The presence of sulfone and *t*-butyl groups was indicated by infrared. The compound decomposed on heating to give sulfur dioxide and isobutylene.[3]

SOLUBILITIES

Solvent	Temp., °C.	Solubility, g./100 ml.
Water	20, 50, 80	1.08, 1.54, 3.18
0.1 *N* HCl	20	1.03
0.1 *N* NaOH	20	0.95
n-Pentane	20	0.82
Diethyl ether	20	5.61
Ethanol	20	16.1

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(3) The compound decomposes or builds up vapor pressure suddenly on heating in the combustion tubes, and mixtures with oxygen were several times obtained which ignited and ruined the analysis. The oxygen analysis was made by the Unterzaucher method.

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A Rapid Method for Fractionating Crude Rare Earth Ores into Mixtures Greatly Enriched with Regard to Particular Rare Earths

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It has been found in this Laboratory that efficiency of producing very pure rare earth oxides by ion-exchange methods can be greatly increased if the crude rare earth mixtures, as leached from the ores, can be first rapidly fractionated into several fractions, enriched in specific rare earths. Normally, the rare earth oxide, as obtained from the ore, consists of from 10 to 14 individual rare earths and rare earth-like elements. Some of these are present in very small amounts and some such as cerium, lanthanum, neodymium and yttrium may represent up to 50% of the total mixture, depending upon the ore involved. When the rare earth mixture is dissolved and adsorbed on the ion-exchange columns, these elements then occupy the major part of the resin band and require considerable time to elute. If the bulk of these less desirable elements can be removed by a preliminary, rapid fractionation, the efficiency of production of the pure heavy rare earths by ion-exchange methods can be increased many fold.

The older type fractionations are usually very slow and laborious. However, Schwarzenbach and Freitag,[1] Marsh,[2] Beck,[3] Vickery[4] and others, have pointed out that the rare earths do form very tight complexes with chelating agents such as Versene (ethylenediaminetetraacetic acid) and Marsh[2] and Vickery[4] have shown that fractionations using these complexes are more rapid than the older methods. However, their methods are still laborious and give smaller enrichments than might be desired. Recent determinations of the equilibrium constants of the rare earth–Versene complexes by Vickery[4] and by Wheelwright, Spedding and Schwarzenbach[5] show that the apparent equilibrium constants, determined at fixed ionic strength, differ by a factor of 10^5 across the rare earth series. It should therefore be possible to take advantage of this fact in effecting a rapid fractionation of the mixed rare earths. The purpose of this note is to indicate one of the ways in which this can be accomplished.

Most of the methods for separating the rare earths by ion-exchange columns, for example, the citrate elution as developed by this Laboratory,[6] depend upon an adsorption of a band of rare earths on the resin and the subsequent elution of this band down the column in a manner roughly analogous to chromotography. However, a much more rapid process could be effected if the ion-exchange columns were used—in a manner analogous to water-softening—to differentially adsorb one rare earth or group of rare earths and allow the others to pass through without being appreciably adsorbed. This technique has been tried by Fitch and Russell,[7] using other chelating agents, but the enrichments obtained have not been great enough to be entirely satisfactory for a preliminary separation to precede the citrate separation to obtain pure rare earths.

Our present process consists essentially of complexing part of the rare earths in a mixture with Versene, then separating the complexed rare earth ions from the uncomplexed ions by passing the solution through an ion-exchange column. The complexed ions pass through the column while the uncomplexed ions are adsorbed on the resin. Care must be taken that the capacity of the resin is such that it is capable of adsorbing all of the uncomplexed rare earths. The rare earth–Versene stability constants range from $10^{14.72}$ for La to $10^{19.65}$ for Lu, with Y appearing in the series between Tb and Dy. Since the rare earth mixture we used in this experiment contained about 60% Y, 15% heavy rare earths and 25% light rare earths, it was decided to complex the heavy rare earths Lu to Dy, make the initial separation with an ion-exchange column, and then remove the Y and the lighter rare earths from the column by passing successive solutions, containing a predetermined amount of Versene, through the column. While this experiment was performed with the resin in a column, it might be more desirable to place the resin in a tank, adsorb the rare earth mixture on the resin, and then intimately mix it with successive fixed amounts of Versene. The complexed rare earths could be removed by draining or filtering, and of course an equilibration period of about 24 hours should be allowed for each solution. We are continuing this work and it is obvious that the conditions can be greatly improved. However, the preliminary experiments were so promising and efficient that we felt that they should be reported at this time. This can best be illustrated by giving the procedure and data for one of our runs.

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Procedure

A neutral solution containing 312 g. of mixed rare earths weighed as oxide, was obtained by dissolving a known larger amount of the rare earth material in a limited amount of hydrochloric acid and recovering the undissolved rare earth. A previously prepared solution of diammonium dihydrogen versenate, containing the theoretical amount of Versene required to complex the heavy rare earths in the mixture, and adjusted to a *p*H of 10, was then added to the rare earth solution, and the combined solution diluted to 90 liters. After equilibrating for 24 hours, the *p*H of the solution was adjusted to 4.5 with a little hydrochloric acid. Following a second 24-hour equilibration period, this solution was passed rapidly through a short bed of Dowex-50, and the column washed free of complexed rare earths with a few liters of distilled water. The rare earth material remaining on the resin was removed fractionally by pouring four successive predetermined amounts of Versene solution, which had been adjusted to a *p*H of 9.5, through the column at a slow flow rate, taking 24 hours for each fraction, so as to let the liquid remain in contact with the resin long enough to approach equilibrium conditions.

Results and Discussion

To obtain an analysis of the five fractions, 20 g. of oxide from each fraction was adsorbed on standard, small ion-exchange columns and eluted with citric acid according to our usual procedure for obtaining pure rare earths. This spread the fractions out into 20 to 30 secondary fractions, each of which contained only two to four rare earths. These secondary fractions could then be analyzed spectrographically and spectrophotometrically without running into the interferences which would occur in a direct analysis of the larger fractions. Also, much better material balances could be obtained. The results are presented in Table I.

TABLE I

RARE EARTH OXIDES RECOVERED IN ONE RUN ON GADOLINITE ORE (GRAMS)

Elements	Sample I	Sample II	Sample III	Sample IV	Sample V	Total
Lu	1.67	...	...	...	...	1.67
Yb	14.02	1.69	...	...	...	15.71
Tm	1.55	1.22	...	...	...	2.77
Er	5.58	9.83	...	...	...	15.41
Ho	1.04	3.57	0.25	...	...	4.86
Dy	2.15	11.17	9.04	0.30	...	22.66
Tb	0.06	0.13	0.10	0.75	0.69	1.73
Gd	...	...	...	7.37	5.80	13.17
Sm	...	...	...	3.87	5.42	9.29
Nd	...	...	...	3.75	7.45	11.20
Pr	...	...	...	0.37	0.68	1.05
Ce	...	...	...	.81	2.27	3.08
La	...	...	...	.81	2.27	3.08
Y	13.81	65.17	72.80	25.80	13.22	190.80
Total	39.88	92.78	82.19	43.83	37.80	296.48

It will be noticed that under these very preliminary conditions, which are almost certainly far from optimum, most of the heavy rare earths are concentrated away from the light rare earths and from most of the yttrium. Such a preliminary separation will permit us to add five times as much heavy rare earths on the ion-exchange columns as we could previously and therefore step up our production of these pure rare earths accordingly.

At the present time, we are studying the possibility of greatly improving this process by investigating such variables as a higher temperature to approach the various equilibria more rapidly, and utilizing more concentrated solutions to increase the yields.

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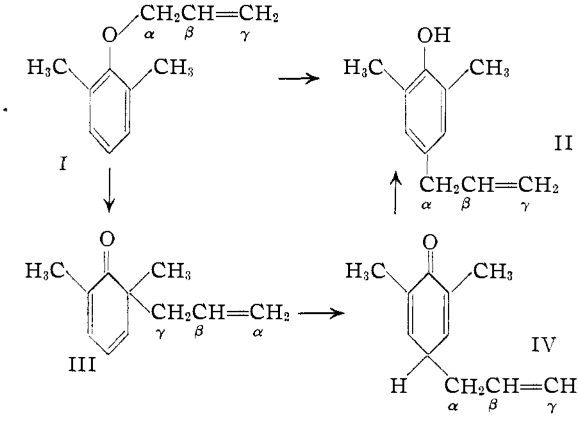
COMMUNICATIONS TO THE EDITOR

THE MECHANISM OF THE *PARA*-CLAISEN REARRANGEMENT

Sir:

Consideration of the literature[1–6] dealing with the *para*-Claisen rearrangement, of which the change I → II is an example, led us to suspect the intermediate formation of isomeric cyclohexadienones, *e.g.*, III and IV. Since III is a type which should readily participate in Diels–Alder additions, it was hoped that this substance, if present in the reaction mixture, might be trapped when the rearrangement was conducted in the presence of some suitable dienophile.



Allyl 2,6-dimethylphenyl ether, in a solution of maleic anhydride, was heated (200° for 2.5 hours, CO_2 atm.) and the acidic reaction products separated. One of these, m.p. 143.3–143.6°, obtained

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