitrile), added proton source (acetic acid, trifluoroacetic acid), or the nature of the inert electrolyte. No parallel substitution products are observed during electroremoval of the 2,2-dichloroethoxy or 2,2,2-tribromoethoxy derivatives, and none is reported during zinc reduction of 2,2,2-trichloroethoxy units.[1,2]

The electroremoval of the 2-haloethoxycarbonyl group from sulfhydryl units is directed in a simple way to high yields of either the free thiol or the disulfide-bonded dimer. Isolation of the thiol requires an inert atmosphere during reduction followed by addition of acetic acid before isolation. If air is not removed, the reduction proceeds smoothly to afford the disulfide (entries 7 and 8, Table II). As an example of deprotection of sulfhydryl groups and as a preliminary test of possible racemization during the reduction, *N*-acetyl-L-cysteine methyl ester ($[\alpha]^{25}D$ +20.91°, 2.31% solution in ethyl acetate) was converted to *N*-acetyl-*S*-(2,2,2-trichloroethoxycarbonyl)-L-cysteine methyl ester (mp 71–72.3°) in 92% yield after column chromatography. Electroremoval of the S-protecting group afforded *N*-acetyl-L-cysteine methyl ester in high purity and 88% yield with $[\alpha]^{25}D$ +19.85° (1.68% solution in ethyl acetate) after an isolation procedure involving addition of a small excess of acetic acid and simple aqueous extraction to remove lithium perchlorate. Overall for the two steps, the retention of configuration is 97.5%.

The selective removal of similar protecting groups is demonstrated by controlled potential reduction of two equimolar mixtures: (1) 2,2-dichloroethoxycarbonyl-*p*-toluidine with 2,2,2-trichloroethyl benzyl carbonate and (2) 2,2,2-trichloroethyl benzoate with 2,2,2-tribromoethyl benzoate. In each case, the appropriate choice of reduction potential (based on polarographic data) led to complete reaction of the more easily reduced species with negligible conversion of the other component.

$$p\text{-}CH_3C_6H_4NHCO_2CH_2CHCl_2 + C_6H_5CH_2OCO_2CH_2CCl_3 \xrightarrow[CH_3OH]{-1.70\ V} p\text{-}CH_3C_6H_4NHCO_2CH_2CHCl_2 + C_6H_5CH_2OH\ (72\%) + C_6H_5OCO_2CH_2CHCl_2\ (26\%)$$

$$C_6H_5CO_2CH_2CCl_3 + C_6H_5CO_2CH_2CBr_3 \xrightarrow[CH_3OH]{-0.70\ V} C_6H_5CO_2CH_2CCl_3\ (91\%) + C_6H_5CO_2H\ (85\%)$$

Further work is underway to increase the variety of electroremovable derivatives of the simple functional groups involved here, as well as extensions to new protecting groups for other functionality.

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(7) Nitrogen is equally effective for most applications.

(8) New York State Regents Predoctoral Fellow.

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A Test of the Closed-Shell Overlap-Repulsion Model for the Ethane Barrier[1]

Sir:

The elusive nature of the origin of the internal rotation barrier in ethane has been stressed repeatedly.[2] In a recent paper,[3] it was suggested that a number of possible contributions to the barrier cannot play an essential role because they do not behave consistently in two minimum-basis-set, Slater-orbital, SCF–LCAO–MO calculations that yield equal values (3.3 kcal/mol) for the barrier but differ in their choice of geometries; in one,[4] the same bond lengths and bond angles ("fixed" geometry) are used for staggered and eclipsed ethane, while the other[5] employs minimum-energy "optimized" geometries for the individual conformations. In this communication we test the closed-shell overlap-repulsion model for the barrier proposed some years ago[6] by making a corresponding comparison. Since the original model calculation was based on the "fixed" geometry approximation, we have extended it to the "optimized" geometries[5] for the two conformers. Localized bond-orbital functions of the same form (eq 2 and 3 of ref 5) as employed previously are used, with the carbon hybrids directed along the bonds and the coefficient of the 1s orbital on hydrogen set equal to the optimum value found in the "fixed" geometry calculation.[6] The Hartree product formed from these nonorthogonal, localized bond functions gives a nega-

(1) Supported in part by a grant from the Natural Science Foundation.
(2) E. B. Wilson, Jr., *Advan. Chem. Phys.*, 2, 367 (1959).
(3) I. R. Epstein and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **92**, 6094 (1970); see, also, W. England and M. S. Gordon, *ibid.*, **93**, 4643 (1971).
(4) R. M. Pitzer and W. N. Lipscomb, *J. Chem. Phys.*, **39**, 1995 (1963).
(5) R. M. Stevens, *ibid.*, **52**, 1397 (1970).
(6) O. J. Sovers, C. W. Kern, R. M. Pitzer, and M. Karplus, *ibid.*, **49**, 2592 (1968).

tive barrier, while an antisymmetrized product (Slater determinant) of the same functions yields a satisfactory barrier value (see Table I). Since the only difference between the Hartree product and Slater determinant calculation is the antisymmetrization of the wave function in the latter, the present result serves to confirm the conclusion based on the fixed geometry calculation; namely, the repulsive overlap of the closed-shell bond functions manifested as a result of the Pauli exclusion principle is the essential element in the internal rotation barrier of ethane; the additional delocalization introduced in an SCF function for the molecule is less important.

Table I. Comparison of Energy Contributions to the Ethane Barrier

	"Fixed" geometry, kcal	"Optimized" geometries, kcal
Bare nucleus	+4.7	−74.0
Hartree product	−0.5	−2.2
Antisymmetrized product	2.6	3.1

Since a detailed analysis of the new calculation would essentially duplicate the one given previously, we do not reproduce it here. However, it is of interest to note that the use of optimized geometries leads to a very large negative barrier from the bare nuclei, which contrasts with the fixed geometry result (see Table I). Thus, in the optimized geometry calculation, the "classical" shielding of the nuclei by the localized electrons, as described by the Hartree product function, plays a significant role in cancelling the effect of the geometry change on the barrier; *i.e.*, the difference in the nuclear–electron attraction integrals approximately balances the proton contribution. Such shielding occurs also in the fixed geometry calculation (see Table I), although the terms are much smaller in magnitude and of opposite sign.[7]

In conclusion, it should be cautioned that the present calculation, which confirms the previous analysis of the internal rotation barrier in ethane, does not in any way require that the same essential elements be responsible for the barriers in all molecules; *e.g.*, for systems with lower symmetries, such as H_2O_2, other contributions may be important as well.

(7) The large electron–nuclear interaction contribution suggests that the barrier may be more sensitive to bond polarity in the optimized, than in the fixed, geometry model.[6]

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*Book Reviews**

Atlas of Electronic Spectra of 5-Nitrofuran Compounds. By J. EIDUS, A. YA. EKMANE, K. K. VENTERS, and S. A. HILLER. Ann Arbor Science Publishers, Inc., distributed by International Scholarly Book Services, Inc., Portland Ore. 1970. xiii + 153 pp. $12.00.

This is a translation of a book published in Latvia in 1958. The motivation for dealing with such a narrow group of substances is their importance in medical and veterinary practice. After a 44-page section dealing with general electronic absorption characteristics of furans, there follow in graphic form, supplemented by numerical values for the maxima and their intensities, the uv–visible spectra of 50 5-nitrofuran derivatives. Each spectrum is shown twice, once plotted with a linear and once with a logarithmic intensity scale. The references cited include many from difficultly accessible Russian sources.

Dictionaire Chimique Anglais-Français. By R. CORNUBERT (Faculté des Sciences, Nancy). Dunod, Paris. 1970. xii + 217 pp. 48 F.

The usual chemical dictionaries available to the English-speaking chemist are those leading from French to English, and do not satisfy the occasionally felt need for the reverse. This paper-bound volume fills such a need.

Discovering Natural Laws: The Experimental Basis of Physics. By MILTON A. ROTHMAN (Trenton State College). Doubleday and Co., Inc., Garden City, N. Y. 1972. xii + 227 pp. $1.45 (paper); $5.95 (hardbound).

This is a book that falls outside the conventional curriculum, but it has something to give to the undergraduate and graduate student, the high school student, the layman, and the teacher. It takes up the universally accepted laws, such as the conservation laws, and presents the specific experimental foundations on which they are based. The author, who is both a teacher of physics and a writer of science fiction, writes easily and well, and his work can be enjoyed by chemists and physicists of widely varying extents of scientific sophistication.

Environment and Society in Transition. Edited by P. ALBERTSON and M. BARNETT. New York Academy of Science, New York, N. Y. 1971. 699 pp. $30.00.

This soft-bound book is Volume 184 of the Annals of the Academy and contains the proceedings of the International Joint Conference of the American Geographical Society and the American Division of the World Academy of Art and Science, held in 1970. It consists of a large number of papers by a distinguished and international group of specialists drawn from the general areas of space and earth science, biological and medical sciences, physical sciences and engineering, anthropology, sociology and psychology, and economics, political science and law. Chemistry is represented by "Recent Advances in Chemical Sciences" by Ernst Bergmann, and "The Chemical Sciences" by Minoru Tsutsui. The discussions and reports of various working groups, some general addresses, and a summary and conclusion to the conference complete the work, which has no index.

Isonitrile Chemistry. Edited by IVAR UGI (University of Southern California). Academic Press, New York, N. Y. 1971. xii + 278 pp. $14.50.

Isocyanides have had a long but thin history and were not generally regarded as important until the 1960's, when a new and more practical synthesis was developed by Ugi and his coworkers. It is now timely that a book on the subject should appear, and it is most appropriate that Dr. Ugi should be the editor.

The treatment in this book is quite comprehensive and includes not only the usual organic chemistry but also chapters on the structure of isocyanides, the isocyanide–nitrile rearrangement, and metal complexes having isocyanide ligands. The ten chapters are written by fifteen contributors, who are from Germany, Japan, and the United States. There are many long tables, and the coverage of the subjects is similar to that in "Organic Reactions" chapters in

* Unsigned book reviews are by the Book Review Editor.