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DEPARTMENT OF THE ARMY
Fort Detrick
Frederick, Maryland
SYNTHESIS AND REACTIONS OF AZO-ACYL COMPOUNDS

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(After Experiments of J. Humpel 1), J. Holzapfel 2) and H. O. Luderitz 2)


Although J. Thiele 4) oxidized hydrazodicarbonamide to diazotized hydrazide and O. Durmus and Heidenreich 5) converted hydrazodicarbonamide to diazotized hydrazide by treatment with concentrated nitric acid, secondary aromatic acid hydrazides, such as dibenzhydrazide, diacetylhydrazides, etc., do not yield azo compounds with these and the usual oxidizing agents.

Hildebrandt and Gassner 3) have shown that hydrazides may be converted to secondary azo-hydrazides, by means of diazotized hydrazides and sodium hydroxide or lime solution, in a method that involves action of sodium ferricyanide under suitable conditions.

The solubility of a secondary azo-hydrazide may be controlled by the corresponding azo compound may under certain circumstances be precipitated by treatment with the concentrated solution of the secondary azo-hydrazide -- if soluble -- when the azo compound is treated with a few drops of dilute solution of 11.3 solution.

4) 227, 29 (1892). 5) 277, 772 (1893); J. PR. [2] 70, 265 (1904); L. 2, 76, 294 (1906).
Thus diacethydrazide and dibutyrylhydrazide exhibit a yellow coloration, while diformhydrazide only gives off gas, since the azo compounds are highly sensitive toward water.

It has nevertheless been possible, according to the procedure developed by Stolle and Benrath with the exclusion of water to prepare azodiformyl, CHO-N=N-CHO, if only in an ethereal solution.

The reaction of iodine or bromine with acid hydrazides \(-\text{metallized}^{1}\) compounds takes place -- assuming the latter to be O-compounds -- according to the following scheme:

\[ \text{R.C(OMe)N=N=C(OMe).R + I}_2 \rightarrow \text{R.CO.N=N.CO.R + 2MeI}. \]

The disilver salts are the most suitable; they are, however, often not preparable and in general are also unstable. If one starts out from the monosilver salt, then only one half of the hydrazo compound is converted to the azo compound, whose preparation in the pure state is accordingly made difficult:

\[ 2\text{R.C(OAg)N=N=C(OAg).R} + \text{I}_2 \rightarrow \text{R.CO.N=N.CO.R} + 2\text{AgI}. \]

When using mercury compounds the mercury iodide dissolved in the ether is eliminated by shaking with potassium iodide solution, or when the azo compound is sensitive to water, with metallic mercury, so as to convert it in the ether-insoluble lower oxide.

While the azo compounds prepared from the secondary symmetric hydrazides of aromatic acids are relatively stable, azodiacetyl and azodibiacetyl,

\[ \text{CH}_3\text{CO.N=N.CO.CH}_3 \text{ (C}_6\text{H}_5\text{CH.CO.N=N.CO.CH}(\text{C}_6\text{H}_5)), \]

have been obtained, as mentioned above, only as crude products in the form of a red oil, and azodiformyl only in ethereal solution. The latter decomposes instantaneously upon addition of water with evolution of gas, and azodiacetyl is hardly less sensitive.

Hydrazodicarbonimide, hydrazidicarbonphenylimide, amino-carbanilide, benzalidourazol may likewise be converted to the corresponding azo compounds:

\[ \text{N.H.CO > N.R} \rightarrow \text{N.CO > N.R}, \]

\[ \text{R = H, C}_6\text{H}_5, \text{NH}_2, \text{ or N=CH-C}_6\text{H}_5. \]

Azo dicarbonimide and the corresponding azido derivative are so sensitive to water that they may be obtained only in a completely anhydrous medium.

Reducing agents, such as hydrogen iodide, hydrogen sulfide and phenylhydrazine reconvert the azodiacyl compounds to the secondary hydrazo-compounds, which usually separate immediately from the ethereal solution of the former.
By titration of the iodine liberated from an acidified potassium-iodide solution the amount of azo compound in a given solution may be determined.

Stolle and Benrath 1) have ascertained, on action of water on azodibenzoyl, the formation of tribenzoyl hydrazine and benzaldehyde in addition to a little dibenzyldrazide with evolution of one atom of the total nitrogen, and given the equation

\[ 2 \text{C}_6\text{H}_5\text{CO.N:C:O.C}_6\text{H}_5 + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_5\text{COOH} + \text{N}_2 + \text{C}_6\text{H}_5\text{CO.N:C:O.C}_6\text{H}_5 \]

for the course of the reaction.

Azodinaphthoyl yields trinaphthoylhydrazine, and azobisdiethylacetyl the corresponding tracylhydrazine.

The assumption that in these cases the hydrolytic splitting takes place only unilaterally,

\[ \text{R.CO.N:N.CO.R} + \text{H}_2\text{O} = \text{R.CO.H} + \text{HN.CO.R} \]

that the resulting dimido derivative immediately decomposes with evolution of nitrogen,

\[ \text{HN.N.CO.R} = \text{H} + \text{N} + \text{CO.R} \]

and that the radicals H and RCO add on the second azodiacyl molecule

\[ \text{R.CO.N:N.CO.R} + \text{H}_2\text{O} = \text{R.CO.H} + \text{HN.N.CO.R} \]

is supported by the fact that benzaldehyde adds to azodibenzoyl on heating to 150° under formation of tribenzoylhydrazine,

\[ \text{C}_6\text{H}_5\text{CHO} + \text{C}_6\text{H}_5\text{CO.N:N.CO.C}_6\text{H}_5 \rightarrow (\text{C}_6\text{H}_5\text{CO})_3\text{N.N.CO.C}_6\text{H}_5 \]

and to azo-(bisdiethylacetyl) on heating under formation of benzoyl-(bisdiethylacetyl)hydrazine,

\[ \text{C}_6\text{H}_5\text{CHO} + (\text{C}_2\text{H}_5)_2\text{N.CO.N.CO.(C}_2\text{H}_5)_2 \rightarrow (\text{C}_2\text{H}_5)_2\text{N.CO.N.CO.(C}_2\text{H}_5)_2 \]

It could be shown that benzaldehyde 2) also adds to azobenzene under formation of benzoyl hydrazobenzene,

\[ \text{C}_6\text{H}_5\text{CHO} + \text{C}_6\text{H}_5\text{N:C:O.C}_6\text{H}_5 = \text{C}_6\text{H}_5\text{CO.N:C:O.C}_6\text{H}_5 \]

where the yield of benzoyl hydrazobenzene, however, was very small under the chosen experimental conditions (120° and no sunlight).

Tafel 3) as well as Gattermann, Johnson and Holzle 4) have observed
during the oxidation of acyl phenylhydrazines the formation of acyl-phenylhydrazines; if one assumes the corresponding azo compound to be an intermediate compound, then the course of the reaction would fully correspond to the formation of tribenzoyl hydrazine from azodibenzoyl.

Finner ¹) has ascertained a one-sided hydrolytic splitting of an azocompound when boiling diphenyltetrazine with alcoholic KOH:

\[ C_{12}H_{12}C\equiv N\equiv N > C\equiv C.H + H_2O + NH_3 + HCN + C_6H_5 + N_2, \]

where benzylbenzhydrazide forms with evolution of nitrogen ²).

Since the formation of dibenzhydrazide in addition to tribenzoyl hydrazine was detected in the decomposition of azodibenzoyl, it is evident that a bilateral hydrolytic splitting, too, has taken place, as assumed by Thiele ³) to occur upon the action of HCl on azodibenzoimide, and of water, acids and alkalis on azodicarboxylic acid salts.

The cyclic derivatives of azodicarboxylic acid investigated so far are accordingly decomposed by water under bilateral hydrolytic splitting:

\[ \begin{array}{c}
2 N.C.O \equiv N.R + 2 H_2O \rightarrow N_2 + 2 CO_2 + NH_3 + R + \dfrac{N.H.C.O}{N.H.C.O} + N.H.
\end{array} \]

R = H, NH₂, N=CH-C₆H₅ or C₆H₅.

The behavior of azodiacyl compounds at higher temperatures must be investigated in greater detail. Azodibenzoyl yields, on introduction into a flask heated to 200-300⁰, benzil, though in small yield:

\[ C_{12}H_{12}C\equiv N\equiv N.C.H = C.H.C.O.C.O.C.H + N_2. \]

The decomposition of azodinapthoyl upon heating is apparently not a smooth one. It appears that dinaphthoyl is formed in part under evolution of nitrogen. Perhaps there occurs also an addition of the acid residue on unchanged azo compound under formation of tetraacyclidrazine:

\[ 2 R.C.O.N\equiv N.C.O.R = (R.C.O)\equiv N.C.O + CO + CO, \]

and a further decomposition of this into furodiazo and acid anhydride:

\[ (R.C.O)\equiv N.C.O.C.O.R = R.C.O + CO. \]

When azodicarbonanil, N-\( \equiv \)C.O.N.C.H₃, is heated by itself, CO and nitrogen are evolved, and at the same time small amounts of phenylicyclicate and another substance are formed, the latter having the constitution:

\[ C.H.N\equiv CO < CO. N.C.O - N.C.H. \]

The formation, also noted, of small amounts of hydrazodicarbonamid is to be attributed most likely to the presence of some water.

Thus it seems that a portion of the azo compound undergoes decomposition into nitrogen and the unstable radical \( \text{C}_6\text{H}_5\text{N CO} \).

This radical in part splits off CO under formation of carbonil, and on the other hand adds to the unchanged azo compound to form the bis-phenylimide of hydrazine tetracarboxylic acid. This decomposition supposedly takes place in accordance to the two equations:

\[
\begin{align*}
1. \quad \text{C}_6\text{H}_6\text{N CO} & \rightarrow \text{C}_6\text{H}_5\text{CO} + \text{N}_2 + \text{CO}, \\
2. \quad 2\text{C}_6\text{H}_6\text{N CO} & \rightarrow 2\text{C}_6\text{H}_5\text{CO} + \text{N}_2 + \text{C}_6\text{H}_5 + \text{N}_2
\end{align*}
\]

However, the decomposition must take place also according to another scheme, since the amount of nitrogen evolved was found to be less than would be expected even in the case of a complete decomposition in the sense of the second equation.

Likewise the difficultly soluble compound formed upon heating the azo compound obtained from (benzylideneamido)-uralozol must represent a bicyclic ring \( \text{I} \):

\[
\begin{align*}
\text{C}_6\text{H}_5\text{N CO} & \rightarrow \text{C}_6\text{H}_5\text{CO} + \text{N}_2 + \text{CO}.
\end{align*}
\]

Here, too, about one quarter of the total nitrogen is split off in gas form.

Most recently Diels and Fritzsche \(^2\) have obtained addition products of azodicarbonyl acid diethyl ester with aniline and dimethylaminiline.

I myself was able to ascertain by a few experiments with azodicarbonyl which was still at my disposal, that the latter decomposes upon reaction with aniline, into benzanilid and dibenzhydraside under evolution of approximately one half of the nitrogen, according to the equations:

\[
\begin{align*}
\text{C}_6\text{H}_5\text{CO} \rightarrow \text{C}_6\text{H}_5\text{CO} + \text{N}_2 + 2\text{H}_2
\end{align*}
\]

Dimethylaminiline reduces azodicarbonyl almost quantitatively to dibenz hydraside, while it is itself converted to oxidation products to be investigated in more detail at a future date, among them tetramethylphenoxydiacids.

\(^2\) Diels and Fritzsche, G. 31, I, 477 (1901) have obtained similar rings from guanazol hydrochloride and dicyandiamide, and from guanazol and biuret. \(2\). B. 44, 5018 (1911).
EXPERIMENTAL PART

Dibenzhydrazide-Mercury, C₁₈H₁₂N₂O₆₃Hg₅O₆₂C₆H₄₅.

A warm, alcoholic solution of dibenzhydrazide (1 mole) and sodium ethylate (2 moles) is treated with an alcoholic solution of mercuric chloride (1 mole). White, heavy precipitate.

0.3836 g substance: 21.7 cc N (18°, 744 mm) = 0.6254 g substance:
0.754 g HgS.

C₁₄H₁₀O₂N₂Hg. Calculated N. 6.39 Hg. 45.6
Found 6.31 44.7

Azodibenzoyl, C₆H₄-CO-N=CO-C₆H₄, from dibenzhydrazide-mercury (1 mole) and bromine (2/3 of theoretical amount) in ethereal solution. The filtrate is freed from mercuric bromide by shaking with mercury, and concentrated in vacuo. Yield about 90% (based on bromine used).

Mercuric oxide and iodine are without effect on dibenzhydrazide in ether; mercuric oxide and bromine yield azodibenzoyl, even though the yield of pure product is low.

1 g Azodibenzoyl was introduced in small quantities into a flask heated to 270° while simultaneously passing in CO₂, each time causing a light deflagration. The alcoholic solution of the decomposition product was freed from 0.17 g diphenylfurodiazol by precipitation with alcoholic silver nitrate solution. Steam was passed through the alcoholic filtrate and the small amount of benzal which went over extracted from the distillate with ether and identified after evaporation by mixed melting point test and color reaction with potash.

Addition of benzaldehyde to azodibenzoyl. Azodibenzoyl was heated for 5 1/5 hours with double the weight of benzaldehyde to 110°, thereby 0.83 g tribenzoyl hydrazine and 0.17 g diphenylfurodiazol (corresponding to 0.2 g tribenzoyl hydrazine and indeed resulting from it) were obtained with evolution of 0.025 g nitrogen, all calculated on 1 g azodibenzoyl.

If the entire amount of nitrogen evolved originates from the decomposition of azodibenzoyl by water (which is very difficult to exclude completely), then according to the equation

2C₆H₄-CO-N=N-C₆H₄ + H₂O → 2C₆H₄-CO-N=N-C₆H₄ + CO₂ + H₂O

0.3 g tribenzoylhydrazine forms from 0.42 g azodibenzoyl. 1.03 g - 0.5 g = 0.73 g tribenzoyl hydrazine must therefore have resulted from 1 g = 0.42 g = 0.58 azodibenzoyl through addition of benzaldehyde.

Di-p-chlorobenzoylhydrazine sodium, C₆Cl₄H₄C(ONa)=N=N-C₆Cl₄H₄, separates from the hot alcoholic solution of di-p-chlorobenzoylhydrazine -

1) From p-chlorobenzoyl chloride (2 moles), hydrazine sulfate (1 mole) and NaOH. Felt-like needles from hot alcohol, m.p. 289°.
(1 mole) after addition of sodium hydroxide (1 mole), on cooling, in
dull lustred yellowish leaflets.

0.1879 substance: 0.0395 g Na₂SO₄ = 0.2395 g Substance:
0.2071 g AgCl.

Found 6.74 21.35

Di-p-chlorobenzoylhydrazine-silver from the sodium salt (1 mole)
in alcoholic solution with aqueous silver nitrate solution (1 mole).
Yellowish-white powder, turning greyish after a longer period of time.

0.1836 g substance: 0.0345 g AgCl. 0.1523 g substance: 9.05 cc
N (20°, 760 mm).

C₃₂H₂₂O₆Cl₂Ag. Calc. Ag 25.83, N 6.71
Found 25.32 6.53

Ano-di-p-chlorobenzene, C₁₀H₈=CO-N=N-C₆H₅Cl₂, from di-p-chloro-
benzoylhydrazine silver and iodine in ethereal solution. Yellow needles,
melting at 147° while turning dark and with strong gas evolution.

0.1796 g substance: 0.3607 g CO₂, 0.0433 g H₂O. = 0.0522 g substance:
0.53 cc N (15°, 755 cc).

C₂₅H₂₄O₆N₂Cl₂. Calc. C 54.73, H 2.63, N 9.13
Found 54.72 2.70 9.33

Routinely soluble in ether, alcohol and particularly benzene. Insoluble
in water. Aqueous hydrogen sulfide and ammonium sulfide dissolve
and yield a red ethereal solution immediately under precipitation of
di-p-chlorobenzoylhydrazine (m.p. 289°).

Di-a-naphthoylhydrazine-silver, C₁₀H₇=CO-N=N-C₆H₅Cl₂, from
di-a-naphthoylhydrazine (11) (1 mole) and sodium hydroxide (1.6516) in
aqueous-alcoholic solution with silver nitrate (1 mole). Weakly yellow
powder.

0.1225 substance: 0.03 g Ag.

C₂₅H₂₄O₆N₂Cl₂: Calculated Ag 24.14. Found Ag 24.50.

Acid anaphthoyl, C₁₀H₇CON=NOClH₂, from di-a-naphthoylhydrazine-
silver and ethereal iodine solution. Nice, orange-red needles, m.p. 120°.

0.1692 g substance: 0.4833 g CO₂, 0.067 g H₂O. 0.1119 g substance:
8.41 cc N (160°, 742 mm).

1. From a-naphthoyl chloride, hydrazine sulfate and sodium hydroxide,
m.p. 260°.
\[
\text{C}_{22}\text{H}_{14}\text{O}_2\text{N}_2 \quad \text{Calc. C 78.07, H 4.19 N 8.26} \\
\text{Found 77.9 4.39 8.56}
\]

Difficultly soluble in cold ether, more readily in hot ether, quite readily in alcohol, very soluble in benzene, insoluble in water.

Reducing agents like hydrogen sulfide, ammonium sulfide, thiourea, hydrazine hydrate and hydrogen iodide convert azodinaphthoyl into dinaphthoyl hydrazine, m.p. 260°. Azodinaphthoyl splits off nitrogen on careful heating to 140-150°, and yields, though in poor yield, a yellow substance difficultly soluble in ether and alcohol and soluble in benzene, m.p. 187°, which is probably dinaphthoyl, \(\text{C}_{20}\text{H}_{12}\text{O}_2\text{N}_2\).

0.1199 g substance: 0.3732 g CO₂, 0.052 g H₂O.

\[
\text{C}_{22}\text{H}_{14}\text{O}_2\text{N}_2 \quad \text{Calculated: C 85.1, H 4.6} \\
\text{Found: 84.9 4.85}
\]

Water reacts with azodinaphthoyl gradually; faster on slight heating, with formation of trinaphthoylhydrazine (m.p. 135°), anthraquinoid acid and some di-naphthoylhydrazine, with half the total amount of nitrogen evolving.

Trinaphthoylhydrazine was also obtained by reacting azodinaphthoyl chloride and dinaphthoylhydrazine-silver. White crystals, m.p. 220°.

0.179 g substance: 0.5276 g CO₂, 0.071 g H₂O. 0.124 g substance: 0.05 cc N (16°, 747 mm).

\[
\text{C}_{22}\text{H}_{14}\text{O}_2\text{N}_2 \quad \text{Calculated C 80.13, H 4.5, N 5.0} \\
\text{Found 80.38, 4.44, 5.65}
\]

Readily soluble in hot alcohol, very slightly in cold, insoluble in water. On heating with alkalis it readily splits off a hydrazoyl group with formation of dinaphthoylhydrazine.

Acetylbenezoylhydrazine-sodium from acetylbenzoylhydrazide \(^\text{2)}\) and sodium ethylate in alcoholic solution. White precipitate, soluble in water and hot dilute alcohol but not in absolute alcohol.

0.3504 g substance: 39.2 cc N (13.5°, 764 mm). = 0.473 g substance: 0.1634 g Na₂SO₄.

\[
\text{C}_{12}\text{H}_{10}\text{O}_2\text{Na} \quad \text{Calculated N 14.00, Na 11.5} \\
\text{Found 14.07 11.2}
\]

Acetylbenezoylhydrazine-mercury from acetylbenezoylhydrazine-sodium \(^\text{2)}\), sodium ethylate (1 mole) and mercuric chloride (1 mole) in alcoholic solution, as white precipitate.

\(^\text{2)}\) //id. [2], 50, 296 (1894).
0.3378 g substance: 21.4 cc N (14°, 762 mm).

C₉H₈O₂N₂H₄. C₉H₈O₂. N 7.45 Found 7.48

Acetylacetoacetyl, CH₃-CO-N=N-CH₃, from acetylbenzoylhydrazine-
mercury in an ethereal iodine solution, as pure oil.

0.2822 g substance: 0.5915 g CO₂, 0.113 g H₂O = 0.2098 g substance:
31.6 cc N (15°, 753 mm).

C₉H₈O₂N₂. Calculated C 61.3, H 4.9%, N 7.45%. Found 61.5, 4.82, 7.45.

Titration of the iodine liberated from the acidified potassium-
iodide solution indicated that the oil contained about 80% of compound.
Combustion tests reveal a contamination with acetylbenzoylhydrazine,
C₉H₈O₂N₂, only by the very high hydrogen value.

Water reacts with the compound causing the evolution of nitrogen;
the acetylbenzoylhydrazine (m.p. 171°) recovered from the reaction
product, in addition to dibenzhydrazide, shows that in part at least a
reaction corresponding to the equations

CH₃.CO.N:N.CO.CH₃ + 3H₂O → CH₃.CO.N₂H.N.CO.CH₃ + 3H₂O
CH₃.CO.N:N.CO.CH₃ + 3H₂O → N₂ + CH₃.CO.N₂H.N.CO.CH₃

has taken place.

Methylphenylfuradiazol, ... , has been prepared since in the decomposition of acetylbenzene ito formation
was expected. 5 g acetylbenzoylhydrazine was heated with 10 g
phosphorus oxychloride 4 hours on the water bath. The reaction product
was carefully treated, after addition of ether, with ice, and the residue
remaining after the evaporation of the ether solution was recrystallized
from dilute methanol. Shiny tablets, m.p. 67°.

0.2034 g substance: 30.8 cc N (22.5°, 752 mm).

C₉H₇O₂. Calculated N 17.55% Found 16.95.

Ready soluble in alcohol, ether, benzene, acetone and chloroform.
slightly in water. The alcoholic solution yields with alcoholic silver
nitrate solution a double compound crystallizing from hot alcohol as
shiny needles, m.p. 169°. The ethereal solution of methylphenylfuradiazol
gives with chloroform mercuric chloride solution a white double compound,
 soluble in excess ether.
Diacetyldibenzoylhydrazine, \( \text{C}_{18}H_{16}O_4N_2 \)

was prepared both from acetyl chloride and dibenzoylhydrazide-mercury, and from benzoyl chloride and diacetylhydrazide mercury. Lecithin from other, m.p. 109°.

0.2244 g substance = 0.5184 g CO\(_2\), 0.0947 g H\(_2\)O, 0.3973 g substance:

50.6 cc N (15°, 753 mm).

\[ \text{C}_{18}H_{16}O_4N_2 \]

Calculated: C 66.63, H 4.96, N 6.66

Found: 65.95, 4.94, 8.72

Dissolved in alcohol and ether, insoluble in water. Only by dilution, it dissolves in sodium hydroxide, which indicates the readiness of at least one acetyl group to split off.

Dibenzoylhydrazide-Silver, \( \text{HC(OAg)} = \text{N} = \text{CH(OAg)} \),

1: chlorohydraside (1 mole), ammonia (2 moles) and silver nitrate (2 moles) in alcohol, cold solution. Yellowish-white, thick-white paste, which soon becomes crystalline and nearly white, and gradually decomposes.

0.4419 g substance = 0.5032 g substance:

0.2758 g Ag.

\[ \text{C}_{18}H_{16}O_4N_2 \text{Ag} \]

Calculated: Ag 7.47

Found: 7.30

When heated rapidly, it explodes vigorously under a current of metallic silver. In the silver determination it was evaporated, before igniting, with a few drops of alcohol and dilute nitric acid, or a trace of hydrazine hydrate.

Dibenzoylhydrazide-Mercury,

from dibenzoylhydrazide (1 mole), sodium ethylate (2 moles) and mercury chloride (2 moles) in aqueous-alcoholic solution. Fine, white precipitate.

0.392 g substance = 0.6794 g HgS.

\[ \text{C}_{18}H_{16}O_4N_2 \text{Hg} \]

Calculated: Hg 69.83

Found: 70.35

Anaerophenyl, \( \text{HC(OH)} = \text{N} = \text{CHO} \)

could be obtained at first only in ethereal solution by reacting iodine with dibenzoylhydrazide-silver. The raspberry-red filtrate left, upon evaporation in vacuo, a relatively small amount of greasy residue having a burning acid smell, which reduced ammoniacal silver nitrate solution.

Since 0.2 g water are already sufficient to decompose 1.5 g of the new compound, the former must be excluded even more carefully than before, perhaps by the addition of barium oxide and magnesia.
The ethereal solution is almost instantaneously decolorized upon the addition of water, with vigorous gas evolution taking place at the point where the water contacts it. Phenylhydrazine reduces acetylstilbene to diacetyldiazene.

**Ethylstilbene—mercury,** \((\text{C}_{13}\text{H}_{12}\text{N})_2\cdot\text{C}_8\text{H}_{8}\)

from acetylstilbene (1 mole), sodium ethylate (1 mole) and mercuric chloride (2 moles) in aqueous solution. Fine, white precipitate, which settles very slowly.

0.3080 g substance: 24.78 cc N (20.5°, 755.5 mm). = 0.4590 g substance: 0.2324 cc HgO.

\(\text{C}_6\text{H}_5\text{O}_2\text{N}_2\). Calculated N 8.91, Hg 63.73. Found: 9.19, 62.3

**Acetylstilbene** (C\(_6\)H\(_5\)-CO-CH\(_2\)-CO-CH\(_2\)\(_2\)\(_2\))- from diacetyldiazene—mercury and aceto-

**Acetylstilbene** is first slightly dissolved in water, with the evolution of hydrogen; then it is decomposed almost immediately into carbon monoxide evolution, yielding small amounts of a pink substance which dissolves in ether giving a pink solution.

**Acetylstilbene** is reduced by hydrogen chloride to diacetyldiazene, with separation of iodine; the reduction is slower with hydrogen sulfide.

Secondary Ethylstilbene Acid Hydrazide, \((\text{C}_{13}\text{H}_{12}\text{N})_2\cdot\text{C}_8\text{H}_{8}\cdot\text{N}_2\cdot\text{C}_2\text{H}_5\) \(_2\text{C}_2\text{H}_5\) from diacetylstilbene chloride (obtained by reacting the acid with thionyl chloride) and hydrazine hydrate in the presence of soda. White needle from alcohol, mp 230°.

0.4462 g substance: 46.3 cc N (120°, 744 mm).

\(\text{C}_6\text{H}_5\text{O}_2\text{N}_2\text{H}_2\). Calculated N 12.28. Found: 12.17.

Readily soluble in hot alcohol, slightly in ether, insoluble in water.

**Diacetyldiazene—mercury**

from secondary diethylstilbene hydrazide (1 mole), sodium ethylate (1 mole) and mercuric chloride (1 mole) in alcoholic solution. White precipitate, settling slowly.

0.4166 g substance: 22.8 cc N (180°, 764 mm).

\(\text{C}_6\text{H}_5\text{O}_2\text{N}_2\text{H}_2\). Calculated N 6.57. Found: 6.51.
iodobisdiethylacetyl, \((\text{C}_2\text{H}_5)_2\text{CH}=\text{CO}-\text{N}=\text{N}-\text{CO-CH}(\text{C}_2\text{H}_5)_2\), from the mercury salt of the secondary hydrazide with ethereal bromine solution, and addition of magnesium. The mercury bromide going into solution was eliminated by shaking with mercury. The intensely red, viscous residue remaining after evaporation was taken up in a little dry ether in order to separate admixed secondary hydrazide. The oil remaining after evaporation of the solvent consisted, according to titration of the iodine liberated from the acidified potassium-iodide solution, of 90% pure compound. As an impurity, the essential compound present is probably secondary diethylacetic acid hydrazide, so that the nitrogen determination gave approximately the true value.

0.3094 g substance: 32.4 cc \(N \) (18°, 749.8 mm).

\(\text{C}_2\text{H}_5\text{N}_2\text{O}_2\text{N}_2\). Calculated N 12.39. Found N 11.87.

When heated acetyldiethylacetyl degrades slightly; with ammonium sulfide its ethereal solution gives a white precipitate of secondary diethylacetic acid hydrazide. Water decomposes the acid hydrazide in a gradual fashion with formation of triethyl orthoformate, whereby one half of the total amount of nitrogen is given off:

\[
2[(\text{C}_2\text{H}_5)_2\text{CH} \cdot \text{CO} \cdot \text{N} \cdot \text{N} \cdot \text{CO} \cdot (\text{C}_2\text{H}_5)_2] + \text{H}_2\text{O} \\
= \text{N}_2 + [(\text{C}_2\text{H}_5)_2\text{CH} \cdot \text{CO}_2\text{H}] \\
+ [(\text{C}_2\text{H}_5)_2\text{CH} \cdot \text{CO}_2\text{N} \cdot \text{N} \cdot \text{CO} \cdot (\text{C}_2\text{H}_5)_2].
\]

Benzoyletylylacetyl adds to acetyldiethylacetyl, forming benzyldiethylacetylhydrazine, m.p. 129°.

Trideylacetylhydrazine, \((\text{C}_2\text{H}_5)_2\text{CH} \cdot \text{CO} \cdot \text{N} \cdot \text{N} \cdot \text{CO} \cdot (\text{C}_2\text{H}_5)_2\), from secondary diethylacetic acid hydrazide (½ mole) and diethylacetyl chloride (1 mole) in pyridine solution at 100°. Colorless prism, m.p. 95°.

0.2588 g substance: 0.6131 g \(\text{CO}_2\), 0.2365 g \(\text{H}_2\text{O}\). 0.2682 g substance: 10.5 cc \(N\) (19°, 762 mm).


Found 66.14 10.41 8.15

Readily soluble in alcohol, ether and benzene; insoluble in water.

Benzyldiethylacetylhydrazine,

from secondary diethylacetic acid hydrazide (1 mole) + benzylic chloride (2 mole) in pyridine solution. Small prisms, m.p. 123°.

0.2079 g substance: 9.7225 g \(\text{CO}_2\), 0.2152 g \(\text{H}_2\text{O}\). 0.3071 g substance: 23.5 cc \(N\) (23°, 757 mm).

\(\text{C}_{27}\text{H}_{34}\text{O}_2\text{N}_2\). Calculated C 68.67. H 8.64. N 8.64.

Found 68.44 8.3 8.87.
It is readily soluble in benzene, alcohol and ether, slightly in water; when precipitated in finely divided form from the alcoholic solution by water, it dissolves on addition of a drop of heat.

A chinoniochloride, N₄CO=NH₃, is formed from 2 moles of silver nitrate and 1 mole of vanillin in a 10% solution of alcohol, immediately decomposed with water with vigorous evolution and mixture temperature increase:

\[ 2 \text{N}_4\text{CO}=\text{NH}_3 + \text{2AgNO}_3 \rightarrow \text{N}_4\text{CO}+\text{2H}_2\text{O} + \text{2Ag} + \text{2NO}_3 \]

The alcoholic solution liberates iodine immediately from distilled HzO solution, and gives a blue-violet precipitate with alcoholic silver nitrate solution; this precipitate redissolves upon addition of ammonia to a NH₃ solution, which almost immediately becomes colored, apparently due to the formation of metallic silver.

The yield of the compound is very poor, which is probably due to the non-uniform composition of the silver salt, containing:

\[ \text{N}_4\text{CO}+\text{Ag}_2\text{O} \]

From which cannot yield any diazodicarbamide.

The silver salt of hydrazodicarbonamide from hydrazodicarbonamide (2 moles) and silver nitrate (1 mole) in aqueous alcoholic solution, imitates precipitates, soluble in ammonia and nitric acid.

**Calculated for Cu₃(N₂O₂)₃Ag:**

- Cu 35.96%
- N 35.96%
- Ag 28.08%

The silver salt of hydrazodicarbonamide from hydrazine (1 mole), 2 moles (2 moles) and silver nitrate (2 moles) in aqueous alcoholic solution, when used colorless, yellow, cheese-like precipitate, readily soluble in ammonia and dilute nitric acid.

**Calculated for Cu₃(N₂O₂)₂Ag:**

- Cu 57.52%
- N 37.48%
- Ag 50.82%

**Azodicarbonamide: N₂C=O**

From the azodicarbonamide of the hydrazo compound with sulfuric acid solution, finely formed, grainy, crimson-red crystals, giving a violet solution in ether.

**Calculated for Cu₃(N₂O₂)₂Ag:**

- Cu 36.04%
- N 55.02%
- Ag 25.77%
- H 2.87%
- O 23.92%

The compounds, Cu₂O, CuO (1934), have been added to obtain cubic I of the oxidation of hydrazodicarbonamide with lead peroxide in a few days.
U. Sily soluble in ether, benzene and ligroin, decomposes by instant solubility in alcohol and alkanes, with vigorous evolution of gas; with water and dilute acids the decomposition is sometimes slower. It evolves a decomposition according to the equation given on page 5, with evolution of one-third of the total nitrogen. Barium hydroxide, in the cold to the decomposition of the acetylenic amide, evolution of nitrogen and formation of a white precipitate which, heated for some time with water, exhibits the aniline reaction and is probably composed of barium acetylenic or anilinedicarboxylate.

Acetylenic amide decomposes on heating with gas evolution and formation of phenyl isocyanate (detected by smell and evaporation with phosphorus pentoxide) and a substance crystallizing from ethereal benzene above water in dark, shiny leaflets subliming on strong heating, into bright needles, without melting. Analysis gave values agreeing with the formula

$$\text{C}_4\text{H}_6\text{N}_2\text{O}_2\text{N}$$

C. 59.6\%  H 3.4\%  N 17.6\%

Dissolve salt of acetylenecarboxylic

from ethylamine\(\text{H}_2\text{N}\) (2 mole), sodium ethylate (2 molar) and water nitrate (2 molar) in aqueous-alcoholic solution, white precipitate, which apparently contains some monosilver salt.

C. 49.3\%  substance: 0.0452 g Ag.

C. 59.6\%  Calculated Ag 65.45. Found Ag 59.5.

Anodicament (acetylenic amide),

$$\text{C}_4\text{H}_6\text{N}_2\text{O}_2\text{N}$$

s in the cooling bath of the hydroxy compound with ethanolic solution of ethylamine and magnesium. The gummy yellow hydric solution precipitated upon evaporation the extrudable whitish crystalline compound in the form of a violet powder, deflagrating at above 75°. The volatile solution, when shaken with acidified potassium iodide solution, 0.15 min., liberates iodine and gradually becomes acetylenic, yielding acetylene.

Dissolve salt of (sulphodiamido)-Ursol

C. 59.6\%  substance: 0.0452 g Ag.

C. 49.3\%  Calculated Ag 65.45. Found Ag 59.5.

17. 12\(\text{CO}_2\), 459, 460 (1895).
0.259 substance: 0.0771 g Ag.

C.R. 20 v. C. Calculated 45 2.052 Found 45 2.75

C. Buys on heating, in the silver determination, some hydrazine

is reduced, whereby reduction sets in during the cold wash

column of metallic silver.

A solid compound of acetacarboxylate (amido-lido), \( \begin{align*}
Na \cdot & (\text{amido-lido})_2 \\
\text{X} & (\text{amido-lido})_2 \\
\end{align*} \)

forms a distinct spot of the hydrazine compound with other rod-like

crystals which are transformed, at about 250°, into a mass substance

melting at about 260°.

C.H. O. Calculated: C 0.2622 g CO₂, 0.035 g H₂O = 0.2599 g substance:

50.2° C (20° F.)

C, N, O, S. Calculated C 53.47, H 2.77, N 22.72

Found 53.38 2.58 22.77

Under these conditions the mass compound under determination, i.e., the

compound, melts about one quarter of the total amount of hydrazine

is evolved.

On heating the mass compound decomposes and gives off about

quarter of the total amount of hydrazine, being converted into a semicrysta-

lized, substance from glacial acetic acid in shiny scales (m.p. about

250°). The nitrogen determination gave a value agreeing with the

constitution.

C.H.O.S. Calculated C, H, N, S.

C, H, O, S. Calculated: C 22.56, H 2.56. Found: C 22.52.

Kerosene Sule of Hydroxycarboxylate Ester 1)

from hydroxycarboxylate ester (2 mols), acetic anhydride (2 mols), and

water solution (1 mol) in alcoholic solution. White precipitate,

insoluble in water and alcohol, which slightly deflagrates upon heating.

C.H.O.S. Substance: 16.1 cc N (27°, 753 mm.) = 0.4421 g substance:

0.365 g N

C. N. O. S. Calculated: C 7.49, H 5.96

7.93 5.73

By heating the mercury salt with benzoyl chloride in carbon tetrachloride at 20°, dibenzoylhydroxycarboxylate ester is obtained. White


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crystals, m.p. C°; very soluble in ether, less soluble in alcohol, benzene, ligroin, insoluble in water.

0.3268 g substance: 0.3268 g CO₂, 0.0686 g F₂O₁. = 0.3268 g substance: 9.4 cc N (18.5°, 750 mm).

CO₃·2CO₂·N₂. Calculated C 62.5, H 5.21, N 7.2.

Found 62.72, 5.36, 7.53.

Acetodicyclohexyl ester 1)

From the mucous oil of hydroxacyclohexyl ester with ethereal sodium solution. Pale yellow oil, purified by fractional distillation in vacuo.

0.1727 g substance: 25 cc N (18.5°, 750 mm).


Addition of oxalyl chloride to acetobenzene.

Acetobenzene was heated with the parts by means of benzene.
C₂H₅CO₂·H₂. to about 110° on the air bath and washed ten times with the addition with sodium bicarbonate. From the residue was benzyloxycarbonyl-
benzene was obtained by washing with ether; this compound was purified by fuming with ether to alcohol, heated at 138° and was found to be identical with the
acetobenzene prepared from benzyl chloride and hydroxy acetone in dry
pyridine 2).

1) Prepared by Frank and Hajdúreich (J. pr. [2], 52, 472 (1903)) by fractional distillation of hydroxacyclohexyl ester with fuming nitric acid.

2) Frank, J. pr. [2], 136, 555 (1903).