and 5 cc. of hydrochloric acid was heated for twenty-five minutes, diluted with an equal volume of water and the yellow, crystalline precipitate of 2,5-di-(*p*-methoxyphenyl)-3,4-benzofuran recrystallized from alcohol; mixed m. p. 126–127°.[25]

When oxidized the furan yielded 2-(4″-methoxyphenyl-4′-methoxybenzophenone; mixed m. p. 157–158°.

2-Benzyltriphenylcarbinol.—To phenylmagnesium bromide, prepared from 3.5 g. of bromobenzene, 0.5 g. of magnesium and 20 cc. of ether, there was added 3.0 g. of 2-benzylbenzophenone,[26] dissolved in 20 cc. of ether. The mixture was heated for three hours, the crystalline precipitate filtered, decomposed with ice and ammonium chloride and the crystalline 2-benzyltriphenylcarbinol recrystallized from alcohol; m. p. 133–134°.

Anal. Calcd. for $C_{26}H_{22}O$: C, 89.09; H, 6.33. Found: C, 88.70; H, 6.35.

The carbinol turns orange-red when moistened with concd. sulfuric acid and then rapidly becomes colorless due to the formation of 9,9-diphenyl-9,10-dihydroanthracene; mixed m. p. 195–196°.[27] The same transformation was effected when an acetic acid solution of the carbinol was boiled for three minutes. To identify the dihydroanthracene further, a portion was oxidized with sodium dichromate and sulfuric acid in acetic acid to 9,9-diphenylanthrone-10; mixed m. p. 191–192°.[28]

A mixture of 0.5 g. of 2-benzyltriphenylcarbinol, 10 cc. of water and 5 cc. of nitric acid was refluxed for three hours and the crystalline 9,9-diphenylanthrone-10 obtained recrystallized from acetic acid; mixed m. p. 191–192°; when reduced with zinc dust and acetic acid the anthrone was reduced to 9,9-diphenyl-9,10-dihydroanthracene; mixed m. p. 194–195°.

Summary

A reaction mechanism has been suggested to account for the formation of a 2,5-diaryl-3,4-benzofuran from the interaction of certain diarylphthalins and sulfuric acid.

In two instances it has been shown that a 2,5-diaryl-3,4-benzofuran can be obtained by reaction of an arylmagnesium halide with 2-cyanobenzaldehyde; 2-benzyltriphenylcarbinol can be converted very readily into 9,9-diphenyl-9,10-dihydroanthracene.

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[25] Blicke and Weinkauff [THIS JOURNAL, **54**, 1458 (1932)] reported the same melting point.

[26] Seidel, *Ber.*, **61**, 2275 (1928).

[27] Liebermann and Lindenbaum [*ibid.*, **38**, 1803 (1905)] reported 195–196°, Barnett, Cook and Nixon [*J. Chem. Soc.*, 508 (1927)] 200°. Although the melting points of 9,9-diphenyl-9,10-dihydroanthracene and 9,9-diphenylanthrone are nearly identical, we found that a mixture composed of equal parts of the two substances melted at 170–175°.

[28] Haller and Guyot [*Bull. soc. chim.*, [3] **17**, 878 (1897)] and Copisarow [*J. Chem. Soc.*, **111**, 17 (1917)] reported 192°.

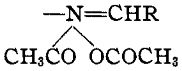
ANN ARBOR, MICHIGAN RECEIVED DECEMBER 26, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF COLORADO]

The Action of Acetic Anhydride upon Dibenzylidenehydrazine[1]

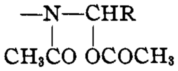
BY JOHN B. EKELEY AND J. WILLIAM LEFFORGE

The addition of acetic anhydride to the group —N=CHR (R = aryl) might occur in one of the following ways



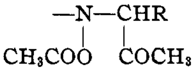
$$\begin{array}{c}\mathrm{-N{=}CHR}\\ \diagup\diagdown\\ \mathrm{CH_3CO\quad OCOCH_3}\end{array}$$

I



$$\begin{array}{cc}\mathrm{-N-}&\mathrm{CHR}\\ |&|\\ \mathrm{CH_3CO}&\mathrm{OCOCH_3}\end{array}$$

II



$$\begin{array}{cc}\mathrm{-N-}&\mathrm{CHR}\\ |&|\\ \mathrm{CH_3COO}&\mathrm{COCH_3}\end{array}$$

III

There is no evidence pointing to III.

Passerini and Macentcelli[2] assumed I in the addition of the anhydride to benzylideneaniline from the analogous addition of bromine as shown by James[3] and others. The above assumption was disputed by Ekeley, Swisher and Johnson,[4] who pointed out that the work of Ekeley and others[5] showed that in the case of benzylideneanthranilic acid the anhydride adds as in II.

The experimental observations herein recorded point definitely to II, since they show that from a reaction mixture of one mole of dibenzylidenehydrazine and three moles of acetic anhydride there can be isolated 14% 2,5-dimethyl-1-oxy-3,4-diazole, 19% of *sym*-diacetylhydrazine, and 40% of benzylideneacetylhydrazine based on one mole of dibenzylidenehydrazine.

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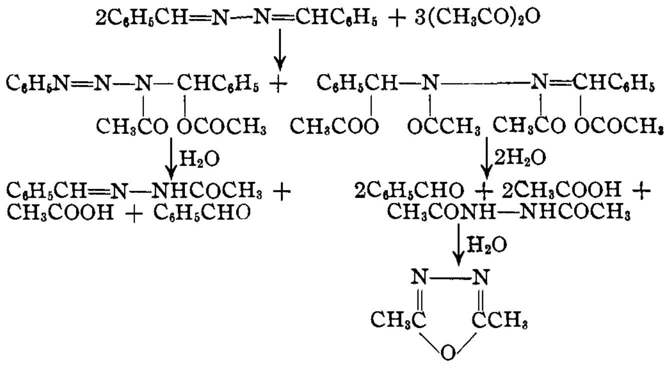
[1] Several years ago the senior author heated 20 g. dibenzylidenehydrazine intermittently with excess acetic anhydride. After each cooling of the solution the dibenzylidenehydrazine separated out unchanged. After some ten heatings, the boiling solution was forgotten on the hot plate. When later discovered all the acetic anhydride had been driven off and a colorless high boiling liquid was condensing and running down the sides of the flask, all of the dibenzylidenehydrazine having disappeared. On being cooled, the liquid solidified to a grayish white crystalline solid (high yield) which was easily separated into two colorless crystalline substances of different solubilities, melting points and composition, both containing nitrogen. After recrystallization many times, many checking analyses were obtained for each, which did not correspond to any possible compounds. After the products were used up, very many attempts to repeat the reaction failed, no reaction whatever being observed.

[2] Passerini and Macentcelli, *Gazz. chim. ital.*, **58**, 64 (1929).

[3] James, *Ber.*, **32**, 2277 (1899).

[4] Ekeley, Swisher and Johnson, *Gazz. chim. ital.*, **62**, 81 (1932).

[5] THIS JOURNAL, **34**, 161 (1912); **35**, 282 (1913); **36**, 603 (1914); **37**, 582 (1915); **44**, 1756 (1922).



Experimental

A mixture of one molecular quantity of dibenzylidenehydrazine with about three of acetic anhydride was distilled until the temperature of the distilling mixture reached 127° (624 mm., Boulder, Colorado), and was then refluxed intermittently for about thirty-five hours. The yellow-brown reaction mixture, upon being cooled, deposited crystals of dibenzylidenehydrazine, but upon standing without heating for about two weeks, the crystals dissolved. The mixture was then distilled under reduced pressure (20 mm.) until the temperature of the boiling residue was 120°.

1. **Distillate.**—The distillate was fractionated at 624 mm. into portions boiling at 100–105° (acetic acid), 105–120°, and 120–127°. These last were each refractionated twice yielding below 125° (acetic anhydride), 125–158° (very small, discarded), and 158–169°, a clear liquid with odor like that of acetamide, but much stronger. This was diluted with five times its volume of ether in a separatory funnel, and well washed with 5% aqueous sodium bicarbonate until the washings were neutral. The ether layer was evaporated, the residue dried over anhydrous calcium chloride and distilled. The distillate boiling at 165–169° was a clear oil with all the properties of 2,5-dimethyl-1-oxy-3,4-diazole. The yield was 14% based on one mole of dibenzylidenehydrazine.

2. **Residue.**—The residue was diluted with toluene to three times its volume and extracted with twice the diluted volume of hot water in a specially devised extraction apparatus. The extract was cooled to 0°, yielding crystals which were filtered off. Three successive evaporations of the filtrate to one-half original volumes each yielded more crystals when cooled to 0°. The four crystal portions were combined, (a). The filtrate was evaporated under reduced pressure on the water-bath to a thick sirup. Stirring the sirup with sufficient dry ether by means of a glass rod yielded more crystals. These were separated and extracted with ether in a Soxhlet. The ether extract on evaporation yielded crystals which were combined with (a). To these were added crystals obtained later from the toluene residue. The residue after extraction with ether was recrystallized from amyl alcohol, dried at 100°, and shown to be *sym*-diacetylhydrazine in yield of 19%, based on one mole of dibenzylidenehydrazine.

The toluene solution after extraction with hot water gave, on cooling, crystals similar to (a), which were combined with the latter (see above). The final toluene filtrate was shown to contain stilbene and dibenzylidenehydrazine. The combined crystals (a) were recrystallized twice from 60% alcohol, once from xylene, washed with ether and dried at 100°. They were benzylideneacetylhydrazine in yield of 40%, based on one mole of dibenzylidenehydrazine.

Summary

1. Acetic anhydride reacts with dibenzylidenehydrazine, forming benzylideneacetylhydrazine and diacetylhydrazine, part of the latter losing water to become 1,3-dimethyl-1-oxy-3,4-diazole.

2. When acetic anhydride adds to the —N=CHR (R = aryl) group the acetyl group goes to the N and the ester group to the C atom of the double bond.

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