

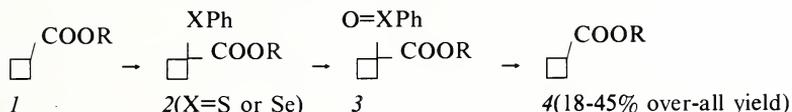
## CHEMISTRY

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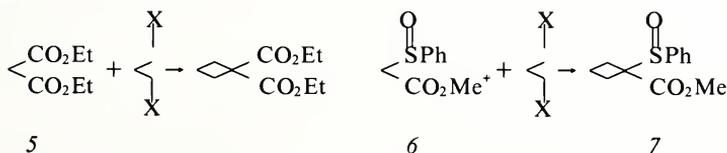
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### Abstracts

**A General Synthesis of Cyclobut-1-enecarboxylates.** STEPHEN R. WILSON and LAWRENCE R. PHILLIPS\*, Department of Chemistry, Indiana University, Bloomington, Indiana 47401.——A general synthesis is described for cyclobut-1-enecarboxylates from cyclobutanecarboxylates via sulfenylation-dehydrosulfoxylation and selenenylation-dehydroselenoxylation. Treatment of cyclobutanecarboxylates *1* with lithium diisopropylamide at low temperatures followed by quenching of the ester enolate with either diphenyl disulfide or diphenyl diselenide gave *2*. Oxidation of *2* to give *3* (either the sulfoxide or selenoxide, respectively) was done with sodium metaperiodate or hydrogen peroxide. Dehydroselenoxylation proceeded smoothly at room temperature



whereas heating was required to effect dehydrosulfoxylation to give *4*. Examples were given and discussed to demonstrate the scope and limitations of the reaction sequence. An interesting parallel between diethyl malonate *5* and methyl 1-phenylsulfinoacetate *6* became apparent during this investigation. *6* was alkylated with 1,3-diiodopropane in dimethylformamide in the



presence of two equivalents of sodium hydride to give *7* in 39% yield. Thus, a synthetic route has been described to make potentially interesting cyclobut-1-enecarboxylates which were formerly unavailable.

**Recent Progress in Radiocarbon Dating at Ball State University.** RICHARD MULFORD, Department of Geography-Geology, and JOHN H. MEISER, Department of Chemistry, and DAVID E. KOLTENBAH, Department of Physics, Ball State University, Muncie, Indiana 47306.——The entire radiocarbon dating process is discussed. Emphasis is placed on sample collection, sample preparation, and data calculation. Peat samples were collected from post-Wisconsin peat bogs north of Muncie In Delaware County. The sample is cleaned megascopically of all foreign material. To remove carbonates and humic

acid the sample is boiled in 2N HCl and .1N NaOH respectively for a period of 2 hours. The liquid in the final solution is boiled off leaving a carbon residue. Volatiles are removed by pyrolyzing the carbon sample in the reactor. Metallic lithium is added with the pyrolyzed sample and heated to 900° C forming lithium carbide. Distilled water is added to the lithium carbide producing acetylene and hydrogen gas. The acetylene gas is subjected to an acetone-dry ice bath, and ascarite-phosphorous pentoxide trap for purification. The acetylene gas is trimerized to benzene by use of a vanadium pentoxide catalyst. The radioactive benzene vial is counted in a Beckman Liquid Scintillation Center and the radiocarbon date is calculated.

**The Synthesis and Characterization of Phosphine-Nitrile Systems.** IVAN SAVAL, JONATHAN WORSTELL, and BRUCE N. STORHOFF, Department of Chemistry, Ball State University, Muncie, Indiana 47306.——Synthetic methods based on Michaelis-Arbuzov and/or metal-halogen exchange reactions have been found to provide convenient routes to phosphine-nitrile systems. Both the previously reported *o*-NCC<sub>6</sub>H<sub>4</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> and the novel *o*-NCC<sub>6</sub>H<sub>4</sub>P(N(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub> have been obtained in good yield from the readily available starting materials R<sub>2</sub>PCl and *o*-NCC<sub>6</sub>H<sub>4</sub>Br. The novel (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>CN has been obtained in good yield from (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>POC<sub>2</sub>H<sub>5</sub> and Cl(CH<sub>2</sub>)<sub>3</sub>CN. The Chemical and spectroscopic properties of the novel phosphines are discussed.

**Palladium (II) Complexes of Potentially Bidentate Phosphine-Nitrile Ligands.** HOREB TRUJILLO and BRUCE N. STORHOFF, Department of Chemistry, Ball State University, Muncie Indiana 47306.——Several novel palladium (II) complexes of the stoichiometries L<sub>2</sub>PdX<sub>2</sub> and (LPdX<sub>2</sub>)<sub>n</sub> where L is (cyanomethyl)diphenylphosphine, (2-cyanoethyl)diphenylphosphine, (3-cyanopropyl)diphenylphosphine, or (*o*-cyanophenyl)diphenylphosphine have been synthesized. In the complexes of the stoichiometry L<sub>2</sub>PdX<sub>2</sub> (X = Cl, Br, SCN) the ligands have been found to function as monodentate phosphines. Both ligand and halogen bridging have been detected for the (LPdX<sub>2</sub>)<sub>n</sub> complexes. The nitrile groups in these palladium complexes display diverse patterns of reactivities, and some of these are discussed.

**Stereochemical Probes: A Test to Distinguish *Erythro* and *Threo* Diastereomers.** PAUL L. BOCK, Ball State University, Muncie, Indiana 47306.——A widely used nmr technique employing diastereomeric RCHDCHDX compounds as stereochemical probes is based on the *assumption* that *anti* conformations are preferred so that <sup>1</sup>erythro is larger than <sup>1</sup>threo; hence *erythro* and *threo* diastereomers can be identified, and the stereochemistry of reactions can be monitored. If, however, the *gauche* conformations were preferred, then <sup>1</sup>threo would be the larger coupling constant, and incorrect stereochemical assignments would be made. This study suggests that assignments of *erythro* and *threo* configurations can be made regardless of which conformation is favored. The technique involves observing the coupling constants at two different temperatures. The one that changes the most for a given change in temperature will be <sup>1</sup>erythro.

**The Behavior of the Bismuth-Bismuth Oxide Electrode in pH Determinations.** JOHN A. RICKETTS and PAUL A. LANG, Chemistry Department, DePauw

University, Greencastle, Indiana 46135.——The electrochemical behavior of the galvanic couple,  $\text{Bi}/\text{Bi}_2\text{O}_3(\text{s}) \text{H}^-//$  saturated calomel electrode was studied as a function of pH at 25°C. Two types of electrodes were employed, a slug electrode and a semimicro electrode. The effect of various pretreatments of the electrode surface before the potential difference was measured were studied, and it was found that polishing of the electrode surface with fine emery paper gave the most reproducible results. In the pH range 5-8 the potential-pH relationship is best represented by the equation,  $E(\text{volts}) = 0.191 - 0.0589 \text{ pH}$  with the bismuth electrode being negative with respect to the calomel electrode. On the hydrogen scale the standard reduction potential for the  $\text{Bi}-\text{Bi}_2\text{O}_3$  couple becomes  $E(\text{red. volts}) = 0.434 - 0.0589 \text{ pH}$ . The performance of the  $\text{Bi}-\text{Bi}_2\text{O}_3$  electrode as the indicating electrode in the potentiometric titration of acid with base was compared with that of the glass electrode and the  $\text{Sb}-\text{Sb}_2\text{O}_3$  electrode. It was found that the  $\text{Bi}-\text{Bi}_2\text{O}_3$  indicated an equivalence point nearer to that observed with the glass electrode than did the  $\text{Sb}-\text{Sb}_2\text{O}_3$  electrode.

**Wabash River Water Analyses in the Vicinity of Sugar and Coal Creeks, Vigo County, Indiana.** JOSEPH R. STEFKER and JONATHAN O. BROOKS, Department of Chemistry, Indiana State University, Terre Haute, Indiana 47809.——Concentrations of over a dozen inorganic elements were determined weekly for a year. Recent sodium concentrations have doubled, mostly as chloride and bicarbonate, over prior years. Sodium, calcium, and iron are their lowest in summer, early-fall, and fall-winter, respectively. Nitrate levels were at 60% of their May maximum of 3mg/l in August and September. Nitrate/phosphate ratios peaked in both May and July. Sugar Creek assayed higher in potassium and Coal Creek assayed higher in calcium, iron and sulfate compared to the Wabash River. Assays corrected to a designated basal flow indicated a smooth increase in mineral flow with river stage.

**Reaction Rates and Equilibria at Tricoordinate Phosphorus.** J. A. MOSBO, Department of Chemistry, Ball State University, Muncie, Indiana 47306.——Reaction rate and equilibrium data for alcohol and amine exchange at phosphorus have been obtained for a series of 2-substituted-1,3,2-diazaphosphorinanes and 2-substituted-1,3-dimethyl-1,3,2-diazaphosphorinanes. The data are interpreted in terms of the electronic and steric characteristics of the exchanging groups and the 1,3 substituents. The dependence of the reaction rates and equilibrium positions upon added acid are also discussed.

**Reactions of Hypofluorous Acid with Organic Compounds.** E. H. APPELMAN, Argonne National Laboratory, Argonne, Illinois 60439, and K. G. MIGLIORESE and M. N. TSANGARIS\*, Department of Chemistry, Indiana University Northwest, Gary, Indiana 46408.——The recent preparation of hypofluorous acid provides a unique opportunity to study the reactions of this extremely reactive molecule with organic compounds. To date, only the reaction of hypofluorous acid with aromatic hydrocarbons to yield phenols has been reported. We have studied the reactions of hypofluorous acid with various alkenes and alkynes. With alkenes, the major products appear to be  $\alpha$ -fluoroalcohols while in the case of alkynes, the products are  $\alpha$ -fluoraldehydes and ketones. The mechanistic implications of these results will be discussed.

**A Research Chemist's Formula for Retirement.** F. O. RICE, Fellow-by-Courtesy, The Johns Hopkins University.—In 1968 I resigned from the University of Notre Dame where I had held a position in the Radiation Laboratory since 1962 as Visiting Research Professor. I built a good laboratory in the basement of my home and there, with the help of an assistant, I continue my research work for a few hours each day. I obtain my assistant by advertising for a high school student who has had at least one year of chemistry and is interested in continuing in chemistry or chemical engineering after he finishes high school: after a period of training this arrangement is entirely satisfactory; a capable student can be trusted to carry out directions without close supervision. Such an arrangement requires, in addition to a good laboratory and assistant, three other things: shop, glassblowing and storeroom and ordering facilities. I am particularly indebted to the University of Notre Dame, through its Chemistry Department and Radiation Laboratory, for such help. Notre Dame is only a mile or so from my home and I make frequent use of their readily available assistance. I want also to thank the Johns Hopkins University Chemistry Department for an annual research grant, as well as the Bureau of Standards Polymers Division for help on several occasions. I have been working during the past few years on problems I had tried many years ago but which gave negative results. It seemed worthwhile to apply the newer techniques and increased knowledge now available. Evering and I had originally shown that, under the action of heat, ordinary organic compounds decompose into free radicals (J. Am. Chem. Soc., 54, 3529 (1932)). The following years were occupied studying methyl, and other univalent, carbon radicals. We had also attempted to study methylene, using as our source diazomethane, but this compound is so treacherously explosive that we finally abandoned the work. At present I am taking it up again, using the reaction between dichloro organic compounds and metallic sodium in the vapor state.

**Dielectric Properties of Bromanil (2,3,5,6-tetrabromo-1,4-benzoquinone).** EUGENE P. SCHWARTZ, Department of Chemistry, DePauw University, Greencastle, Indiana 46135.—Dielectric properties of benzene solutions of the title compound were determined at a radio — and at a visible frequency. The compound was found to show an atomic polarization of about 9.4 cc., which is appreciably larger than the value previously reported. In contrast to the behavior of the parent compound (1,4-benzoquinone), for bromanil most of this polarization is accounted for by a maximum loss in the microwave region at a wavelength near 1 cm. Possible sources of this loss are discussed.

**New Methods of Analysis of Isomeric Diols.** MICHAEL WHALON and TERRY L. KRUGER, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—Studies of diols with  $\text{Eu}(\text{fod})_3$  allow easy analysis of the compounds for structure and purity. The *meso*-2,4-pentanediol and *meso*-1,3-cyclohexanediol appear to coordinate twice to one Eu atom. The  $\delta$  vs R/S ratio plot and coupling constants both support this conclusion. In contrast, *trans*-1,2-cyclopentanediol can attach two  $\text{Eu}(\text{fod})_3$  and is structured so that a bidentate complex is unlikely. A computer-programmed fit of the data for the *meso*-2,4-pentanediol was necessary to extract the coupling constants.

**Determination of Iron in Breakfast Cereals by X-Ray Fluorescence.** PHILIP A. KINSEY and RICHARD E. RUTLEDGE, University of Evansville, Evansville, Indiana, 47702.—An x-ray fluorescence method for the determination of iron in breakfast cereals were developed. The cereal was ground and pelletized in a press and the intensity of the  $K\alpha$  line of iron measured. A least squares working curve of intensity vs. iron concentration was determined over the concentration range, 10 to 200 ppm, using iron standards prepared by serial dilution of Spex HiPure  $Fe_2O_3$  in microcrystalline cellulose. The standards were analyzed by a spectrophotometric method to verify their concentration and homogeneity. It was necessary to reduce the  $Fe_2O_3$  particle size until it would pass through a 250 mesh sieve to obtain uniformity in the standards. Samples of a iron fortified cereal and an unfortified cereal were collected over a five month period and analyzed. A much greater variability in iron content was found in the fortified cereal. In conclusion, the x-ray method was fast and gave reproducible results for analyzing iron in breakfast cereals.

**Identification of the *cis* and *trans* Isomers of 4-t-Butylcyclohexanecarbonitrile.** CATHERINE A. DICK, TERRY L. KRUGER, and BRUCE N. STORHOFF, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—The effects of the lanthanide shift reagent tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato) europium ( $Eu(fod)_3$ ) on the proton NMR spectra of the *cis* and *trans* isomers of 4-t-butylcyclohexanecarbonitrile have been determined. For both isomers, the signal from the proton that is geminal to the nitrile group is shifted downfield to a point where it is well-separated from the remainder of the signals. The shifted signals can be interpreted by application of the Karplus equation and used to unequivocally distinguish the *cis* from the *trans* form.

**Applications of Transactional Analysis to the Laboratory Situation.** TERRY L. KRUGER, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—A popular theory, transactional analysis (TA), of personality structure was sketched and applied to everyday problems concerning chemists. Examples from lecture and from laboratory were used to illustrate the use of the theory. Games such as Grade Grubber, NIGYYSOB, IDU, and No Time were discussed within the framework of the theory. Work by Piaget and by Kelley was shown as supporting the usefulness of TA.

**Michael-Like Reactions: The Reaction of Diphenylphosphine with 1-Cycloalkene Carbonitriles.** DOUGLAS GRINSTEAD, JOSEPH WU, TERRY KRUGER, and BRUCE STORHOFF, Ball State University, Muncie, Indiana 47306.—Michael-like additions of diphenylphosphine,  $Ph_2PH$ , to 1-cyanocyclohexene and 1-cyanocyclopentene have been investigated. The reactions are base catalyzed and give the corresponding (2-cyanocycloalkyl)diphenylphosphines in 60-80% yields. The effects of the type of base on the isomer distributions of the products have been determined. For aqueous hydroxide, the  $Ph_2PC_5H_8CN$  product consists of two isomers (*ca.* 65:35), whereas the  $Ph_2PC_5H_{10}CN$  product is a single isomer. The reaction product from  $C_5H_7CN$  and  $Ph_2PH$  in the presence of potassium *tert*-butoxide also consists of two isomers. However, the isomer ratio is *ca.* 15:85. Results from deuteration studies are also presented.

**An Investigation of the Feasibility of Classifying and Identifying Soil Samples of Forensic Interest on the Basis of Elemental Composition by X-ray Fluorescence Spectrometry.** R. SEGAL, Lone Star Industries, Greencastle, Indiana 46135, D. J. REULAND and W. A. TRINLER, Chemistry Department, Indiana State University, Terre Haute, Indiana 47809.——Two potential forensic applications of soil analysis by X-ray fluorescence (XRF) were studied. First, the possibility of cataloging soils on the basis of XRF data on oxide composition was investigated. Soils belonging to three soil series: Elston, Warsaw and Iva, were collected and analyzed. Data are presented as loss-free oxide percentages and as oxide ratios. Oxides measured were: silicon, aluminum, iron, potassium, calcium, magnesium and titanium. No significant differences were found in the composition of the three soil series for either the seven oxides or ten oxide ratios. Secondly, soils from five environmentally differing locations were collected and analyzed. The five areas were selected with the criterion that the chemical composition of each might be affected by the environmental conditions. An eroded area, soil next to railroad tracks, a plowed field, soil located downwind from a portland cement manufacturer, and soil from a reclaimed stripmined area were analyzed. Data are presented as loss-free oxides and as oxide ratios. Variations in composition for the five sampled locations were studied for their use as tracers. Significant differences in the compositions of several samples were noted.