

relative cross sections of these molecules, we obtain a crude lower limit of 6×10^{-5} mm. for the Al_2H_6 pressure at maximum intensity. That the actual pressure was higher than this value was demonstrated by measuring both the rates of aluminum evaporation from the aluminum droplet and deposition of aluminum on the wall of the apparatus under conditions where hydrides were observed mass spectrometrically. The differences were attributed to hydride formation since the aluminum deposition occurred only in the immediate vicinity of the droplet. From these data and aluminum vapor pressure data, the calculated hydride pressures ranged from 10^{-4} to 10^{-3} mm.

The observed ready dimerization of AlH_3 is entirely expected since the latter can be assumed to be sp^2 hybridized with only three filled orbitals. Dimerization to a structure similar to B_2H_6 ⁶ would involve the formation of two hydrogen bridge bonds with an increase in coordination number of Al from 3 to 4. AlH_3 would then be expected to be no more stable than BH_3 , relative to dimerization.

It was not possible to sustain aluminum droplet temperatures much in excess of 1300° with the apparatus described above. A more elaborate evaporator is under construction and will be used to determine whether higher gaseous alanes can be prepared at considerably higher aluminum vapor pressures.

Acknowledgment.—The authors gratefully acknowledge the technical assistance of Mr. G. W. Albright.

(6) W. N. Lipscomb, *J. Chem. Phys.*, **22**, 985 (1954).

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RECEIVED OCTOBER 8, 1964

Aromatic Alkylation *via* Diazotization

Sir:

We have been able to detect the presence of cymene in the diazotization of isopropylamine by butyl nitrite and an equivalent amount of a carboxylic acid dissolved in excess toluene. No previous report of alkylation by this procedure has been found in the literature although a similar method has been used for arylation.¹

Acetic acid (0.02 mole) was added to toluene (3 ml.) in a test tube containing a clay boiling chip. A mixture of isopropylamine (0.02 mole) and butyl nitrite (0.02 mole) in 3 ml. of toluene was added in increments of 1 ml. over a period of 2 hr. Occasional warming was performed to facilitate gas evolution. The reaction mixture was allowed to stand overnight, refluxed with 25 ml. of 15% aqueous sodium hydroxide, rinsed with water in a separatory funnel, and finally shaken twice with two separate portions of cold, concentrated sulfuric acid. The hydrocarbon layer remaining was washed with water and dried with calcium chloride. Analysis was carried out by means of g.l.c., thermal conductivity detector, 60 ml./min. flow rate of helium, 50- μ l. sample at attenuation of 2; 5% Bentone 34, 0.5% XF 1150 on Diatoport S: *p*-cymene retention time = 8 min. and *o*- and *m*-cymene = 9.5 min.; 5% polyphenyl ether on Anachrome P, 60-70 mesh: *p*- and *m*-cymene = 10.5 min. and *o*-cymene =

11.5 min. From the first column, the per cent *p*-cymene was obtained, from the second column, the per cent *o*-cymene; the per cent *m*-cymene was obtained by difference.

The total yield of cymenes, based on isopropylamine, was about 3 to 4%, the major products being propylene and isopropyl acetate. The yield of cymenes was nearly the same over a surprisingly large variety of conditions as indicated by the following changes of standard procedure: (1) substitution of pivalic or mesitoic acid or acetic anhydride for acetic acid; (2) change of reaction temperature from 25 to 60° ; (3) stirring, mechanical or sonic cavitation, or no stirring; (4) tenfold increase in toluene concentration; and (5) increased surface area such as crushed clay plate (nitrogen evolution rate increases but not yield). Decrease in acetic acid concentration causes separation of two phases and lowering of the yield.

In such a nonpolar medium the question arises whether a free-radical or ionic mechanism is applicable. We have answered this question by observing the results of the diazotization of *n*-propylamine in benzene using the same conditions as described. About a 1% yield of hydrocarbon was obtained of which 55% was isopropylbenzene and 45% *n*-propylbenzene. These results are similar to those run previously in which the mechanism is an ionic one without doubt.^{2,3} To emphasize the improbability of a free-radical mechanism applying to the above results, we quote that not a single reliable demonstration of a primary to secondary migration of a hydrogen atom ($\text{H}\cdot$) has been observed in free radicals to date.⁴

Although the yield of this reaction is too low to be of synthetic value, it is within a satisfactory range to carry out orientation and competition studies. The orientation in isopropylation of toluene was 40-44% *o*-, 24-25% *m*-, and 32-36% *p*-cymene in four different experiments. The competition results were quite interesting as shown in Table I.

TABLE I
CYMENE/CUMENE RATIOS^a

A	B	C
Toluene/benzene molar ratio	Cymene/cumene product ratio ^b	Apparent rate ratio ($k_{\text{C}_6\text{H}_5\text{CH}_3}/k_{\text{C}_6\text{H}_6}$), [B \times 1/A]
0.25	0.25	1.0
1.0	0.93	0.93
2.5	2.0	0.8
4.0	3.15	0.79

^a Acetic acid (0.02 mole) in 3 ml. of toluene-benzene mixtures treated with isopropylamine (0.02 mole) and butyl nitrite in 3 ml. of the same toluene-benzene mixtures in a test tube containing a clay boiling chip. ^b Determined by comparison of Gaussian curve areas in g.l.c.

Benzene is more reactive than toluene. Benzene is even more reactive than *p*-xylene ($k_{p\text{-xylene}}/k_{\text{C}_6\text{H}_6}$ ca. 0.6). Only one other alkylation experiment is known where benzene has been found to be more reactive than toluene: the alkylation of aromatic hydrocarbons

(2) R. M. Roberts and D. Shienghong, *J. Am. Chem. Soc.*, **82**, 732 (1960). Isopropylbenzene (66%) and *n*-propylbenzene (33%) are produced from *n*-propyl chloride, benzene, and aluminum chloride.

(3) H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961, p. 122. Isopropyl alcohol (58%) and *n*-propyl alcohol (42%) are prepared from diazotization of *n*-propylamine in aqueous solution.

(4) R. K. Freidlina, V. N. Kost, and M. Y. Khorina, *Russ. Chem. Rev.*, **31**, No. 1, 4 (1962).

(1) S. Huang, *Hua Hsueh Hsueh Pao*, **25**, 171 (1959); *Chem. Abstr.*, **54**, 4489 (1960); J. I. G. Cadogan, *J. Chem. Soc.*, 4257 (1962).

using a boron trifluoride-phosphoric acid mixture.⁵ We prefer not to comment on this paper since the reaction appears to be heterogeneous in nature.

The results of diazotization cannot be interpreted on the basis of the relative electronic or chemical properties of the aromatic hydrocarbons. Our tentative interpretation is that a cage effect is in operation. The isopropylamine-nitrous acid intermediates, including the original isopropylamine-acetic acid salt, are surrounded by the more polar components, particularly the free acetic acid molecules. The benzene, toluene, and *p*-xylene are distributed sparsely in the cage according to their sizes or shapes rather than in relation to their bonding abilities. According to bulk, the population of benzene molecules in the cage is very small but greater than that of toluene or of *p*-xylene. Thus, the isopropyl intermediate has the opportunity to attack in the sequence: acetic acid \gg benzene $>$ toluene $>$ *p*-xylene. The only other interpretation possible is that the intermediate carbonium

(5) R. N. Volkov and S. V. Zavgorodnii, *Dokl. Akad. Nauk, SSSR*, **133**, 843 (1960).

ion is so reactive that it attacks the aromatic hydrocarbons in a statistical manner. This interpretation is not so attractive because the *meta/para* ratio in isopropylation of toluene is about 0.7, rather than close to the statistical factor of 2. The invariant yield gives weight to the cage theory also.

A great deal of work remains to be done, but it is important at this time to point out (1) that aromatic alkylation by diazotization has been accomplished, and (2) that unusual activity sequences in competition reactions carried out in nonpolar solvents were encountered. It is well for chemists to be alerted to the possibility that activity sequences having nothing to do with electronic effects may be encountered in other reactions involving nonpolar solvents.

Acknowledgment.—The authors are indebted to the National Science Foundation for support of this work.

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RECEIVED AUGUST 21, 1964

BOOK REVIEWS

Progress in Reaction Kinetics. Volume II. By G. PORTER, F.R.S., Editor, Professor of Physical Chemistry, University of Sheffield. The Macmillan Co., 60 Fifth Ave., New York 11, N. Y. 1964. vii + 391 pp. 16 \times 24 cm. Price, \$15.00.

With the publication of this second volume, this series may be described as having "arrived" in terms of the importance and seriousness of its contribution to the broad field of chemical kinetics. The present work offers a selection of eight articles, mainly by well-recognized authorities, the subject matter being about equally divided between gas phase and solution kinetics. Its catholicity of coverage is also indicated by the fact that fields such as photochemistry, biochemistry, polymer chemistry, as well as physical organic and inorganic chemistry, are involved. This diversity of subjects is perhaps but a reflection of the fact that the techniques of chemical kinetics are becoming as broadly used a tool in the sciences as thermodynamics. And this in turn has raised a difficult problem of jurisdiction which must surely be plaguing the editors of this and other "Advances in . . ." or "Progress in . . ." series.

Drs. G. C. Fettis and J. H. Knox have contributed a timely and well-done article on halogen atom reactions. They have gone beyond the usual bounds of reviewers in trying to systematize and rationalize the data, both internally from an empirical point of view and externally with regard to transition-state theory. Of particular interest is their criticism of the the classical Bodenstein work on $\text{Br} + \text{H}_2$ and their proposed revision of the rate constant for this reaction *vis-à-vis* $\text{Cl} + \text{H}_2$ and $\text{I} + \text{H}_2$. They list some very interesting tables of *A* factors calculated by transition-state theory which show the present state of the art fairly well, *i.e.*, agreement with observed values to about $\pm 40\%$ on the average and disparity factors seldom beyond $1/3$ or 3 in the extreme.

Another very timely and thorough article is on Hg photosensitized reactions by Dr. R. J. Cvetanović, one of the outstanding practitioners of this difficult art. There has been a good deal of controversy about the nature of the primary and secondary steps in Hg^* reactions, and this is very ably presented here if not settled. A very strong case is made that for olefins the major process is the formation of highly excited molecules or biradicals. Their multiplicity, singlet or triplet, is still being

actively investigated. Quite fascinating are the recent reports of cyclic products from butenes and pentenes. The recent history of isotopic enrichment studies of Hg mostly by Gunning, *et al.*, is also included.

Dr. H. M. Frey who is well known for his studies on the decompositions of small ring compounds contributes a very compact and readable survey of CH_2 and simple carbene reactivity. The intensity of interest in this subject is indicated the fact that this will make the fourth such survey to appear this year.

Strongly related to each of the three preceding articles is the fourth chapter by R. B. Cundall on the kinetics of *cis-trans* isomerizations. This is again a very well-written survey of the early and recent history of the subject covering gas phase, catalyzed and uncatalyzed reactions, as well as solution phase reactions including photosensitization by Hg and triplet-state molecules. It is a pity that this otherwise well-done article appears to be marred by having an unusual number of errors in some of the tables.

As noted by the authors, Dr. M. Szwarc and Dr. J. Smid, anionic polymerization is a revitalized, rather than a new field. The present article on the kinetics of propagation of anionic polymerization and copolymerization is a most thorough and scholarly account of the field from earliest days by one of its most famous revivers, Dr. M. Szwarc. The stage of sophistication recently achieved in this art using modern physico-chemical techniques is well illustrated by the discussion of ion-pair and ion-pair dimers involved in some of the systems studied.

An equally new and "hot" field of fast reactions in solutions is presented by one of its discoverers, Dr. M. Eigen. Chapter VI, "The Rate Constants of Protolytic Reactions in Solution," by M. Eigen, W. Kruse, G. Maass, and L. DeMaeyer, discusses the theory and findings on diffusion-controlled reactions mostly in aqueous solutions. The methods employed are the relaxation techniques introduced by Dr. Eigen and co-workers, and useful tables list almost all of the extant data. The field appears ripe for a discussion of these data in terms of structure but this is not a major concern of this chapter.

The difficult but important biochemical subject, "Rates of Reaction of some Haem Compounds," is lucidly covered by Dr. Q. H. Gibson in a short section. These include reversible complex formation and some enzyme reactions.