grams of mixtures of known composition, was given by true fraction of *endo* isomer = 1.03 × apparent fraction of *endo*. In the methacrylic and *trans*-crotonic series, no correction was needed. The peak areas on an individual chromatogram, and the relative areas on separate chromatograms of a given mixture, were sufficiently reproducible to allow analysis of a component with an absolute variation of about 0.1% in the absolute value of the % composition. Parallel additions of the same components under identical conditions were reproducible to about the same precision.

**Diels-Alder Additions.**—Temperature control at 30° and 26° was maintained to ±0.05° with a thermostat. At 3°, a refrigerated compartment and at 66° and 56°, boiling methanol and acetone vapor baths controlled temperatures to ±0.5°. At 0°(±1°) and −35°(±3°) appropriate freezing mixtures were used; at 139 ±1° xylene, and at 170 ± 1°, phenetole were used as boiling vapors. For runs at $\leqq$30°, separate solutions of the reagents in the appropriate solvent were brought to thermal equilibrium, mixed and re-immersed in the thermostat. For runs at 56°, 66° and 100°, 2 ml. of cyclopentadiene was sealed in a thin-walled glass bulb. This was placed in a sturdy test-tube, covered with a solution of 2 ml. of the dienophile in 15–20 ml. of the solvent, and the whole inserted in the vapor-bath. After temperature equilibrium had been reached, the cyclopentadiene bulb was crushed with a clean glass rod and the reaction allowed to proceed. For the runs at 139° and 170°, where loss of dienophile by evaporation during the attainment of temperature equilibrium was excessive, the experiments were performed with a magnetically controlled break-seal device (designed by Mr. A. Remanick of this Laboratory). Into the apparatus was sealed a thin-walled bulb long enough to reach into the compartment containing the dienophile solution. A glass rod, onto which was sealed a small iron bar, rode in a track and was held away from the thin wall with a magnet. Diene solution was placed in the bulb, dienophile solution in the compartment, the whole apparatus was sealed off and brought to temperature in the vapor bath. The magnet was then removed, whereupon the heavy rod dropped, smashing the bulb wall and delivering the diene into the dienophile solution.

The time necessary to achieve convenient yields of products varied from 0.5 hour to several days, depending upon the temperature and dienophile. Initial concentrations of the reactants were in the range 0.5–1.5 *M*.

The proportions of isomers were strictly independent of the yield of products and of the proportions of reactants used initially. This demonstrates that fractionation of the adducts by preferential reaction of one of a pair of adduct isomers with excess cyclopentadiene was not a factor. The product ratio was unchanged by the incursion of any thermal isomerization at temperatures up to 139°. This was demonstrated by the recovery of pure *exo* adduct uncontaminated by even a trace of *endo* when pure *exo*-5-norbornene-2-carboxylic ester was heated at 139° in decalin; the equilibrium mixture is[12] about 1:1 *endo:exo*. Change of the product composition of the adducts with α-hydrogen (IIIa, IIIc, IVa, IVc) by epimerization in the basic solvents pyridine and triethylamine was also not a factor. Samples of adduct mixtures IIIa–IVa and IIIc–IVc were kept in these solvents for reaction periods and at temperatures corresponding to those under which the additions were carried out. A sample of the test mixture was kept without solvent under the same conditions as control. The isomer compositions as determined by vapor chromatography are given in Table III. The IIIa–IVa mixture given in Table III is *not* an equilibrium mixture.[12] Any isomerization in the IIIc–IVc mixture would have led to a mixture of four different adducts—two *cis* and two *trans*. There was no indication in the vapor chromatograms of any substance other than IIIc and IVc.

TABLE III

EPIMERIZATION EXPERIMENTS

| Isomer mixture | Solvent | Temp., °C. | Recovd., % N | Recovd., % X |
|---|---|---|---|---|
| IIIa–IVa | None | 30 | 74.8 | 25.2 |
| IIIa–IVa | Pyridine | 30 | 74.8 | 25.2 |
| IIIa–IVa | $Et_3N$ | 30 | 74.8 | 25.2 |
| IIIc–IVc | None | 30 | 21.0 | 79.0 |
| IIIc–IVc | Pyridine | 30 | 21.0 | 79.0 |
| IIIc–IVc | $Et_3N$ | 30 | 21.2 | 78.8 |
| IIIc–IVc | None | 66 | 21.1 | 78.9 |
| IIIc–IVc | Pyridine | 66 | 21.1 | 78.9 |
| IIIc–IVc | $Et_3N$ | 66 | 21.1 | 78.9 |

The products from the additions and control runs were worked up (with the exceptions indicated below) by evaporation of the reaction mixture to a small volume *in vacuo* and bulb-to-bulb distillation of the residue *in vacuo*. In the case of solvent decalin, which interfered with the analysis when present in large quantity, the products were extracted with methanol. A control experiment showed that no fractionation of products occurred during this procedure. Acetic acid and dimethylformamide also interfered with the analyses. The reaction mixtures in these cases were diluted with water, extracted with ether, washed with water, dried over magnesium sulfate, evaporated and distilled.

**Direct Determination of Z-value for 1,2-Dimethoxyethane.**—The absorption spectrum of 1-ethyl-4-carbomethoxypyridinium iodide in 1,2-dimethoxyethane was determined in the region of the long wave length band by the method of Kosower.[16a] The maximum occurred at 4607 ± 4 Å. (average of four scans); Z = 62.1 kcal./mole.

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# COMMUNICATIONS TO THE EDITOR

## CATALYTIC HYDROGENATION OF ORGANIC COMPOUNDS BY PENTACYANOCOBALTATE(II)

*Sir:*

The absorption of molecular hydrogen by aqueous potassium cyanocobaltate(II) was first reported by Iguchi in 1942[1]; the chemistry involved in this reaction has been elucidated recently[2] and the structure of the reduced complex has been formulated as the hydrido-ion, $[Co^{III}(CN)_5H]^{3-}$.

The possibility of utilizing this hydrogen-activating system for the reduction of organic compounds appears to have been neglected except for the early observation by Iguchi[3] that increased quantities of hydrogen were absorbed in the presence of sodium cinnamate or isatin; however, no identification of products was carried out.

We wish to report the catalytic hydrogenation of a variety of organic substrates by means of this cobalt(II) coördination compound in aqueous solution. As shown in the table, the types of compounds which have been reduced include aliphatic dienes,[4] conjugated aromatic olefins, α,β-unsatu-

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(1) M. Iguchi, *J. Chem. Soc. Japan*, **63**, 634 (1942).

(2) N. Kelso King and M. E. Winfield, *J. Am. Chem. Soc.*, **83**, 3366 (1961), and references therein.

(3) M. Iguchi, *J. Chem. Soc. Japan*, **63**, 1752 (1942).

(4) It has been brought to our attention that German Patent

TABLE I

| Substrate | Ratio, moles substrate/ $K_3[Co(CN)_5]$ | Mole % $H_2$ absorbed[a] | Initial rate of $H_2$ absorp. (ml./min.) | Products |
|---|---|---|---|---|
| Isoprene | 6.7 | 79 | 12 | ~85% 1,4-, ~15% 1,2-addition |
| 1,3-Cyclohexadiene | 7.0 | 96 | 60 | Cyclohexene |
| Styrene | 2.9 | 89 | 21 | Ethylbenzene |
| Tiglic aldehyde | 3.4 | 57 | 22 | α-Methylbutyraldehyde |
| Methacrylic acid[b] | 3.3 | 97 | 35 | Isobutyric acid |
| Sorbic acid[c] | 3.3 | 87 | 57 | 2-Hexenoic acid |
| Cinnamic acid[c] | 3.3 | 49 | 8 | β-Phenylpropionic acid |
| Methyl methacrylate | 3.1 | 84 | 4–24 | Methyl isobutyrate, isobutyric acid |
| Benzil[c] | 1.7 | 88 | .. | Benzoin |
| Cyclohexene oxide | 3.3 | 45 | 9 | Cyclohexanol |
| Styrene oxide | 2.9 | 53 | 4 | β-Phenylethanol |
| Azoxybenzene | 1.7 | 68 | .. | Azobenzene |

[a] Based on 1 mole $H_2$/mole substrate; does not include hydrogen absorbed by catalyst. [b] Added as the sodium salt. [c] An equivalent of potassium hydroxide also was added.

rated acids (as salt or ester) and aldehydes, 1,2-diketones, epoxides and azoxy compounds.

Hydrogenations generally were carried out using a cyanide/cobalt ratio of 5.1 at a cobalt concentration of 0.15 *M* although other ratios and concentrations also were effective. The reductions described here were carried out at room temperature and a hydrogen pressure of one atmosphere; the extent and rate of the reaction were followed by measurement of hydrogen absorption. Water-insoluble substrates were added either directly or, prior to addition, were dissolved in a non-polar solvent such as benzene.

The catalyst was not only specific with respect to the type of functional group reduced, but also was sensitive to other structural features of the substrate molecule. For example, styrene and α-methylstyrene were reduced readily while 1,1-diphenylethylene, indene, and propenylbenzene were not; acrylic acid was reduced only at elevated temperatures, while acrylic acids substituted in the α-position by $C_6H_5$, $CH_3$ or $HOOCCH_2$ groups were reduced at room temperature.

Propionaldehyde yielded the dimeric aldehyde, α-methylvaleraldehyde, evidently *via* a base-catalyzed aldol condensation. Cinnamaldehyde yielded the aldol condensation product of β-phenylpropionaldehyde, 2-benzyl-5-phenylpent-2-enal.

It is of interest that certain substrates such as nitrobenzene and benzoquinone were not reduced catalytically unless added to the prehydrogenated catalyst in less than stoichiometric quantities. After this quantity had been reduced, further "incremental additions" could be made until the molar quantity of substrate which was reduced exceeded that of the cobalt present in the catalyst system. Thus, the catalytic hydrogenation of these compounds and regeneration of the catalyst were demonstrated. Azobenzene and hydroquinone were formed, respectively. Allyl chloride or allyl acetate yielded propylene rapidly in good yield. Hydrogen peroxide and certain inorganic salts also have been reduced.

No other homogeneous hydrogenation system[5] is known to reduce such a wide variety of substrates catalytically under such mild conditions. A more detailed description of this work, as well as observations on the course of the reductions, will be made at a future date.

1,114,183 concerning the reduction of butadiene to butene by pentacyanocobaltate(II) has been issued to Imperial Chemical Industries.

(5) For a review of such systems, see J. Halpern in *Advances in Catalysis*, **11**, 303 (1959), and J. Halpern, J. F. Harrod and B. R. James, *J. Am. Chem. Soc.*, **83**, 753 (1961).

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## MACRORETICULAR ION EXCHANGE RESINS

*Sir:*

A new polymerization technique has been discovered that yields a cross-linked ion exchange structure entirely different from the conventional homogeneous gels and having a truly macro-porous structure similar to those of conventional adsorbents such as alumina and bone char. The polymerization technique involves the suspension polymerization of styrene–divinylbenzene copolymers in the presence of a substance that is a good solvent for the monomer but a poor swelling agent for the polymer. These polymers have been converted to a sulfonic acid cation exchanger (Amberlyst 15) by conventional sulfonation techniques and to a quaternary ammonium anion exchanger (Amberlyst XN-1001) by chloromethylation followed by amination with trimethylamine.

The pore properties of the dry macroreticular ion exchange resins were studied by means of nitrogen adsorption at −195° and by measurement of the true density (helium displacement) and apparent density (mercury displacement). A summary of these measurements is given in Table I along with comparison data for Amberlite IR-120 and Amberlite IRA-400, conventional sulfonic acid cation and quaternary ammonium anion exchange resins, respectively. It is quite evident that any pore structure that exists in the conventional resin gel structure disappears on drying