heated at reflux for 0.5 hour. After cooling, the product was removed by filtration and purified by recrystallization from isopropyl alcohol to give 2.65 g.

2-Amino-5-methylaminopyrimido(4,5-d)pyrimidine (XVI, R'' = H, R' = CH$_3$).—One gram of 2-ethylthio-5-methylaminopyrimido(4,5-d)pyrimidine was heated with 30 ml. of ethanol saturated with ammonia in an autoclave at 135° for 5 hours. The product which had separated out of solution was purified by recrystallization from aqueous ethanol to give 0.5 g.

2,5-Bis-(methylthio)-pyrimido(4,5-d)pyrimidine, (XIV, R = CH$_3$).—To 15 ml. of 7.5% aqueous sodium carbonate was added 0.4 g. of 2-methylthio-5-mercaptopyrimido(4,5-d)pyrimidine and the mixture was heated to 35–40° in an oil-bath. To the resulting solution was added 0.5 ml. of dimethyl sulfate and the two-phase system was stirred manually until homogeneous. At this time a light yellow solid began to separate from the reaction mixture. The flask was removed from the oil-bath and the mixture stirred vigorously with a magnetic stirrer for 5 minutes. The mixture was refrigerated overnight and the solid product collected by filtration, washed with alcohol and dried to give 0.32 g. of a pale yellow solid.

2-Methylthio-5-benzylaminopyrimido(4,5-d)pyrimidine (XV, R = CH$_3$, R' = C$_6$CH$_5$CH$_2$).—To a suspension of 0.07 g. of 2,5-bis-(methylthio)-pyrimido(4,5-d) pyrimidine in 8 ml. of absolute ethanol was added 0.5 ml. of benzylamine. The mixture was stirred for 15 hours at room temperature. The solid which had formed was collected by filtration, washed with ethanol and ether and dried to give 0.075 g. of pale yellow material, which yielded white needles upon recrystallization from ethanol.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA, IOWA CITY, IOWA]

The Rearrangement of 1,1-Dimethyl-1-*p*-nitrobenzylamine-2-acetimide

BY S. WAWZONEK AND E. YEAKEY[1]

RECEIVED MAY 9, 1960

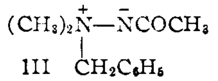
1,1-Dimethyl-1-benzylamine-2-acetimide and 1,1-dimethyl-1-*p*-nitrobenzylamine-2-acetimide rearrange to 1,1-dimethyl-2-benzyl-2-acetylhydrazine and 1,1-dimethyl-2-*p*-nitrobenzyl-acetylhydrazine, respectively. The structure of the latter was demonstrated by synthesis from the dimethylhydrazone of *p*-nitrobenzaldehyde. Alkylation of 1,1-dimethyl-1-*p*-nitrobenzylamine-2-acetimide with methyl iodide gave 1,1-dimethyl-1-*p*-nitrobenzyl-2-α-methoxyethylidenehydrazonium iodide. Hydrolysis of the acetimide with hydrochloric acid gave 1,1-dimethyl-1-*p*-nitrobenzylhydrazonium chloride. Treatment of the latter with sodium methoxide gave dimethyl-*p*-nitrobenzylamine, formaldehyde and ammonia.

The successful synthesis of trimethylamine-*p*-toluenesulfonimide (I)[2] and trimethylaminebenzimide (II)[3] suggested a study of the chemical

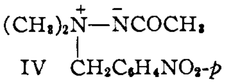
$$(CH_3)_3\overset{+}{N}—\overset{-}{N}SO_2C_6H_4CH_3\text{-}p \qquad (CH_3)_3\overset{+}{N}—\overset{-}{N}COC_6H_5$$

properties of these compounds and a comparison of their behavior with the sulfilimines

In this work the rearrangement of 1,1-dimethyl-1-benzylamine-2-acetimide (III) and 1,1-dimethyl-1-*p*-nitrobenzylamine-2-acetimide (IV) has been investigated. Since the benzyl derivative III was an oil, most of the reactions were carried out with the *p*-nitrobenzyl compound IV.

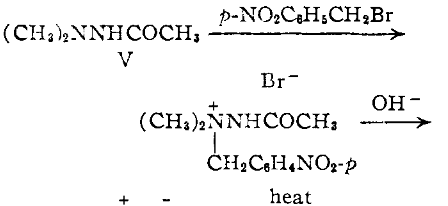


$$\underset{\text{III}\quad CH_2C_6H_5}{(CH_3)_2\overset{+}{N}—\overset{-}{N}COCH_3}$$



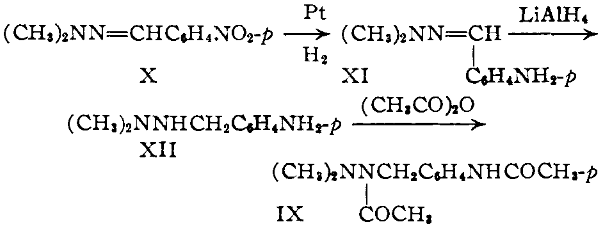
$$\underset{\text{IV}\quad CH_2C_6H_4NO_2\text{-}p}{(CH_3)_2\overset{+}{N}—\overset{-}{N}COCH_3}$$

Both compounds were prepared from 1,1-dimethyl-2-acetylhydrazine (V)[4] through the corresponding hydrazonium salt VI. The 1,1-dimethyl-1-*p*-nitrobenzylamine-2-acetimide (IV) rearranged when distilled under reduced pressure to 1,1-dimethyl-2-*p*-nitrobenzyl-2-acetylhydrazine (VII). The structure of the rearranged product (VII) was demonstrated by conversion to 1,1-dimethyl-2-*p*-acetaminobenzyl-2-acetylhydrazine (IX) which was synthesized from the dimethylhydrazone of *p*-nitrobenzaldehyde (X) by the steps



$$\underset{\text{V}}{(CH_3)_2NNHCOCH_3} \xrightarrow{p\text{-}NO_2C_6H_5CH_2Br} \overset{Br^-}{\underset{CH_2C_6H_4NO_2\text{-}p}{(CH_3)_2\overset{+}{N}NHCOCH_3}} \xrightarrow{OH^-}$$

$$\underset{\text{IV}\quad CH_2C_6H_4NO_2\text{-}p}{(CH_3)_2\overset{+}{N}—\overset{-}{N}COCH_3} \xrightarrow{\text{heat}} \underset{\text{VIII}\quad CH_2C_6H_4NO_2\text{-}p}{(CH_3)_2NNCOCH_3}$$

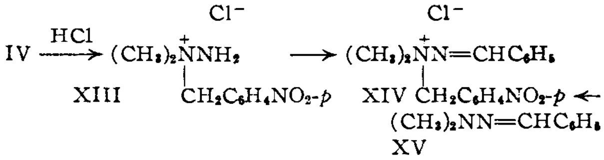


$$\underset{\text{X}}{(CH_3)_2NN{=}CHC_6H_4NO_2\text{-}p} \xrightarrow[H_2]{Pt} \underset{\text{XI}\quad C_6H_4NH_2\text{-}p}{(CH_3)_2NN{=}CH} \xrightarrow{LiAlH_4}$$

$$\underset{\text{XII}}{(CH_3)_2NNHCH_2C_6H_4NH_2\text{-}p} \xrightarrow{(CH_3CO)_2O} \underset{\text{IX}\quad COCH_3}{(CH_3)_2NNCH_2C_6H_4NHCOCH_3\text{-}p}$$

Acid hydrolysis of 1,1-dimethyl-2-*p*-nitrobenzyl-2-acetylhydrazine gave 1,1-dimethyl-2-*p*-nitrobenzylhydrazine.

Proof for the structure of the aminimide IV was the acid hydrolysis to 1,1-dimethyl-1-*p*-nitrobenzylhydrazonium chloride (XIII) which was difficult to purify. This salt (XIII) was converted into



$$\text{IV} \xrightarrow{HCl} \overset{Cl^-}{\underset{\text{XIII}\quad CH_2C_6H_4NO_2\text{-}p}{(CH_3)_2\overset{+}{N}NH_2}} \longrightarrow \overset{Cl^-}{\underset{\text{XIV}\quad CH_2C_6H_4NO_2\text{-}p}{(CH_3)_2\overset{+}{N}N{=}CHC_6H_5}} \longleftarrow \underset{\text{XV}}{(CH_3)_2NN{=}CHC_6H_5}$$

the picrate and formed a hydrazone (XIV) with benzaldehyde. The latter compound was also synthesized by the alkylation of the dimethylhydrazone of benzaldehyde (XV) with *p*-nitrobenzyl chloride.

Prolonged acid treatment of the aminimide IV gave *p*-nitrobenzyl chloride.

Reduction of the aminimide IV with tin and hydrochloric acid gave 1,1-dimethylhydrazine; cleav-

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(1) Abstracted in part from the Ph.D. Thesis of E. Yeakey, August, 1960 and presented at the 138th Meeting of the American Chemical Society, New York, N. Y., Sept., 1960.

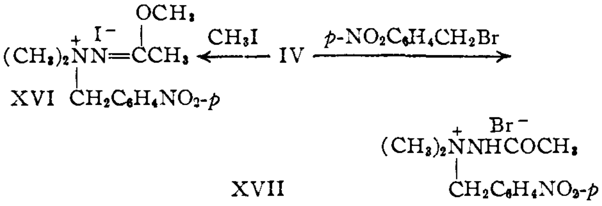
(2) S. Wawzonek and D. Meyer, THIS JOURNAL, **76**, 2918 (1954).

(3) R. L. Hinman and M. Flores, *J. Org. Chem.*, **24**, 660 (1959).

(4) R. L. Hinman, THIS JOURNAL, **78**, 1645 (1956).

age of the *p*-nitrobenzyl group occurred in a manner similar to that observed with 1,1,1-trimethyl-2-benzyl-2-*p*-toluenesulfonylhydrazonium chloride.[2]

Alkylation of the aminimide IV with methyl iodide gave 1,1-dimethyl-1-*p*-nitrobenzyl-2-α-methoxyethylidenehydrazonium iodide (XVI) and a small amount of *p*-nitrobenzyliodide. The same reaction with *p*-nitrobenzyl bromide gave 1,1-dimethyl-1-*p*-nitrobenzyl-2-acetylhydrazonium bromide (XVII); solvolysis of the *p*-nitrobenzyl bromide occurred in the ethanol and formed hydrogen bromide which reacted with the aminimide IV.

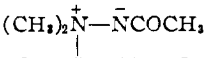


$$\underset{\text{XVI}}{(CH_3)_2\overset{+}{N}(CH_2C_6H_4NO_2\text{-}p)N{=}C(OCH_3)CH_3\ I^-} \xleftarrow{CH_3I} \text{IV} \xrightarrow{p\text{-}NO_2C_6H_4CH_2Br} \underset{\text{XVII}}{(CH_3)_2\overset{+}{N}(CH_2C_6H_4NO_2\text{-}p)NHCOCH_3\ Br^-}$$

Evidence for the structure of XVI was its hydrolysis to 1,1-dimethyl-1-*p*-nitrobenzylhydrazonium chloride (XIII).

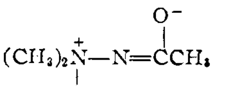
An attempt to prepare 1,1-dimethyl-1-*p*-nitrobenzylaminimide from 1,1-dimethyl-1-*p*-nitrobenzylhydrazonium chloride (XIII) by treatment of the latter with sodium methoxide in methanol gave dimethyl-*p*-nitrobenzylamine. Formaldehyde and ammonia were also formed in this reaction. This decomposition resembles that observed with trimethylmethoxyammonium hydroxide[5] and related compounds and suggests that methoxide ion causes a displacement of the amino group as the amide ion. Conversion of the latter by methanol into ammonia would drive the reaction to completion. The resulting dimethyl-*p*-nitrobenzylmethoxyammonium methoxide would decompose into dimethyl-*p*-nitrobenzylamine, formaldehyde and methanol as was observed.

The results obtained indicate that aminimides with benzyl groups (IV) rearrange in a similar fashion to that observed with the corresponding sulfilimines.[6] The *O*-alkylation of the aminimide IV observed with methyl iodide indicates that the resonance form XVIII contributes to the structure of the aminimide. Comparison of the infrared spectra of the aminimide IV and of 1,1-dimethyl-1-*p*-nitrobenzyl-2-α-methoxyethylidinehydrazonium iodide (XVI) indicates that this contribution is a substantial one. The α-methoxyethylidene derivative XVI gives a broad band from 6.10 to 6.18 μ and the aminimide gives a band at 6.35 μ in Nujol. Both bands are probably due to the C=N stretching frequency. The shift in the aminimide is no doubt due to the ionic character involved.



$$(CH_3)_2\overset{+}{N}(CH_2C_6H_4NO_2\text{-}p)\text{—}\overset{-}{N}COCH_3$$

IV



$$(CH_3)_2\overset{+}{N}(CH_2C_6H_4NO_2\text{-}p)\text{—}N{=}C(O^-)CH_3$$

XVIII

Experimental[7]

1,1-Dimethyl-1-benzyl-2-acetylhydrazonium Chloride.—A mixture of 1,1-dimethyl-2-acetylhydrazine[4] (5 g.) and benzyl chloride (10 g.) in 25 ml. of dry benzene was refluxed for 2 hours, cooled, and the solid removed by filtration. The yield of white needles, m.p. 139–141° after recrystallization from a mixture of ethanol–ethyl acetate, was 8 g. (71%). The compound was water soluble and gave silver chloride with silver nitrate solution.

Anal. Calcd. for $C_{11}H_{17}N_2OCl$: C, 57.75; H, 7.44; N, 12.25. Found: C, 57.87; H, 7.22; N, 12.07.

1,1-Dimethyl-1-benzylamine-2-acetylimide (III).—A solution of 1,1-dimethyl-1-benzyl-2-acetylhydrazonium chloride (5 g.) in 10 ml. of water was treated with 0.1 *N* sodium hydroxide to a phenolphthalein end-point. The aqueous solution was evaporated almost to dryness under reduced pressure and extracted with five 25-ml. portions of chloroform. After removal of the chloroform under reduced pressure 3 g. of a yellow glassy oil remained which could not be induced to crystallize. A satisfactory analysis of the water-soluble oil could not be obtained. The picrate when crystallized from ethanol melted at 87–88°.

Anal. Calcd. for $C_{17}H_{19}N_5O_8$: C, 48.46; H, 4.51. Found: C, 48.23; H, 4.53.

1,1-Dimethyl-2-benzyl-2-acetylhydrazine.—Distillation of the oily aminimide occurred at 173–175° (5 mm.) and gave a clear viscous liquid, n^{25}D 1.5285, which was water insoluble. This liquid analyzed for 1,1-dimethyl-2-benzyl-2-acetylhydrazine.

Anal. Calcd. for $C_{11}H_{16}N_2O$: C, 68.80; H, 8.34; Found: C, 69.33; H, 8.38.

1-1-Dimethyl-1-*p*-nitrobenzyl-2-acetylhydrazonium Bromide (VI).—To 40 g. of *p*-nitrobenzyl bromide in 100 ml. of dry benzene 1,1-dimethyl-2-acetylhydrazine (20 g.) was added and the mixture was refluxed for 1 hour. The yield of pale yellow crystals obtained by cooling and removal of the solvent was 51 g. (85%) after recrystallization from a mixture of absolute ethanol and ethyl acetate; m.p. 156–158°.

Anal. Calcd. for $C_{11}H_{16}N_3O_3Br$: C, 41.50; H, 5.04; N, 13.21. Found: C, 41.38; H, 4.89; N, 13.57.

1,1-Dimethyl-1-*p*-nitrobenzylamine-2-acetylimide (IV).—Five grams of 1,1-dimethyl-1-*p*-nitrobenzyl-2-acetylhydrazonium bromide was dissolved in 20 ml. of water and titrated to a phenolphthalein end-point with 5 *N* sodium hydroxide. The solution was evaporated to dryness and extracted with five 25-ml. portions of chloroform. Removal of the chloroform under reduced pressure gave 3.2 g. (86%) of pale yellow crystals. This water-soluble compound when recrystallized from a mixture of ethyl acetate–petroleum ether gave white crystals melting at 175–177°.

Anal. Calcd. for $C_{11}H_{15}N_3O_3$: C, 55.62; H, 6.32. Found: C, 55.51; H, 6.14.

The picrate of 1,1-dimethyl-1-*p*-nitrobenzylamine-2-acetylimide when recrystallized from ethanol melted at 139–141°.

Anal. Calcd. for $C_{17}H_{17}N_6O_{10}$: C, 43.69; H, 4.07; N, 17.38. Found: C, 43.65; H, 3.79; N, 17.43.

1,1-Dimethyl-2-*p*-nitrobenzyl-2-acetylhydrazine (VII).—Ten grams of 1,1-dimethyl-1-*p*-nitrobenzylamine-2-acetylimide was distilled at 180–182° (3 mm.) and gave 5 g. (50%) of a colorless oil which upon cooling gave white platelets. The solid, after recrystallization from hexane, melted at 100–102°. The black tarry residue left in the still pot was not investigated further.

Anal. Calcd. for $C_{11}H_{15}N_3O_3$: C, 55.62; H, 6.32. Found: C, 55.52; H, 6.33.

1,1-Dimethyl-2-*p*-acetaminobenzyl-2-acetylhydrazine (IX). **Method A.**—A solution of 1,1-dimethyl-2-*p*-nitrobenzyl-2-acetylhydrazine (1.7 g.) in 50 ml. of 95% ethanol was treated with hydrogen at a pressure of 40 pounds for 4 hours using platinum oxide (0.2 g.) as a catalyst. The catalyst was removed by filtration and the ethanol removed under reduced pressure. The resulting oil was not purified but was refluxed with 4 ml. of acetic anhydride in 10 ml. of dry benzene for 5 hours. Removal of the benzene and excess acetic anhydride under reduced pressure gave 0.5 g. (28%)

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(5) J. Meisenheimer, *Ann.*, **397**, 273 (1913).

(6) A. S. F. Ash and F. Challenger, *J. Chem. Soc.*, 2792 (1952).

(7) Melting points are corrected and boiling points are not.

of white plates, which melted at 170–171° after recrystallization from benzene.

Anal. Calcd. for $C_{13}H_{19}N_3O_2$: C, 62.60; H, 7.64; N, 16.87. Found: C, 62.54; H, 7.69; N, 16.67.

Method B.—Ten grams of the dimethylhydrazone of *p*-nitrobenzaldehyde[8] was suspended in 150 ml. of 95% ethanol and reduced with hydrogen at a pressure of 40 pounds for 6 hours using platinum oxide (0.3 g.) as a catalyst. Removal of the catalyst by filtration and the ethanol under reduced pressure gave 6.5 g. (76%) of yellow crystals which, after recrystallization from hexane, melted at 86–87°. The yellow color and the elemental analysis indicated that this compound was the dimethylhydrazone of *p*-aminobenzaldehyde.

Anal. Calcd. for $C_9H_{13}N_3$: C, 66.20; H, 7.98. Found: C, 65.94; H, 7.76.

Seven grams of the dimethylhydrazone of *p*-aminobenzaldehyde in 25 ml. of dry tetrahydrofuran was added dropwise with stirring to 4.0 g. of lithium aluminum hydride in 75 ml. of tetrahydrofuran. The mixture was stirred for 2 days during which time the reaction mixture turned from green to gray. After decomposition with water the tetrahydrofuran solution after filtration was dried over sodium sulfate. Removal of the tetrahydrofuran under reduced pressure gave 1,1-dimethyl-2-*p*-aminobenzyl-2-acetylhydrazine boiling at 164–165° (18 mm.), yield 5 g., $n^{25}D$ 1.5785.

Anal. Calcd. for $C_9H_{15}N_3$: C, 65.40; H, 9.09; N, 25.47. Found: C, 65.31; H, 8.86; N, 25.00.

Four grams of 1,1-dimethyl-2-*p*-aminobenzylhydrazine was added to 9 ml. of acetic anhydride in 20 ml. of dry benzene and refluxed for 2 hours. The benzene and excess acetic anhydride when removed under reduced pressure gave a white solid (4.3 g.) which was recrystallized from benzene; m.p. 170–171°. A mixture with the product from method A melted at the same point. The infrared spectra of the two were identical.

1,1-Dimethyl-1-*p*-nitrobenzylhydrazonium Chloride (XIII).—Five grams of 1,1-dimethyl-1-*p*-nitrobenzylamine-2-acetimide in 10 ml. of water was refluxed with 20 ml. of concentrated hydrochloric acid for 2 hours. Removal of the water and excess hydrochloric acid under reduced pressure gave a green oil (4.4 g.) which when recrystallized from isopropyl alcohol gave white hygroscopic cubes, m.p. 116–118°. This compound was water soluble and gave a positive test for chloride with silver nitrate solution.

Anal. Calcd. for $C_9H_{14}N_3O_2Cl$: C, 46.62; H, 6.04. Found: C, 47.99; H, 6.77.

Reaction of the chloride salt with picric acid in ethanol gave 1,1-dimethyl-1-*p*-nitrobenzylhydrazonium picrate, which melted at 202–204° after recrystallization from ethanol.

Anal. Calcd. for $C_{15}H_{16}N_6O_9$: C, 42.45; H, 3.77; N, 19.80. Found: C, 42.49; H, 3.81; N, 19.53.

Prolonged refluxing (3 days) of the aminimide IV (20 g.) gave upon cooling *p*-nitrobenzyl chloride (3.0 g.) which after one crystallization from hexane melted at 69–71°. The literature[9] reports a value of 71–72°. Further characterization was made by converting this compound into N-*p*-nitrobenzylphthalimide melting at 175–176°. The literature[10] value is 173–174°.

The water layer gave a viscous green oil which was not characterized further.

1,1-Dimethyl-1-*p*-nitrobenzyl-2-benzylidenehydrazonium Chloride (XIV). **A.**—Condensation of 1,1-dimethyl-1-*p*-nitrobenzylhydrazonium chloride (0.5 g.) with benzaldehyde (2 ml.) in refluxing ethanol (5 ml.) for 10 minutes yielded white crystals which melted at 152–154° after recrystallization from a mixture of ethanol and ethyl acetate. This compound was water soluble and gave a positive chloride test with silver nitrate.

Anal. Calcd. for $C_{16}H_{18}N_3O_2Cl$: C, 60.05; H, 5.64; N, 13.02. Found: C, 59.71; H, 5.62; N, 13.14.

B.—A solution of *p*-nitrobenzyl chloride (5 g.) and the dimethylhydrazone of benzaldehyde (5.0 g.) was heated in benzene (5 ml.) for 24 hours. The white crystals (3.0 g.) obtained melted at 154–155° after recrystallization from a mixture of ethanol and ethyl acetate. The solid did not depress the melting point of the product from method A and had an identical infrared spectrum in potassium bromide.

1,1-Dimethyl-2-*p*-nitrobenzylhydrazine.—Five grams of 1,1-dimethyl-2-*p*-nitrobenzyl-2-acetylhydrazine in ethanol (25 ml.) was refluxed with 50 ml. of concentrated hydrochloric acid for 2 hours. The solution was made basic with sodium hydroxide and extracted with three 25-ml. portions of ether. Removal of the ether gave an orange oil which was distilled at 144–145° (4 mm.). The distillate crystallized upon cooling and melted at 60–61° after recrystallization from hexane; yield 2 g. This compound slowly decomposed upon standing.

Anal. Calcd. for $C_9H_{13}N_3O_2$: C, 55.38; H, 6.66. Found: C, 55.46; H, 6.46.

The picrate of 1,1-dimethyl-2-*p*-nitrobenzylhydrazine after recrystallization from ethanol melted at 127–128°.

Anal. Calcd. for $C_{15}H_{16}N_6O_9$: C, 42.45; H, 3.77; N, 19.80. Found: C, 42.36; H, 3.72; N, 19.21.

Reactions of 1,1-Dimethyl-1-*p*-nitrobenzylamine-2-acetimide. 1. Reduction.—To a mixture of 10 g. of 1,1-dimethyl-1-*p*-nitrobenzylamine-2-acetylimide and 24 g. of granulated tin in 20 ml. of water, 40 ml. of concentrated hydrochloric acid was added in small portions with cooling. After the addition was complete the mixture was refluxed for 2 hours, cooled, and filtered to remove the excess tin. The filtrate was made strongly basic with sodium hydroxide and was steam distilled into dilute hydrochloric acid. The acid distillate upon evaporation to dryness gave 3 g. (74%) of yellow hygroscopic needles which could not be recrystallized satisfactorily. The picrate, recrystallized from ethanol, melted at 142–144°. A mixture with the picrate of unsymmetrical dimethylhydrazine melted at 142–144°. The literature[4] reports a value of 145–146°.

The other products from the reaction, *p*-toluidine and acetic acid, were not isolated.

2. Reaction with Methyl Iodide.—To 10 g. of 1,1-dimethyl-1-*p*-nitrobenzylamine-2-acetylimide in 25 ml. of chloroform 50 ml. of methyl iodide was added and the mixture was refluxed for 12 hours. Upon cooling and filtering 14 g. of yellow needles was obtained. The 1,1-dimethyl-1-*p*-nitrobenzyl-2-α-methoxyethylidenehydrazonium iodide was water soluble, gave a positive silver nitrate test and melted at 137–138° after recrystallization from an ethanol–ethyl acetate mixture.

Anal. Calcd. for $C_{12}H_{18}N_3O_3I$: C, 37.99; H, 4.75; N, 11.08. Found: C, 38.24; H, 4.63; N, 10.50.

The filtrate upon evaporation to dryness gave a black tar which was dissolved in boiling ethanol and treated with charcoal; 1 g. of *p*-nitrobenzyl iodide was obtained melting at 127–128°. The literature reports[9] a melting point of 127°.

Hydrolysis of 1 g. of 1,1-dimethyl-1-*p*-nitrobenzyl-2-α-methoxyethylidenehydrazonium iodide with 10 ml. of concentrated hydrochloric acid under reflux conditions for 1 hour gave a black viscous oil when the excess hydrochloric acid was removed under reduced pressure. The picrate of the oil, recrystallized from 95% ethanol, melted at 195–197°; a mixture with 1,1-dimethyl-1-*p*-nitrobenzylhydrazonium picrate also melted at 195–197°.

3. Reaction with *p*-Nitrobenzyl Bromide.—Five grams of 1,1-dimethyl-1-*p*-nitrobenzylamine-2-acetylimide in 25 ml. of absolute ethanol was allowed to react with 5 g. of *p*-nitrobenzyl bromide for 2 weeks at room temperature. The mixture was poured into 50 ml. of water and the excess *p*-nitrobenzyl bromide was removed by filtration. The filtrate when evaporated to dryness under reduced pressure gave 1 g. of 1,1-dimethyl-1-*p*-nitrobenzyl-2-acetylhydrazonium bromide, which melted at 157–158°.

Reaction of 1,1-Dimethyl-1-*p*-nitrobenzylhydrazonium Chloride with Sodium Methoxide.—A solution of the hydrazonium chloride XIII (5 g.) in methanol (10 ml.) when treated with 1.1 g. of sodium methoxide in 10 ml. of methanol gave an immediate precipitate of sodium chloride. The methanol was removed by distillation and was accompanied by the evolution of ammonia. The distillate showed the presence of formaldehyde when tested with chromotropic acid.

The residue upon extraction with chloroform gave 3.3 g. of a black oil which was identified as dimethyl-*p*-nitrobenzylamine by conversion to the methiodide and picrate. The

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[8] O. C. Brady and G. P. McHugh, *J. Chem. Soc.*, **121**, 1651 (1922).

[9] G. Kumpf, *Ann.*, **224**, 96 (1884).

[10] H. Salkowski, *Ber.*, **22**, 2137 (1889).

picrate melted at 140–142° after recrystallization from ethanol. The literature[11] reports a melting point of 149°.

Anal. Calcd. for $C_{15}H_{15}N_5O_9$: C, 44.05; H, 3.67. Found: C, 44.11; H, 3.91.

The methiodide after recrystallization from a mixture of ethanol and ethyl acetate melted at 197–198°. The literature[12] reports a melting point of 198°. A mixture with an authentic sample melted at 197–198°. The infrared spectra of the two methiodides were identical in Nujol.

Acknowledgment.—Support of this research by the National Science Foundation is gratefully acknowledged. Infrared spectra were obtained with a model 21 Perkin–Elmer infrared spectrophotometer purchased in part with funds from the National Science Foundation.

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[11] G. M. Bennett and G. H. Willis, *J. Chem. Soc.*, 256 (1929).

[12] E. Stedman, *ibid.*, 1902 (1927).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES, CALIF.]

Macro Rings. XXIII. Carbonylchromium Complexes of Paracyclophanes and Model Compounds[1]

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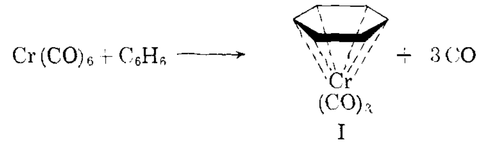
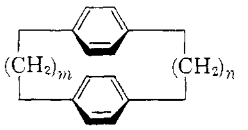
Tricarbonylchromium complexes of the paracyclophanes and model open-chain compounds have been prepared. With the [*m.n*]paracyclophanes, only mono-complexes formed when *m* and $n \leqq 4$. Bis-complexes were prepared with difficulty from cycles with $m = 4$, $n = 5$, and $m = n = 6$. Complexes of the smaller cycles possessed abnormal ultraviolet absorption spectra compared to either spectra of the larger cyclic, or of open-chain model organometallic compounds. Attempts to convert [4.4]paracyclophane tricarbonylchromium to [4.4]paracyclophanechromium with the metal between the two benzene rings failed.

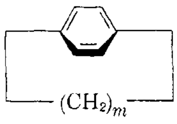
The description of a general method[2] for the synthesis of tricarbonylchromium complexes of aromatic hydrocarbons[3] (*e.g.*, I) provided a new tool for the study of transannular effects in the paracyclophanes[4] (II and III). Points of interest in such a study are as follows. (1) Compounds that possess structure II might complex with either one or two moles of tricarbonylchromium. If the lower homologs of II formed mono-complexes and the higher bis-complexes, this might be taken as evidence for transannular electronic interactions between the two rings in the former substances. (2) Differences in spectral properties of the complexes of II might correlate with changes in the distances between the two benzene rings as the values of *m* and *n* change. (3) Possibly mono-complexes of II could be induced to lose three moles of carbon monoxide to form an organometallic compound with chromium between the two rings and bound directly to each. In these studies, complexes of hydrocarbons such as III and open-chain analogs of II served as models.



I



II



III

Twenty-one different paracyclophanes were used in this study, and their preparations have been described in previous papers in this series.[5] All of these hydrocarbons formed mono-tricarbonylchromium complexes when heated with hexacarbonylchromium in diethylene glycol dimethyl ether. The names of the compounds employed, and the analytical and physical data pertaining to their complexes are reported in Table I. All of the open-chain model compounds listed in Table I gave mono-complexes. A mixture of complexes which could not be separated was obtained with 1,4-bis-(4-ethylphenyl)-butane. Only two bis-complexes, those of [4.5]- and [6.6]paracyclophane, were obtained, and then in poor yield. Variation in the relative amounts of hexacarbonylchromium employed and changes in solvent did not seem to affect the relative amounts of mono- and bis-complexes formed from [6.6]paracyclophane.

Discussion

Clearly the mono-complexes with structure IV show little inclination to react with hexacarbonylchromium, particularly those homologs in which *m* and *n* are 4 or less. This fact suggests that the electron-withdrawing character of the tricarbonylchromium group[2] exerts its influence both on the aromatic ring to which it is directly bonded, and on the second aromatic nucleus. Thus the two benzene rings of the [*m.n*]paracyclophanes have to be able to get as far apart as in the [4.5]- or [6.6]-homologs before the two rings can behave as independent units, and form bis-complexes (V). This effect is similar to that observed in the one-to-one complexes formed between the [*m.n*]-

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[1] This work was sponsored by the Office of Ordnance Research, U. S. Army.

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[4] D. J. Cram, *Rec. Chem. Prog.*, **20**, 71 (1959).

[5] (a) D. J. Cram and H. Steinberg, THIS JOURNAL, **73**, 5691 (1951); (b) D. J. Cram and N. L. Allinger, *ibid.*, **76**, 726 (1954); (c) N. L. Allinger and D. J. Cram, *ibid.*, **76**, 2362 (1954); (d) D. J. Cram and H. U. Daeniker, *ibid.*, **76**, 2743 (1954); (e) J. Abell and D. J. Cram, *ibid.*, **76**, 4406 (1954); (f) D. J. Cram, N. L. Allinger and H. Steinberg, *ibid.*, **76**, 6132 (1954); (g) D. J. Cram and M. F. Antar, *ibid.*, **80**, 3103 (1958); (h) D. J. Cram and M. F. Antar, *ibid.*, **80**, 3109 (1958); (i) D. J. Cram and K. Dewhirst, *ibid.*, **81**, 5963 (1959).