*Acknowledgment.* The authors are indebted to these members of the National Bureau of Standards: Fred P. Czech for infrared spectroscopy and Erle R. Deardorff for microanalyses.

Diamond Ordnance Fuze Laboratories
Washington 25, D. C.

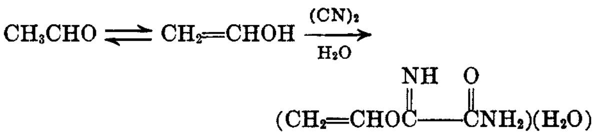
---

## Reaction of Cyanogen with Organic Compounds. XIV. Compounds Containing Hydrogen Activated by Neighboring Groups[1]

Henry M. Woodburn and Thomas J. Dolce[2]

*Received March 11, 1959*

Previous papers in this series[3] have described many reactions of cyanogen with the hydrogen of functional groups. However, little has been done with the cyanogen reactions of hydrogen activated by neighboring groups. Traube[4] has reported on malonic ester, acetoacetic ester, and acetylacetone and Langenbeck[5] showed that acetaldehyde reacts with cyanogen. However, the structure of the product indicates that hydrolysis was an accompanying step:



$$CH_3CHO \rightleftharpoons CH_2{=}CHOH \xrightarrow[H_2O]{(CN)_2} (CH_2{=}CHO\overset{NH}{\overset{\|}{C}}{-\!-}\overset{O}{\overset{\|}{C}}NH_2)(H_2O)$$

The present study was undertaken to discover other active hydrogen compounds which would react with cyanogen. Table I lists the compounds with which some measure of success was obtained. In every case the product consisted of a substance in which one molecule of the organic reagent had added to one molecule of cyanogen.

Other compounds which were studied but were recovered unchanged were nitromethane, 2-nitropropane, 1-nitrobutane, phenylacetonitrile, succinonitrile, benzaldehyde, and cyclopentadiene.

Attempts were made without success to add a second molecule of cyanogen to the condensation products of cyanogen with acetylacetone and with acetoacetanilide. In addition the following compounds, all of which contain but one active hydrogen, failed to react: ethyl butylmalonate, 3-chloroacetylacetone, ethyl $\alpha$-acetylacetoacetate, triphenylmethane, and 4-pyridyldiphenylmethane.

In no case was it possible to obtain products in which the ratio of organic reagent to cyanogen was 2:1 instead of 1:1

### EXPERIMENTAL

Pure, compressed cyanogen in cylinders was supplied by the American Cyanamid Company. The gas was led from the cylinder into a trap cooled by Dry-Ice–acetone where it became solid and permitted the tube to be weighed before and after a reaction. The rate of vaporization was easily controlled by warming or cooling the tube.

Except for nitroparaffins and aldehydes where the nature and strength of a basic solvent appeared to be critical, all the successful reactions took place in the presence of alcohol and a small amount of sodium. Three procedures illustrative of the above are given.

TABLE I

Reaction of Cyanogen with Compounds Containing Active Hydrogen

| | | | | Analysis | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Calcd. | | | Found | | |
| Reagent | Product | M.P. | Yield, % | C | H | N | C | H | N |
| $C_2H_5NO_2$ | $CH_3CHNO_2C({=}NH)CN$ | 117–119 | 7.5 | 37.8 | 4.0 | 33.1 | 37.9 | 4.4 | 33.3 |
| $C_2H_5CH_2NO_2$ | $C_2H_5CHNO_2C({=}NH)CN$ | 67–69 | 4.7 | 42.6 | 5.0 | 29.8 | 42.6 | 4.9 | 30.4 |
| $C_6H_5NHCO$<br>$\vert$<br>$CH_2COCH_3$ | $C_6H_5NHCOCHC({=}NH)CN$<br>$\vert$<br>$COCH_3$ | 204–205 | 43.0 | 62.0 | 4.8 | 18.3 | 62.4 | 5.1 | 18.1 |
| $CH_2CNCO_2C_2H_5$ | $CHCNCO_2C_2H_5$<br>$\vert$<br>$C({=}NH)CN$ | 168–170 | 2.4 | 50.9 | 4.3 | 25.4 | 50.7 | 4.5 | 25.2 |
| $CH_2(CN)_2$ | $(CN)_2CHC({=}NH)CN$ | 171 | 6.5 | 50.8 | 1.7 | 47.5 | 50.4 | 2.2 | 47.2 |
| $(CH_3)_2CHCHO$ | $(CH_3)_2C{=}CHOC({=}NH)$<br>$\vert$<br>$CONH_2{\cdot}H_2O$ | 108–110 | 22.7 | 45.0 | 7.6 | 17.5 | 45.2 | 7.5 | 17.0 |
| $C_3H_7CHO$ | Gummy product | | | Infrared spectrum closely resembled that from isobutyraldehyde product | | | | | |

*Reaction with nitroethane.* A solution of 22.1 g. (0.29 mole) of nitroethane was prepared in 200 ml. of 1*N* aqueous sodium hydroxide and cooled to 0°. Three-tenths of a mole (15.6 g.) of cyanogen was bubbled into the solution. The mixture darkened quite rapidly and after a short time a small amount of crystalline material formed. When all the cyanogen had been added, the dark mixture was extracted immediately with 200 ml. of ether and the extract dried over anhydrous magnesium sulfate while standing in the ice chest. Evaporation of the ether left 2.8 g. (7.5% yield) of yellow solid. Recrystallization from ether with decolorizing carbon present gave pure material forming yellow needles which melted at 117–119°.

---

[1] From the dissertation presented by Thomas J. Dolce in partial fulfillment of the requirements for the Ph.D. degree, February 1958. The financial assistance of Research Corporation is gratefully acknowledged.

[2] Present address: Research Laboratory, Celanese Corporation, Summit, N. J.

[3] Paper No. 1 of this series appeared in *J. Org. Chem.*, **14**, 555 (1949).

[4] W. Traube, *Ber.*, **31**, 2938 (1898).

[5] W. Lagenbeck, *Ann.*, **469**, 16 (1929).

*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.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF BUFFALO
BUFFALO 14, N.Y.

---

# Reaction of Diazoethane and 1-Diazopropane With Aliphatic Aldehydes

RICHARD F. SMITH

*Received September 3, 1959*

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.

*Acknowledgment.* This work was supported by a generous Grant-in-Aid from the Research Founda-

TABLE I

REACTIONS WITH DIAZOETHANE

| Aldehyde | Product | Yield, % | B.P., °C. Found | B.P., °C. Lit. | Derivative,[a] M.P., °C. Found | Derivative,[a] M.P., °C. 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).