reflux for 6 hr., during which about 15 ml. of colorless liquid was collected in the cold trap. This material was purified by two bulb-to-bulb distillations using Dry Ice–isopropyl alcohol baths; about a third of the material did not distil at room temperature. The product gave a positive test (for acidic hydrocarbons) with Nessler's reagent.(5)

Anal. Calcd. for C_4H_6: C:H, 7.94. Found: C:H, 7.67, 7.56.

The product decomposed in condensed phases (pure liquid or CCl_4 solution) at normal temperatures. It was stable for at least 4 days in the vapor phase or in the liquid phase at liquid-nitrogen temperature.

The infrared spectrum of II showed medium bands in the double-bond region at about 1780 and 1800 cm.$^{-1}$.

Treatment of 1-Methylcyclopropene with Triphenylmethyl Fluoroborate.—A solution of triphenylmethyl fluoroborate in acetic anhydride was prepared from 9.91 g. (0.038 mole) of triphenylcarbinol by the method of Dauben, Honnen, and Harmon.(6) A solution of 0.04 mole (manometric) of 1-methylcyclopropene in 25 ml. of acetic anhydride was added at 0°. After 30 min. the mixture was warmed to room temperature. After 2 days there was no fading of the orange color of the triphenylcarbonium ion.

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Reactions of N-Benzylideneanilines with N-Bromosuccinimide and with Succinimide[1]

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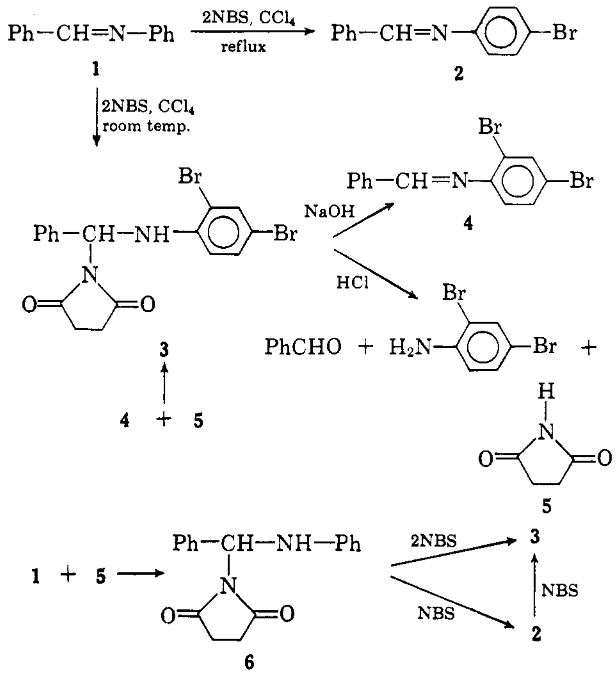
Various active hydrogen compounds have been known to add across the carbon–nitrogen double bond of Schiff bases.[2] *t*-Amyl hypochlorite also has been regarded as an addend in its reactions with Schiff bases.[3] The present study was undertaken to see if N-bromosuccinimide (NBS) would likewise undergo addition reactions with N-benzylideneaniline (**1**) and some of its derivatives.

The imine **1** and 2 mole equiv. of NBS, when refluxed in carbon tetrachloride for 3 hr., gave N-benzylidene-4-bromoaniline (**2**) in 95% yield. However, when the same reactants were stirred at room temperature for 6 hr., the product was N-(α-succinimidobenzyl)-2,4-dibromoaniline (**3**), isolated in 22% yield (Scheme I). The structure **3** was supported by the following. The elemental analysis agreed with the formula $C_{17}H_{14}Br_2N_2O_2$. It was converted to N-benzylidene-2,4-dibromoaniline (**4**) when treated with dilute sodium hydroxide in ethanol. It was degraded to benzaldehyde, succinimide, and 2,4-dibromoaniline when treated with dilute hydrochloric acid in ethanol.

Scheme I



The infrared spectrum of **3** exhibited bands at 5.85 and 2.95 μ indicating the presence of a cyclic amide function and an N-H group, respectively.[4] The latter band would be absent for the structure in which the succinimido group is attached to the nitrogen atom. Furthermore, many existing analogies[2] justify the attachment of the succinimido group to the benzylic carbon. Nitromethane, for example, adds to **1** forming N-(2-nitro-1-phenylethyl)aniline.[5] The final structural confirmation came from the synthesis of **3** in 76% yield by heating equimolar amounts of **4** and succinimide (**5**) in refluxing ethanol for 15 hr.

This synthesis of **3** demonstrated the capability of succinimide to act as an active hydrogen compound toward Schiff bases. Michael addition of succinimide to α,β-unsaturated aldehydes with the aid of sodium ethoxide has been reported in a few cases, however.[6] Heating equimolar amounts of **1** and succinimide in ethanol under reflux for 10 hr. gave N-(α-succinimidobenzyl)aniline (**6**) in 84% crude yield. The structure **6** followed in analogy with structure **3**. The infrared spectrum of **6** showed bands at 5.92 and 3.00 μ corresponding to a cyclic amide function and an N-H group, respectively.[4] The adduct **6** was not very stable: it reverted to **1** after two conventional recrystallizations from ethanol. When refluxed for 20 min. with 2 mole equiv. of NBS in carbon tetrachloride, **6** was converted to **3** in 17% yield. On the other hand, the reaction of **6** with 1 equiv. of NBS in carbon tetrachloride, at reflux or under stirring at room temperature for 1 hr., produced **2** in 80 or 88% yield, respectively, instead of the expected, still unknown compound, N-(α-succinimidobenzyl)-4-bromoaniline (**7**). This was rather surprising, since **6** could be dibrominated with retention of the succinimido moiety to form **3**. That the succinimide molecule has to be eliminated when **6**

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(1) A grateful acknowledgment is hereby made to the Republic of China National Council on Science Development for a grant which supported this work.

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is monobrominated may be taken to reflect the instability of **7**. Indeed, **2** and succinimide did not form adduct **7** after 27 hr. of heating in ethanol or 13 hr. of heating in carbon tetrachloride.

Equimolar amounts of **2** and NBS in carbon tetrachloride gave **3** in 26% yield when refluxed for 4 hr. This reaction may be considered to proceed by bromination of **2** by NBS to form **4**, to which succinimide added. It might be possible also that NBS first added to **2**, in analogy with the addition of *t*-amyl hypochlorite to Schiff bases,[3] forming an N-bromo compound which subsequently rearranged to **3**. A variety of reaction paths can be considered for the formation of **3** from **1** and NBS, but any one involving addition of succinimide to the possible intermediate **2** must be excluded.

A nitro group on either ring of **1** apparently facilitated addition of succinimide. Thus, N-benzylidene-4-nitroaniline and N-(4-nitrobenzylidene)aniline readily afforded N-(α-succinimidobenzyl)-4-nitroaniline and N-(α-succinimido-4-nitrobenzyl)aniline, respectively. On the other hand, N-benzylidene-2,4-6-tribromoaniline[7] failed to give an adduct, apparently because it tended to decompose to tribromoaniline and benzaldehyde before addition could possibly occur. N-Benzylidene-1-(and 2-) naphthylamines[8,9] did not give adducts either probably because their ground-state energies are lower than that of **1**.

Experimental[10]

Reaction of N-Benzylideneaniline (1) with N-Bromosuccinimide (NBS). A.—A mixture of 1[11] (1.81 g., 0.01 mole) and NBS (3.68 g., 0.02 mole) in carbon tetrachloride (20 ml.) was refluxed for 3 hr. and cooled to room temperature. The solid (2.67 g.) was filtered off, and the filtrate was evaporated to dryness. The residue (2.47 g., 95% yield) was recrystallized from methanol to obtain N-benzylidene-4-bromoaniline[12] (**2**), m.p. 60–62°.

B.—The same amounts of reactants as in A were stirred at room temperature for 6 hr. The solid (2.70 g.) was collected by suction and washed with water. The residue (0.97 g., 22% yield) was recrystallized from ethyl acetate to obtain N-(α-succinimidobenzyl)-2,4-dibromoaniline (**3**), m.p. 146.5–147°. The infrared spectrum showed bands at 2.95, 5.63, 5.85, and 6.30 μ.

Anal. Calcd. for $C_{17}H_{14}Br_2N_2O_2$: C, 46.60; H, 3.22; Br, 36.48; N, 6.39. Found: C, 46.60; H, 3.18; Br, 36.11; N, 6.27.

Reaction of N-(α-Succinimidobenzyl)-2,4-dibromoaniline (3) with Sodium Hydroxide.—A mixture of **3** (0.3 g.), ethanol (10 ml.), and 10% aqueous sodium hydroxide solution (0.3 ml.) was gently refluxed for 15 min. The solution was then evaporated to dryness and the residue was washed with water. The remainder (0.17 g.) was recrystallized from methanol to obtain N-benzylidene-2,4-dibromoaniline[13] (**4**), m.p. 67–69°. The water washing was neutralized with dilute hydrochloric acid and evaporated to dryness. The residue was then extracted with two 5-ml. portions of hot absolute ethanol, and the ethanol solution was evaporated to dryness. The remaining solid (0.05 g.) was recrystallized from benzene to obtain succinimide, m.p. 121°.

Reaction of N-(α-Succinimidobenzyl)-2,4-dibromoaniline (3) with Hydrochloric Acid.—A mixture of **3** (0.3 g.) and ethanol (12 ml.) was gently heated to boiling, to which was added 10% aqueous hydrochloric acid (0.34 ml.). Boiling was continued for 3 min. longer, when all the solid dissolved. The solution was evaporated to dryness, when the smell of benzaldehyde was noted. The residue was washed with water and the remainder (0.16 g.) was recrystallized from 85% ethanol to obtain 2,4-dibromoaniline,[14] m.p. 78–79°. The water washing was evaporated to dryness and the residue (0.06 g.) was recrystallized from benzene to obtain succinimide, m.p. 121°.

Addition of Succinimide (5) to N-Benzylidene-2,4-dibromoaniline (4).—A mixture of **4** (33.9 g., 0.1 mole) and **5** (9.9 g., 0.1 mole) in ethanol (100 ml.) was refluxed for 15 hr. and the solution was allowed to cool. The solid (33.5 g., 76% yield) formed was collected by suction, washed with water, and recrystallized from ethyl acetate to obtain N-(α-succinimidobenzyl)-2,4-dibromoaniline (**3**), m.p. 146.5–147°, identical with the product from the reaction of **1** with NBS.

Addition of Succinimide (5) to N-Benzylideneaniline (1).—A mixture of **1** (1.81 g., 0.01 mole), **5** (0.99 g., 0.01 mole), and ethanol (10 ml.) was refluxed for 10 hr. and the solution was allowed to cool. The solid formed was collected by suction and washed with water. The remaining solid (1.67 g., m.p. 92–108°) was recrystallized three times from ethanol to obtain N-(α-succinimidobenzyl)aniline (**6**), m.p. 92–93°. This was done by dissolving the crude product in ethanol at room temperature and cooling the solution in an ice–salt bath to effect crystallization. The conventional technique of recrystallization converted the product to the starting materials. The mother liquid from the crude product afforded 0.5 g. more of **6**, m.p. 87–106°. The total crude yield was 84%. The infrared spectrum showed bands at 3.00, 5.66, 5.92, and 6.22 μ.

Anal. Calcd. for $C_{17}H_{16}N_2O_2$: N, 9.99. Found: N, 9.78, 9.77, 9.68.

Reaction of N-(α-Succinimidobenzyl)aniline (6) with NBS. A.—A mixture of **6** (1.40 g., 0.005 mole), NBS (1.84 g., 0.01 mole), and carbon tetrachloride (20 ml.) was refluxed for 20 min. When cool, the solid (1.10 g. of succinimide) was filtered off. The filtrate was evaporated at room temperature to dryness and the residue (0.37 g., 17% yield) was recrystallized from ethyl acetate to obtain N-(α-succinamidobenzyl)-2,4-dibromoaniline (**3**).

B.—A mixture of **6** (1.40 g., 0.005 mole), NBS (0.92 g., 0.005 mole), and carbon tetrachloride (20 ml.) was refluxed for 1 hr. When cool, the solid (0.87 g. of succinimide) was filtered off. The filtrate was evaporated to dryness at room temperature and the residue (1.04 g., 80% yield) was recrystallized from methanol to obtain N-benzylidene-4-bromoaniline (**2**).

When the same amounts of reactants as above were stirred at room temperature for 1 hr., there were obtained 0.84 g. of succinimide and 1.14 g. (88% yield) of **2**.

Reaction of N-Benzylidene-4-bromoaniline (2) with NBS.—A mixture of **2** (2.60 g., 0.01 mole), NBS (1.84 g., 0.01 mole), and carbon tetrachloride (20 ml.) was refluxed for 4 hr. and cooled to room temperature. The solid present was collected by suction, washed with water, and recrystallized from ethyl acetate to obobtain N-(α-succinimidobenzyl)-2,4-dibromoaniline (**3**), 1.14 g., 26% yield.

Addition of Succinimide (5) to N-Benzylidene-4-nitroaniline (8).—A mixture of **8**[15] (0.92 g., 0.004 mole), **5** (0.4 g., 0.004 mole), and benzene (10 ml.) was refluxed for 8 min. The resulting solid product (0.67 g., 51% yield) was recrystallized from toluene to obtain N-(α-succinimidobenzyl)-4-nitroaniline, m.p. 180–181°. The infrared spectrum showed bands at 2.96, 5.65, 5.90, and 6.25 μ.

Anal. Calcd. for $C_{17}H_{15}N_3O_4$: C, 62.76; H, 4.65; N, 12.92. Found: C, 62.77, 62.67; H, 4.50, 4.83; N, 12.72, 12.77.

Addition of Succinimide (5) to N-(4-Nitrobenzylidene)aniline (9).—A mixture of **9**[16] (0.23 g., 0.001 mole), **5** (0.1 g., 0.001 mole), and benzene (5 ml.) was refluxed for 9 hr. The solid product (0.33 g., 100% crude yield) was recrystallized from toluene to obtain N-(α-succinimido-4-nitrobenzyl)aniline, m.p. 143–144°. The infrared spectrum showed bands at 2.95, 5.65, 5.87, and 6.22 μ.

Anal. Calcd. for $C_{17}H_{15}N_3O_4$: C, 62.76; H, 4.65; N, 12.92. Found: C, 62.72; H, 4.64; N, 12.77, 12.67.

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