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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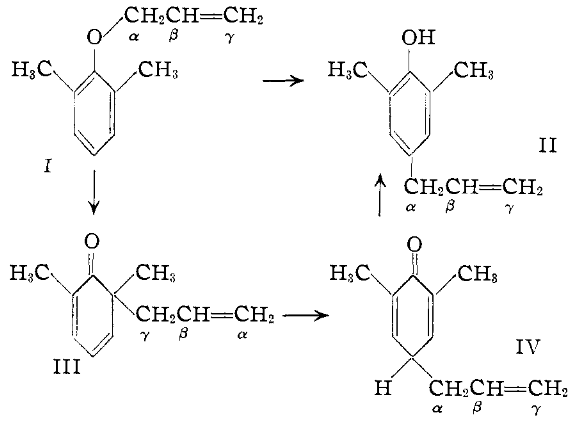
COMMUNICATIONS TO THE EDITOR

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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(1) O. Mumm, *et al.*, *Ber.*, **70**, 2214 (1937); **72**, 100 (1939); **72**, 1523 (1939).

(2) D. S. Tarbell and J. F. Kincaid, THIS JOURNAL, **62**, 728 (1940).

(3) C. D. Hurd and M. A. Pollack, *J. Org. Chem.*, **3**, 550 (1939).

(4) E. R. Alexander and R. W. Kluiber, THIS JOURNAL, **73**, 4304 (1951).

(5) D. S. Tarbell, chapter in "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 1.

(6) H. B. Watson, *Ann. Repts. Chem. Soc.*, 206 (1939).

in 6.3% yield, is evidently one of the possible stereoisomeric Diels-Alder adducts of III, from the following data: calcd. for $C_{15}H_{16}O_4$: C, 69.21; H, 6.20. Found: C, 69.30; H, 6.31. Infrared: 5.42, 5.63 μ (cyclic 5-ring anhydride) and 5.83 μ (6-ring saturated ketone). Ultraviolet: No high intensity maxima; λ_{max} 300 mμ, ϵ = 64. The adduct was slowly soluble in sodium hydroxide solution, decolorized permanganate rapidly, and was converted after the uptake of exactly two molar equivalents of hydrogen (Pt catalyst) to a tetrahydro derivative, m.p. 115.1–115.4° (calcd. for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.15; H, 7.74.) which was saturated to permanganate, and gave an infrared spectrum whose carbonyl region was substantially identical with that of the adduct.

The phenol (II) gave no trace of adduct under identical conditions, with an identical isolation procedure. The ether (I) gave no trace of adduct with maleic anhydride at 100° for three hours. However the pure ether, when heated alone at 200° for ten minutes, produced a mixture actually containing some dienone, since a small amount of the adduct could be isolated after treatment of the mixture with maleic anhydride at 100° for three hours. Finally, pyrolysis of the pure adduct in Nujol solution (200° for 3.75 hours) yielded phenol (II), isolated as the phenylurethan, m.p. 141.5–143°, identical with an authentic sample,[2] in 2% over-all yield. Evidently the dienone (III), when released from its adduct, can rearrange further to the final product (II).

The data require that I → III → (IV) → II is a reaction path actually used, if not the sole reaction path. In analogy to the *ortho* Claisen rearrangement, the dienone (III) is presumably formed from I through a six-membered transition state in which the bonds are made and broken simultaneously.[1,6] But unlike the enolizable dienone formed in the *ortho* rearrangement, III can return to an aromatic system only by an additional longitudinal flip of the allyl group, to give IV, which then enolizes to II. In a sense, the change III → IV is comparable to the thermal transformation of ethyl 1-cyclohexenylallylcyanoacetate to ethyl (2-allylcyclohexylidene)-cyanoacetate,[7] an all-carbon allylic rearrangement.

This mechanism for the *para*-Claisen rearrangement predicts no α-γ inversion of the allyl group in the over-all process, a result borne out by several previous experiments,[1,8] is consistent with the finding that an optically active allyl residue retains activity in *para* migration[4], and is in agreement with the fact[2] that both *ortho* and *para* rearrangements have comparable entropies of activation.

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RECEIVED NOVEMBER 24, 1952

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[7] A. C. Cope, *et al.*, THIS JOURNAL, **62**, 441 (1940); **63**, 1843 (1941); **63**, 1852 (1941).

[8] NOTE ADDED APRIL 30, 1953.—Although some of the experiments of Mumm, *et al.* (ref. 1), seemed inconsistent with this view, these have very recently been repeated (S. J. Rhoads, R. Raulins and R. D. Reynolds, THIS JOURNAL, **75**, 2531 (1953)) and the difficulty resolved. *Cf.* also J. P. Ryan and P. R. O'Connor, *ibid.*, **74**, 5866 (1952), who demonstrated the point with *labelled* compounds.

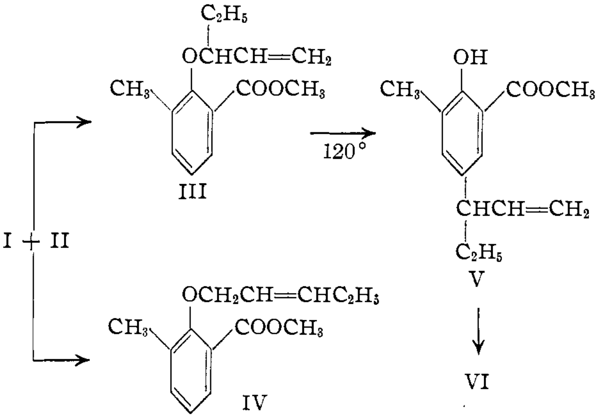
[9] Process Research, Merck & Co., Inc., Rahway, N. J.

ON THE *PARA*-CLAISEN REARRANGEMENT

Sir:

Renewed interest in the *para*-Claisen rearrangement[1,2] prompts us to report our findings on reinvestigation of the work of Mumm, Hornhardt and Diederichsen[3] on the preparation and rearrangement of the α- and γ-ethylallyl ethers of methyl cresotinate, III and IV. Contrary to the conclusions reached by the earlier workers, we have obtained evidence that the *para*-rearrangement proceeds *without inversion* of the migrating group in both III and IV.

The reaction of sodio-methyl cresotinate, I, with α-ethylallyl chloride, II, in methanol gives rise to a mixture of III and IV as well as a phenolic fraction containing both possible C-allylated phenols. The separation of the neutral and phenolic fractions *cannot* be accomplished with 2 *N* sodium hydroxide (*cf.* ref. 3) but requires the use of Claisen alkali.



Vacuum distillation of the ethereal fraction gives material with a negative ferric chloride test, b.p. 92–116° at 0.2 mm., $n^{25}D$ 1.5072–1.5119. Methanolic potassium hydroxide hydrolysis of the higher boiling end fraction of this material yields the acid corresponding to the γ-ether, IV, m.p. 63.5–64°, identical by mixed m.p. with an authentic sample. Hydrolysis of the lower boiling end fraction of the ethereal material proceeds *without rearrangement* (*cf.* ref. 3) furnishing an oil which crystallizes at −5° but remelts at room temperature. Ozonolysis of the ethereal fraction produces formaldehyde in amounts corresponding to 40 ± 5% of an ether with a terminal methylene group. Ozonolysis of the same ethereal material, followed by hydrogen peroxide-acetic acid oxidation permits the isolation of 2-carboxy-6-methylphenoxyacetic acid (20–30%), identical with that produced by the oxidation of pure IV. Comparision of the infrared spectra of the ethereal fraction, authentic γ-ether and a model compound, the allyl ether of methyl cresotinate, confirms the presence of IV in the α-ether preparation, but the characteristic 10.7–10.8μ peak of the terminal methylene group is also detectable.

Separation of III and IV by fractional distillation is precluded by the thermal sensitivity of the

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[1] J. P. Ryan and P. R. O'Connor, THIS JOURNAL, **74**, 5866 (1952).

[2] H. Schmid and K. Schmid, *Helv. Chim. Acta*, **35**, 1879 (1952).

[3] O. Mumm, H. Hornhardt and J. Diederichsen, *Ber.*, **72**, 100 (1939); O. Mumm and J. Diederichsen, *ibid.*, **72**, 1523 (1939).