Reaction with acetoacetanilide. In 290 ml. of 95% ethanol which contained a catalytic amount of sodium (less than 0.1 g.) was dissolved 62.0 g. (0.35 mole) of acetoacetanilide. The solution was cooled to 0° and treated with 18.2 g. (0.35 mole) of cyanogen. Crystals began to separate almost immediately and continued to do so as the reaction proceeded. Filtered immediately and dried, the solid weighed 34.5 g. (43% yield). Recrystallized from acetone the product formed minute, light yellow needles which melted at 204–205°.

Reaction with isobutyraldehyde. Twenty-four g. (0.33 mole) of isobutyraldehyde was placed in a 500-ml. flask fitted with a stirrer, and 70 ml. of 2% sodium carbonate solution was added. The aldehyde was insoluble in the carbonate solution, but the presence of the base appeared necessary to cause a reaction. With the flask cooled by an ice bath, 17.2 g. (0.33 mole) of cyanogen was passed in. Vigorous stirring was needed since the product which began to form after a few minutes was gummy and tended to clog the addition tube. The gummy material gradually became a light tan foamy mass. This was filtered with some difficulty, and placed in a vacuum desiccator overnight to dry. It became a light yellow, crusty solid weighing 12.0 g. (22.7% yield).

Recrystallized from ethanol with decolorizing carbon present, a solid was obtained which melted at 108–110° with decomposition.

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Reaction of Diazoethane and 1-Diazopropane With Aliphatic Aldehydes

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The major products obtained in the reaction of aldehydes with diazomethane are the methyl ketone or the oxide. As pointed out by Gutsche, in an excellent review article, aromatic and aliphatic aldehydes most frequently react to give mixtures of both ketones and oxides. In the few cases studied however,[1] aromatic aldehydes reacted with higher diazoalkanes to yield the ketones as the major products in good yields.

Because of the selective formation of ketones in the higher diazoalkane–aromatic aldehyde reaction, it seemed of interest to study the reaction of higher diazoalkanes with aliphatic aldehydes. It was found that ketones (see Table I) were formed in 51–78% yields from the reaction of the readily available[2] diazoethane and 1-diazopropane with five simple aliphatic aldehydes. Widely boiling foreruns were obtained in many cases, but were not examined for oxide content.

From the few cases studied, it would appear that the reaction of higher diazoalkanes with aliphatic aldehydes may provide a convenient synthetic method for the small scale conversion of aliphatic aldehydes to the corresponding alkyl ketones.

EXPERIMENTAL

Boiling points and melting points are uncorrected.

General method of reaction of aldehydes with diazoalkanes. The diazoalkanes were prepared from the nitrosoalkylurethanes by the method of Wilds and Meader.[2] Ethereal solutions of diazoethane (from 0.15 mole[3] of the urethane) or 1-diazopropane (from 0.20 mole of the urethane) were treated with 0.1 mole of the aldehyde. The reaction was allowed to proceed overnight at room temperature. The ether and excess diazoalkane were removed by distillation and the products were obtained by distillation through a 12" Vigreux column.

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TABLE I

REACTIONS WITH DIAZOETHANE

Aldehyde	Product	Yield, %	B.P., °C.		Derivative,[a] M.P., °C.	
			Found	Lit.	Found	Lit.
Propionaldehyde	3-Pentanone	62	99–100	102[b]	155–157D	156[b]
n-Butyraldehyde	3-Hexanone	56	122–125	121–123[c]	129–130D	130[d]
Isobutyraldehyde	2-Methyl-3-pentanone	58	109–113	111–113[e]	110–111D	111–113[f]
n-Valeraldehyde	3-Heptanone	72	144–147	148[g]	100–102S	103[g]
n-Heptaldehyde	3-Nonanone	71	185–190	187[h]	109–111S	111–112[i]
REACTIONS WITH 1-DIAZOPROPANE						
Propionaldehyde	3-Hexanone	51[j]	121–123	121–123[c]	129–130D	130[d]
n-Butyraldehyde	4-Heptanone	74	141–144	144[g]	131–132S	132[g]
Isobutyraldehyde	2-Methyl-3-hexanone	64	131–133	134–136[k]	116–118S	119[k]
n-Valeraldehyde	4-Octanone	74	164–167	170[l]	94–95S	96[l]
n-Heptaldehyde	4-Decanone	78	204–207	202–206[m]	117–118H	117–119[n]

[a] D = 2,4-dinitrophenylhydrazone; S = semicarbazone; H = hydantoin. [b] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, John Wiley & Sons, New York, 4th ed., p. 316. [c] L. I. Smith, H. E. Ungnade, W. M. Lauer, and R. M. Leekley, *J. Am. Chem. Soc.*, **61**, 3079 (1939). [d] R. B. Wagner and H. D. Zook, *Synthetic Organic Chemistry*, John Wiley & Sons, New York, 1953, p. 352. [e] F. C. Whitmore and L. P. Block, *J. Am. Chem. Soc.*, **64**, 1619 (1942). [f] H. Fournier, *Bull. soc. chim.*, **7**, 836 (1910). [g] M. L. Sherrill, *J. Am. Chem. Soc.*, **52**, 1982 (1930). [h] A. I. Vogel, *J. Chem. Soc.*, 610 (1948). [i] Ref. *d.*, p. 354. [j] The yield of distilled product was 41%. An additional 10% was isolated as the 2,4-dinitrophenylhydrazone by treatment of a forerun (b.p. 96–120°) with excess of Brady's solution. [k] B. E. Hudson and C. R. Hauser, *J. Am. Chem. Soc.*, **63**, 3163 (1941). [l] L. Boueveault, *Bull. soc. chim. France* (3) **35**, 629 (1906). [m] P. Karrer, B. Shibata, A. Wettstein, and L. Jacubowicz, *Helv. Chim. Acta*, **13**, 1292 (1930). [n] M. S. Kharash and H. N. Friedlander, *J. Org. Chem.*, **14**, 248 (1949).

tion of the State University of New York. The author also wishes to express his thanks to the Foundation for a Summer Research Fellowship.

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(1) C. D. Gutsche, *Org. Reactions*, VIII, 364 (1954).

(2) A. H. Wilds and A. L. Meader, Jr., *J. Org. Chem.*, **13**, 763 (1948).

(3) The molar quantities were chosen to give a slight excess (about 10%) of the diazoalkane (based on the average yields of diazoalkane given by Wilds and Meader[2]). In an experiment conducted by Mr. E. Otremba in these laboratories, it was established that 3-pentanone does not react with ethereal diazoethane at room temperature. Thus, it was assumed that the ketonic product would not react with excess diazoalkane. A polar solvent is evidently necessary to promote the reaction of acyclic ketones with diazoalkanes (ref. 1, p. 375).

Reaction of Aluminum Phenoxide with Nitriles

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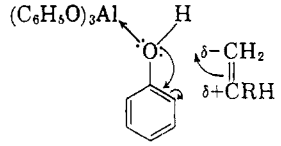
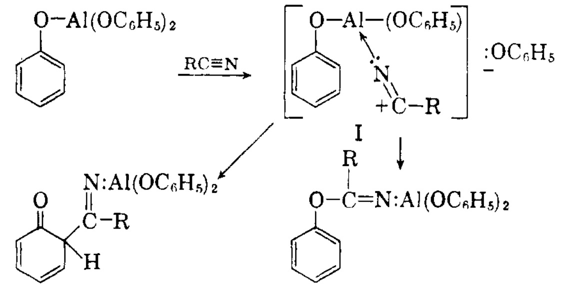
In a previous report it was shown that the cyanoethylation of phenol in the presence of anhydrous aluminum chloride and dry hydrogen chloride gave a small amount of the *ortho-* addition product, the δ-lactone of β-(*o*-hydroxyphenyl) propionic acid.[1] Our interest in the possibility of increasing the yield of this *ortho-* isomer was prompted by the work of Kolka, Napolitano, and Ecke, who found that alkylation of the phenolic salt of aluminum with alkenes at temperatures of 240° to 320° and pressures of 200 to 800 p.s.i. gave unusually high yields of *ortho-* alkylated products.[2] However, in our laboratory when acrylonitrile and aluminum phenoxide were caused to react together under similar conditions, a resin was obtained as the principal reaction product, and neither dihydrocoumarin nor *p*-hydroxyphenylpropionitrile were isolated. An infrared spectral examination of the resin showed that the cyano-group had completely disappeared, and strong aromatic carbonyl bands appeared, indicating that, under these relatively severe reaction conditions, polymerization of the olefin had taken place with considerable cross linking of the resin through the formation of carbonyl groups linked to the aromatic ring. Bands corresponding to both *ortho-* and *para-* substitution were noted. That cross linking of the polymer took place in a Hoesch-type reaction of the nitrile was confirmed in an experiment in which acetonitrile was substituted for acrylonitrile in the reaction with aluminum phenoxide. *o*-Hydroxyacetophenone and *p*-hydroxyacetophenone were recovered in yields of 3 and 4%, respectively based upon equivalents of aluminum consumed.

In the alkylation of phenol with ethylene or propylene the suggestion is advanced that a cyclic concerted mechanism operates, in which aluminum phenoxide is coordinated with excess phenol with simultaneous attack of the olefin upon the *ortho-* position of the benzene ring:[2]



However, this mechanism as constructed here implies an electron shift toward the ring though opposed by both the coordination of aluminum and the proton of phenol. A suggested mechanism more applicable to the aluminum phenoxide-nitrile system might be the displacement of a phenoxide ion from aluminum phenoxide by the nitrogen atom and its electron pair. An attack is then possible upon the *ortho-* position of the new phenoxide complex (I) to give an *ortho-* substituted dienone (II) or, alternately, upon the oxygen atom of the displaced phenoxide ion to form an imidic ester complex (III). Cleavage of the latter would permit amidation of the *para-* position of phenol.



II III

An interesting study of the Fries rearrangement parallels the above suggestion. Cullinane and Edwards[3] have studied the rate of rearrangement of substituted phenyl acetates and have found that the kinetics were consistent with a mechanism which assumes the displacement of the acyl group from the oxygen atom by a second mole of catalyst. The acyl carbonium ion attack upon the *ortho-* or *para-* position of the phenolic moiety is said to be irreversible, contrary to the results obtained by Rosenmund and Schnurr.[4]

Finally, in some experiments with aluminum phenoxide and ethyl acrylate a small amount of β-phenoxypropionic acid was isolated indicating

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(3) W. M. Cullinane and B. F. R. Edwards, *J. Chem. Soc.*, 434 (1958) and *J. Chem. Soc.*, 3016 (1957).

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