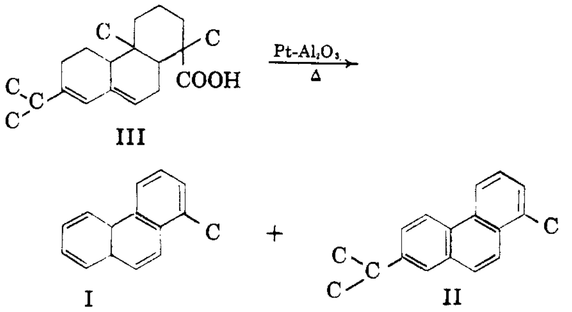
that the following reactions occur during the process:



+ C_4–C_5 alkylphenanthrenes, CO_2, H_2, CH_4, C_2H_6, and C_3H_8 + partial degradation products

1-Methylphenanthrene and 1-methyl-7-isopropylphenanthrene were obtained in pure form. Hydrocarbons consisting of C_4 and C_5 alkylphenanthrenes were also isolated from the reaction mixture.

EXPERIMENTAL[7]

1-Methyl-7-isopropylphenanthrene. A 66% solution of abietic acid (Mathieson, Coleman and Bell, tech. grade) in benzene was prepared by dissolving 1260 g. of the acid in 735 ml. of the hydrocarbon solvent. The solution then was passed over a Pt-alumina catalyst in a fixed-bed continuous-flow unit. Operating conditions were as follows: Temperature = 480°, Hydrogen pressure = 50 p.s.i.g., Liquid hourly space velocity (vol. oil/vol. catalyst/hr.) = 0.8, H_2/oil mole ratio = 4/1. Gaseous products were analyzed by mass spectrometry. The total liquid product yielded 810 g. after the benzene solvent had been removed. A preliminary separation was made by means of a vacuum Engler distillation. The 315–400° cut (69%) containing the alkylphenanthrenes was chromatographed over alumina. The polyaromatic fraction from this operation (66%) then was distilled in a 30-plate 1-inch Oldershaw column at 24/1 reflux ratio. The fraction which had a b.p. 245–248°/22 mm. proved to be 1-methyl-7-isopropylphenanthrene and gave an over-all yield of 16.2%. Recrystallization of this fraction from aqueous ethanol afforded a product of m.p. 98–99°, similar to that in the literature.[8] The *picrate* melted at 124–125°.[8] Mass spectrometric analysis indicated the compound to be 99% methylisopropylphenanthrene.

Anal. Calc'd for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.12; H, 7.63.

Anal. Calc'd for *picrate* $C_{24}H_{21}N_3O_7$: N, 9.07. Found: N, 9.18.

1-Methylphenanthrene. The fraction boiling at 217–219°/22 mm. during the final distillation above consisted of 1-methylphenanthrene. On recrystallization from aqueous ethanol the compound had m.p. 119–120°[9] and the *picrate* melted at 137–138°.[9] Mass spectrometric analysis indicated the product to be 99% methylphenanthrene. The yield was 5.4%.

Anal. Calc'd for $C_{15}H_{12}$: C, 93.71; H, 6.29. Found: C, 93.37; H, 6.30.

Anal. Calc'd for picrate $C_{21}H_{15}N_3O_7$: N, 9.97. Found: N, 9.93.

C_4 and C_5 Alkylphenanthrenes. A liquid product (1.2%) was obtained during the final distillation above which had b.p. 257–259°/22 mm. Mass spectrometric analysis indicated this sample to be >95% C_4 and C_5 alkylphenanthrenes, n_D^{20} 1.6450.

RESEARCH LABORATORY
SHELL OIL COMPANY
HOUSTON, TEXAS

---

[7] All melting points uncorrected.

[8] Haworth, Letsky, and Mavin, *J. Chem. Soc.*, 1784 (1932); 1-methyl-7-isopropylphenanthrene, m.p. 98–99°; *picrate*, m.p. 123–124°.

[9] Bachmann and Wilds, *J. Am. Chem. Soc.*, **60**, 624 (1938); 1-methylphenanthrene, m.p. 120–121°; *picrate*, m.p. 136–136.5°.

The Reaction of 1,1-Dibenzoyl-2,2-dimethylhydrazine with Lithium Aluminum Hydride

RICHARD L. HINMAN

Received May 21, 1956

Recently reported work from this laboratory has shown that the lithium aluminum hydride reductions of acylhydrazines containing the group —CONH— are slow and that the yields of alkylhydrazines are generally poor.[1,2] In this class are found such compounds as benzhydrazide, 1-benzoyl-2,2-dimethylhydrazine, and 1,2-diacetylhydrazine. When the hydrogen of the —CONH— is replaced by a methyl or a phenyl group, reduction to the corresponding alkylhydrazine is rapid and the yields are fairly good (40–60 per cent).[1,2] This group of acylhydrazines includes such substances as 1-benzoyl-1-methylhydrazine,[2] and 1,2-diacetyl-1,2-dimethylhydrazine.[1] As would be expected, when both types of groups are contained in the same molecule, the group which lacks the hydrogen undergoes preferential reduction.[3]

To explore further the scope of this correlation between structure and ease of reduction the reaction of a 1,1-diacyl-2,2-dimethylhydrazine with lithium aluminum hydride was examined. Since the —CONH— group is absent, rapid reduction would be expected. 1,1-Dibenzoyl-2,2-dimethylhydrazine (I) was selected because of its availability.[1] From the reduction, carried out with a 100% excess of lithium aluminum hydride in refluxing tetrahydrofuran for two hours, the following products were isolated: 1-benzyl-2,2-dimethylhydrazine (21% yield), 1-benzoyl-2,2-dimethylhydrazine (18%), and a mixture of benzyl alcohol and benzaldehyde in which the alcohol predominated. A basic gas, which was evolved during decomposition of the excess hydride, was identified as *unsym*-dimethylhydrazine. None of the starting material was recovered. These facts are summarized in equation (1).

$$(1)\ \underset{\text{I}}{(C_6H_5CO)_2NN(CH_3)_2} \longrightarrow C_6H_5CONHN(CH_3)_2 + C_6H_5CH_2NHN(CH_3)_2 + C_6H_5CH_2OH + C_6H_5CHO + (CH_3)_2NNH_2$$

---

[1] R. L. Hinman, *J. Am. Chem. Soc.*, **78**, 1645 (1956).

[2] R. L. Hinman, *J. Am. Chem. Soc.*, **78**, 2463 (1956).

[3] R. Huisgen, F. Jakob, W. Siegel, and A. Cadus, *Ann.*, **590**, 1 (1954).

It is apparent that 1,1-dibenzoylhydrazine, lacking the group —CONH—, undergoes relatively rapid reduction.

The various products can be accounted for by application of the mechanism advanced by Weygand for the reduction of amides by lithium aluminum hydride.[4] Since it has been established that 1-benzoyl-2,2-dimethylhydrazine is not reduced by lithium aluminum hydride under the conditions employed in this experiment,[2,5] 1-benzyl-2,2-dimethylhydrazine must be formed by partial reduction of 1,1-dibenzoyl-2,2-dimethylhydrazine, followed by cleavage[4] of the intermediate formed in this way.

It seemed possible that 1-benzoyl-2,2-dimethylhydrazine could be formed by hydrolysis of residual 1,1-dibenzoyl-2,2-dimethylhydrazine in the basic solution resulting from the decomposition of the excess lithium aluminum hydride. The reaction mixture therefore was carefully examined for benzoic acid, but no significant quantity of base-soluble material could be found.

Other pathways which have been used to explain the reduction products of amides have been reviewed.[6] The formation of alkylamines rather than dialkylamines in the reaction of diacyl aromatic amines with lithium aluminum hydride has been reported.[7] It has also been shown that the isomeric 1,2-dibenzoyl-1,2-dimethylhydrazine also undergoes some cleavage to benzyl alcohol during reduction by lithium aluminum hydride. However, the tetraalkylhydrazine, 1,2-dibenzyl-1,2-dimethylhydrazine was isolated in 41% yield.[1] No benzaldehyde was detected.

The 1,1-dibenzoyl-2,2-dimethylhydrazine used in this work had previously been obtained together with 1-benzoyl-2,2-dimethylhydrazine from the reaction of benzoyl chloride and *unsym*-dimethylhydrazine under Schotten-Baumann conditions.[1] In an effort to improve the yield (previously about 40%) the benzoylation was carried out in pyridine. By this procedure 1,1-dibenzoyl-2,2-dimethylhydrazine was obtained in 67% yield.

The success of this procedure and the fact that Fox and Gibas have been able to prepare 1-nicotinyl-2,2-dimethylhydrazine using pyridine as a solvent,[8] suggested that the monobenzoylation of *unsym*-dimethylhydrazine in pyridine might be an improvement over previously described procedures.[1] Although the yield of crude product from the reaction in pyridine was high (73%), the pure product was obtained in only 33% yield because of difficulties in purification.

EXPERIMENTAL[9]

Reaction of 1,1-dibenzoyl-2,2-dimethylhydrazine with lithium aluminum hydride. A solution of 13.4 g. (0.05 mole) of 1,1-dibenzoyl-2,2-dimethylhydrazine[1] in 100 ml. of dry tetrahydrofuran was added rapidly to a stirred solution of 3.8 g. (0.10 mole) of lithium aluminum hydride in 150 ml. of the same solvent. The colorless solution was heated at the reflux temperature for two hours, then cooled in ice, after which the excess of lithium aluminum hydride was decomposed by the drop-wise addition of *n* ml. of water, followed by *n* ml. of 15% sodium hydroxide and then by 3 *n* ml. of water, where *n* = grams of lithium aluminum hydride originally used. During the decomposition a strong amine-like odor was noticed. Since the current of hydrogen produced in the decomposition entrained the volatile material, it was passed through an ethereal solution of picric acid. The yellow crystals which precipitated consisted of *unsym*-dimethylhydrazinium picrate, as shown by the undepressed mixture m.p. with an authentic specimen.[1] After the decomposition had been completed, the white precipitate was removed by filtration and washed several times with tetrahydrofuran and once with methanol. The filtered solid dissolved completely in 20% hydrochloric acid. When the acidic solution was extracted with ether, and the ether was evaporated, less than 0.1 g. of residue remained. The filtrate from the decomposed reaction mixture was concentrated under reduced pressure to about 30 ml., extracted twice with 20-ml. portions of 10% hydrochloric acid, and dried over sodium sulfate (solution A). When the hydrochloric acid extracts were made basic to litmus with 10% sodium hydroxide an oily layer formed. This basic mixture was extracted with three 20-ml. portions of ether, and the combined extracts were dried over sodium sulfate (solution B). After removal of the solvent, the residual material from solution B was separated into two fractions by distillation through a short Vigreux column. The first portion consisted of 1.6 g. (21%) of a colorless liquid, b.p. 61–62° (0.55 mm.), which rapidly turned yellow on standing. Treatment of a small portion of the distillate with methyl iodide in ether produced white crystals, which melted at 216–217° after two recrystallizations from 80% ethanol. The product had the composition of *1,1,1-trimethyl-2-benzylhydrazinium iodide.*

Anal. Calc'd for $C_{10}H_{17}IN_2$: C, 41.53; H, 4.88; N, 9.69. Found: C, 41.71; H, 5.58; N, 9.51.

The pot residue from the distillation of solution B crystallized on cooling. After one recrystallization from a mixture of ethyl acetate and pet. ether (60–70°), and one from a mixture of carbon tetrachloride and pet. ether (60–70°), the white needles melted at 106–107°. The mixture m.p. with an authentic specimen of 1-benzoyl-2,2-dimethylhydrazine was undepressed. The yield was 1.5 g. (18%).

Ethereal solution A was distilled at atmospheric pressure to give 3.8 g. of colorless liquid, b.p. 198–203°, n_{D}^{20} 1.5365. This material was a mixture of benzaldehyde and benzyl alcohol with the latter predominant, as shown by the following observations. Treatment of a solution of 0.25 ml. of the distillate in 3 ml. of 50% ethanol with 0.2 ml. of phenylhydrazine and one drop of glacial acetic acid produced tan needles, which weighed 80 mg. and melted at 154–155° after one crystallization from an ethanol-water mixture. The mixture m.p. with an authentic specimen of benzaldehyde phenylhydrazone was undepressed (reported m.p.[10] 156°).

When 0.1 ml. of the distillate was subjected to Brewster's

---

(4) F. Weygand, G. E. Berhardt, H. Linden, F. Schafer, and I. Eigen, *Angew. Chemie*, **65**, 525 (1953).

(5) More precisely the species resisting reduction is $[C_6H_5CONN(CH_3)_2]^{\ominus}$.

(6) N. G. Gaylord, *Reduction with Complex Hydrides*, Interscience Publishers, Inc., New York, N. Y., 1956, pp. 544, 633.

(7) B. Witkop and J. D. Patrick, *J. Am. Chem. Soc.*, **74**, 3861 (1952).

(8) H. H. Fox and J. T. Gibas, *J. Org. Chem.*, **20**, 60 (1955).

(9) Melting points and boiling points are uncorrected.

(10) R. Behrend and K. Leuchs, *Ann.*, **257**, 227 (1890).

procedure[11] for the preparation of a 3,5-dinitrobenzoate, 0.15 g. of a cream-colored solid was obtained, which melted at 109–111° and did not depress the m.p. of an authentic sample of benzyl 3,5-dinitrobenzoate [reported m.p.[12] 113–113.5° (corr.)].

Department of Chemistry
State University of Iowa
Iowa City, Iowa

---

(11) J. H. Brewster and C. J. Ciotti, Jr., *J. Am. Chem. Soc.*, **77**, 6214 (1955).

(12) R. E. Buckles and J. E. Maurer, *J. Org. Chem.*, **18**, 1585 (1953).

Transmission through the Phenylamino-Group of the Effect of Substituents in the Benzene Ring

D. G. O'Sullivan and P. W. Sadler

Received May 21, 1956

The carbonyl group possesses a stretching frequency in the 1800–1650 cm.$^{-1}$ region of the infrared spectrum.[1,2] Certain sets of compounds containing the substituted benzoyl group give carbonyl maxima which are linear functions of the σ values of the substituents.[3,4,5] The latter numbers are monotonically related to the decrease of electron density in the region of the particular benzene-ring carbon atom, produced by a substituent in either the *meta*- or *para*-position.[6] The effect of substituents may, however, be further transmitted through an NH group attached to the benzene ring as is shown by the tabulated carbonyl frequencies of *meta*- and *para*-substituted acetanilides and *iso*-nitrosoacetanilides. For comparison, carbonyl frequencies of substituted acetophenones and benzophenones[4] are also included in Table I. Amongst other compounds that show this effect are benzoic acid monomers and dimers,[3] benzoyl peroxides,[7] and isatins.[8] The carbonyl frequencies of all these compounds in solution approximately obey the equation $\nu - \nu_0 = 15\sigma$, where $\nu_0 = 1684$ (acetanilides), 1680 (*iso*nitrosoacetanilides), 1690 (acetophenones), 1663 (benzophenones), 1742 (benzoic acid monomers), 1696 (benzoic acid dimers), and 1740 (isatins). The good correlation between carbonyl frequency and σ function in acetanilides occurs despite the very extensive hydrogen bonding, presumably involving the carbonyl group, that is present in these compounds. Of the compounds examined, only *p*-phenylacetanilide exhibits an unusual carbonyl absorption, which may arise from partial hydrogen bonding.

TABLE I

Carbonyl Stretching Frequencies of Acetanilides A, Isonitrosoacetanilides B, Acetophenones C, and Benzophenones D, with the σ Values of Their Substituents

Substituent	σ	Carbonyl Frequencies A[a]	B[a]	C[b]	D[b]
p-NH_2	−0.660			1677	1651
p-MeO	−0.268	1678		1684	1658
p-Me	−0.170	1682	1677		1661
m-Me	−0.069	1683	1679		
None	0	1685	1680	1692	1664
p-Ph	0.009	1682 1686sh.			
p-F	0.062	1685	1680		
m-MeO	0.115	1686	1682		
p-Cl	0.227	1688	1683	1692	1666
m-F	0.337	1689	1685		
m-I	0.352	1690	1685		
m-Cl	0.373	1690	1686		
m-NO_2	0.710	1696	1690	1701	

[a] In chloroform. [b] In carbon tetrachloride.

Certain physical properties and many chemical reaction rates may be correlated with σ values of substituents. As an illustration, in Table II, rates of de-acylation of substituted *o*-nitroacetanilides[9–12] are compared with the carbonyl frequencies of the corresponding acetanilides. It has been shown that the nitro-group in the *ortho*-position exerts a constant effect in all cases, so that the comparison is valid.[9–12]

TABLE II

σ-Values and Carbonyl Frequencies (ν) of Acetanilides Compared with Rates of De-acylation (ρ) of Corresponding *o*-Nitroacetanilides

Substituent	σ	ρ	ν
p-NH_2	−0.660	0.06	
p-MeO	−0.268	0.6	1678
p-Me_2N	−0.205	0.06	
p-Me	−0.170	0.6	1682
m-Me	−0.069	1	1683
None	0	1	1685
p-Cl	0.227	4	1688
p-Br	0.232	4	
m-Cl	0.373	10	1690
m-Br	0.391	10	
m-NO_2	0.710	12	1696
p-NO_2	1.27[a]	18	

[a] Value quoted by Hammett[5] for derivatives of *p*-nitroaniline.

---

(1) Bellamy, *The Infra-red Spectra of Complex Molecules*, Methuen and Co., London, 1954.

(2) Jones and Sandorfy, *Chemical Applications of Spectroscopy* (Editor: W. West), Interscience Publishers, New York, 1956, p. 443.

(3) Flett, *Trans. Faraday Soc.*, **44**, 767 (1948).

(4) Fuson, Josien, and Shelton, *J. Am. Chem. Soc.*, **76**, 2526 (1954).

(5) Hammett, *Physical Organic Chemistry*, McGraw-Hill Book Co., New York, 1940, p. 188.

(6) Jaffe, *J. Chem. Phys.*, **20**, 279 (1952).

(7) Davison, *J. Chem. Soc.*, 2456 (1951).

(8) O'Sullivan and Sadler, *J. Chem. Soc.* (in the press).

(9) Wepster and Verkade, *Rec. trav. chim.*, **67**, 411 (1948).

(10) Wepster and Verkade, *Rec. trav. chim.*, **67**, 425 (1948).

(11) Wepster and Verkade, *Rec. trav. chim.*, **68**, 77 (1949).

(12) Wepster and Verkade, *Rec. trav. chim.*, **68**, 88 (1949).