

such as relative radical stability and ring strain in dictating direction of cleavage.<sup>3</sup> Rate of cleavage of *n*-alkyl *vs.* methyl is greater than 10 to 1 (no. 1, 4, 5). Rate of cleavage of *sec*-alkyl (isopropyl) exceeds *n*-alkyl (ethyl) by 20 to 1 (no. 1). This latter order is reversed when cleavage of "*n*-alkyl" is part of a five-membered ring, *i.e.*, rate of cleavage of isopropyl *vs.* cleavage of one of the two equivalent ring carbon-carbon bonds in 1-isopropylcyclopentoxyl (no. 2) is 1 to 14. The bulk of this difference probably is associated with relief of ring strain in the five-membered ring (6 kcal. per mole from heat of combustion data).

**Hydrogen Abstraction<sup>4</sup> *vs.* Fragmentation.**—Examples 4, 5 and 7 indicate that intramolecular hydrogen abstraction may compete successfully with fragmentation. The preferred point of abstraction is four carbon atoms removed from the oxygen atom.<sup>5</sup> (Intermolecular attack on cyclohexene by the alkoxy radicals of Table I competes poorly with 1,5-intramolecular hydrogen abstraction or fragmentation<sup>4</sup>.) Rate of 1,5-intramolecular abstraction of secondary C-H (per hydrogen) *vs.* fragmentation of *n*-alkyl (butyl) is 2.7 to 1 (no. 4); rate of 1,5-abstraction of primary C-H (per H) *vs.* fragmentation of neopentyl is 1 to 16 (no. 5). If one makes the assumption that the rate constant for abstraction of hydrogen from cyclohexene is the same for the alkoxy radicals in examples 4 and 5, then the data may be extended to indicate a preference for 1,5-abstraction of secondary C-H *vs.* primary C-H of 10 to 1<sup>6</sup> and a preference for cleavage of neopentyl *vs.* *n*-butyl of 4 to 1.

**Acknowledgment.**—We are indebted to the National Science Foundation and the Sloan Foundation for support of this work.

(4) See C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108, 6113 (1960), for a study of intermolecular hydrogen abstraction by the *tert*-butoxyl radical (hydrocarbon chlorination by *tert*-butyl hypochlorite).

(5) Compare with the Hofmann-Löffler-Freytag reaction, E. J. Corey and W. R. Hertler, *J. Am. Chem. Soc.*, **82**, 1657 (1960).

(6) Compare with intermolecular abstraction by *tert*-butoxyl of tertiary C-H *vs.* secondary C-H *vs.* primary C-H of 44 to 8 to 1 (ref. 4).

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#### MECHANISM OF THE DIELS-ALDER REACTION<sup>1</sup> Sir:

The thermal interconversions of  $\alpha$ - and  $\beta$ -1-hydroxydicyclopentadiene with *syn*- and *anti*-8-hydroxydicyclopentadiene, respectively, with retention of optical activity<sup>2</sup> suggest that other Diels-Alder dimers<sup>3</sup> might undergo analogous rearrangements. The conversions of 8-ketodicyclopentadiene<sup>4</sup> and a chlorinated derivative<sup>5</sup> to the

(1) Supported in part by the Office of Naval Research.

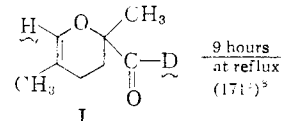
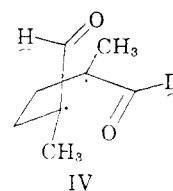
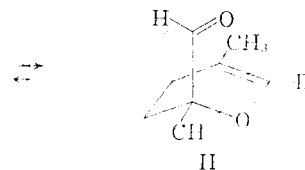
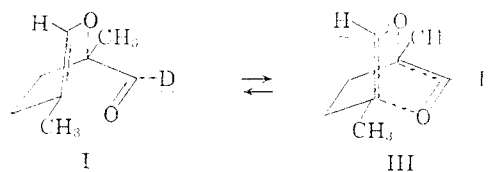
(2) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

(3) Products of Diels-Alder additions in which a single component serves both as diene and dienophile.

(4) R. C. Cookson, J. Hudec and R. O. Williams, *Tetrahedron Lett.*, No. 22, 29 (1960).

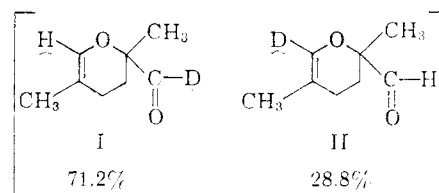
(5) P. Yates and P. Eaton, *ibid.*, No. 11, 5 (1960).

corresponding 1-ketodicyclopentadienes support this prediction; we now report that optically active deuterium-labeled (at the aldehyde hydrogen) methacrolein dimer,<sup>6</sup> I, rearranges to II in a similar manner, under conditions where there is substantial competitive formation of methacrolein by the reverse Diels-Alder reaction. A possible course of the rearrangement is



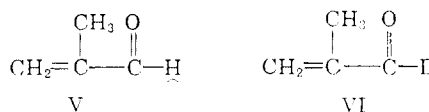
$$\alpha_D^{27} - 71.35 \pm 0.05^\circ$$

(neat,  $l = 1$  dm)



$$\alpha_D^{26} - 71.00 \pm 0.04^\circ$$

(neat,  $l = 1$  dm)



Species III might be the transition state or else an intermediate, but in either case its geometry is formulated as being highly restricted.<sup>7</sup> The over-

(6) Prepared from inactive unlabeled methacrolein dimer by a Cannizzaro oxidation to the corresponding acid,<sup>a,b</sup> then resolution through the brucine salt, conversion of the sodium salt of the acid to the acid chloride with oxalyl chloride,<sup>c</sup> formation of the corresponding *N*-methylanilide and reduction with lithium aluminum deuteride.<sup>d</sup>  
<sup>a</sup> R. R. Whetstone, U. S. Patent 2,479,283 (1949); <sup>b</sup> G. C. Stoner and J. S. McNulty, *J. Am. Chem. Soc.*, **72**, 1531 (1950); <sup>c</sup> A. L. Wilds and C. H. Shunk, *ibid.*, **70**, 2427 (1948); <sup>d</sup> F. Weygand, G. Eberhardt, H. Linden, F. Schäfer and I. Eigen, *Angew. Chem.*, **65**, 525 (1953).

(7) The bicyclo[2.2.1]heptane formalism (I-IV) is used only to make clear the general character of the transformation which is taking place and should not be taken as a description of the precise geometry of the species involved. Actually, as has been pointed out to us by Professor

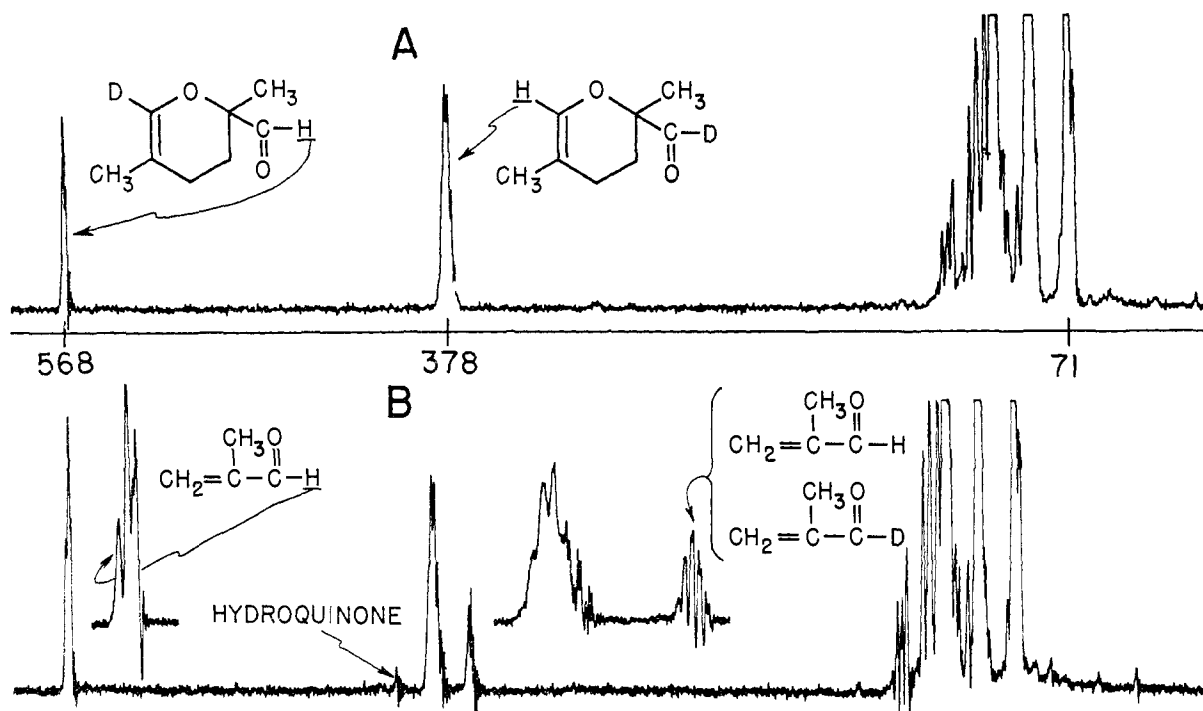


Fig. 1.—Proton n.m.r. spectra at 60 Mc. of rearranged dimers; chemical shifts are in cps. from tetramethylsilane ( $\equiv 0$  cps.) as internal standard: (A) distilled dimer mixture after 9 hours at  $171^\circ$  in an open system; (B) crude product mixture after 7 hours at  $180^\circ$  in a sealed tube. The inset enlargements of the aldehyde and vinyl regions were taken at a reduced sweep rate. One of the vinyl hydrogen resonances of methacrolein is buried under that of the dimer. For comment on the unusual splitting of the dimer aldehyde proton resonance, see D. R. Davis, R. P. Lutz and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 246 (1961).

all process converts the aldehyde deuterium to a vinyl substituent and would occur with *retention* of optical configuration. Rearrangement by way of a diradical intermediate such as IV would be expected to lead to more or less racemization.

The experimental data for rearrangement of I at  $171^\circ$  are summarized in the diagram (I  $\rightarrow$  VI).

Methacrolein, formed by dissociation of the dimer, distilled from the reaction mixture and was condensed at  $-78^\circ$ . No other by-products were detected. The optical activity of the rearranged dimer, which represents 99.5% retention of configuration, was determined for a sample twice vacuum-distilled to remove traces of methacrolein which remained persistently dissolved. The relative amounts of I and II were determined by electronic integration of the n.m.r. absorption signals of the aldehyde and vinyl hydrogens in the distilled dimer mixture (see Fig. 1-A).

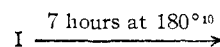
Another rearrangement was carried out in a sealed n.m.r. tube; the experimental results (given in mole per cent.) are summarized in (I  $\rightarrow$  [V + VI]).

The relative amounts of rearranged and unrearranged dimers and of methacrolein formed were

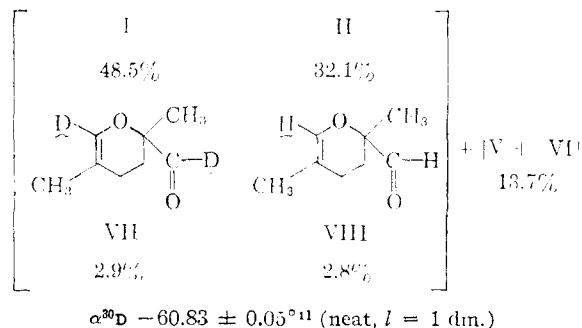
R. B. Woodward, the substituents attached to the two carbon-carbon partial double bonds of III probably would be very nearly planar.

(8) Thermometer bulb immersed in the boiling liquid; rearrangement proceeded at an inconveniently slow rate at  $160^\circ$ . Hydroquinone (0.8%) was used to inhibit polymerization; nonetheless, 4.1% of polymeric residue was formed. In a sealed tube in the absence of inhibitor, 30% of the starting material was converted to polymer in 7 hours at  $180^\circ$ .

(9) Root-mean-square error.



$$\alpha^{26D} - 71.44 \pm 0.05^\circ \\ (\text{neat}, l = 1 \text{ dm.})$$



determined directly in the reaction mixture by n.m.r. (see Fig. 1-B). The amounts of VII and VIII, expected through random recombination of V and VI by a forward Diels-Alder reaction (with a corresponding loss of optical activity), were determined with a mass spectrometer.

Assuming the reactions are first order, we calculate approximately that  $k_r = 1.8 \times 10^{-3} \text{ min.}^{-1}$  for non-dissociative rearrangement and that  $k_d$

(10) Hydroquinone (0.9%) added; <2.7% of polymeric residue was formed.

(11) The observed 14.9% loss of optical activity requires formation of 3.2% each (of the total product) of VII and VIII if the only pathway for loss of activity involves dissociation to methacrolein followed by random recombination.

$= 5.2 \times 10^{-4} \text{ min.}^{-1}$  for dissociation (reverse Diels-Alder reaction) at  $180^\circ$ ; these values represent a difference in free energy of activation of 1.1 kcal. per mole. More accurate determinations of the kinetic parameters are planned.

While our experiments offer no new insight into the mechanism of the Diels-Alder reaction, they exclude participation of a diradical intermediate with a long enough lifetime to permit racemization. Strong moral support is provided for the presumption<sup>2</sup> that the rearrangements and the reverse Diels-Alder reaction proceed along the same energy path. The possibility that different energy paths are involved (the rearrangements are formally Cope rearrangements)<sup>13</sup> is not rigorously excluded; but at least with methacrolein dimer, both reactions occur simultaneously.

Our thanks are due to Dr. S. L. Manatt and Mr. D. M. Kuwada of the Jet Propulsion Laboratory for their good offices and technical help in obtaining the mass spectra.

(12) A. C. Cope and E. M. Hardy, *J. Am. Chem. Soc.*, **62**, 441 (1940), and later papers.

CONTRIBUTION No. 2685

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RECEIVED MARCH 11, 1961

#### FIRST OBSERVATION OF AQUEOUS TETRAVALENT AMERICIUM<sup>1</sup>

Sir:

Americium chemistry has been studied by workers at laboratories in the U.S., U.K., and U.S.S.R. for over ten years. However, only americium valence states of (III), (V), and (VI) have been

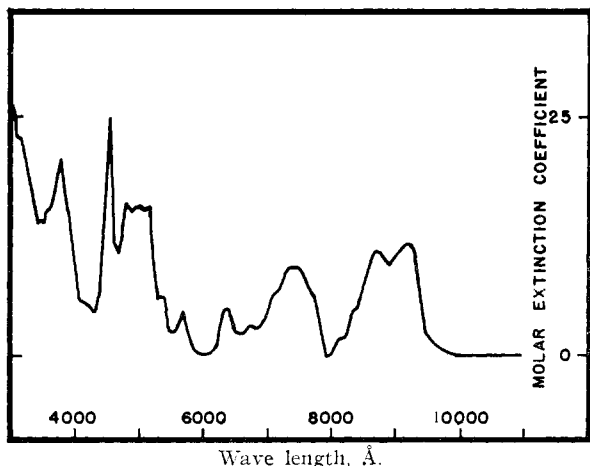


Fig. 1.—Absorption spectrum of Am(IV) in  $15M \text{ NH}_4\text{F}$ ; 5 cm. quartz cells,  $15M \text{ NH}_4\text{F}$  reference solution.

characterized in aqueous solution. Compounds of tetravalent americium prepared by anhydrous means are known, and tetravalent americium has been looked for in aqueous solution, e.g., during the reduction of Am(V) and (VI); during the disproportionation of Am(V); and on dissolution of americium dioxide. Although evidence was found for reactions involving Am(IV) as a kinetic intermediate, all previous work agrees that Am(IV)

(1) This work was sponsored by the U. S. Atomic Energy Commission.

has not heretofore been detected in solution.<sup>2</sup> We find that a solution of pure tetravalent americium can be prepared in saturated ammonium fluoride.

Black Am(OH)<sub>3</sub> was freshly prepared by heating Am(OH)<sub>3</sub> with  $0.2 M \text{ NaOCl}$ - $0.2 M \text{ NaOH}$ .<sup>3</sup> It was treated with saturated aqueous ammonium fluoride in an attempt to produce a solid ammonium-Am(IV) fluoride compound. To our surprise, the slurry of Am(OH)<sub>3</sub> completely dissolved in the  $15 M \text{ NH}_4\text{F}$  solution to give an americium concentration of  $0.01 M$ . The resulting clear (pink-red) solution showed absorption peaks which could not be attributed to any soluble americium species previously known. Moreover, this spectrum bore a striking resemblance to the absorption spectrum of solid AmF<sub>4</sub>.<sup>4</sup>

PRINCIPAL Am(IV) PEAKS			
AmF <sub>4</sub> (solid)	Am(IV) in $15 M \text{ NH}_4\text{F}$	AmF <sub>4</sub> (solid)	Am(IV) in $15 M \text{ NH}_4\text{F}$
9180	9230 Broad, asym	5680	5687
8620	8730	5360	5393
7440	7400 Broad	4860	4818
7030	..	4530	4560
6390	6387	3760	3777

The absorption spectrum of Am(IV) in  $15 M \text{ NH}_4\text{F}$  was obtained from 3,000 to 12,000 Å. (Fig. 1). The peak at 4560 Å. ( $\epsilon = 25$ ) is sharp and well separated from principal peaks of other americium valence states. It is useful for identification and determination of Am(IV).

Heating the solution of Am(IV) in  $15 M \text{ NH}_4\text{F}$  to  $90^\circ$  does not cause disproportionation of Am(IV) or its chemical reduction by water.

Treatment of Am(IV) in  $15 M \text{ NH}_4\text{F}$  with ozone at room temperature yields Am(VI) which, on reduction, again forms the soluble Am(IV) complex. Reduction of Am(IV) to Am(III) is observed due to Am<sup>241</sup> alpha radiation. Iodide also reduces Am(IV) to Am(III).

Treatment of Am(OH)<sub>3</sub> with saturated RbF or KF also gives solutions containing primarily Am(IV). Both Th(IV) and U(IV) are soluble in high concentrations of potassium, rubidium and ammonium fluorides. It would be expected that Pu(IV) and Np(IV) would behave similarly. Structures of the crystalline alkali-Am(IV) fluorides obtained from solution are currently being investigated by F. H. Kruse and L. B. Asprey of this laboratory.

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(2) L. B. Asprey and S. E. Stephanou, AECU-924 (1950); S. E. Stephanou, L. B. Asprey and R. A. Penneman, AECU-925 (1950); L. Eyring, H. R. Lohr and B. B. Cunningham, *J. Am. Chem. Soc.*, **74**, 1186 (1952); L. B. Asprey, *ibid.*, **76**, 2019 (1954); S. R. Gunn and B. B. Cunningham, *ibid.*, **79**, 1563 (1957); G. R. Hall and P. D. Heruiman, *J. Chem. Soc.*, 2214 (1954); G. N. Yakovlev and V. N. Kosyakov, *Proc. Int'l. Conf. Peaceful Uses of Atomic Energy*, **7**, 363 (1956), and **26**, 373 (1958); R. A. Penneman and L. B. Asprey, *ibid.*, **7**, 355 (1956); G. R. Hall and T. L. Markin, *J. Inorg. & Nuclear Chem.*, **4**, 296 (1957); and R. A. Penneman and T. K. Keenan, National Academy of Sciences NS-3006 (1960).

(3) R. A. Penneman, J. S. Coleman and T. K. Keenan, "Preparation and Reactions of Am(IV) Hydroxide," *J. Inorg. Nuclear Chem.*, **17**, 138 (1961).

(4) L. B. Asprey and T. K. Keenan, *ibid.*, **7**, 27 (1958).