model DU. Reagent benzene was used as a reference for the spectroscopic measurements. Before each set of kinetic runs the optical density of a standard solution of formaldehyde 2,4-dinitrophenylhydrazone [λ_{max} 345 mμ (ϵ 18,500)] in benzene was measured in order to check the reproducibility of the spectrometer. The maximum variation of these optical density measurements from their mean was less than 1%. The reactions were followed by measuring the optical densities of the reaction mixtures at the wave length of maximum absorption of the borofluoride complexes (approximately 360 mμ; see Table III). For the 4-methoxy-*trans*-benzalacetophenone oxide runs, the maximum at 383 mμ was employed. The oxides, benzene and boron trifluoride etherate all have negligible absorption in this region. For the purpose of calculation the first optical density reading taken was considered to be 0% reaction and the final, maximum optical density reading was taken as 100% reaction. In several of the cases the final optical density reading was demonstrated to remain constant for at least an hour. In all cases the pseudo-first order rate constants were determined graphically from plots of time *vs.* log [(final − init. optical density)/(final − obsd. optical density)]. For the rearrangement of *trans*-benzalacetophene oxide, Table VII summarizes the effect of change in boron trifluoride etherate concentration at a constant oxide concentration and Table VIII demonstrates that changes in the oxide concentration at constant boron trifluoride etherate concentration do not alter the rate constant. The deliberate addition of a small amount of water (to make the solution 0.0037 M in water) prior to a kinetic run had a small effect on the rate ($k = 1.77 \times 10^{-3}$ with added water, $k = 1.27 \times 10^{-3}$ without added water). Addition of greater amounts of water caused the reaction mixture to become turbid precluding optical measurements. For each set of kinetic runs a sample of *trans*-benzalacetophenone oxide was run as a standard in an effort to minimize possible errors in the relative rates which would result from differing concentrations of boron trifluoride etherate and differing amounts of water which might be present. Table V lists the average relative rates obtained with the average deviation from the mean. Each of the entries in the table represents the average of at least three kinetic runs.[15]

In two cases (Ig and Ih) the rearrangements were run under the conditions of the kinetic measurements but on a

sufficient scale to permit the isolation of the products. A solution of 25.3 mg. (9.40 $\times$ 10^{-5} mole) of the oxide Ig and 6 ml. (0.048 mole) of boron trifluoride etherate in 1000 ml. of benzene was allowed to stand at 30° for 2.5 hr., after which period the optical density indicated 70% reaction. The solution was washed with aqueous sodium acetate and then with water and concentrated under reduced pressure to

TABLE VIII

EFFECT OF VARIOUS CONCENTRATIONS OF *trans*-BENZALACETOPHENONE OXIDE ON THE RATE OF REARRANGEMENT IN THE PRESENCE OF A 0.0424 M SOLUTION OF BORON TRIFLUORIDE ETHERATE

Initial oxide concn., M	Pseudo-first order rate constant, sec.$^{-1}$ $\times$ 10^3
8.74 $\times$ 10^{-5}	1.33
4.37 $\times$ 10^{-5}	1.27
2.62 $\times$ 10^{-5}	1.35

approximately 30 ml. The resulting solution was diluted with ether, washed with water, and then concentrated to dryness under reduced pressure. A solution of the residue in 5 ml. of ethanol was treated with 18.3 mg. (1.69 $\times$ 10^{-4} mole) of phenylhydrazine and one drop of acetic acid. The resulting solution was refluxed for 30 min., diluted with water and cooled. The crude pyrazole VIIg which separated (16.8 mg. or 53%, m.p. 220.6-223.8°) was chromatographed on 2 g. of Merck acid washed alumina and then recrystallized from aqueous ethanol. The pure pyrazole VIIg, m.p. 222.5-224.2°, yield 12.0 mg. (38%), was identified by a mixed melting point determination and by comparison of the infrared spectrum with the spectrum of an authentic sample.

In a similar experiment in which a solution of 32.8 mg. (1.29 $\times$ 10^{-4} mole) of the oxide Ih and 6 ml. (0.048 mole) of boron trifluoride etherate in 1000 ml. of benzene was allowed to react for 3 hr., the optical density of the solution indicated 69% reaction. Use of the previously described isolation procedure, employing 19.7 mg. (1.82 $\times$ 10^{-4} mole) of phenylhydrazine, afforded 12.6 mg. (30%) of the crude pyrazole VIIh, m.p. 139.4-143.5°, which was identified by comparison of its infrared spectrum with the spectrum of an authentic sample.

[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY, EVANSTON, ILL.]

High Pressure Thermal Alkylation of Xylenes and Related Compounds by Propylene[1,2]

BY C. N. PILLAI AND HERMAN PINES

The high pressure thermal alkylation reactions of toluene, the three xylenes and *p*-methylanisole by propylene were studied in a flow system at 430° and 410 atmospheres pressure. The alkylation products were *n*-butyl- and isobutylbenzene derivatives. Comparison of the selectivity of these reactions with the previously reported results with other alkylbenzenes lead to the conclusion that steric factors are of greater importance than resonance factors in determining the selectivity of addition. Ring methylation and formation of phenolic materials were also observed during the reaction of *p*-methylanisole.

In the earlier papers of this series, the high pressure thermal alkylation of monoalkylbenzenes by simple olefins has been reported.[3,4] It was found that the addition of a benzyl-type radical to an unsymmetrical olefin at high pressure and temperature had a certain amount of selectivity. The mode of addition resulting in the more stable

intermediate free radical (I < II < III) predominated. It was also found that the magnitude of this selectivity was dependent on the structure of the benzyl-type radical as well as on the structure of the olefin.

Benzyl radicals derived from toluene, ethylbenzene and cumene showed progressively increasing selectivity in their addition to unsymmetrical olefins like propylene[3] and 1-butene.[4] This progressive change in selectivity was considered to be due to one or both of two factors, namely the progressive increase in steric hindrance around the benzylic carbon atom in the series toluene, ethyl-

(1) Part IV of the series, "Thermal Alkylation Reactions." For Part III, see H. Pines and C. N. Pillai, *J. Am. Chem. Soc.*, **82**, 2921 (1960).

(2) This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

(3) H. Pines and J. T. Arrigo, *J. Am. Chem. Soc.*, **79**, 4958 (1957).

(4) H. Pines and C. N. Pillai, *ibid.*, **81**, 3629 (1959).

benzene and cumene and the progressive increase in the stability of the benzylic radical with increasing methyl substitution on the α-carbon atom.

It was suspected[4] that the steric factor was the more important of the two. It was of interest to determine, if possible, the relative importance of these two factors. For this purpose, the alkylation of ring-substituted toluene by propylene was undertaken. By this means, it was hoped to keep the steric factor constant while changing the stability factor.

In the present paper, the high pressure thermal alkylations, by propylene, of toluene, o-, m- and p-xylene and p-methylanisole are reported.

Experimental

The thermal alkylation studies at 430° and 410 atmospheres and a flow rate of 45 cc. per hour were carried out in the reactor previously described.[3] As before, the technique consisted of passing a mixture of the alkylbenzene and propylene, the former in excess, down a stainless steel tube kept at the required temperature and pressure.

The rate of flow was selected so that the conversion was low and the side reactions at a minimum. The products were collected in suitable receivers during the run. The reaction products from toluene and the xylenes were worked out as reported before.[4] Non-aromatic components were separated, after selective hydrogenation, by displacement chromatography over silica gel. The aromatic components were analyzed by vapor phase chromatography over a 16-ft. column made of silicon oil (D.C. silicon 550, 40% by weight) deposited on firebrick. Most of the major components were also identified by their infrared spectra.

Pure samples of butyltoluenes were synthesized for comparison of their retention times and infrared spectra with the compounds obtained in the alkylation reactions. The syntheses were made by treating the corresponding tolylmagnesium bromides with n- or isobutyraldehyde to form the corresponding tolylpropylcarbinols. The latter on hydrogenolysis in the presence of copper chromite catalyst yielded the corresponding tolylbutanes.

The liquid product from p-methylanisole was distilled to remove traces of materials that boiled below 160°. A fraction composed of p-methylanisole and its monoalkylation products boiling above 160° was collected and analyzed as indicated below. The residue in the distillation flask which was a tarry material that could not be distilled below 290°, was not analyzed.

TABLE I
ALKYLATION OF SUBSTITUTED TOLUENES, $C_6H_4(CH_3)R$, BY PROPYLENE

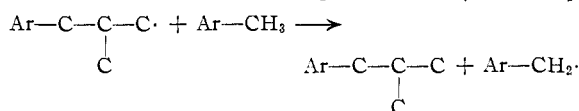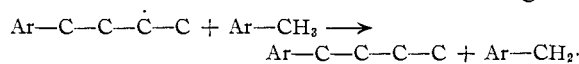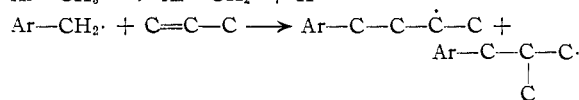| Experiment	1[a]	2	3	4	5	6
$C_6H_4(CH_3)R$, R =	H	H	o-CH₃	m-CH₃	p-CH₃	p-OCH₃
Reactants, moles						
Alkylbenzene	4.31	1.47	1.93	1.78	1.04	0.52
Propylene	0.85	0.21	0.53	0.54	0.29	0.16
Molar ratio[b]	5.1	7.2	7.3	6.6	7.1	3.2
Yields based on propylene charged[c], mole %						
Monoadducts	17	27	37	37	31	11
Polymn. of propylene	16	9	8	7	6	...
Alkylbenzene reacted, mole %	6.4	5.6	11.6	13.7	11.4	8.6
Yields based on alkylbenzene reacted, mole % $C_6H_4(R)R'$,						
R = C₂H₅	3.0	4.9	1.3	2.5	2.3	4.7
n-C₃H₇	...	0.7	1.2	1.3	1.7	2.1
i-C₄H₉	9.4	13.3	18.7	14.9	15.1	8.3
n-C₄H₉	47.6	53.3	67.2	63.4	59.7	24.6
Monoadduct yield, mole %, based on Me groups available	3.7	3.8	5.1	5.6	4.5	3.5
Selectivity	5.1	4.0	3.6	4.3	3.9	3.0

[a] From ref. 3. [b] Ratio of moles of CH₃ groups on the alkylbenzene to moles of olefin. [c] Small amounts of diadducts were formed. The rest of the propylene was recovered.

The p-methylanisole mixture was selectively hydrogenated over copper chromite catalyst to remove side chain unsaturation. The mixture could not be resolved by vapor phase chromatography on the silicon oil column previously described. Hence, it was hydrogenated over nickel to a mixture of 1-methoxy-4-alkylcyclohexanes. This mixture, on passing over an alumina catalyst at 400°, split off methyl alcohol to yield a mixture of alkylcyclohexenes. Cyclohexyl methyl ether over the same catalyst gave pure cyclohexene. Hence, it was assumed that no skeletal isomerization was taking place during this step. The mixture of olefins was hydrogenated to the mixture of alkylcyclohexanes, which could be readily analyzed by vapor phase chromatography over the silicon oil column. This mixture showed peaks corresponding to methyl-, dimethyl-, ethyl-, n-propyl-, isobutyl- and n-butylcyclohexane. A sample of the original liquid product on extraction with alkali gave phenolic materials corresponding to about 4–5% by weight of the original charge.

The data from the various experiments are summarized in Table I.

Discussion

The alkylation reaction can be represented by the following equations, where Ar represents a phenyl or a substituted phenyl group

$$Ar—CH_3 \longrightarrow Ar—CH_2\cdot + H\cdot$$

$$Ar—CH_2\cdot + C{=}C—C \longrightarrow Ar—C—C—\overset{\cdot}{C}—C +$$
$$Ar—C—\underset{\underset{C}{|}}{C}—C\cdot$$

$$Ar—C—C—\overset{\cdot}{C}—C + Ar—CH_3 \longrightarrow$$
$$Ar—C—C—C—C + Ar—CH_2\cdot$$

$$Ar—\underset{\underset{C}{|}}{C}—C—C\cdot + Ar—CH_3 \longrightarrow$$
$$Ar—\underset{\underset{C}{|}}{C}—C—C + Ar—CH_2\cdot$$

The selectivity in these reactions represents the ratio of the yield of n-butylbenzene derivative to that of isobutylbenzene derivative. The data in the table show that the methyl substituent in the o-, m- or p-position does not affect the selectivity of the addition of the corresponding benzyl radical to propylene. If stability is the factor determining selectivity, o- and p-xylene, since they should yield radicals similar in stability to that from ethylbenzene,[5] should have given a selectivity of about 7 as did ethylbenzene.[3] However, their selectivity is the same as that of toluene. Hence, it appears that steric factors are more important in determining selectivity than stability factors. This is further supported by the fact that m-xylene has about the same selectivity as toluene, o-xylene and p-xylene.

p-Methylanisole was studied to see if the methoxyl substituent had any effect on the selectivity. The fact that the methoxyl substituent assists the dissociation of hexaarylethanes[6] indicates that it is a radical stabilizer. Hydrogen abstraction studies on substituted alkylbenzenes[7] also point to the same conclusion.

Results with p-methylanisole are complicated by the formation of phenols. However, it is

(5) The benzylic C–H bond dissociation energies for o- and p-xylene and for ethylbenzene are about 74 kcal./mole and for m-xylene and toluene, about 77.5 kcal./mole; M. Szwarc, Chem. Revs., 47, 75 (1950); C. H. Leigh and M. Szwarc, J. Chem. Phys., 20, 844 (1952).

(6) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 380.

(7) K. M. Johnston and G. H. Williams, Chemistry & Industry, 328 (1958).

seen that the selectivity is not appreciably different from that of toluene and the xylenes. This affords added support to the conclusion that resonance effects are not of appreciable importance in determining selectivity.

The three xylenes have the same reactivity toward propylene as judged by the yield of monoadduct based on methyl groups available (see Table I). This reactivity is essentially the same as that exhibited by toluene. About 80–90% of the reacted xylenes are accounted for as monoalkylation products. Diadducts and diarylalkanes account for the remainder of the alkylbenzene reacted. In reactions with the xylenes, 30–40% of the propylene charged were converted to monoalkylation products. Polymerization of propylene was less important than in the 1-butene experiments.[4] Some diadducts were also formed, but these were not analyzed. The remainder of the propylene charged was recovered unchanged.

Reactivity of p-methylanisole toward alkylation by propylene cannot be accurately assessed by the results obtained in the present study. Approximately 5% of the p-methylanisole was converted to phenols. The nature of these was not determined. The analysis of monoalkylated p-methylanisole given in the table was arrived at on the assumption that the alkylcyclohexanes obtained by the procedure described in the Experimental section were derived from the corresponding p - methoxy- or p - hydroxyalkylbenzenes. That some dimethylcyclohexane was also detected shows that probably some rearrangement of p-methylanisole to xylenols took place or, alternately, ring methylation of p-methylanisole by methyl radicals took place. Such pyrolytic reactions of alkyl phenyl ethers to form alkylphenols have been reported.[8]

(8) W. J. Hickinbottom, *Nature*, **142**, 830 (1938); **143**, 520 (1939); N. M. Cullinane and S. J. Chard, *J. Chem. Soc*, 821 (1945); R. D. Obolentzev, *J. Gen. Chem. (U.S.S.R.)*, **16**, 1459 (1946).

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY, EAST LANSING, MICH.]
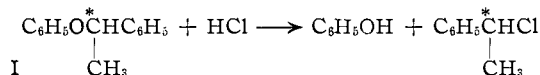
Cleavage of Optically Active α-Phenethyl Phenyl Ether with Hydrogen Chloride
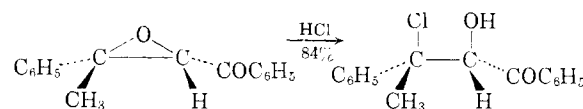
BY HAROLD HART AND RAYMOND J. ELIA[1,2]

Hydrogen chloride cleaves optically active α-phenethyl phenyl ether at 40° to give α-phenethyl chloride and phenol with a minimum of 85–90% retention of configuration, in toluene, 3-pentanone or isobutyl alcohol as solvent (0.25 M solutions). The reaction is kinetically first order in each reactant; the second-order rate constants show a rather small increase with increasing dielectric constant and/or hydroxylic nature of the solvent.

Some years ago we reported[3] that α-phenethyl phenyl ether is cleaved by hydrogen chloride at 50° in benzene with a minimum of 38% retention of configuration (62% racemization). A similar configurational result, with varying retentions of optical purity, was obtained with the corresponding p-tolyl and mesityl ethers, neat, in benzene or in acetone. Retention of configuration required a mechanism for ether cleavage different from those which had previously been considered,[4] and it was suggested that, consonant with the behavior of α-phenethyl systems in other reactions,[5] an SNi ion-pair mechanism was operative.

Subsequently it was shown that cis- and trans-dypnone oxides react stereospecifically with hydrogen chloride, in acetic acid or ethanol, to give chlorohydrin with retention of configuration.[6] Brewster pointed out[7] that the acidic hydrolysis (dilute

$$C_6H_5O\overset{*}{C}HC_6H_5 + HCl \longrightarrow C_6H_5OH + C_6H_5\overset{*}{C}HCl$$
$$\quad\quad\quad | \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad |$$
$$I \quad\quad CH_3 \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad CH_3$$

hydrochloric acid) of trans-α-methylstilbene oxide[8] also proceeds with retention; attention has also been called[6,7] to earlier acidic hydrolyses of cyclic epoxides which give cis-diols. In all cases, a phenyl group is attached to the epoxide carbon at which cleavage occurs.

In view of the high stereospecificity of the epoxide cleavages,[6,7] it seemed desirable to establish with greater precision than in our exploratory study[3] the extent of retention of optical purity in the cleavage of I. It is the purpose of this paper to describe both the stereochemical results and the reaction kinetics in several solvents.

Results

Stereochemistry.—A solution approximately 0.25 M in hydrogen chloride and α-phenethyl phenyl ether was maintained at 40° for a given time, then extracted with 20% alkali to remove the phenol and hydrogen chloride, washed with water, dried and distilled. The rotation of recovered α-phenethyl chloride was compared with the rotation of the chloride originally used to synthesize the ether (via the Claisen procedure). The observed loss in rotation should, in the absence of other factors, represent the total racemization in the two reactions (ether

(3) H. Hart and H. S. Eleuterio, *J. Am. Chem. Soc.*, **76**, 1379 (1954).

(4) For a review, see R. L. Burwell, Jr., *Chem. Revs.*, **54**, 625 (1954).

(5) Numerous examples are cited by E. L. Eliel in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 79 ff.

(6) H. H. Wasserman and N. E. Aubrey, *J. Am. Chem. Soc.*, **78**, 1726 (1956).

(7) J. H. Brewster, *ibid.*, **78**, 4061 (1956).

(8) M. Tiffeneau and J. Levy, *Bull. soc. chim. France*, **49**, 1810 (1931).