described above, in about 60% yield. The m. p.'s and N contents of those not found in the literature are presented in Table I.

TABLE I

PHENYLHYDRAZONES OF β-FORMYLPROPIONIC ACID

Substituents of phenylhydrazine	M. p., °C. cor., dec.	Nitrogen, % Calcd.	Found	
2-Nitro	155–156	17.7	17.4	17.4
2-Chloro	180–185.5	12.4	12.3	12.2
2,4-Dichloro	181–182	10.7	10.4	10.6

4,5-Dihydro-2-(*o*-nitrophenyl)-3(2)-pyridazone.—One gram (0.0042 mole) of the *o*-nitrophenylhydrazone of β-formylpropionic acid was dissolved in concentrated sulfuric acid. After twenty-four hours at room temperature, the solution was poured into a large amount of water. The aqueous solution was extracted with ether, and the ether extract dried with Drierite. The ether was allowed to evaporate and the residue crystallized from hot benzene. There was obtained 0.5 g. (54%) of crystals of m. p. 99–102°. Several recrystallizations from ethanol with addition of water raised the m. p. to 101.5–102°. The compound was not soluble in 5% hydrochloric acid solution, nor immediately soluble in cold 5% sodium hydroxide solution. It dissolved slowly in cold, rapidly in hot, sodium hydroxide solution to give a deep red-brown solution. The color of the solution changed to yellow upon acidification. Analysis indicated this compound to be the pyridazone.

Anal. Calcd. for $C_{10}H_9O_3N_3$: N, 19.2. Found: N, 19.4, 19.2.

Acknowledgments.—Dr. S. W. Loo, now of the Botany Department of the University of Peking, was very helpful in the testing of the compounds. We are indebted to General Mills for a generous supply of technical grade glutamic acid.

Summary

The preparation of a series of substituted 2-methyl-3-indoleacetic acids and of a series of substituted phenylhydrazones of β-formylpropionic acid has been described.

AMES, IOWA RECEIVED[15] APRIL 8, 1948

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[15] Original manuscript received July 10, 1947.

[CONTRIBUTION FROM PHILLIPS PETROLEUM COMPANY, RESEARCH DEPARTMENT]

Relative Rates of Propylation of Monoalkylbenzenes

BY FRANCIS E. CONDON

Repeated observations by many workers that monoalkylation of benzene is accompanied by considerable polyalkylation have indicated that aromatic alkylation, like halogenation[1] and nitration,[2] is faster for an alkylbenzene than for benzene.[3] As indicated by Francis and Reid,[4] the rate of alkylation of a monoalkylbenzene relative to that of benzene can be evaluated from the composition of the reaction mixture. Although they favored the view that the rates are equal, some of their calculations showed that, under some conditions, benzene appeared to be twice as readily ethylated as ethylbenzene.[5] They pointed out, however, that this may not represent the true relative reactivities of benzene and ethylbenzene because the reaction mixture was not homogeneous and because of the possibility of simultaneous dealkylation of polyethylbenzenes.

In the work reported herein, the rates of propylation of toluene, ethylbenzene, cumene and *t*-butylbenzene relative to the rate of propylation of benzene were determined, in competition-type experiments, in homogeneous reaction mixtures and under conditions which were shown to be ineffective for dealkylation of the polyisopropylbenzenes produced. In one series of runs, boron fluoride etherate, which is completely miscible with these hydrocarbons, was used as a catalyst. In other runs, aluminum chloride was the catalyst and nitromethane was the solvent.[6]

I. Experimental Part

Materials.—Commercial C. P. benzene and toluene were distilled, discarding the first and last ten per cents., approximately.

Ethylbenzene, *p*-cymene (both Eastman Kodak Co. White Label) and *t*-butylbenzene (from hydrogen fluoride alkylation of benzene with isobutylene) were distilled in a Podbielniak Hypercal column with Heligrid packing[7]; only middle fractions of constant boiling point were used.

Nitromethane from the Commercial Solvents Corporation was distilled from an ordinary Claisen flask and the first and last ten per cents., approximately, were discarded.

Boron fluoride etherate was obtained from Eastman Kodak Company. The formula $BF_3 \cdot (C_2H_5)_2O$ was assumed.

Reagent quality anhydrous aluminum chloride was used.

The propylene was a high-purity product of Phillips Petroleum Company.

Alkylation Procedure.—Alkylation was carried out in a 500-cc. flask provided with a mercury-sealed Hershberg stirrer,[8] an inlet tube for propylene, a thermometer, and a reflux condenser, the top of which communicated through a Drierite-filled drying tube with a water-bubbler that indicated any escape of propylene. The flask was charged with a mixture of 100–150 g. of aromatic hydrocarbons and boron fluoride etherate or nitromethane and aluminum chloride. The stirrer was started and the

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(1) de la Mare and Robertson, *J. Chem. Soc.*, 279 (1943).

(2) Ingold, Lapworth, Rothstein and Ward, *ibid.*, 1959 (1931).

(3) See, for example, Fieser and Fieser, "Organic Chemistry," D. C. Heath and Co., Boston, 1945, p. 535; Price, in "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, 1946, p. 5.

(4) Francis and Reid, *Ind. Eng. Chem.*, **38**, 1194 (1946).

(5) Coincidentally, relative rates calculated from the data of Slanina, Sowa and Nieuwland, THIS JOURNAL, **57**, 1547 (1935), indicate that benzene is apparently about twice as readily propylated as cumene.

(6) Schmerling, paper presented before the Petroleum Division, ACS Meeting, New York, September, 1947.

(7) Podbielniak, *Ind. Eng. Chem.*, *Anal. Ed.*, **13**, 639 (1941).

(8) Hershberg, *ibid.*, **8**, 313 (1936).

temperature of the mixture was adjusted to 40° by a water-bath. Propylene, dried with Drierite, was introduced above the surface of the mixture only as rapidly as it was absorbed. After two and one-half to five hours in the boron fluoride runs, or one-half to three hours in the aluminum chloride runs, the addition of propylene was stopped, and the catalyst was washed out with water and with sodium hydroxide solution. Enough of the latter was used to remove all nitromethane. After a final wash with water, the mixture was dried with calcium chloride. Tests showed that this rather extensive treatment did not alter the composition of mixtures of aromatic hydrocarbons; and recoveries after fractional distillation quite generally reached 96-97 mole per cent. of the aromatics charged.

Analytical Procedure.—The products were analyzed by fractional distillation in a Podbielniak Hypercal column. Cut points were selected on the basis of analyses of mixtures of known composition. A high-boiling residue, generally less than 10% of the material distilled, was not completely analyzed, but its molecular weight was determined cryoscopically in benzene or, in many cases, was estimated from its probable composition as a mixture of polyalkylbenzenes, so that the composition of the total mixture could be computed in mole fractions.

Calculations.—The relative rate of propylation (benzene = 1) was calculated for toluene, ethylbenzene and *t*-butylbenzene by the well-known formula[2]

$$k'/k = \log (c'/c_0')/\log (c/c_0)$$

derived from the rate equations for irreversible propylation

$$dc/dt = -k(C_3H_6)c \text{ and } dc'/dt = -k'(C_3H_6)c'$$

in which c_0 and c, and c_0' and c', are initial and final mole fractions of benzene, and of alkylbenzene, respectively, in the hydrocarbon part of the reaction mixture. The relative rate of propylation of cumene was evaluated from the formula

$$\log (c + c' - (k'/k)c') = (k'/k) \log c$$

which was derived (for a reaction mixture initially containing no cumene) from the rate equations

$$dc/dt = -k(C_3H_6)c \text{ and } dc'/dt = k(C_3H_6)c - k'(C_3H_6)c'$$

and which is equivalent to the formula derived by Francis and Reid.[4]

Tests for Dealkylation.—Three experiments were made to determine if dealkylation of polyisopropylbenzenes occurred during propylation of benzene, inasmuch as such dealkylation would lead to too low a relative rate of propylation of cumene.

Experiment 1.—A homogeneous mixture of benzene (508 g., 76.0 mole per cent.), polyisopropylbenzenes (mol. wt. = 200; mainly triisopropylbenzenes obtained by vacuum distillation of accumulated residues boiling above 215° from benzene–propylene alkylations) (125.5 g., 7.3 mole per cent.), nitromethane (83.0 g., 15.7 mole per cent.), and aluminum chloride (10.8 g., 1.0 mole per cent.) was stirred at 40° for several hours and samples were withdrawn at intervals for analysis. The results were

Time, minutes	0	33	95	181	323	555
Composition, wt. %						
Benzene	79.6	79.6	79.8	80.2	79.7	79.2
Diisopropylbenzenes	1.5	2.1	2.0	1.6	1.9	2.2
Residue	18.9	18.3	18.2	18.2	18.4	18.6

No cumene was found in any of the samples, nor did the composition of the mixture apparently change.

Experiment 2.—A homogeneous mixture of benzene (304.6 g., 59.9 mole per cent.), polyisopropylbenzenes (76.2 g., 5.8 mole per cent.), nitromethane (111.0 g., 27.9 mole per cent.), and aluminum chloride (55.7 g., 6.4 mole per cent.) was treated as in Expt. 1. The results of analysis of samples were

Time, minutes		0	33	136
Composition, wt. %	Benzene	80.0	77.9	76.3
	Cumene	..	2.4	5.1
	Diisopropylbenzenes	..	0.9	3.2
	Residue	20.0	18.8	15.4

Depropylation took place under these conditions. The conditions of this experiment were, however, more conducive to depropylation than the conditions used in the propylation experiments. The concentrations of both the polyisopropylbenzenes and the catalyst were higher than in the propylation runs.

Experiment 3.—A homogeneous mixture of benzene (61.3 mole per cent.), *p*-cymene (21.7 mole per cent.), nitromethane (15.8 mole per cent.), and aluminum chloride (1.2 mole per cent.) was stirred at 65° and propylene was passed into it for two hours. The catalyst was washed out with water and the nitromethane with sodium hydroxide solution, and the alkylate was dried and analyzed by fractional distillation. No toluene was found, indicating that depropylation of the cymene did not take place; furthermore, the recovered cymene was pure *p*-cymene, with no *o*- and no *m*-cymene, indicating that no depropylation of the isopropylcymenes produced in the reaction took place.

In addition, it is noteworthy that no xylenes were found among the products of propylation of toluene-containing mixtures, indicating that no demethylation took place during propylation; and no diethylbenzenes were found among the products of propylation of ethylbenzene-containing mixtures, indicating that no deëthylation took place.

II. Results

The results from 51 competition experiments are summarized in Table I. In the first row are averages of two runs each in which the reaction mix-

TABLE I

RELATIVE RATES OF PROPYLATION AT 40° (BENZENE = 1)

Catalyst	Toluene	Ethylbenzene	Cumene	*t*-Butylbenzene
Boron fluoride	2.09 ± 0.10	1.73 ± 0.06	....	1.23 ± 0.06
Aluminum chloride	2.10 ± 0.15	1.81 ± 0.14	1.69 ± 0.05	1.40 ± 0.16

tures contained 27 mole per cent. boron fluoride and 27 mole per cent. diethyl ether. In the second row are averages of from 7 runs in the case of *t*-butylbenzene to 19 runs in the case of cumene, for aluminum chloride concentrations of 1.0 to 7.7 mole per cent. and nitromethane concentrations of 12.7 to 42 mole per cent. No dependence of the rate ratios on either of these concentrations could be found in runs in which one was varied while the other was held constant, although the results for any one compound were quite scattered, as is indicated by the rather large average deviation from the mean. This scattering is attributable to limitations in the analytical method (fractional distillation). The fact that the relative rates were independent of the aluminum chloride concentration, within experimental error, whereas the rate of depropylation was demonstrated to be dependent on the aluminum chloride concentration (see Experimental Part), indicates that not enough depropylation was taking place in those runs in which the conditions were most favorable for it (high aluminum chloride concentration and long contact time) to influence detectably the apparent relative rates. (Noteworthy here are results of some preliminary attempts to measure relative rates of alkylation with isobutylene. It appeared that *t*-butylbenzene was three to six times as readily butylated as benzene when the aluminum chloride concentration was about 4 mole per cent. but 12–14 times as readily when the catalyst concentration was only 1.3 mole per cent. The lower apparent relative rate is attributable to a greater amount of dealkylation, which would be easier for a *t*-butyl than for an isopropyl group, in the presence of the greater catalyst concentration.)

III. Discussion

The relative rates of propylation of the alkylbenzenes listed in Table I are in the same order as their relative rates of chlorination and bromination.[1] In order to account for this order of reactivity, both steric hindrance in the ortho position, increasing with the size of the alkyl group, and a no-bond resonance involving the α-hydrogen atoms of the alkyl group have been suggested.[9] The most important factor in propylation appears to be steric hindrance in the ortho positions. The propylation of toluene gives 31% *o*-, 25% *m*-, and 44% *p*-cymene,[10] and the propylation of cumene gives 7% *o*-, 43% *m*-, and 50% *p*-diisopropylbenzene[11]; and, relative to one position in benzene, the rate of propylation of toluene is $6 \times 2.10 = 12.6$, and that of cumene is $6 \times 1.69 = 10.1$; so that the relative rate of propylation of toluene in an ortho position is $12.6 \times 0.31/2 = 1.95$, and the relative rate of propylation of cumene in an ortho position is $10.1 \times 0.07/2 = 0.35$; similarly, the relative rates of propylation of toluene and cumene in a meta position are $12.6 \times 0.25/2 = 1.6$ and $10.1 \times 0.43/2 = 2.2$, respectively, and in the para position, $12.6 \times 0.44 = 5.5$ and $10.1 \times 0.50 = 5.1$, respectively.[12] That is, the rates of propylation in the meta and para positions are approximately the same for toluene and cumene, whereas the rate of propylation in an ortho position of cumene is only about one-sixth the rate of propylation in an ortho position of toluene, and the difference, which is attributable to steric hindrance, is sufficient to account for all the difference in reactivities of toluene and cumene.

Acknowledgment.—Phillips Petroleum Company made possible the publication of this work.

Summary

The relative rates of propylation of benzene, toluene, ethylbenzene, cumene and *t*-butylbenzene are 1, 2.1, 1.8, 1.7 and 1.4, respectively. Steric hindrance in the ortho positions, increasing with the size of the alkyl group, appears to be the principal cause of the differences in rates of propylation of the alkylbenzenes.

BARTLESVILLE, OKLAHOMA RECEIVED FEBRUARY 2, 1948

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[9] See Berliner and Bondhus, THIS JOURNAL, **68**, 2355 (1946), for a review and additional references.

[10] Simons and Hart, *ibid.*, **69**, 979 (1947). Averages were taken of all the values reported.

[11] Melpolder, Woodbridge and Headington, *ibid.*, **70**, 935 (1948).

[12] It is supposed that the isomeric dialkylbenzenes are formed principally by direct alkylation at the various available positions, and not to any great extent by isomerization nor by dealkylation of trialkylbenzenes as suggested by Price and Ciskowski, *ibid.*, **60**, 2499 (1938).