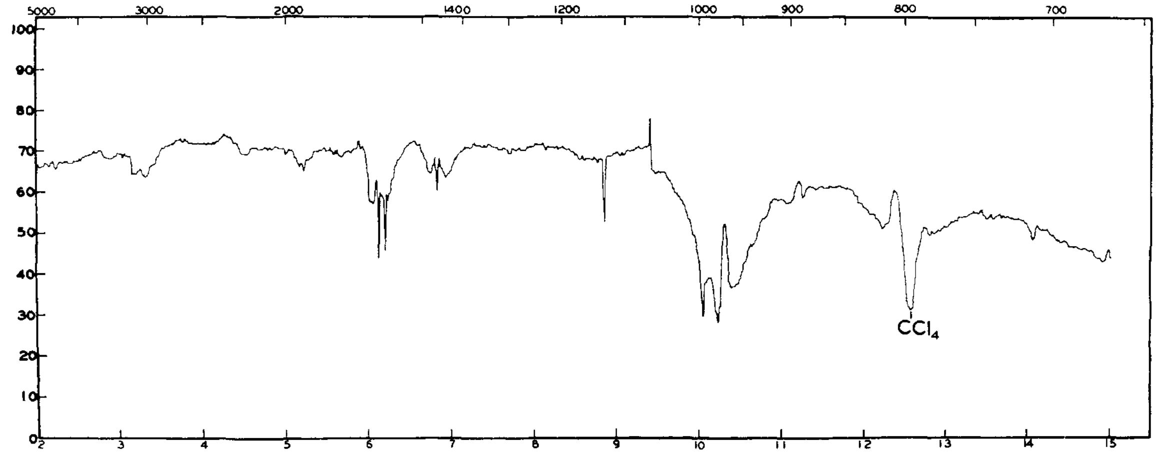

Fig. 2.—Infrared spectrum of diazirine.

Diazirine has been handled routinely as a gas and neat liquid[10] although it exploded once upon warming after being frozen in a liquid nitrogen trap; several times gaseous samples exploded when air was admitted.

Acknowledgment.—This investigation was supported by Army Ordnance Contract DA-01-021-ORD-11909.

[10] This contrasts with the observation in reference (4) that diazirine is explosive at −40°.

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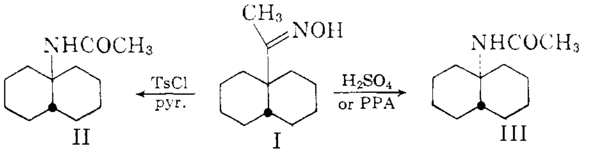
STEREOISOMERIZATION OF MIGRATING GROUP DURING BECKMANN REARRANGEMENT

Sir:

It is a cardinal principle of rearrangements to electron-deficient nitrogen that the reaction occurs with retention of configuration of the migrating group. Previous work[1] has established the validity of this conclusion for a variety of rearrangements including that under consideration here, the Beckmann rearrangement.[2]

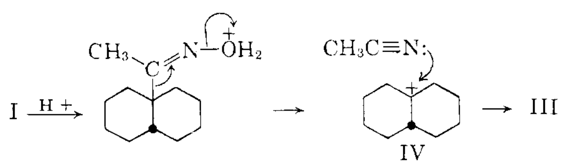
We wish to report the first violation of this rule of retention of configuration, and the consequent demonstration of an alternate mechanism for Beckmann rearrangements in strong acid, in the rearrangement of 9-acetyl-*cis*-decalin oxime (I). The oxime, m.p. 107.5–108.5° (calcd. for $C_{12}H_{21}NO$: C, 73.79; H, 10.84; N, 7.17. Found: C, 73.72; H, 10.81; N, 7.35) was prepared from the ketone, b.p. 84° (1 mm.) (calcd. for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 80.13; H, 11.41), which was synthesized by treatment of the acid chloride of *cis*-decalin-9-carboxylic acid[3] with dimethylcadmium. Reaction of I with *p*-toluenesulfonyl chloride in pyridine at room temperature afforded, in 92% yield, N-(*cis*-9-decalyl)-acetamide (II),[4] m.p. 126°, shown identical by mixed m.p. determination and comparison of infrared spectra with an authentic sample.[5]

On the other hand, treatment of oxime I with concentrated sulfuric acid or polyphosphoric acid overnight at room temperature yielded N-(*trans*-9-decalyl)-acetamide (III),[4] m.p. 183°, again identified by comparison with an authentic sample. The *cis* amide (II) was recovered unchanged under these conditions.



The stereoisomerization which occurs in the decalyl moiety during the conversion of I to III requires the existence of an alternate mechanism for the Beckmann rearrangement, in addition to the well-known stereospecific process.[2] We propose the pathway shown in Chart I for the rearrangement in acid: (1) fragmentation of the protonated oxime into acetonitrile and the 9-decalyl carbonium ion (IV), a step which finds ample analogy in the cleavage of α-trisubstituted oximes,[6] and (2) recombination of these fragments in a Ritter[7] reaction.

CHART I



In support of this postulate, we find, first, that acetonitrile can be identified as a product of the reaction of I with phosphorus pentachloride and, second, that the addition of acetonitrile to ion IV can be verified by treating the nitrile separately

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[1] Summarized by G. W. Wheland, in "Advanced Organic Chemistry," 3rd edition, John Wiley and Sons, Inc., New York, N. Y., 1960, pp. 597–610.

[2] J. Kenyon and D. P. Young, *J. Chem. Soc.*, 263 (1941); A. Campbell and J. Kenyon, *ibid.*, 25 (1946).

[3] R. E. Pincock, E. Grigat and P. D. Bartlett, *J. Am. Chem. Soc.*, **81**, 6332 (1959).

[4] W. Hückel and M. Blohm, *Ann.*, **502**, 114 (1933); W. G. Dauben, R. C. Tweit and R. L. MacLean, *J. Am. Chem. Soc.*, **77**, 48 (1955).

[5] Authentic samples of the *cis* and *trans* amides were kindly furnished by Prof. W. G. Dauben, University of California, to whom we express our gratitude.

[6] See R. K. Hill and R. T. Conley, *J. Am. Chem. Soc.*, **82**, 645 (1960), for examples and additional references.

[7] J. J. Ritter and P. P. Minieri, *ibid.*, **70**, 4045 (1948).

with β-decalol in sulfuric acid to yield III.[8] The factors responsible for the sole formation of the *trans* isomer in this reaction may be similar to those operating in the carbonylation of IV, where *trans* decalin-9-carboxylic acid is the kinetically favored product.[3]

This demonstration of the existence of an alternate mechanism for the Beckmann rearrangement when stable carbonium ions may be produced in strong acid media raises the possibility that some reported rearrangements[9] carried out under these conditions are actually of the fragmentation–recombination type; it further serves as a warning to avoid these conditions in experiments in which retention of configuration is desired.

[8] The formation of N-(*trans*-9-decalyl)-formamide from β-decalol and potassium cyanide in sulfuric acid has been reported by H. Christol, R. Jacquier and M. Mousseron, *Bull. soc. chim.*, France, 1027 (1957).

[9] *E.g.*, H. A. Bruson, F. W. Grant and E. Bobko, *J. Am. Chem. Soc.*, **80**, 3633 (1958).

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ORGANIC COMPOUNDS IN MICROWAVE DISCHARGE

Sir:

The subjection of compounds to microwave discharge has found utility in inorganic synthesis[1] primarily because of the efficient production of atoms and radicals. The chemical literature contains only one report of the application of this technique in organic chemistry and then only to methane.[2] The efficient production of acetylene in this example apparently results from the reactions of radicals. Such radical reactions are reminiscent of the extensive degradation and tar formation observed in the general behavior of organic compounds in other electrical discharges or with radiation in a chemistry that dates back to 1796.[3] In marked contrast, we have found that under some conditions organic compounds in microwave discharge produce relatively high yields of identifiable transformation products that bespeak a new and interesting chemistry.

In our experiments, an organic compound entrained in a helium stream was passed through a quartz tube in a microwave cavity such that a glow discharge was maintained. The products were collected in a trap cooled in liquid nitrogen and identified by their gas chromatographic retention times and infrared spectra. Some tar and carbonaceous material were formed, as well as noncondensable gases (hydrogen, methane and acetylene were identified by gas chromatography). Generally, aliphatic compounds reacted in low conversion to give a large number of products, whereas their aromatic analogs formed a smaller number of products in higher yields. One representative series of results obtained in this reaction (the transformation of toluene) is shown in Table I. The virtual absence ($<0.005\%$) of biaryls or bibenzyls suggests that ion-molecule reactions are of greater importance than radical combinations in these experiments. A duplicate run with helium carrier gas is reported to show the independence of product composition from the percentage conversion.

TABLE I

MICROWAVE DISCHARGE PRODUCTS OF TOLUENE

Toluene, g.	0.87	1.74	0.87	0.17
Non-volatiles, g.	0.19	0.42	[a]	[a]
Condensate, g.[b]	0.41	0.79	0.60	0.13
Helium, l./min.	11	11	0	11
Methane, ml./min.	0	0	0	80
Hydrogen, ml./min.	0	0	80	0
Composition of condensate, %[c]				
Low boilers[d]	18	20	5	27
Benzene	42	40	75	37
Toluene	(68)	(83)	(88)	(76)
Ethylbenzene	23	23	11	25
m,p-Xylene	1	1	1	1
Styrene	7	7	4	6
Phenylacetylene	5	4	3	3
Unidentified[e]	4	5	1	1

[a] No tar formation was observed. [b] The poor material balance appears to be a result of inefficient trapping. Under reaction conditions, with no glow discharge, about 25% of the organic substrate was lost. [c] Percentage composition of unreacted starting material is given in parentheses; other yields are normalized as percentage of the remainder determined by relative areas of peaks in g.c. [d] These compounds are aliphatic and alicyclic unsaturates. [e] Many additional compounds are formed (most in less than 0.5% yield) possibly by secondary processes.

Experiments in which the concentration of toluene in the helium stream was varied showed that tar formation *increased* with increasing dilution of the toluene.[4] Although details of the various reactions are still under study, a plausible explanation at present is that the initial reaction is between an electron plasma and toluene. The cross-section for electron impact of toluene is doubtless much greater than that of helium; hence, as the toluene concentration is decreased the average electron energy is increased. Under the reaction conditions, a methane–helium mixture alone showed only little transformation. It is of interest not only that the presence of methane caused only minor changes in the product composition, but also that lower tar production resulted, perhaps because methane also serves to moderate the electron energy.

When hydrogen alone is used as a carrier gas, the proportion of benzene in the product is increased significantly; nevertheless, there seems to be no drastic change in the nature of the reactions involved. The chemistry of these reactions is being investigated currently. Of especial interest is the

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[1] *Cf.* W. L. Jolly, "Synthetic Inorganic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1960, p. 113.

[2] P. L. McCarthy, *J. Chem. Phys.*, **22**, 1360 (1954). A tritium discharge in juxtaposition to solid and liquid organic compounds has been used for radioactive labeling [N. A. Ghanem and T. Westermark, *J. Am. Chem. Soc.*, **82**, 4432 (1960)]. A. P. Wolf (personal communication) has been studying rearrangements in toluene resulting from microwave discharge and other high energy conditions.

[3] M. Fourcroy, *Ann. chim.*, (1) **21**, 48 (1796). The early literature of this chemistry is reviewed by G. Glockler and S. C. Lind, "The Electrochemistry of Gases and other Dielectrics," John Wiley and Sons, Inc., New York, 1939.

[4] Vapor phase photolysis of toluene at low pressure yields volatile gases and polymer: R. R. Hentz and M. Burton, *J. Am. Chem. Soc.*, **73**, 532 (1951).