The A-60 proton n.m.r. spectrum of the 43% constituent consists of a triplet centered at $\delta = 5.7$ (I) $(CH_3)_4Si$ external $= 0.0$ with $J = 53$ c.p.s. The components of the triplet are further split to doublets (J = 5 c.p.s.), and at very high resolution, the further splitting of the doublets to quadruplets can be detected ($J \approx 1$ c.p.s.). The pattern thus is wholly consistent with that predicted for the previously unreported 2-bromo-1,1,1,2,3,3-hexafluoropropane (II) ($n^{24}D$ 1.3059). The proton spectrum of the other isomer, 3-bromo-1,1,1,2,3,3-hexafluoropropane (I) ($n^{24}D$ 1.3032), consists of a doublet centered at $\delta = 4.7$ with J = 44 c.p.s. The doublet components further resolve to quartet–quadruplet combinations (J1 doublet = 10 c.p.s.; J2 doublet = 5.5 c.p.s.; J quad. = 5.5 c.p.s.) by virtue of the asymmetry of the central carbon atom.[5]

Ultraviolet-initiated Addition of Hydrogen Bromide to Hexafluoropropene.—A mixture of 11.5 g. (0.08 mole) of hexafluoropropene and 6.3 g. (0.08 mole) of anhydrous hydrogen bromide was sealed in a 50-ml. Pyrex Carius tube and irradiated with a G.E. C3-H85 lamp at a distance of *ca.* 6 inches for 6 days. The tube was cooled to −78° and opened. The liquid reaction product was distilled through a small spinning-band column to give 13.5 g. (76% yield) of 1:1 adduct mixture boiling at 34–35°/760 mm. The proton n.m.r. spectrum of this material showed that it consisted of a mixture of isomers I and II in a ratio of 62:38.

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[5] (a) P. M. Nair and J. D. Roberts, *J. Am. Chem. Soc.*, **79**, 4565 (1957). (b) J. J. Drysdale and W. D. Phillips, *ibid.*, **79**, 319 (1957).

The Synthesis of Dihydropyrimidines from Benzamidine and α,β-Unsaturated Ketones

E. F. SILVERSMITH

Contribution No. 330 from the Research and Development Division, Organic Chemicals Department, E. I. du Pont de Nemours and Company, Inc., Wilmington, Delaware

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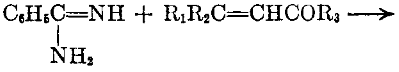
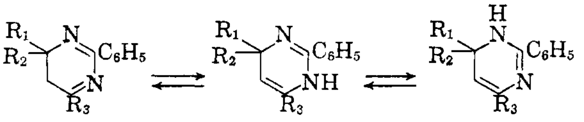
The reaction of amidines (*e.g.*, benzamidine, I) with α,β-unsaturated ketones is an attractive approach to the synthesis of dihydropyrimidines bearing an alkyl or aryl group at the 2-position. Traube and Schwarz[1] treated benzamidine (I) with mesityl oxide (IIa) in the absence of solvent and obtained a product, m.p. 91°, to which they assigned structure IIIa. Ruhemann[2] found that the reaction of benzamidine with 3-benzylidene-2,4-pentanedione at 100° results in the loss of an acetyl group with formation of a dihydromethyldiphenylpyrimidine, to which structure IV ($R_1 = H$, $R_2 = C_6H_5$, $R_3 = CH_3$) was assigned. Dodson and Seyler[3] used the reaction of benzamidine with various α-benzylidene ketones (II, $R_1 = H$, $R_2 = C_6H_5$) for the preparation of 6-substituted-2,4-diphenylpyrimidines; the presumed dihydropyrimidine intermediates, to which structure III ($R_1 = H$, $R_2 = C_6H_5$) was assigned, were not isolated.



$$C_6H_5\underset{NH_2}{C}{=}NH + R_1R_2C{=}CHCOR_3 \longrightarrow$$

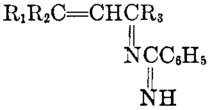
I

IIa. $R_1 = R_2 = R_3 = CH_3$
b. $R_1 = CH_3$, $R_2 = R_3 = C_6H_5$



III IV V

a. $R_1 = R_2 = R_3 = CH_3$
b. $R_1 = CH_3$, $R_2 = R_3 = C_6H_5$



$$R_1R_2C{=}CH\underset{\substack{\| \\ NCC_6H_5 \\ \| \\ NH}}{C}R_3$$

VIa. $R_1 = R_2 = R_3 = CH_3$
b. $R_1 = CH_3$, $R_2 = R_3 = C_6H_5$

In our hands the reaction of benzamidine with mesityl oxide in ethanol or under Traube and Schwarz's conditions[1] yielded a compound melting several degrees higher than reported[1] and having an analysis consistent with the formula $C_{13}H_{16}N_2$. The infrared spectrum (carbon tetrachloride solution) has a band at 2.89 μ (N—H), which contradicts IIIa but is consistent with the tautomerized structures IVa and Va and the open-chain structure VIa. The proton nuclear magnetic resonance spectrum, taken in carbon tetrachloride solution with tetramethylsilane as internal standard, also rules out IIIa. Absorption occurs at 8.83 τ (*gem*-dimethyl), 8.23–8.25 τ (doublet, methyl), 5.60 τ (vinylic hydrogen), and 2.25–2.79 τ (multiplet, phenyl group) with approximate relative areas of 6:3:1:5. The absorption of the amino hydrogen, which is undoubtedly broad,[4] could not be detected with certainty. Structure VIa can be ruled out by comparing the τ-value of the *gem*-dimethyl groups with those of model compounds, as summarized in Table I. The *gem*-dimethyl grouping absorbs close to that of isopropylamine and at considerably higher τ than that of mesityl oxide, demonstrating that the two methyls are attached to a saturated carbon.

An analogous reaction occurs between benzamidine and dypnone (IIb); the elemental analysis, molecular weight, and infrared and n.m.r. spectra demonstrate that the product is IVb or Vb. The infrared spectrum has an N—H maximum at 2.91 μ, while n.m.r. peaks are present at 8.35 τ (methyl), 4.64 τ (vinylic hydrogen), and 2.00–3.00 τ (multiplet, phenyl) with approximate area ratios of 3:1:15. Structure VIb is ruled out by the data in Table I. The τ-value of the methyl protons of the reaction product is close to those of α-methylbenzylamine (a model for structure Vb) and N-benzylidene-α-methylbenzylamine (a model

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[1] W. Traube and R. Schwarz, *Ber.*, **32**, 3163 (1899).

[2] S. Ruhemann, *J. Chem. Soc.*, **83**, 1371 (1903).

[3] R. M. Dodson and J. K. Seyler, *J. Org. Chem.*, **16**, 461 (1951).

[4] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 270.

TABLE I

N.M.R. MAXIMA OF METHYL GROUPS IN REACTION PRODUCTS AND MODEL COMPOUNDS

Compound	N.m.r. maxima[a]
Product of benzamidine–mesityl oxide reaction	8.23–8.25,[b] 8.83[c]
Isopropylamine	8.92–9.02[b]
Mesityl oxide	7.89–7.91–7.92,[b] 8.14–8.17[b,d]
Product of benzamidine–dypnone reaction	8.35
α-Methylbenzylamine	8.60 to 8.75[e]
N-Benzylidene-α-methylbenzylamine	8.42–8.53[b]
Dypnone	7.45–7.48[b]

[a] τ-Values, relative to internal tetramethylsilane. [b] Hyphenated numbers indicate multiplets. [c] Area ratio of doublet to singlet: 1:2. [d] Area ratio of triplet to doublet: 2:1. [e] Amino hydrogens absorb in the same region, and methyl bands can not be assigned with certainty.

for IVb), but considerably higher than those of dypnone (a model for VIb).

At present we are unable to decide between structures IV and V for the condensation products. One is tempted to favor V which has conjugated endocyclic double bonds. However, structures similar to both IV[2,5] and V[5a,5b,6] have appeared in the literature.

Experimental

2-Phenyl-4,4,6-trimethyl-1,4(or 3,4)-dihydropyrimidine (IVa or Va).—A mixture of 15.66 g. (0.10 mole) of benzamidine hydrochloride, 9.8 g. (0.10 mole) of freshly distilled mesityl oxide, 6.60 g. (0.10 mole) of potassium hydroxide, and 300 ml. of absolute ethanol was heated at reflux for 3 hr. The mixture was cooled, filtered to remove potassium chloride, and concentrated *in vacuo*, leaving a brown oil which was boiled with 300 ml. of hexane. The mixture was filtered while hot, the filtrate was cooled to room temperature and poured onto an alumina chromatographic column. Elution with hexane yielded 12.6 g. (63%) of yellow solid, m.p. 85–97°. The product was purified by boiling with 700 ml. of petroleum ether (b.p. 30–60°), filtering while hot, and cooling the filtrate in Dry Ice, giving 9.1 g. (45%) of pale yellow crystals, m.p. 97.0–98.5°.

Anal. Calcd. for $C_{13}H_{16}N_2$: C, 78.0; H, 8.1; N, 14.0. Found: C, 78.2, 78.2; H, 8.1, 8.2; N, 14.1, 14.2.

The hydrogen chloride–mercuric chloride double salt, m.p. 183–185° (lit., m.p. 179°), was prepared as previously described.[1]

The reaction of benzamidine with mesityl oxide in the absence of solvent[1] gave a crude product, m.p. 68–82°, which was too soluble in ether[1] to make recrystallization from this solvent practical. Recrystallization from petroleum ether as described above resulted in a 63% yield of yellow solid, m.p. 89.0–94.5°, which had an infrared spectrum identical to that of the product obtained in ethanol. A second recrystallization raised the m.p. to 93.0–95.5°.

4-Methyl-2,4,6-triphenyl-1,4(or 3,4)-dihydropyrimidine (IVb or Vb).—The above procedure was repeated on a 0.05-mole scale, using dypnone instead of mesityl oxide. The brown oil remaining after solvent removal was boiled with 100 ml. of benzene. The mixture was filtered while hot, treated with 300 ml. of hexane, and boiled till the volume was 150 ml. Cooling gave two crops of yellow crystals: 1.15 g., m.p. 117–119°, and 3.54 g., m.p. 109–117°, a total yield of 29%. Recrystallization from hexane raised the m.p. of the first fraction to 121.0–122.5°.

Anal. Calcd. for $C_{23}H_{20}N_2$: C, 85.2; H, 6.2; N, 8.6; mol. wt., 324. Found: C, 85.6, 85.4; H, 6.3, 6.2; N, 8.7, 8.5; mol. wt. (ebullioscopic in benzene), 322, 330.

N-Benzylidene-α-methylbenzylamine.—This compound was prepared by the method of Nerdel, Becker, and Kresze.[7]

Infrared spectra were run in carbon tetrachloride solution on a Perkin-Elmer Infracord, Model 137B.

N.m.r. spectra were determined on a Varian A60 spectrometer, using 0.6 *M* solutions in 5:1 carbon tetrachloride–tetramethylsilane.

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[5] (a) W. H. Hill, U. S. Patent 2,628,716 (1953); (b) Wellcome Foundation Ltd., British Patent 734,842 (1955); (c) G. E. McCasland, E. Blanz, Jr., and A. Furst, *J. Org. Chem.*, **24**, 999 (1959).

[6] W. H. Hill, British Patent 633,353 (1949); T. D. Heyes and J. C. Roberts, *J. Chem. Soc.*, 328 (1951).

[7] F. Nerdel, K. Becker, and G. Kresze, *Ber.*, **89**, 2862 (1956).

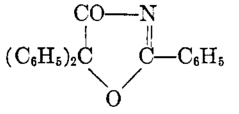
The Reaction of Benzilic Acid with Benzonitrile

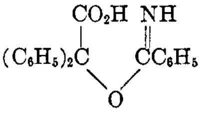
C. W. BIRD

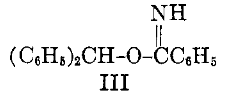
Department of Chemistry, Queen Elizabeth College, University of London, London W.8, England

Received June 7, 1962

Only one example of a 4-oxazolone is reported in the literature.[1] From the treatment of benzilic acid and benzonitrile with concentrated sulfuric acid there was obtained a compound A, $C_{21}H_{15}NO_2$, readily hydrolyzed to a compound B, $C_{21}H_{17}NO_3$. By analogy with prior work[2] on the formation of oxazoles from benzoin and nitriles under the same conditions, compounds A and B were assigned the structures I and II, respectively. These formulations apparently were confirmed by subsequent transformations. Thus compound B was converted back into compound A by refluxing with acetic anhydride. Both compounds A and B, on reduction with hydriodic acid, gave benzamide and diphenylacetic acid. Further, compound A, on heating either alone or with strong alkali, was decarboxylated to a neutral compound C, $C_{20}H_{17}NO_3$. This was identical to the product obtained by treating benzonitrile and benzhydrol with hydrogen chloride gas and thus thought to be III.


I


II


$$(C_6H_5)_2CH\text{-}O\text{-}\overset{\overset{\text{NH}}{\|}}{C}C_6H_5$$
III

The marked stability of compounds B and C to

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[1] F. R. Japp and A. Findlay, *J. Chem. Soc.*, **75**, 1027 (1899).

[2] F. R. Japp and T. S. Murray, *ibid.*, **63**, 469 (1893).