The Reaction with Pinacolone and Ethyl α-Bromophenylacetate.—A 20% yield of ethyl phenylacetate, identified as indicated previously, was obtained from the reaction of 0.15 molar quantities of pinacolone, ethyl α-bromophenylacetate and potassium *t*-butoxide. Unreacted pinacolone was recovered in 32% of the amount originally added. A 33% yield of diethyl 2,3-diphenylsuccinate, identified by a mixed melting point determination with the product previously identified as diethyl 2,3-diphenylsuccinate from the isobutyrophenone—ethyl α-bromo phenylacetate reaction, was also obtained. The presence of diethyl diphenylmaleate in the reaction mixture was shown by the isolation of diphenylmaleic anhydride from the saponified distillation residue.

The Reaction with Acetophenone and Ethyl α-Bromophenylacetate.—A 28.2% yield of ethyl phenylacetate was obtained from the reaction of 0.15 molar quantities of acetophenone, ethyl α-bromophenylacetate and potassium *t*-butoxide. Unreacted acetophenone was recovered in 45% of the amount originally added. Diethyl diphenylsuccinate and diethyl diphenylmaleate were identified in the tarry distillation residue, but the amounts present could not be accurately determined.

Acknowledgment.—We wish to express our appreciation for the financial aid given us through a Cottrell grant from Research Corporation.

ORONO, MAINE

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

The Synthesis of Alkylhydrazines. II. The Reduction of 1-Acyl-2-alkylidenehydrazines with Lithium Aluminum Hydride

BY RICHARD L. HINMAN

RECEIVED AUGUST 3, 1956

Several 1-acyl-2-alkylidenehydrazines have been reduced with lithium aluminum hydride in refluxing tetrahydrofuran. In every case two products were obtained: a 1,2-dialkylhydrazine and a 1-acyl-2-alkylhydrazine. The 1,2-dialkylhydrazines were easily oxidized in air to hydrazones which were identified by their ultraviolet absorption spectra.

Only a few examples have been reported of 1,2-dialkylhydrazines in which the alkyl groups are not identical. Of the few synthetic routes which have been employed only two are at all general in application. One method involves the reaction of an alkylhydrazine with an aldehyde or ketone and reduction of the resulting hydrazone by catalytic or chemical methods.[1] When an *unsym*-dialkylhydrazine is used, this method is useful for the preparation of trialkylhydrazines.[2]

A different approach involves the alkylation of a 1-alkyl-1,2-diacylhydrazine to give a 1,2-dialkyl-1,2-diacylhydrazine from which the acyl groups are then hydrolyzed. Starting with isopropylhydrazine and following this method, Ramsperger prepared 1-isopropyl-2-methylhydrazine.[1b] The direct alkylation of hydrazine is of course not feasible because alkylation generally occurs on the nitrogen which already bears an alkyl group.[2c,3]

In the approach to the problem reported in this paper it was hoped that the two alkyl groups could be introduced by the reduction of a 1-acyl-2-alkylidenehydrazine with lithium aluminum hydride. The requisite hydrazine derivatives are easily obtained, and the over-all reaction sequence is shown in equation 1. Since it is known that the

$$\mathrm{RCO_2R \longrightarrow RCONHNH_2 \longrightarrow}$$

$$\mathrm{RCONHN{=}CR_1R_2 \xrightarrow{LiAlH_4} \underset{I}{RCH_2NHNHCHR_1R_2}} \quad (1)$$

$$\mathrm{+\ \underset{II}{RCONHNHCHR_1R_2}}$$

carbonyl group of an acylhydrazine containing the group –CONH– is usually reduced with difficulty,[4,5] the isolation of products of type II was also anticipated. However, it was hoped that long periods of reaction would give good yields of I at the expense of II.

The results of the reductions of several 1-acyl-2-alkylidenehydrazines are summarized in Table I.

TABLE I

SUMMARY OF THE REDUCTIONS OF 1-ACYL-2-ALKYLIDENEHYDRAZINES WITH LITHIUM ALUMINUM HYDRIDE

Reactant[a]	Excess of LAH, %	Time of reduction, hr.	Yield of 1,2-dialkylhydrazine, %	Yield of acylhydrazine, %
$C_3H_7CONHN{=}C(CH_3)_2$	100[b]	20	48	13
$C_3H_7CONHN{=}CHC_6H_5$	90[b]	27	12	43
$C_3H_7CONHN{=}CHC_6H_5$	167[b]	48	30	28
$C_6H_5CONHN{=}CHCH_3$	100	90	5	45
$C_6H_5CONHN{=}CHCH_3$	100[c]	30	[e]	65
$C_6H_5CONHN{=}CHC_6H_5$[c,d]	..	8	[e]	70
$C_6H_5CONHN{=}CH_2$	100[f]	24	[g]	..

[a] Solution of reactant added to solution of hydride except where noted otherwise. [b] One mole of $LiAlH_4$ required for reduction of both functional groups. [c] Soxhlet technique. [d] Private communication from Dr. Louis Carpino, University of Massachusetts. [e] Isolation not attempted. [f] Powdered hydrazone added to solution of hydride in tetrahydrofuran. [g] Only starting material recovered.

It will be noted that the yield of dialkylhydrazine is higher when the acyl group is butyryl rather than benzoyl. Even 90 hr. of refluxing 1-benzoyl-2-ethylidenehydrazine with lithium aluminum hydride in tetrahydrofuran produced only 5% of 1-benzyl-2-ethylhydrazine. These results follow the pattern of earlier work[4] in which it was shown that the –CONH– group of an acylhydrazine is more difficult to reduce when the acyl group is benzoyl rather than of the aliphatic type. The failure of

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[1] (a) H. L. Lochte, W. A. Noyes and J. R. Bailey, THIS JOURNAL, **44**, 2556 (1922); (b) H. C. Ramsperger, *ibid.*, **51**, 918 (1929); (c) C. D. Garrick, G. W. Drake and H. L. Lochte, *ibid.*, **58**, 160 (1936).

[2] (a) T. Curtius, *J. prakt. Chem.*, [2] **62**, 84 (1900); (b) H. Franzen and F. Kraft, *ibid.*, **84**, 137 (1911); (c) F. Klages, *Ann.*, **547**, 1 (1941); (d) J. G. Aston, J. B. Class and T. S. Oakwood, THIS JOURNAL, **75**, 2937 (1953).

[3] O. Westphal, *Ber.*, **74**, 759 (1941).

[4] R. L. Hinman, THIS JOURNAL, **78**, 1645, 2463 (1956).

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

1-benzoyl-2-methylenehydrazine to undergo reduction can be ascribed to the extreme insolubility of the hydrazone in tetrahydrofuran.

The reduction of 1-acyl-2-alkylidenehydrazines therefore appears to be useful for the preparation of 1,2-dialkylhydrazines only when the acyl group is not benzoyl. Even then the yields are low, although doubling or tripling the reaction times used in this study would probably result in better yields. On the other hand, if short reaction times are employed, the reduction of 1-acyl-2-alkylidenehydrazines is useful for the preparation of 1-acyl-2-alkyl-hydrazines, which are not easily obtained otherwise. The latter reduction can also be effected by hydrogenation in the presence of a platinum oxide catalyst.[6]

The identification of the products from the reductions warrants separate discussion. The 1-acyl-2-alkylhydrazines were cleaved readily by Raney nickel to the corresponding amides,[7] as shown for 1-*n*-butyryl-2-benzylhydrazine in equation 2. The latter compound could be reoxidized to 1-*n*-butyryl-2-benzylidenehydrazine by copper sulfate.

$$C_3H_7CONHNHCH_2C_6H_5 \xrightarrow[\text{refluxing ethanol}]{\text{Raney Ni}} C_3H_7CONH_2 \quad (2)$$

The 1,2-dialkylhydrazines, on the other hand, were more difficult to identify because of their ready oxidation in air to hydrazones. After standing for a few days in a stoppered bottle, 1-benzyl-2-*n*-butylhydrazine, for example, no longer yielded the solid hydrochloride or dibenzoyl derivatives in purifiable form.

To establish the nature of the oxidation product the ultraviolet absorption spectrum of 1-benzyl-2-butylhydrazine was determined. The spectrum of the freshly distilled material had only one peak, λ_{max}, 289 mμ, probably due to contamination by the hydrazone. The absorbancy increased steadily during the following weeks, and a new peak of lower intensity appeared at 222 mμ. After three months the spectrum was almost identical with that reported for benzaldehyde methylhydrazone.[8] The structure of the oxidation product was confirmed by comparison of its spectrum with that of an authentic sample of benzaldehyde *n*-butylhydrazone.

Attempts to reduce the pure hydrazone to 1-benzyl-2-butylhydrazine under a pressure of one atmosphere of hydrogen using catalysts of platinum oxide or palladium on charcoal were unsuccessful.

Although azo compounds are frequently prepared by the oxidation of 1,2-dialkylhydrazines, the formation of benzaldehyde *n*-butylhydrazone has precedents in the formation of hydrazones by oxidation of 1-alkyl-2-phenylhydrazines.[9] When one of the groups is of the benzyl type, the benzaldehyde hydrazone may be the only product isolated.[10,11]

The liquid product from the reduction of 1-benzoyl-2-ethylidenehydrazine also had a spectrum of the same general type, having two peaks of λ_{max} 222 and 288 mμ, from which it is assumed that the product of the reduction is 1-benzyl-2-ethylhydrazine, which undergoes rapid oxidation to benzaldehyde ethylhydrazone.

From the reaction of week-old 1-benzyl-2-butylhydrazine and potassium cyanate in aqueous acetic acid a small quantity of crystalline material X was obtained. From the nitrogen analysis this product was limited to four possible compounds: 1-benzyl-2-butylsemicarbazide (I), 1-butyl-2-benzylsemicarbazide (II), butyraldehyde 2-benzylsemicarbazone (III) or benzaldehyde 2-butylsemicarbazone (IV), of which II and IV are shown below. The ultraviolet absorption spectrum of X

$$\underset{\text{II}}{C_6H_5CH_2NHN(C_4H_9)CONH_2} \qquad \underset{\text{IV}}{C_6H_5CH{=}NN(C_4H_9)CONH_2}$$

had its principal peaks at 286 and 293 mμ, thereby eliminating compounds I and II, the general type of which absorbs at shorter wave lengths.[12] Furthermore, the spectrum of an authentic specimen of benzaldehyde 2-methylsemicarbazone[13] was almost identical with that of the unknown, as shown in Table II,[14] thereby establishing that the unknown has structure IV. The slight shift toward longer wave lengths in passing from the methyl to the butyl derivative is similar to that observed with the methyl[8] and butylhydrazones of benzaldehyde. A bathochromic shift also occurs in passing from the dimethylhydrazone to the diethylhydrazone of benzaldehyde.[8]

A solid derivative was also obtained from 1-butyl-2-isopropylhydrazine and potassium cyanate. By analogy it is assumed that the product is a semicarbazone. Because a sufficient quantity of pure product was not available, the spectrum could not be determined.

TABLE II

	λ_{max}, mμ (a_M)
Compound X (4.1×10^{-5} *M*)	219 (21,000), 286 (28,500), 293 (29,000)
Benzaldehyde 2-methylsemicarbazone (4.7×10^{-5} *M*)	218 (17,700), 285 (25,700), 292 (24,700)

Experimental[15]

1-Acyl-2-alkylidenehydrazines.—These are known compounds with the exception of 1-benzoyl-2-methylidenehydrazine, which was prepared by boiling for five minutes and then refrigerating for 12 hours a solution of equimolar quantities of benzhydrazide and formaldehyde (37% aqueous

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[6] H. L. Yale, K. Losee, J. Martins, M. Holsing, F. M. Perry and J. Bernstein, THIS JOURNAL, **75**, 1933 (1953).

[7] C. Ainsworth, *ibid.*, **76**, 5774 (1954); **78**, 1636 (1956).

[8] D. Todd, *ibid.*, **71**, 1353 (1949).

[9] P. Grammaticakis, *Compt. rend.*, **204**, 1262 (1937); **210**, 303 (1940).

[10] G. H. Coleman, H. Gilman, C. E. Adams and P. E. Pratt, *J. Org. Chem.*, **3**, 99 (1938).

[11] Mild oxidation of symmetrical hydrazo compounds, even that derived from acetophenone, appears to yield the azo compound as the initial product: W. A. Schulze and H. L. Lochte, THIS JOURNAL, **48**, 1030 (1926).

[12] P. Grammaticakis, *Bull. soc. chim.*, 690 (1950).

[13] A. Michaelis and E. Hadanck, *Ber.*, **41**, 3285 (1908).

[14] The spectra of *m*- and *p*-hydroxybenzaldehyde 2-methylsemicarbazones exhibit similar characteristics: L. K. Evans and A. E. Gillam, *J. Chem. Soc.*, 565 (1943).

[15] Melting points and boiling points are uncorrected. Ultraviolet absorption spectra were determined with a Cary recording spectrophotometer, Model 11, using 1 cm. cells and 95% ethanol as the solvent.

solution) in twice their volume of 67% ethanol. The cream-colored needles which formed were recrystallized from the minimum quantity of absolute ethanol. The resulting white needles melted at 167–169°. The average yield was 70%. An analytical sample was prepared by three recrystallizations from absolute ethanol.

Anal. Calcd. for $C_8H_8N_2O$: C, 64.59; H, 5.43. Found: C, 64.71; H, 5.39.

Reductions with Lithium Aluminum Hydride.—Unless otherwise noted, these reactions were carried out by adding a solution of the 1-acyl-2-alkylidenehydrazine in dry tetrahydrofuran dropwise to a stirred solution of the hydride in the same solvent at a rate sufficient to cause gentle reflux. At the end of the specified reaction time, the reaction mixture was cooled in ice, and the excess hydride was decomposed by the cautious dropwise addition of *n* ml. of water, then *n* ml. of 15% sodium hydroxide solution, and finally 3 *n* ml. of water, where *n* = the number of grams of hydride originally used. The white precipitate was removed by filtration and washed thoroughly with solvent. The filtrate was dried over sodium sulfate, filtered and distilled *in vacuo* to remove the volatile solvents. The residue was then distilled through a small Vigreux column under reduced pressure.

Where noted, the Soxhlet technique was employed, the compound to be reduced being extracted from the cup into the solution of hydride in the pot. The work-up was that described above.

Reduction of 1-*n*-Butyryl-2-isopropylidenehydrazine.—Hydride, 7.6 g. (0.2 mole) in 100 ml. of tetrahydrofuran; 1-*n*-butyryl-2-isopropylidenehydrazine[16] 14.2 g. (0.1 mole) in 100 ml. of solvent; reaction time, 20 hr. From the distillation was obtained 6.2 g. (48%) of a colorless liquid (A), b.p. 67–71° (26 mm.), and 1.8 g. (13%) of a pale yellow viscous oil (B), b.p. 135–140° (27 mm.).

Treatment of a portion of B with phenyl isothiocyanate by the usual procedure[17] produced white needles, which, after three crystallizations from a mixture of ethanol and water, melted at 152–153° and had the composition of 1-*n*-butyryl-2-isopropyl-4-phenylthiosemicarbazide.

Anal. Calcd. for $C_{14}H_{21}N_3OS$: C, 60.18; H, 7.58. Found: C, 60.16; H, 7.69.

From treatment of A, presumably 1-butyl-2-isopropylhydrazine, with benzoyl chloride by the Schotten–Baumann method, an unidentified yellow oil was obtained.

A solution of A in ether reacted with oxalic acid to give a white powder, m.p. 155–156°. However, its analysis did not correspond to that of any likely product of the reaction.

No solid material was isolated from the reaction of A and picric acid in ether.

From a solution of A and potassium cyanate in 70% aqueous acetic acid, a small quantity of crystalline solid was obtained after addition of an equal volume of water. After three crystallizations from an ethanol–water mixture, the melting point of the solid was 112–113°. It had the composition of a substituted semicarbazide or its oxidation product, a substituted semicarbazone.

Anal. Calcd. for $C_8H_{19}N_3O$: C, 55.45; H, 11.05. Calcd. for $C_8H_{17}N_3O$: C, 56.11; H, 10.01. Found: C, 55.37; H, 11.12.

Reduction of 1-*n*-Butyryl-2-benzylidenehydrazine.—Hydride, 7.6 g. (0.20 mole) in 150 ml. of tetrahydrofuran; 1-butyryl-2-benzylidenehydrazine,[16] 14.2 g. (0.075 mole) in 150 ml. of solvent; reaction time, 48 hr. From the distillation of the crude reaction products two main fractions were obtained. The less volatile one (b.p. 100–140° (0.85 mm.)) crystallized on cooling, and after three crystallizations from a 1:4 mixture of benzene and petr. ether (b.p. 60–70°) the white needles melted at 66–67°. The yield of 1-butyryl-2-benzylhydrazine was 4.0 g. (28%).

Anal. Calcd. for $C_{11}H_{16}N_2O$: C, 68.70; H, 8.39; N, 14.57. Found: C, 68.77; H, 8.44; N, 14.88.

From treatment of a sample of this material with Raney nickel according to the method of Ainsworth,[7] *n*-butyramide was isolated, m.p. and mixed m.p. with an authentic specimen 112–114°.

Redistillation of the lower boiling fraction from the hydride reduction yielded 4.0 g. (30%) of colorless liquid, b.p. 96–99° (0.9 mm.), n^{21}D 1.5248, ultraviolet λ_{max} 289 mμ, A_s 0.502. The absorbancy of this sample increased rapidly on standing, reaching a value of 1.24 after 3 weeks, and 1.95 after 3 months. A new peak λ_{max} 222 mμ appeared during this time. The latter had A_s 1.52 after 3 months.

Solution of a portion of this material in 20% hydrochloric acid was followed immediately by the precipitation of white needles which dissolved in hot chloroform and recrystallized when benzene was added and the mixture cooled. From four such crystallizations an analytical sample was obtained, m.p. 148–150°, which had the composition of the monohydrochloride of 1-benzyl-2-butylhydrazine.

Anal. Calcd. for $C_{11}H_{19}N_2Cl$: C, 61.53; H, 8.92; N, 13.06. Found: C, 61.50; H, 8.98; N, 13.76. 1-Benzyl-2-*n*-butylhydrazine turned yellow when exposed to air, and after a few days no longer dissolved in 10% hydrochloric acid. When the acidic mixture was heated, the odor of benzaldehyde was detected.

1-Benzyl-2-butyl-1,2-dibenzoylhydrazine was prepared by basifying a portion of 1-benzyl-2-butylhydrazine hydrochloride with 20% sodium hydroxide and shaking the basic solution with freshly distilled benzoyl chloride. White crystals were obtained which, after three crystallizations from a mixture of benzene and pet. ether (b.p. 60–70°), melted at 105–107°.

Anal. Calcd. for $C_{25}H_{26}N_2O_2$: N, 7.25. Found: N, 7.14.

Oxidation of 1-*n*-Butyryl-2-benzylhydrazine.—A solution of 5 g. (0.02 mole) of copper sulfate pentahydrate in 45 ml. of water was added dropwise to a boiling solution of 0.95 g. (0.005 mole) of 1-*n*-butyryl-2-benzylhydrazine in 20 ml. of 95% ethanol. The mixture was refluxed for three hours after the addition was complete. The reddish solid was removed by filtration and the filtrate was evaporated to dryness. The green residue was taken up in boiling benzene, filtered and allowed to evaporate to dryness at room temperature. The resulting green needles were recrystallized from a mixture of ethanol and water, and then from a mixture (1:3) of benzene and petr. ether (b.p. 60–70°). The white crystals (0.2 g.) melted at 98–99° and did not depress the m.p. of an authentic sample of 1-*n*-butyryl-2-benzylidenehydrazine.

Benzaldehyde 2-Butylsemicarbazone.—To a solution of 1.0 g. (0.006 mole) of week-old 1-benzyl-2-butylhydrazine in 10 ml. of acetic acid was added a solution of 1.0 g. (0.012 mole) of potassium cyanate in 10 ml. of water. After two hours the mixture was diluted with water. The paste which separated was collected by suction filtration. It crystallized after standing for several days at room temperature in an alcohol–water mixture from which the solvents slowly evaporated. The product was crystallized once from an alcohol–water mixture and thrice from a mixture of benzene and pet. ether (b.p. 60–70°). The white needles melted at 89–90°; ultraviolet λ_{max} 219, 286, 293 mμ (a_M 21,000, 28,500, 29,000).

Anal. Calcd. for $C_{12}H_{17}N_3O$: N, 19.16. Found: N, 18.97.

Reduction of 1-Benzoyl-2-ethylidenehydrazine.—Hydride, 5.7 g. (0.15 mole) in 100 ml. of tetrahydrofuran; 1-benzoyl-2-ethylidenehydrazine,[18] 12.2 g. (0.075 mole) in 150 ml. of solvent; reaction time, 90 hr. Distillation of the crude products gave 0.6 g. (5%) of colorless liquid, b.p. 92–93° (1.4 mm.), n^{20}D 1.5822. Neither a solid hydrochloride nor a benzoyl derivative could be prepared from the product which rapidly turned yellow while standing in a stoppered flask. The ultraviolet absorption spectrum had λ_{max} 222 and 288 mμ, characteristic of an aliphatic hydrazone of benzaldehyde.

The pot residue from the distillation crystallized on cooling. It was recrystallized thrice from a mixture of benzene and pet. ether (b.p. 60–70°). The white needles melted at 86–87°, weighed 5.4 g. (45%), and had the composition of 1-benzoyl-2-ethylhydrazine.

Anal. Calcd. for $C_9H_{12}N_2O$: C, 65.84; H, 7.37; N, 17.07. Found: C, 65.28; H, 7.26; N, 17.01.

Benzamide, m.p. and mixed m.p. with an authentic sample 125–127°, was obtained by treatment of 1-benzoyl-2-ethylhydrazine with Raney nickel.[7]

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(16) R. Stollé and G. Zinsser, *J. prakt. Chem.*, [2] **69**, 487 (1904).

(17) R. L. Shriner and R. C. Fuson, "The Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 3rd Edition, 1948, p. 179.

(18) R. Stollé and E. Münch, *J. prakt. Chem.*, [2] **70**, 393 (1904).

Benzaldehyde *n*-Butylhydrazone.—A 20% aqueous solution of barium hydroxide octahydrate was mixed with an equimolar quantity of *n*-butylamine oxalate,[19] and the precipitate was removed by filtration. The filtrate was distilled and the last fractions were saturated with sodium hydroxide and extracted with ether. The extracts were mixed with a quantity of benzaldehyde equal to the number of moles of *n*-butylamine oxalate originally used. The solution was dried over sodium sulfate. After the ether had been evaporated, the residue was distilled and the fraction boiling at 114–118° (1.2 mm.) was collected. The yield was 11%; ultraviolet λ_{max} 222, 289 mμ (a_M 7850, 11,200).

Anal. Calcd. for $C_{11}H_{16}N_2$: C, 74.93; H, 9.15. Found: C, 74.65; H, 9.03.

IOWA CITY, IOWA

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[19] G. Gever and K. Hayes, *J. Org. Chem.*, **14**, 813 (1949).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

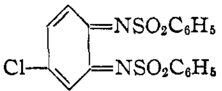
Quinone Imides. XLIII. The Reactions of *o*-Quinonedibenzenesulfonimides

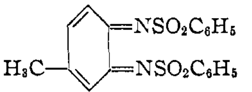
BY ROGER ADAMS AND EDWIN L. DEYOUNG[1]

RECEIVED SEPTEMBER 4, 1956

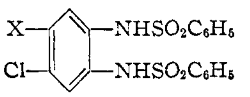
4-Chloro- and 4-methyl-*o*-quinonedibenzenesulfonimide add hydrazoic acid, benzenesulfinic acid and acetylacetone to give presumably the 5-substituted *o*-phenylenedibenzenesulfonamides. The constitution of the hydrazoic acid products was determined by reduction and hydrolysis to the substituted triamines which were synthesized by unequivocal methods. Dimers of the two diimides were formed by the action of nitromethane or cyclopentadiene.

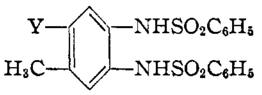
The syntheses of several substituted *o*-quinonedibenzenesulfonimides and their reactions with hydrogen chloride have been reported in a previous paper.[2] When 4-chloro- and 4-methyl-*o*-quinonedibenzenesulfonimide (I and II, respectively) were treated with hydrogen chloride, the major product in each case was the 5-chloro adduct (III and IV).


I


II

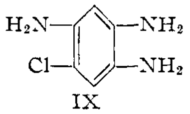
Other addition reactions to *o*-quinonedibenzenesulfonimides have now been studied.

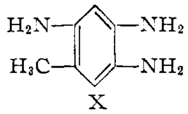

III, X = Cl
V, X = N_3
VII, X = NH_2
XI, X = $SO_2C_6H_5$
XIII, X = $CH(COCH_3)_2$


IV, Y = Cl
VI, Y = N_3
VIII, Y = NH_2
XII, Y = $SO_2C_6H_5$
XIV, Y = $CH(COCH_3)_2$
XV, Y = CH_2COCH_3

The starting materials (I and II), prepared by lead tetraacetate oxidation of the corresponding *o*-phenylenedibenzenesulfonamides,[2] were obtained in good yields and in sufficient purity for use in all addition reactions.

Addition of an aqueous solution of sodium azide to glacial acetic acid solutions of I and II afforded the 5-azido adducts V and VI in good yields. The structures of these adducts were established by reduction of the azido groups to the corresponding amino compounds (VII and VIII), followed by hydrolysis of the resulting disulfonamides to the free triamines IX and X. Structures IX and X were synthesized by unequivocal methods and the products were identical in melting point and spectra with those derived from the azido compounds.


IX


X

Compound IX was made by the following sequence of reactions: 3-chloroacetanilide, 3-chloro-4,6-dinitroacetanilide, 3-chloro-4,6-dinitroaniline,[3] 2-chloro-1,4,5-benzenetriamine. For comparison, 5-chloro-1,2,3-benzenetriamine was prepared by the following steps: 4-chloroaniline, 4-chloroacetanilide, 4-chloro-2,6-dinitroacetanilide, 4-chloro-2,6-dinitroaniline,[4] 5-chloro-1,2,3-benzenetriamine.

Compound X was synthesized as follows: *o*-toluidine, 2-amino-4-nitrotoluene, 2-acetylamino-4-nitrotoluene,[5] 2-acetylamino-4,5-dinitrotoluene, 2-amino-4,5-dinitrotoluene,[6] 2,4,5-toluenetriamine. For comparison, 3,4,5-toluenetriamine was synthesized: *p*-toluidine, *p*-acetotoluidide, 4-acetylamino-3,5-dinitrotoluene, 4-amino-3,5-dinitrotoluene,[7] 3,4,5-toluenetriamine.[7]

The addition of benzenesulfinic acid to I and II took place readily. From analogy to the 5-chloro and the 5-azido adducts, and from the C–H absorption in the infrared spectrum, it is probable that the products are the 5-benzenesulfonyl adducts XI and XII. Thiophenol did not add in presence of either an acidic or basic catalyst; only reduction of the imides resulted.

Acetylacetone, catalyzed with sodium methoxide, added to I and II in dioxane solution to give the monoadducts XIII and XIV. While the structures of these adducts were not proven, the entering diacetylmethyl group is probably in the 5-position. Steric factors are likely to inhibit the entry into the 3-position and if the group had entered the 6-position, *ortho* to the benzene and sulfonamido group, the adducts would probably have cyclized to indoles under the influence of acid.[8]

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[1] An abstract of a part of a thesis submitted by Edwin L. DeYoung to the Graduate College of the University of Illinois, 1956, in partial fulfillment of the requirements for the Degree of Doctor of Philosophy. Minnesota Mining and Manufacturing Co. Fellow, 1953–1956.

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