TABLE VI (*Continued*)

Min.	CH_4, ml.[e]	CH_4, %	Min.	CH_4, ml.[e]	CH_4, %
$(CH_3)_3SiCH_2CH_2CH_2COOH$					
	Run 45[c]			Run 47[d]	
1.0	1.30	5.48	5.0	2.60	9.52
2.0	2.75	11.60	10.0	5.20	19.05
3.0	4.15	17.51	15.0	7.40	27.11
4.0	5.60	23.63	20.0	9.50	34.80
5.0	6.72	28.35	25.0	11.40	41.76
7.0	8.94	37.72	30.0	13.10	47.99
8.0	9.90	41.77	35.0	14.70	53.85
10.0	11.75	49.57	40.0	16.10	58.97
12.0	13.30	56.11	46.0	17.50	64.10
14.0	14.75	62.23	60.0	20.30	74.36
18.0	16.93	71.43	80.0	23.10	84.62
21.0	18.20	76.79	95.0	24.45	89.56
25.0	19.57	82.57	110.0	25.40	93.04
31.0	21.00	88.60	192.0	27.30	100.00
45.0	22.54	95.10			
100.0	23.70	100.00			

[a] 730.1 mm. 25.0°, 1.060 × 10^{-3} mole sample, gas collected at 27°, % CH_4 calcd. [b] 738.4 mm., 15.0°, 0.995 × 10^{-3} mole sample, gas collected at 23°, % CH_4 calcd. [c] 743.3 mm., 25.0°, 1.017 × 10^{-3} mole sample, gas collected at 26.5°, % CH_4 based on final volume. [d] 735.0 mm., 15.0°, 1.180 × 10^{-3} mole sample, gas collected at 28°, % CH_4 based on final volume. [e] Uncorrected.

first-order kinetics and constant reaction rate constants. This was caused by a small amount of cleavage to form butyric acid. When the percentage of methane evolved was calculated from that expected from quantitative cleavage of a methyl group the poor first-order kinetics shown by the dashed line in Fig. 3 was obtained. If, however, the percentage methane was calculated as the percentage of the final volume obtained in each of the reactions, excellent first-order kinetics resulted. This is shown in Figs. 4 and 5 and in Tables IV and V for the cleavages conducted at 25 and 15°. The experimental data for two of these runs appear in Table VI. It is noteworthy that constant values were obtained for a reaction rate constant which was doubly dependent upon the concentration of un-ionized sulfuric acid.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STANFORD UNIVERSITY]

Organic Peroxides. IV. Higher Dialkyl Peroxides

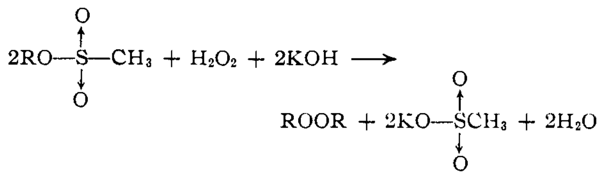
BY FRANK WELCH, HOMER R. WILLIAMS AND HARRY S. MOSHER

RECEIVED AUGUST 30, 1954

Several new primary and secondary saturated dialkyl peroxides have been prepared by the direct alkylation of hydrogen peroxide with two equivalents of alkyl methanesulfonate in homogeneous methanol–water–potassium hydroxide solution. These peroxides have been found to be relatively stable to mineral acids but labile to alkali and to resemble di-*t*-butyl peroxide in their thermal stability and other observed properties.

Dialkyl peroxides have been prepared in the past by three main methods[1]: first, the alkylationof hydrogen peroxide with alkyl sulfates in the presence of base; second, the alkylation of hydrogen peroxide by tertiary carbonium ions or their equivalent; and third, the alkylation of alkyl hydroperoxides with either alkyl sulfates, alkyl hydrogen sulfates or alkyl halides.[1] The first of these methods appears to be limited to the preparation of the lower dialkyl peroxides because of the relative inaccessibility of the alkyl sulfates above butyl. The second method has been reported only for the preparation of ditertiary alkyl peroxides. The third method is the most general and the only usable method for the preparation of unsymmetrical dialkyl peroxides. Since the higher primary and secondary alkyl hydroperoxides have only recently become available,[2] this third method has been limited in the past to those dialkyl peroxides containing a tertiary radical or to the few lower members of the series where the normal or secondary hydroperoxide was available. Thus the di-*n*-alkyl peroxides above propyl have not been reported previously.

It has now been demonstrated that alkyl methanesulfonates can be employed successfully in the alkylation of hydrogen peroxide to give primary and secondary *dialkyl peroxides* in satisfactory yields. The conditions for the dialkylation of hydrogen peroxide differ only in the ratio of the reactants from those previously reported[2] for the monoalkylation. When a large excess of hydrogen peroxide was used, the formation of the hydroperoxide was favored,[2] but when two moles of alkyl methanesulfonate were used for each mole of hydrogen peroxide according to the following equation, the dialkyl peroxide was the predominant reaction product.



$$2RO-\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}}-CH_3 + H_2O_2 + 2KOH \longrightarrow ROOR + 2KO-\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}}CH_3 + 2H_2O$$

When one considers the competing side reactions, basic hydrolysis of the alkyl methanesulfonate, decomposition of the hydrogen peroxide and the intermediate alkyl hydroperoxide, and basic decomposition of the dialkyl peroxide itself, it is quite remarkable that yields as high as 45 to 65% as reported in Table I have been obtained.

Some idea of the relative rate of the desired reaction as compared to the rate of the competing reaction of hydrolysis of the alkyl methanesulfonate is obtained from the data represented in Fig. 1

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(1) For reviews on the preparations of peroxides see: (a) A. Rieche, "Alkyl Peroxyde und Ozonide," Theodor Steinkoff, Dresden, 1931, pp. 27–34; (b) W. Eggersglüss, "Peroxyde," Verlag Chemie, Weinheim, 1950; (c) R. Criegee, "Methoden der Organische Chemie," Vierte Auflage, Vol. VIII, Georg Theime Verlag, Stuttgart, 1952, pp. 9–61; (d) A. V. Tolbolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publ. Inc., New York, N. Y., 1954; (e) N. A. Milas, Encyclopedia of Chemical Technology, Interscience Publ., Inc., New York, N. Y., Vol. 10, 1953, p. 38.

(2) H. R. Williams and H. S. Mosher, THIS JOURNAL, **76**, 2984, 2987, 3495 (1954).

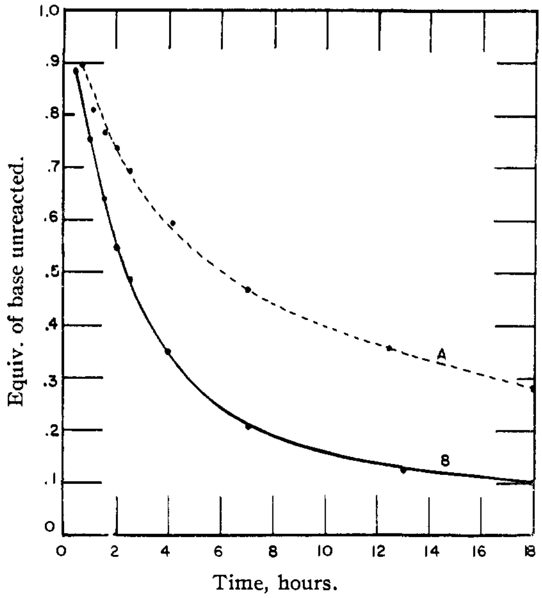

Fig. 1.—Relative rates of disappearance of base in the solvolysis of *n*-butyl methanesulfonate in the presence and absence of hydrogen peroxide: curve A, ------, 7.6 g. (0.050 mole) of *n*-butyl methanesulfonate, 5.6 g. (0.050 mole) of 50% KOH, 3 ml. of water and 18 ml. of methanol; curve B, ——, same reaction mixture as represented by curve A except that the 3 ml. of water was replaced with 3.4 g. (0.025 mole) of hydrogen peroxide.

where the rate of disappearance of base in a reaction mixture containing *n*-butyl methanesulfonate and potassium hydroxide, but lacking the hydrogen peroxide, is compared to the rate of disappearance of base when the hydrogen peroxide is present. The two reaction mixtures are not completely comparable since the presence of hydrogen peroxide may exert an effect on the rate of hydrolysis of the butyl methanesulfonate. However, any such effect should be small as compared to the difference demonstrated. It is therefore readily apparent that the solvolysis reaction with hydrogen peroxide is very appreciably greater than with water.

TABLE I

DIALKYL PEROXIDES

Peroxide	Yield,[a] %	B.p., °C.	Mm.	n^{20}_D[b]	Formula	Analyses[b,d] Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found
n-Butyl	48	61	20	1.4062	$C_8H_{18}O_2$	65.71	65.95	12.41	12.61
s-Butyl	17	59	50	1.4018	$C_8H_{18}O_2$	65.71	65.85	12.41	12.57
i-Butyl	10	34–36	10	1.3996	$C_8H_{18}O_2$	65.71	65.50	12.41	12.21
n-Amyl	57	42	1	1.4168	$C_{10}H_{22}O_2$	68.91	69.01	12.72	12.73
i-Amyl	50	54	5	1.4133	$C_{10}H_{22}O_2$	68.91	68.98	12.72	12.69
n-Hexyl	62	58	0.5	1.4248	$C_{12}H_{26}O_2$	71.23	71.27	12.95	12.91
2-Hexyl[c]	28	39–44	0.5	1.4200	$C_{12}H_{26}O_2$	71.23	70.35	12.95	12.70
n-Heptyl	72	78	1	1.4307	$C_{14}H_{30}O_2$	72.98	73.58	13.13	13.16

[a] All yields are of the crude material which has been distilled once with the exception of *n*-butyl which was the yield on carefully fractionated product. [b] The refractive indices and analyses are for purified materials obtained as indicated in the Experimental section. [c] Infrared spectra indicate contamination by a small amount of alkyl methanesulfonate. [d] Analyses by Charles Koch, Microchemical Specialties Co., Berkeley, Calif.

The crude dialkyl peroxides, which were isolated by extraction with hexane and distillation at reduced pressure, were always contaminated with unreacted alkyl methanesulfonate. Careful fractionation under vacuum was sufficient to obtain analytically pure samples of di-*n*-butyl, di-*s*-butyl, di-*n*-amyl and diisoamyl peroxides; but the volatilities of the higher methanesulfonates were so similar to those of the corresponding dialkyl peroxides that satisfactory separation by distillation could not be achieved. Di-*n*-hexyl peroxide and the higher members were purified by refluxing the crude mixture of the alkyl methanesulfonate and dialkyl peroxide with 40% sulfuric acid to which had been added enough methanol (or isopropyl alcohol) to give a homogeneous solution. This treatment destroyed the alkyl methanesulfonate and left most of the dialkyl peroxide unchanged; any remaining small amount of alkyl methanesulfonate or carbonyl impurities was removed readily by adsorption on alumina.

The infrared spectra were a very sensitive means of testing for impurities due to alkyl methanesulfonate or carbonyl compounds. The spectra of the dialkyl peroxides all had a strong band in the region 8.8 to 8.9 μ which was absent in the spectra of the alkyl methanesulfonates; the latter had a very intense band at 8.5 μ that was lacking in the dialkyl peroxides. Any carbonyl impurities absorbed strongly around 5.9 μ, a region which was devoid of absorption in the pure dialkyl peroxides. In a synthetic mixture which was prepared from purified di-*n*-amyl peroxide and 0.25 weight per cent. each of *n*-amyl methanesulfonate and methyl *n*-propyl ketone, the presence of the two impurities was clearly indicated by these characteristic absorption bands in the infrared taken on a thin film without spacer.

The primary dialkyl peroxides, *n*-butyl, *n*-amyl, isoamyl and *n*-hexyl were obtained in yields of 48 to 67% as indicated in Table I; diisobutyl peroxide was obtained in very poor yield as would be expected.[2] The secondary dialkyl peroxides were obtained in poor yields, and only the di-2-hexyl and di-*s*-butyl peroxides were carried to a satisfactory state of purity as shown by carbon and hydrogen analyses and infrared spectra.

The infrared spectra of the purified dialkyl peroxides are summarized and compared in Table II. None of the dialkyl peroxides reported in Table II showed absorption in the region 2.9–3.0 μ which indicated the absence of contaminating alcohol or hydroperoxide. There was essentially no ab-

TABLE II

INFRARED ABSORPTION BANDS OF DIALKYL PEROXIDES

				Wave length in microns[a]					
n-Propyl[b]	*n*-Butyl	*i*-Butyl	*s*-Butyl	*t*-Butyl[b]	*n*-Amyl	*i*-Amyl	*n*-Hexyl	2-Hexyl	*n*-Heptyl
6.74w	6.73i				6.74i	6.73i	6.76i		6.74i
6.82s	6.82s	6.80s	6.82s	6.80m	6.82s	6.80s	6.82s	6.82s	6.82s
6.94w	6.96i		6.90i	6.86i	6.96i	6.96i	6.96i		6.96i
7.20s		7.18s		7.23s	7.24s	7.20i	7.25s	7.28s	7.24s
7.32s	7.26sb	7.28s	7.26s	7.34s	7.32s	7.28s	7.32s	7.48s	7.32s
7.44i	7.45i	7.44i	7.48s			7.46i			
7.80w	7.68m	7.68m	7.70m		7.71m	7.68w	7.68m		7.68m
	7.98m	7.92w	7.90w	8.04s		7.96m	7.82w	7.98m	7.90w
8.12w	8.18w	8.08w			8.10w	8.18w	8.14w	8.20m	8.20w
				8.38s	8.25m		8.33m		8.40w
	8.70i		8.60i						
8.94m	8.86s	8.86m	8.80s		8.90m	8.76s	8.90s	8.80s	8.90m
			9.00s					8.96s	
9.14w									
9.42s									
9.58s	9.38s				9.52sb	9.48s	9.54sb	9.50s	9.54sb
9.88s	9.74s	9.74s	9.72s	9.78m		9.68w	9.84sb	9.84s	9.70sb
			10.02s		10.00sb	9.96w			9.98sb
			10.12s			10.18w		10.17m	
10.35s	10.30s	10.38s	10.32s			10.36w		10.30i	10.34s
	10.56m	10.60i					10.80s		
		10.84m		10.87w		10.84m		10.88s	
11.02w	11.06m	11.08m	11.94s						11.06w
11.26w					11.24m		11.20i		
11.62w	11.82m	11.84i	11.70w	11.40s	11.72w	11.70w		11.82m	11.50w
		11.98i	12.08m			12.00m		12.06w	11.86w
		12.20m	12.20w						
	12.35w	12.40i			12.25w	12.36w	12.30wb	12.78m	
			12.84m		12.88w		13.10w		12.90w
13.12w	13.52m			13.32m	13.70m	13.04w	13.78s	13.70s	13.80s

[a] The symbols w, m and s refer to weak, medium or strong absorption as shown on a thin film. The designation i denotes an inflection on a larger and stronger band while sb refers to a strong and broad absorption band. [b] The spectra of di-*n*-propyl and di-*t*-butyl peroxides have been added for purposes of comparison.

sorption in the region of 5.9 μ with the purified peroxides which showed the correct carbon and hydrogen analyses, but di-2-heptyl peroxide and some of the other peroxides prior to purification showed moderate absorption at 5.9 μ which indicated the presence of some carbonyl contaminants resulting from decomposition of the dialkyl peroxide. The impurities responsible for this carbonyl absorption usually could be removed by adsorption on activated alumina. The band near 8.9 μ which was common to all of the dialkyl peroxides corresponds to the reported carbon–oxygen stretching vibration in ethers.[3] Alkyl hydroperoxides have all shown absorption near 11.2–11.4 μ, usually weak, which has been correlated with the oxygen–oxygen stretching frequency.[4,5] The corresponding band in these dialkyl peroxides does not seem to be as well defined but appears to be the band from 11.40 μ (for di-*t*-butyl peroxide) to 11.84 μ (for diisobutyl peroxide). The spectrum of the well known di-*t*-butyl peroxide[4] has been added to Table II for purposes of comparison.

Although these dialkyl peroxides were quite stable to strong mineral acids, we have observed, as previously reported by Kornblum and DeLaMare[6] for 1-phenylethyl-*t*-butyl peroxide, that the dialkyl peroxides which have a hydrogen on the peroxidic carbon atom are decomposed by base with the formation of carbonyl compounds.

Acknowledgment.—We wish to thank the California Research Corporation for a grant which made these investigations possible.

Experimental

General Preparative Procedure for Dialkyl Peroxides.—A mixture of 0.1 mole of the appropriate alkyl methanesulfonate,[2] 0.05 mole of "30%" aqueous hydrogen peroxide, and 35 to 60 ml. of methanol as designated in Table III was cooled to 0 to 8°, 0.1 mole of 50% aqueous potassium hydroxide was added over a period of a few minutes with stirring, and the mixture was allowed to come slowly to room temperature. The amount of methanol was chosen to give a homogeneous solution. Potassium methanesulfonate began to separate from the reaction mixtures after periods varying from approximately one to four hours depending upon the structure of the alkyl methanesulfonate and on the amount of water present. Since it had been determined that 30% hydrogen peroxide slowly decomposed in the presence of base in methanol solution of this concentration and at this temperature, a second addition of 0.025 mole of "30%" hydrogen peroxide was made after approximately five hours.[7] The reaction mixture was then allowed

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(3) F. A. Miller, in H. Gilman, "Organic Chemistry, An Advanced Treatise," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 148.

(4) O. D. Shreve, M. R. Heether, H. B. Knight and D. Swern, *Anal. Chem.*, **23**, 282 (1951).

(5) H. R. Williams and H. S. Mosher, *ibid.*, **27**, in press (1955).

(6) N. Kornblum and H. E. DeLaMare, THIS JOURNAL, **73**, 880 (1951).

(7) In one experiment on the preparation of di-*n*-butyl peroxide the second addition of hydrogen peroxide was omitted and the yield was 45% with 18% of *n*-butyl methanesulfonate recovered. It is therefore possible that this second addition of hydrogen peroxide is not necessary.

to stir for an additional 10 to 15 hours. The ratio of reactants, summary of conditions and yields are given in Table III. The reaction mixture was worked up by adding water,[8] in order to dissolve the potassium methanesulfonate, extracting the aqueous solution with several 10-ml. portions of hexane, washing the hexane layer with 5 ml. of 5% potassium hydroxide solution to remove any hydroperoxide, then washing the hexane layer with distilled water until the washings were neutral, and drying the hexane layer over anhydrous sodium sulfate. The solvent was then removed under a slight vacuum through an 8-inch column packed with glass helices and the residue distilled. In the case of the isomeric dibutyl peroxides, vacuum distillation through an 8-inch Vigreux column completely separated the peroxide from the unreacted, higher boiling alkyl methanesulfonate. Redistillation through the same Vigreux column was sufficient to obtain the purified di-*n*-amyl peroxide; but fractionation through a small column was better and was, in fact, necessary for purification of the diisoamyl peroxide. Di-*n*-hexyl peroxide was not completely separated from the *n*-hexyl methanesulfonate by careful fractionation through a 1.2 × 45 cm. column packed with 1/8 inch glass helices, and it was therefore necessary to resort to another method of purification as indicated below in those cases with twelve or more carbon atoms.

TABLE III

PREPARATION OF DIALKYL PEROXIDES

	Alkyl methane-sulfonate g.	Alkyl methane-sulfonate mole	Methanol, ml.	50% KOH soln., g.	Total "30%" H_2O_2, g.[c]	Time, hr.	Crude yield,[a] %
n-Butyl	30.4	0.20	70	22.4	13.6	15	44[b]
2-Butyl	106.4	.70	280	80	60.0	23	17
Isobutyl	15.2	.10	50	11.2	10.2	23	10
n-Amyl	16.6	.10	50	11.2	10.2	18	57
n-Amyl	49.8	.35	150	33.6	28.0	12	48
Isoamyl	16.6	.10	50	11.2	10.2	18	50
2-Pentyl	7.4	.045	20	5.0	4.5	24	20
n-Hexyl	9.0	.05	30	5.6	5.1	22	62
2-Hexyl	9.0	.05	30	5.6	5.1	18	28
n-Heptyl	9.7	.05	30	5.6	5.1	22	72

[a] Yield of the once-distilled peroxide fraction based upon the amount of the alkyl methanesulfonate taken. [b] If the amount of recovered *n*-butyl methanesulfonate is taken into account this yield would be 48%. [c] The hydrogen peroxide used in all of these experiments was 25.3% by titration.

The peroxides could be purified from contaminating alkyl methanesulfonate by refluxing with 5 g. of 40% sulfuric acid and 10 ml. of methanol per gram of peroxide. In the case of di-*n*-heptyl peroxide, isopropyl alcohol was used in place of methanol to make the mixture homogeneous. The time necessary for the hydrolysis of the contaminating heptyl and hexyl methanesulfonates was 11 to 12 hours. The course of the purification could be followed readily by the characteristic absorption band in the infrared at 8.5 μ possessed by the alkyl methanesulfonates but lacked by the dialkyl peroxides studied. The mixture was cooled, diluted with an equal volume of water and extracted with hexane. The hexane extracts were washed with potassium hydroxide solution, washed with water and dried over anhydrous sodium sulfate; and the purified product was recovered by distillation. If the infrared spectra of a test sample indicated the presence of carbonyl contaminants, resulting from decomposition of some of the dialkyl peroxide during the acid treatment, the hexane solution was stirred with alumina and filtered before distillation. The new dialkyl peroxides along with their properties are given in Table I.

Initial experiments on attempted purification of the dialkyl peroxides by basic hydrolysis of the contaminating alkyl methanesulfonate showed that these peroxides were attacked readily by base. Thus the decomposition of di-*n*-amyl peroxide was essentially complete upon refluxing for one hour in 25% aqueous potassium hydroxide in enough methanol to give a homogeneous solution. Di-*n*-heptyl peroxide was decomposed similarly by standing for 15 hours at room temperature in an aqueous potassium hydroxide–methanol solution. No noticeable decomposition as measured by infrared spectra had been observed for several of these dialkyl peroxides after storage for one year at approximately 0°.

STANFORD, CALIFORNIA

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[8] In several experiments the potassium methanesulfonate was filtered and washed with methanol and hexane. The recovery amounted to 55 to 70% in these cases. The amount which was soluble in the aqueous methanol was, of course, not recovered.

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

Sodium Catalyzed Reactions. II.[1] Side-chain Ethylation of Alkyl Aromatic Hydrocarbons Catalyzed by Sodium

BY HERMAN PINES,[2a] J. A. VESELY AND V. N. IPATIEFF[2b]

RECEIVED JULY 16, 1954

It has been found that side-chain ethylation of alkylbenzenes or of related hydrocarbons, such as indan, can be accomplished by treating ethylene with alkylbenzenes in the presence of a catalyst consisting of sodium and a promoter. Promoters which were effective for the side chain ethylation usually consisted of organic compounds which presumably react with sodium to form organosodium compounds. The side-chain ethylation occurs with alkylbenzenes which have at least one hydrogen atom on the α-carbon atom attached to the aromatic ring. Toluene formed *n*-propylbenzene and 3-phenylpentane, cumene yielded *t*-amylbenzene, xylenes formed the corresponding *n*-propyltoluenes, indan produced 1-ethylindan, etc. A mechanism for the reaction is proposed.

The ring alkylation of aromatic hydrocarbons has been the subject of extensive studies in the literature. Catalysts which have been used for this reaction consist of acids or acid-acting compounds. The catalysts used most widely for the ethylation of benzene and of alkylbenzenes are aluminum chloride–hydrogen chloride,[3a] silicophosphoric acid[3b,c] and silica–alumina (cracking catalyst).[3d] None of these catalysts has been reported to cause any side-chain ethylation of the alkylbenzenes present or formed during the reaction.

The present work shows that side-chain ethylation of alkylbenzenes or of related hydrocarbons, such as indan, can be accomplished by treating ethylene with alkylbenzenes in the presence of a catalyst consisting of sodium and a promoter. The

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[1] For paper I of these series see H. Pines, J. A. Vesely and V. N. Ipatieff, THIS JOURNAL, **77**, 347 (1955).

[2] (a) The Ipatieff High Pressure and Catalytic Laboratory, Department of Chemistry, Northwestern University, Evanston, Illinois; (b) Deceased, November 29, 1952.

[3] (a) C. C. Price, "Organic Reactions," Vol. III, Chapt. I, John Wiley and Sons, Inc., New York, N. Y., 1946; (b) V. N. Ipatieff and L. Schmerling, *Ind. Eng. Chem.*, **38**, 400 (1946); (c) W. J. Mattox, *Trans. Am. Inst. Chem. Eng.*, **41**, 463 (1945); (d) A. A. O'Kelly, J. Kellet and J. Plucker, *Ind. Eng. Chem.*, **39**, 154 (1947).