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).

(10) Alfred P. Sloan Foundation Fellow.

(11) Albert Plaut Fellow.

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RECEIVED FEBRUARY 19, 1962

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).

study of reaction mechanism using tritium and deuterium labeled compounds.

(5) (a) Alfred P. Sloan Fellow, 1958–1962; (b) National Science Foundation Postdoctoral Fellow, 1961–1962.

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THE STEREOCHEMISTRY OF CHALCOSE, A DEGRADATION PRODUCT OF CHALCOMYCIN

Sir:

The chemistry and structure of chalcose[1] were reported recently. We now wish to report data indicating that crystalline methyl chalcoside [m.p. 101.5–102°; $[\alpha]^{27}D$ $-21°$ (chloroform)] and chalcose [m.p. 96–99°; $[\alpha]^{24}D$ $+120°$ (2 min.) $\rightarrow$ $+97°$ (10 min.) $\rightarrow$ $+76°$ (3 hr. and 26 hr.) (water)] may be represented sterically as I and II, respectively.

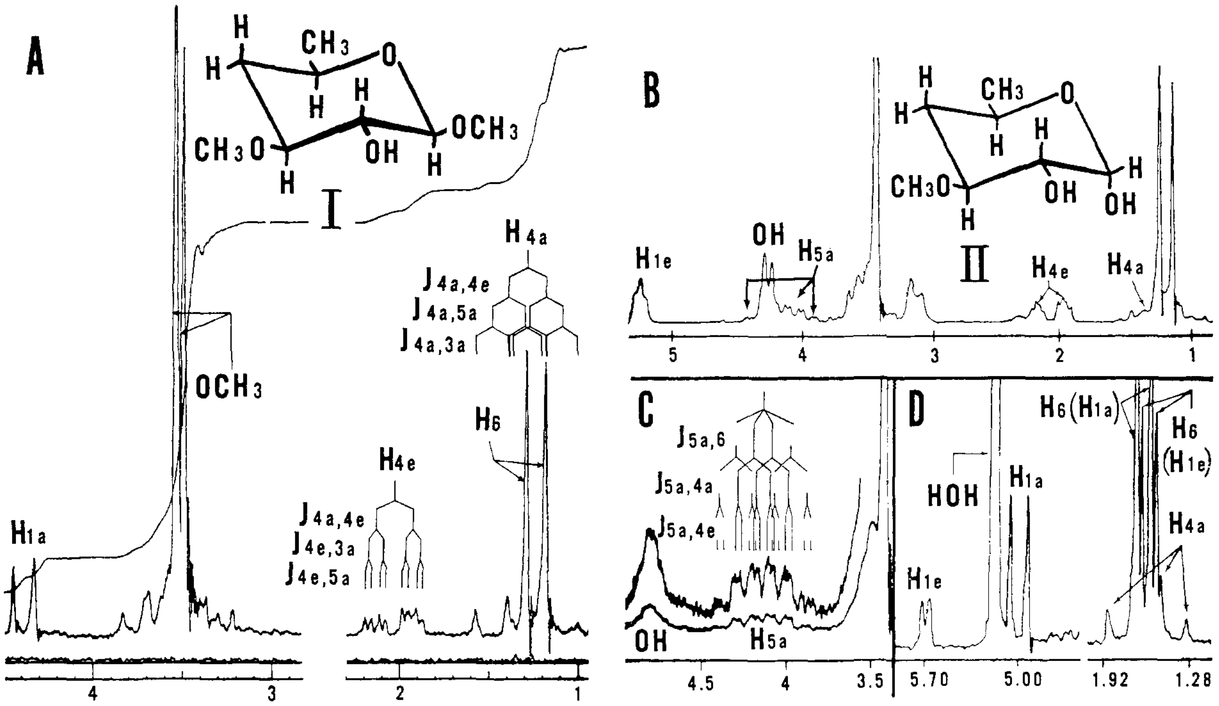

Fig. 1.—N.m.r. spectra at 60 mc. with chemical shifts given in ppm. from tetramethylsilane as zero: (A) methyl chalcoside in pyridine, also showing area integration curve and theoretical splitting patterns derived from assumed constants[4b]; (B) chalcose in deuteriochloroform: (C) the C-5 hydrogen of chalcose in deuteriochloroform (under slightly different conditions from those for Fig. 1B) showing theoretical splitting patterns[4b]; (D) chalcose in deuterium oxide.

Figure 1A shows the n.m.r. spectrum of methyl chalcoside in pyridine. The doublet C-1 anomeric hydrogen signal at $\delta = 4.40$ has a large spin coupling ($J \sim 7$ cps.) which indicates that the C-1 and C-2 hydrogens are axial,[2] as in I. The equatorial C-4 hydrogen signals around $\delta = 2.05$ shows a typical large spin coupling to the axial C-4 hydrogen ($J_{4a,4e}$ $\sim$12.5 cps.).[2,3] The axial C-4 hydrogen signals around $\delta = 1.00$ to 1.58,[3] partly hidden by the doublet C-methyl signal, have a total width of 34.5 cps. This width is practically equal to the sum of three coupling constants ($J_{4a,5}$, $J_{4a,3}$, $J_{4a,4e}$) with which the axial C-4 hydrogen is coupled to the equatorial C-4 hydrogen and to the two neighboring hydrogens on C-3 and C-5.[4] Thus the sum of $J_{4a,5}$ and $J_{4a,3}$ may be calculated to be approximately 22 cps. To account for this large value, as well as for the splitting pattern observed, the C-3 and C-5 hydrogens are assigned axial configurations as in I.[5]

Similar consideration of the n.m.r. spectrum of crystalline chalcose in deuteriochloroform (Fig. 1B and 1C) and in deuterium oxide (Fig. 1D) indicates the presence of axial hydrogens on C-3 and C-5. The C-2 hydrogen, being *trans* to the C-3 hydrogen, therefore must be axial. The C-1 ano-

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[1] P. W. K. Woo, H. W. Dion and Q. R. Bartz, *J. Am. Chem. Soc.*, **83**, 3352 (1961).

[2] From n.m.r. studies of acetylated pyranose, cyclohexane and related ring systems, R. U. Lemieux, R. K. Kullnig, H. J. Bernstein and W. G. Schneider [*ibid.*, **80**, 6098 (1958)] reported these data pertinent to the present discussion: (a) in β-D-xylopyranose tetraacetate, $J_{5a,5e}$ = 12 cps., $\delta_{5e} > \delta_{5a}$ (*cf.* ref. 3); (b) for a number of acetylated pyranoses, δ_{1e} = 5.66–6.11 ppm., δ_{1a} = 5.37–5.75 ppm. (*cf.* ref. 3); (c) for hydrogens on adjacent carbons, $J_{a,a}$ = 5–8 cps., $J_{a,e}$ or $J_{e,e}$ = 2–3.5 cps. (*cf.* ref. 5).

[3] J. N. Shoolery and M. T. Rogers [*ibid.*, **80**, 5121 (1958)] give other examples showing that the equatorial proton absorbs at a larger δ value than its axial counterpart.

[4] (a) This statement was based on calculations first treating three hydrogens, H_{4a}, H_{4e}, $H_{5a\ (\text{or}\ 3a)}$, as an ABX system [J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, p. 132], then splitting each of the resulting lines by the fourth hydrogen $H_{3a\ (\text{or}\ 5a)}$. (b) The following constants (in cps.) were used to derive the theoretical patterns shown in Fig. 1A: $J_{4a,3a} = 11.0$, $J_{4a,5a} = 11.0$, $J_{4e,5a} = 2.1$ (or 5.0), $J_{4e,3a} = 5.0$ (or 2.1), $J_{4a,4e} = 12.5$, $\delta_{4e} - \delta_{4a} = 43.0$; and in Fig. 1C: $J_{4a,5a} = 11.4$, $J_{4e,5a} = 2.3$, $J_{5a,6} = 6.5$.

[5] J. N. Shoolery ["NMR and EPR Spectroscopy" by Varian staff, Pergamon Press, New York, N. Y., 1960, p. 114] tabulates spin coupling constants for cyclohexane systems: $J_{a,a}$ = 6–14 cps., $J_{a,e}$ or $J_{e,e}$ = 0–6 cps.