at 60°, refluxed for 4 hr., and cooled overnight, and the precipitate (needles) was filtered and washed with dilute acid and then water and dried to give 0.620 g., m.p. 170–175°. Two recrystallizations from methanol gave a product, m.p. 188.5–189°. Mixture melting point and infrared and ultraviolet spectra proved it to be bis[2,3,4-trimethylnaphthyl-(1)-methyl] ether.[5] Benzoylation of the acidic filtrate gave 0.511 g., m.p. 105.8–106° (after recrystallization from ligroin), and a mixture melting point with an authentic sample proved it to be N-benzylbenzamide.

Reaction of 2 with Methanolic Hydrochloric Acid.—To a solution of 2 (0.520 g.) in methanol (5 ml.) was added concentrated hydrochloric acid (5 drops). The solution turned pink at once and was refluxed 4 hr., cooled, and poured into water containing excess sodium carbonate. The oily solid so obtained was extracted with hexane; the extract was washed neutral, dried over sodium sulfate, and evaporated to dryness; and the residue was extracted with water (10 ml.) containing concentrated hydrochloric acid (2 drops). The residue, insoluble in acid, weighed 0.150 g., m.p. 73–75°, and recrystallization from methanol gave the pure product, m.p. 76–76.5°, identified by mixture melting point and spectra to be 1-(methoxymethyl)-2,3,4-trimethylnaphthalene.[5] The acidic filtrate was made alkaline, giving 0.270 g. of a solid, m.p. 108–112°, which was recrystallized from hexane to give the starting material, 2, m.p. 115.5–116°. Benzylamine was identified in the filtrate by benzoylation.

Reaction of 2 in Methanol with Dry Hydrogen Chloride.—A solution of 2 (0.554 g.) in dry methanol (10 ml.) was saturated at 20° with HCl gas. The pink solution was evaporated to about 5 ml. and cooled to give crystals, which were filtered and washed with cold methanol to give 0.054 g., m.p. 93.5–94°, identified by infrared spectrum as 1-(chloromethyl)-2,3-4-trimethylnaphthalene.[5] Reaction of it with boiling methanol gave 1-(methoxymethyl)-2,3,4-trimethylnaphthalene.[5]

Ultraviolet Spectral Changes on Protonation of 2.—To a solution of 2 (2.71 mg.) in methanol (10 ml.) was added 3 M hydrochloric acid (1 drop), whereupon the spectrum showed $\lambda_{\max}^{\mathrm{MeOH}}$ mμ (log ε) 252 (2.80) 258 (2.80), 262 sh (2.75), 267 sh (2.64), and 280 sh (2.21). Within 15 min. after the addition of the acid, the solution was neutralized with 4 *M* ammonium hydroxide (1 drop), after which the spectrum was that of 2.

A sample of 2 was hydrogenated in the Brown[2] Hydro-analyzer and found to absorb 1.05 moles of hydrogen/mole of 2. The product was isolated and gave the spectrum: $\lambda_{\max}^{\mathrm{MeOH}}$ mμ (log ε) 205 (4.31), 256 sh (2.88), 261 (2.99), 267 (3.08), 274 (2.99). After acidification (as above), the spectrum showed: $\lambda_{\max}$ mμ (log ε) 210 (4.21), 260 sh (2.76), 263 (2.79), 270 (2.69). Upon neutralization, the solution again gave the original maxima.

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The Reaction of Lead Tetraacetate with Carbethoxyhydrazones[1,2]

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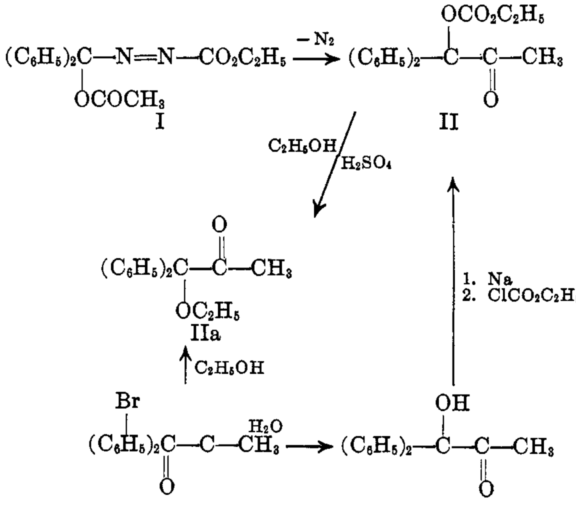
As part of a project designed to study azo and hydrazo aliphatic acid derivatives,[3] it appeared to be of interest to subject available carbethoxyhydrazones to treatment with lead tetraacetate. It was assumed that acetoxyazo esters, $R_2C(OCOCH_3)—N{=}N—CO_2C_2H_5$, would be obtained in high yields according to the reaction described by Iffland, Salisbury, and Schafer[4] for the oxidation of ketohydrazones.

When benzophenone carbethoxyhydrazone was caused to react with lead tetraacetate, a mixture of products resulted. This was separated to give the expected ethyl acetoxydiphenylmethylazocarboxylate (I) in 28% yield, an unknown oxygen-containing compound $C_{18}H_{18}O_4$ (II) in about 15% yield, and benzophenone. It was thought that acetic acid, formed during the reaction, had caused decomposition of the azo ester. Accordingly, the reaction was repeated in the presence of calcium oxide; however, there appeared to be no distinct advantage over the experiments conducted without the latter agent.

Analytical data suggested that II might be ethyl acetylbenzilate[5]; however, a mixture melting point determination and comparison of infrared and n.m.r. spectra of the compounds showed that they were similar but not identical. Alkaline hydrolysis of II produced benzhydrol and a small amount of an unidentified acidic material. Treatment of II with ethanol in the presence of sulfuric acid gave a product, IIa, which on heating with 18% hydrochloric acid was converted to a substance, IIb. An infrared spectrum of the latter showed hydroxyl and carbonyl absorption, and a positive test was obtained with 2,4-dinitrophenylhydrazine reagent. Compound II gave a material similar to IIb when heated with 18% hydrochloric acid. The product IIa was shown to be 1,1-diphenyl-1-ethoxy-2-propanone by analysis and comparison with an authentic sample prepared by ethanolysis of the known 1-bromo-1,1-diphenyl-2-propanone. This suggested that II is acetyldiphenylmethyl ethyl carbonate and was formed from the acetoxyazo ester I by a molecular rearrangement. The structure of II was confirmed by synthesis from the sodium derivative of 1,1-diphenyl-1-hydroxy-2-propanone and ethyl chloroformate.



Iffland and Davies[6] have described a similar rearrangement in which benzophenone 4,4-diethylsemicarbazone was transformed into 2-oxo-1,1-diphenyl-

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[2] Presented in part at the 15th Annual Kansas City Chemistry Conference of the American Chemical Society, Nov. 15, 1963.

[3] M. C. Chaco and Norman Rabjohn, *J. Org. Chem.*, **27**, 2765 (1962).

[4] D. C. Iffland, L. Salisbury, and W. R. Schafer, *J. Am. Chem. Soc.*, **83**, 747 (1961).

[5] Ethyl acetylbenzilate, m.p. 73–74°, was prepared by acetylation of ethyl benzilate. It was observed that ethyl acetylbenzilate undergoes solvolysis when heated with ethanol and sulfuric acid to give ethyl diphenylethoxyacetate, while acetylbenzilic acid under similar conditions affords diphenylethoxyacetic acid and a small amount of ethyl diphenylethoxyacetate.

[6] D. C. Iffland and T. M. Davies, *J. Am. Chem. Soc.*, **85**, 2182 (1963).

propyl diethylcarbamate by treatment with lead tetraacetate.

Attempts to extend the lead tetraacetate reaction to other carbethoxyhydrazones led to difficulties. Acetone, cyclohexanone, and acetophenone carbethoxyhydrazones afforded mixtures of yellow oily products with absorption peaks near 313 and 365 mμ in the ultraviolet. Similar results were, also, obtained with acetone carbethoxyhydrazone and lead tetrabenzoate.

Experimental[7]

Reaction of Benzophenone Carbethoxyhydrazone with Lead Tetraacetate.—A solution of 18.8 g. (0.07 mole) of benzophenone carbethoxyhydrazone,[8] m.p. 112–113°, λ_{max} 277 mμ (ϵ 16,960), in 18 ml. of methylene chloride was added slowly to a solution of 34.3 g. (0.07 mole) of lead tetraacetate in 140 ml. of methylene chloride, which contained 7.8 g. (0.14 mole) of calcium oxide, with vigorous stirring and ice cooling. After all of the hydrazone had been added, the reaction mixture was stirred at room temperature for 30 min. and was filtered. The filtrate was washed with sodium bicarbonate solution and water and was dried over anhydrous sodium sulfate.

The solvent was removed *in vacuo* and the residue was taken up in petroleum ether (b.p. 30–60°). The solution was cooled in a refrigerator and a yellow solid separated. Fractional recrystallization of this material from petroleum ether and *n*-pentane and distillation of the mother liquors at 0.2 mm. afforded three fractions in fairly pure form.

Fraction A (6.4 g.) was recrystallized repeatedly from methanol and 95% ethanol to give a yellow compound which melted at 99–100°.

Anal. Calcd. for $C_{18}H_{18}N_2O_4$: C, 66.24; H, 5.56; N, 8.58. Found: C, 66.10; H, 5.20; N, 8.34.

The ultraviolet spectrum in ethanol showed λ_{max} 375 mμ (ϵ 74.3).

Fraction B (3.1 g.) melted at 84–85° after repeated recrystallizations from *n*-pentane.

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.46; H, 6.08. Found: C, 72.47; H, 5.95.

The ultraviolet spectrum in ethanol had λ_{max} 262 mμ (ϵ 605) and 288 mμ (ϵ 400), and shoulders at 253 mμ (ϵ 454), 260 (562), and 270 (540).

Fraction C (2.7 g.) was shown to be benzophenone by comparison of its infrared and ultraviolet spectra with an authentic sample.

Action of Alkali on Fraction B.—A solution of 0.25 g. of fraction B in 3 ml. of 2 *N* alcoholic potassium hydroxide was heated on a steam bath for 2.75 hr. It was diluted with water and extracted with ether. The ether extract was dried over anhydrous sodium sulfate, and the ether was evaporated to give a residue of 0.12 g., m.p. 59–64°. Its infrared spectrum was identical with that of benzhydrol and a mixture of the compound with authentic benzhydrol (m.p. 67–68°) melted at 61–66°.

The aqueous layer from the hydrolysis was acidified with dilute hydrochloric acid. The precipitate was removed by extraction with ether and worked up to give 0.045 g. of a white solid, m.p. 95–135°.

Treatment of Fraction B with Ethanol and Sulfuric Acid.—A solution of 0.51 g. of fraction B in 10 ml. of absolute ethanol, to which had been added 2 drops of concentrated sulfuric acid, was heated at reflux for 11 hr. The solvent was removed under reduced pressure and the residue was taken up in ether. The ether solution was washed with water, dried over anhydrous sodium sulfate, and concentrated. After drying the residue under high vacuum, there was obtained 0.45 g. of product. Its infrared spectrum was identical with that of 1,1-diphenyl-1-ethoxy-2-propanone described below.

The residue (0.39 g.) was refluxed with an excess of 18% hydrochloric acid for 2 hr. and worked up in the usual fashion. The oil obtained gave a positive test with 2,4-dinitrophenylhydrazine reagent, and its infrared spectrum showed the presence of carbonyl and hydroxyl groups.

1,1-Diphenyl-1-ethoxy-2-propanone.—A solution of 2.71 g. (0.01 mole) of 1-bromo-1,1-diphenyl-2-propanone, prepared by the method of Stevens and Lenk,[9] in 30 ml. of absolute ethanol was refluxed for 10 hr. The alcohol was removed at reduced pressure and the residue was dissolved in petroleum ether. The colored solution was treated with Norit, and the solvent was removed. The residue (1.55 g.) was distilled through a short column, b.p. 108–110° (0.05 mm.), $n^{20}D$ 1.5561.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.22; H, 7.07.

Acetyldiphenylmethyl Ethyl Carbonate.—A solution of 1.21 g. (0.0054 mole) of 1,1-diphenyl-1-hydroxy-2-propanone (m.p. 62–64°), prepared by the hydrolysis of 1-bromo-1,1-diphenyl-2-propanone,[9] in 5 ml. of dry benzene was added with vigorous stirring to a suspension of 0.123 g. (0.0054 g.-atom) of sodium in 8 ml. of dry benzene. After the sodium had disappeared, 0.68 g. (0.0063 mole) of ethyl chloroformate was added and the mixture was heated at reflux with stirring overnight. The solvent was removed *in vacuo*, the residue was boiled with petroleum ether (b.p. 60–70°) and decanted, and the process was repeated. The combined extracts were evaporated to dryness, taken up in a minimum amount of hot pentane, and seeded with a crystal of fraction B obtained from the reaction of lead tetraacetate with benzophenone carbethoxyhydrazone. A solid (0.05 g.) resulted which melted at 84–85°. It did not depress the melting point of fraction B and the two gave identical infrared spectra.

Ethyl Acetylbenzilate.—This ester was prepared from ethyl benzilate by acetylation with acetyl chloride[10] and also with acetic anhydride in the presence of a small amount of sulfuric acid. The compound was recrystallized from petroleum ether (b.p. 60–68°) and melted at 73–74°. Bickel[10] reported a melting point of 65°.

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.46; H, 6.08. Found: C, 72.13; H, 5.87.

Acetylbenzilic Acid.—Benzilic acid (8 g.) was heated overnight at 100° with an excess of acetic anhydride. After hydrolysis of the excess anhydride, the reaction mixture afforded 5.6 g. (66%) of a solid product. It was recrystallized from acetic acid and dried for 3 days at 50° (0.25 mm.), m.p. 105–106°; melting points of 98[11] and 104.5–104.8°[12] have been reported.

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.11; H, 5.22. Found: C, 71.26; H, 5.07.

Ethanolysis of Acetylbenzilic Acid.—A solution of 6.5 g. (0.024 mole) of acetylbenzilic acid in 30 ml. (0.5 mole) of absolute ethanol and 0.3 ml. of concentrated sulfuric acid was heated at 75–80° for 16 hr. The excess ethanol was removed *in vacuo*, the residue was dissolved in ether, and the solution was extracted repeatedly with dilute sodium bicarbonate. The combined bicarbonate solutions were acidified to give 5.3 g. (87%) of a white solid, m.p. 113–114°. This was shown, by comparison of infrared spectra and mixture melting point, to be identical with the ethyl ether of benzilic acid which was prepared by the method of Klinger.[13] A sample of the ether was heated with 18% hydrochloric acid and benzilic acid was obtained.

The ether solution from the original reaction mixture was dried and evaporated to leave a residue of 0.44 g. This was purified by evaporative distillation at 75° (0.1 mm.), $n^{25}D$ 1.5421.

Anal. Calcd. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 75.73; H, 7.29.

The compound was shown to be ethyl diphenylethoxyacetate by comparison of its infrared spectrum with the product prepared by ethanolysis of ethyl acetylbenzilate as described in the next experiment.

Reaction of Ethyl Acetylbenzilate with Ethanol in the Presence of Sulfuric Acid.—A solution of 0.2 g. of ethyl acetylbenzilate in 4 ml. of absolute ethanol which contained 2 drops of sulfuric acid was heated at 100° for a day. The solvent was removed under reduced pressure and the residue was dissolved in ether. The ether solution was washed, dried, and concentrated. The infrared spectrum of the residue was identical with that of the product from the previous experiment.

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[7] Microanalyses were by the Weiler and Strauss Laboratories. The melting points are corrected.

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