

Anal. Calcd. for $C_9H_{15}N_5O_{10}$: C, 30.60; H, 4.24; N, 19.83; OCH_3 , 8.78. Found: C, 31.17; H, 4.49; N, 20.11; OCH_3 , 8.19.

Bis-(2,2-dinitropropyl)-glycyl Chloride.—A mixture of 78 g. (0.23 mole) of bis-(2,2-dinitropropyl)-glycine and 190 ml. of thionyl chloride was refluxed overnight. The solution was evaporated to dryness *in vacuo*, leaving a brown solid. Recrystallization from chloroform gave white crystals, 41.0 g. (50%), m.p. 64–65°.

Anal. Calcd. for $C_8H_{12}N_8O_9Cl$: C, 26.86; H, 3.38; N, 19.14; Cl, 9.91. Found: C, 27.48; H, 3.68; N, 19.27; Cl, 9.70.

5,5-Dinitro-2-piperidone-N-acetic Acid (VI).—A solution of 7.5 g. (0.1 mole) of glycine, 4.0 g. (0.1 mole) of sodium hydroxide and 50 ml. of water was mixed with 22.2 g. (0.1 mole) of methyl 5-hydroxy-4,4-dinitropentanoate. A yellow solution was formed and the temperature rose to 38°. The mixture was allowed to stand overnight. Acidification with dilute sulfuric acid caused an oil to separate, which soon crystallized. The product was collected, washed with water and dried to give 15.2 g. (61.5%) of white solid. Recrystallization from methanol-water and ether gave colorless crystals, m.p. 128–130°. This compound gave a negative test for the methoxyl group.

Methyl 5,5-Dinitro-2-piperidone-N-acetate (VII).—A mixture of 20.0 g. (0.081 mole) of 5,5-dinitro-2-piperidone-N-acetic acid, 150 ml. of methanol and 10 ml. of concentrated sulfuric acid was refluxed for 90 minutes. The solution was diluted with 250 ml. of methylene chloride and washed with water, 5% sodium carbonate solution and water. After drying over sodium sulfate, the solvent was evaporated leaving crystals. Recrystallization from methanol gave

16.0 g. (75.8%) of product, m.p. 126–130°. The mixed melting point with the free acid (m.p. 128–130°) was depressed to 105–111°.

Anal. Calcd. for $C_8H_{11}N_5O_7$: C, 36.79; H, 4.26; N, 16.09. Found: C, 37.51; H, 4.33; N, 16.32.

Bis-(2,2-dinitropropyl)-hydrazine (VIII).—A solution of 52.0 g. of 85% hydrazine hydrate, 300 ml. of water and 75 ml. of glacial acetic acid was heated to 60°. At this temperature a solution of 50.0 g. (0.33 mole) of 2,2-dinitropropanol in 150 ml. of methanol was added within 15 minutes. A viscous oil immediately separated. The mixture was stirred at 60° for one hour. After cooling the oily layer crystallized to give 36 g. (73.0%) of white solid, m.p. 83–85°. Recrystallization from ether or chloroform gave colorless prisms, m.p. 85–86°.

Azo-(2,2-dinitropropane) (IX).—A solution of 5.0 g. (0.017 mole) of bis-(2,2-dinitropropyl)-hydrazine in 50 ml. of methanol was cooled to 0° and bromine was added with vigorous stirring until the bromine was no longer bleached. The temperature was kept below 5° by means of external cooling. After a short time crystals precipitated, which were collected and washed with absolute ether. Recrystallization from methanol gave 2.3 g. (46.3%) of colorless crystals, m.p. 101–101.5°.

Anal. Calcd. for $C_8H_{10}N_8O_8$: C, 24.49; H, 3.43; N, 28.57. Found: C, 24.85; H, 3.49; N, 28.80.

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Sodium and Potassium Alkoxides as Catalysts for Carbanion Reactions of Hydrocarbons¹

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Sodium and potassium alkoxides, when heated to decomposition temperatures, catalyze carbanion reactions such as the dehydrogenation of *d*-limonene, double bond isomerization of olefins, and the side chain alkylation of alkylarenes. Alkoxides of tertiary alcohols are far more effective than those of primary or secondary alcohols. A mechanism for the alkoxide decomposition is proposed, and some similar reactions are discussed.

Organosodium compounds and sodium hydride have been reported to be catalysts for certain reactions that apparently proceed by carbanion mechanism: (a) isomerization of olefins, (b) dehydrogenation of monocyclic terpenes, (c) side chain alkylation of alkylarenes by olefins.³

It has been found that potassium *t*-butoxide can promote reactions a, b as well as c at temperatures of 250–300°, which cause alkoxide decomposition, but that it is most effective for b. Reaction c is promoted by a trace of hydroxide ion with the *t*-alkoxide. An autoclave was used, the experiments being of 4–12 hours duration. Limonene changed into *p*-cymene in yields of 95–97% using either potassium *t*-butoxide or *t*-pentoxide, whereas it

dropped to 3–4% with the isopropoxide, 1.5% with the methoxide, and 0% with the phenoxide or with no alkoxide. The experimental data obtained are summarized in Table I. The solid residue from the *t*-butoxide experiments, on acidification, yielded some 3,5-dimethylphenol and isovaleric acid.

Potassium *t*-butoxide caused 8% isomerization of 1-*p*-menthene on heating for 5.5 hours at 260–265°. The same catalyst, containing a trace of potassium hydroxide, was effective for the formation of *n*-propylbenzene from ethylene and toluene at 279–291°, or *t*-pentylbenzene (containing a trace of 1,1-dimethylindan) from cumene and ethylene. The experimental conditions and yields are summarized in Table II.

Methane was found in the reactions catalyzed by potassium *t*-butoxide while small amounts of ethane as well as methane were obtained from the experiments carried out with potassium *t*-pentoxide. The presence of methane is due to the decomposition of the alkoxide at 280° as shown in Experiment 8. No methane was produced however when powdered potassium hydroxide in *t*-butyl alcohol was heated to the same temperature (ex-

(1) Paper IX of the series of Base Catalyzed Reactions. For paper VIII see H. Pines and M. Kolobielski, *THIS JOURNAL*, **79**, 1698 (1957).

(2) Predoctoral Fellow: Universal Oil Products Company, 1954–1955, Standard Oil Company (Indiana) 1955–1956.

(3) (a) H. Pines, J. A. Vesely and V. N. Ipatieff, *THIS JOURNAL*, **77**, 347 (1955); (b) **77**, 554 (1955); (c) H. Pines and H. E. Eschinazi, *ibid.*, **77**, 6314 (1955); (d) **78**, 1178 (1956); (e) H. Pines and V. Mark, *ibid.*, **78**, 4316 (1956); (f) H. Hart, *ibid.*, **78**, 2619 (1956); (g) A. A. Morton and E. J. Lanpher, *J. Org. Chem.*, **20**, 839 (1955); (h) **21**, 93 (1956).

TABLE I
 REACTIONS OF LIMONENE^a

Expt.	Alkoxide	Conditions		Pressure at max. temp. atm.	Recovered C ₁₀ Fraction			Kind	Gases ^b	Mole %
		Temp., °C.	Hr.		Wt. %	α^{25D}	<i>p</i> -Cymene, %			
1	<i>i</i> -PrOK	291	8.6	51	85	74	4.3	H ₂ CH ₄	0.16 .062	
2	<i>i</i> -PrONa	290 ± 3	6	28	77	86	3.0	H ₂ CH ₄	.072 .054	
3	<i>t</i> -PeOK	251	9	113	99 ^c	0	97	H ₂ CH ₄ C ₂ H ₆	.47 .06 .003	
4	MeONa	300 ± 2	9	10	74	91	1.5	H ₂ CH ₄	.03 .001	
5	PhOK	285 ± 5	7	9	95	100	0	None		
6	None	281 ± 4	7.5	7	85 ^d	97	0	None		
7	<i>t</i> -BuOK	257 ± 5	8.5	122	98	0	95 ^e	H ₂ CH ₄	.38 .24	

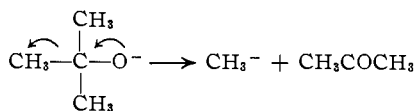
^a 68.1 g. (0.5 mole) of *d*-limonene, $\alpha^{25D} +100$, was used in each experiment with an alkoxide prepared from 0.10 g. atom of sodium or potassium. ^b Small amounts of ethylene ranging from 0.001 to 0.002 mole were obtained from reactions with catalysts prepared from isopropyl, *t*-butyl and *t*-pentyl alcohols. ^c 0.50 g. of *t*-pentyl alcohol was recovered when the solid material from this reaction was treated with water. ^d About 15% of the liquid product consisted of limonene polymers boiling above 150° at 2 mm. ^e A similar experiment carried out at 290° for 4.3 hr. yielded 75% *p*-cymene.

 TABLE II
 REACTION OF AROMATIC HYDROCARBONS WITH OLEFINS IN THE PRESENCE OF POTASSIUM *t*-BUTOXIDE

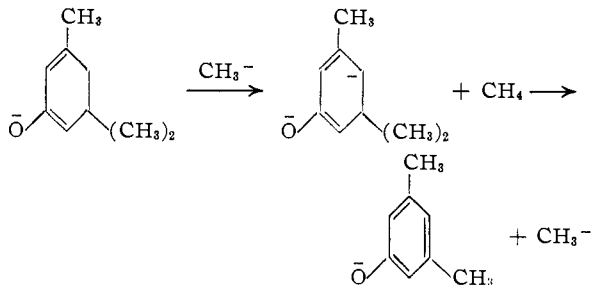
Exptl.	Hydrocarbons charged		Catalyst ^b	Temp., °C.	Product formed (moles)	Methane ^d (moles)
	Aromatic ^a	Olefin (moles)				
10	Toluene	C ₃ H ₆ 0.35	<i>t</i> -BuOK	279	0.0054 ^e	...
11	Toluene	C ₂ H ₄ .2	<i>t</i> -BuOK ^f	291	.026 ^g	0.163
12	Benzene	C ₂ H ₄ .2	<i>t</i> -BuOK	284 ± 4	.0031 ^h .0001 ⁱ	.160
13	Isopropylbenzene	C ₂ H ₄ .2	<i>t</i> -BuOK	285 ± 3	.132 ^j	.162

^a One mole of aromatic hydrocarbon was used in each experiment. ^b The catalyst, *t*-BuOK, was prepared using *t*-BuOH with 0.4 g. (0.022 mole) of water added and 4 g. (0.1 g. atom) potassium. ^c The reaction was carried out for 4-5 hours at the given temperature. ^d Hydrogen was produced in amounts varying from 0.002 to 0.004 mole. ^e The product was isobutylbenzene. The low yield can in part be ascribed to stoppage of the stirrer during the reaction. ^f A similar reaction carried out with potassium *t*-butoxide prepared from anhydrous *t*-butyl alcohol produced insufficient *n*-propylbenzene to purify by distilling on a 12 in. column. ^g The product was *n*-propylbenzene. ^h Biphenyl: m.p. 68-70°, λ_{max} 246 m μ , ϵ_{mol} 16,500. ⁱ *p*-Terphenyl, m.p. 205-211°, λ_{max} 276 m μ , ϵ_{mol} 30,000. ^j The product was composed of *t*-pentylbenzene containing a very small amount of 1,1-dimethylindan. In check reactions carried out under apparently similar conditions the yields were smaller.

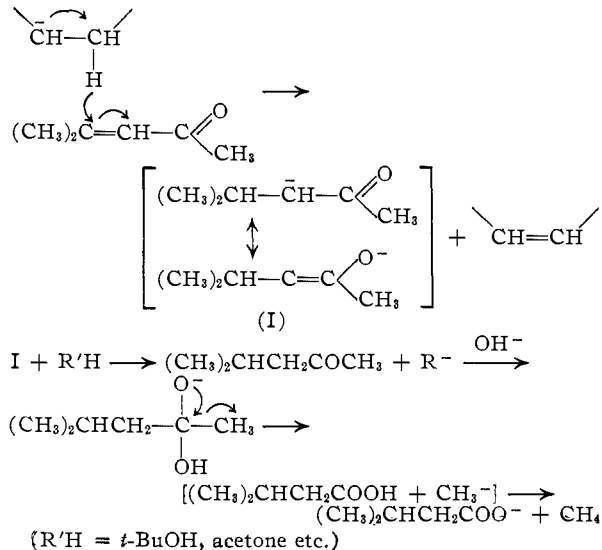
periment 9). To explain these observations it is assumed that the *t*-butoxide ion pyrolyzes into acetone and methide ion



Methide ion then promotes the dehydrogenation, side-chain alkylation, and isomerization effects which were noted. It (or *t*-butoxide) promotes aldolization in part of the acetone forming mesityl oxide, isophorone and water, thereby providing an explanation for the formation of 3,5-dimethylphenol and isovaleric acid



This explains the phenol. To explain the acid, it is assumed that mesityl oxide is changed to 4-methyl-2-pentanone by hydride transfer, after which this ketone is cleaved by the hot hydroxide ion



It will be recalled that acetone is cleaved⁴ into acetate ion by fused alkali at 250°. A similar type of decomposition takes place in the Guerbet reaction and when alcohols are heated with alkali.⁵

Alkoxide decomposition is not suitable for studying relative carbanion stabilities because subsequent condensation and elimination reactions make it impossible to study the primary elimination products, but it is evident from the gases recovered from potassium *t*-pentoxide reaction that the ethyl carbanion is eliminated much less readily than a methyl carbanion. Very little ethane was produced from potassium *t*-pentoxide at 250°.⁶

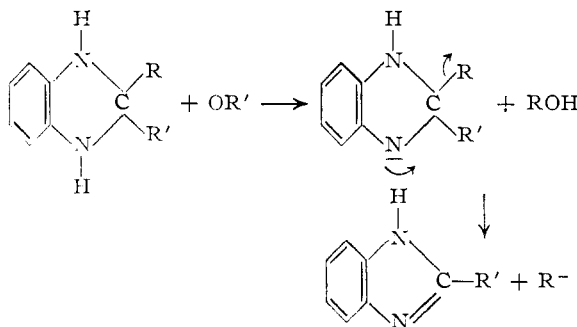
Experimental

Preparation of Alkoxides.—The *t*-pentyl, *t*-butyl, isopropyl and methyl alkoxides were prepared by refluxing 0.1 g. atom of sodium or potassium with 200 ml. of the corresponding anhydrous alcohol in a 500-ml. flask equipped with a reflux condenser and a drying tube. Water, 0.4 g. (0.022 mole) was added to the *t*-butyl alcohol used in making catalysts for the side-chain alkylation of alkylarenes. When a clear solution of the alkoxide was obtained, the excess of the alcohol was distilled off and the remaining alcohol was removed at 100° and at about 10 mm. of pressure. The white solid was then pulverized and introduced into the reaction vessel containing a weighed quantity of the liquid hydrocarbon. The alkoxides thus produced were not completely

(4) H. S. Fry and E. L. Schulze, *THIS JOURNAL*, **48**, 956 (1926).

(5) M. Guerbet, *Compt. rend.*, **128**, 511 (1899); **149**, 129 (1909); **151**, 222, 713 (1912); H. S. Fry and E. Ott, *THIS JOURNAL*, **50**, 1122 (1928); Ch. Weizmann, E. Bergmann and L. Haskelberg, *Chemistry & Industry*, **56**, 589 (1937).

(6) A mechanism similar to the elimination of carbanion by alkoxides has been proposed by Elderfield and co-workers for the elimination of alkyl groups from 2,3-dialkylbenzimidazolones [R. C. Elderfield, *et al.*, *THIS JOURNAL*, (a) **70**, 44 (1948); (b) **73**, 975 (1951); (c) **76**, 1883 (1954)]. Alkoxides have been reported to catalyze the reaction for which the presumed mechanism is



However, when two alkyl groups are attached to the 2-position the group which is eliminated is not the one which should form the more stable carbanion (H. Pines and H. E. Eschinazi, *ibid.*, **78**, 5950 (1956)) even under base catalysis. Therefore it seems probable that the reaction proceeds by a radical type mechanism. This is in accord with the fact that di-*t*-butyl peroxide will also catalyze the reaction.^{6b}

free of alcohol; no quantitative estimation of the alcohol content was made however.

The potassium phenoxide was prepared from phenol and potassium hydroxide.

Apparatus and Procedure.—A 250-ml. capacity Magne-Dash⁷ autoclave was used for all the experiments. The liquid hydrocarbon and the alkoxide were placed in the autoclave. After sealing it the air was displaced from it by means of nitrogen. When required measured amounts of ethylene or propylene were introduced into the autoclave.

The reaction was judged to be finished when the pressure remained constant. The gases were then released, measured and analyzed by a mass spectrometer. The liquid product was filtered and distilled.

Experiments 1-7.—The *d*-limonene used was purified according to the method reported previously.^{3a} It had the following physical constants: b.p. 71° at 20 mm.; n_D^{20} 1.4724, $\alpha_D^{25} +100$. The C₁₀ fraction of the liquid product from each reaction was obtained by distillation at 20 mm. pressure using a 10 in. Vigreux column. Infrared spectra were used to show the presence of *p*-cymene and, in some cases, *p*-menthadienes. The percentage of *p*-cymene was determined using ultraviolet spectra in 95% ethanol according to the method reported previously.^{3a}

Experiment 8.—*t*-Butyl alcohol, 37 g. (0.5 mole) with 1 g. (0.025 g. atm.) of potassium dissolved in it, when heated at 280° for 3.3 hr. yielded 0.087 mole of methane and 0.001 mole of hydrogen.

Experiment 9.—*t*-Butyl alcohol, 37 g. (0.5 mole) with 5.6 g. (0.1 mole) of powdered potassium hydroxide was heated at 292° for 1 hr. but yielded no gas.

Experiment 14.—1-*p*-Menthene had the following physical constants: $\alpha_D^{25} +93.5$, n_D^{20} 1.4560. This hydrocarbon, 34.5 g. (0.25 mole), was heated at 260–265° for 5.5 hr. with potassium *t*-butoxide prepared from 2 g. (0.05 g. atom) of potassium. The gaseous product consisted of 0.160 mole of methane and 0.003 mole of hydrogen. The C₁₀ fraction obtained, $\alpha_D^{25} +35$, n_D^{20} 1.4560, was composed of 92% 1-*p*-menthene 1.5% 2-*p*-menthene, 2.0% 3-*p*-menthene and 4.5% 8-(9)-*p*-menthene. The analytical procedure was the same as reported previously.^{3d}

Alkoxide Decomposition Products.—The white solid recovered from a potassium *t*-butoxide reaction with limonene was neutralized with 10% hydrochloric acid and acidic and phenolic fractions were extracted. A 3,5-dinitrobenzoate was prepared from the phenolic fraction according to the method of Keenan and Phillips.⁸ Only 13.7 mg. of a cream-colored solid was obtained which when recrystallized twice from 95% ethanol melted at 192–194°. Mixed melting point with an authentic sample of the 3,5-dinitrobenzoate of 3,5-dimethylphenol was 192–194°; literature⁸ 195.4°.

The acid fraction obtained gave an anilide which melted at 108°. A synthetic sample prepared from isovaleryl chloride and aniline melted at 107°. Mixed melting point with that isolated from reaction was 107°; literature⁹ 109–110°.

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(7) Autoclave Engineers, Inc., Erie, Pa.

(8) G. L. Keenan and M. Phillips, *THIS JOURNAL*, **53**, 1924 (1931).

(9) E. K. Harvill, R. M. Herbst, E. C. Schreiner and C. W. Roberts, *J. Org. Chem.*, **15**, 662 (1950).