are m.p. 156°, α +81°, λ 240 mμ (ϵ 17,080); and for **2b** they are m.p. 194°, α +27°, λ 237 mμ (ϵ 14,500). In this nonsensitized run no cholest-4,6-dien-3-one (**5**) was evident from the infrared or ultraviolet spectra of the fractions from chromatography.

Photosensitized Oxygenation.—A solution of 1 (0.60 g.), hematoporphyrin (0.005 g.), and methylene blue (0.005 g.) in pyridine (70 ml.) was oxygenated and irradiated 42 hr. in the cold room as before. The crude product was an oil (0.55 g.) which gave a positive test for hydroperoxide and which had λ 242 mμ (ϵ 5450). Its infrared spectrum (neat) showed strong peaks around 3330 and 1680 cm.$^{-1}$ (characteristic of OOH and α,β-unsaturated ketone, respectively); a weak shoulder at 1725 cm.$^{-1}$ and the absence of bands at 952 and 795 cm.$^{-1}$ indicated that very little starting material remained. The product was reduced with sodium iodide in the normal way except acetic acid was omitted. After reduction the product had λ 240 mμ (ϵ 6100); this maximum was overshadowed by a new maximum that appeared at 285 mμ when the ultraviolet solution was treated with a little hydrochloric acid or potassium hydroxide (ϵ 9300 and 9100, respectively). Separate runs showed that, when the acetic acid was not omitted in the sodium iodide treatment, the dienone chromaphore developed during the reduction. Based on the reported[17] values for cholesta-4,6-dien-3-one (**5**, λ 284 mμ, ϵ 26,300)[17] the acid or base treatment gave rise to *ca.* 35% of dienone **5**. A portion of the reduced material was acetylated in the usual way[3b] to esterify secondary hydroxyl groups, and the product (0.123 g.) in benzene–hexane (1:3) was chromatographed on alumina (5 g.). Dienone **5** was formed on the column and was eluted with benzene–hexane (2:5) as a solid (0.032 g.) whose melting point (75–76°) was undepressed by authentic **5** (m.p. 77–79°)[17]; the infrared spectra were also identical.

The remainder of the reduced product (0.370 g.) prior to acetylation was dissolved in benzene–hexane (1:1) and deposited on a column of alumina (13 g.), and elution with the same solvent was commenced after a 15-min. waiting period. Several solid and semisolid fractions (total 0.111 g.) were obtained whose individual infrared and ultraviolet spectra were essentially the same as that of dienone **5**. Elution with benzene gave a hardened oil (0.030 g.) whose infrared spectrum was identical with that of authentic cholest-4-ene-3,6-dione, and whose ultraviolet spectrum showed λ 253 mμ (ϵ 9600). Benzene–ether (6:1) eluted several yellow solid fractions (total 0.065 g.) whose individual melting points fell between 145 and 174°. Their ultraviolet spectra (λ 237–238 mμ, ϵ 11,200–12,000) and infrared spectra (ν 3450, 1680, 1270, 1230, 1190, 1035, 1015, 875 cm.$^{-1}$) indicated that these fractions contained varying proportions of cholest-4-en-6β-ol-3-one (**2b**) and cholest-4-en-6α-ol-3-one (**4b**). Further elution of the column with ether gave brown, gummy material (0.050 g.) that seemed polymeric and was not investigated.

Acknowledgment.—We are grateful to Mr. Anthony Baum and Mr. Zaki Abdulla for valuable laboratory assistance.

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[17] A. L. Wilds and C. Djerassi, *J. Am. Chem. Soc.*, **68**, 1713 (1946). A sample of the authentic dienone was prepared by Dr. J. F. Bagli.[4b]

Synthesis of 1-Methylcyclopropene

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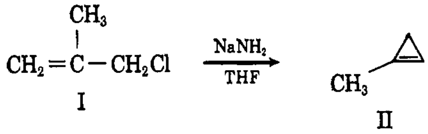
During some attempts to prepare methylenecyclopropane by γ-elimination of hydrogen chloride from methallyl chloride (I), a synthesis of the hitherto unknown 1-methylcyclopropene (II) was found. When I was treated with commercial sodamide in gently refluxing, anhydrous tetrahydrofuran and the gas evolved was passed through a wash of initially 1 *N* sulfuric acid to remove the ammonia, a readily condensed gas was obtained which gave a positive test for an acidic hydrocarbon with potassium iodomercurate (Nessler's reagent) and analyzed (C:H ratio) for C_4H_6. It showed three n.m.r. signals, δ = 0.83 (doublet, $J \sim 2$ c.p.s.), 2.13 (doublet, $J \sim 1$ c.p.s.), and 6.40 p.p.m. (partially resolved multiplet) with relative areas 2:3:1. On this basis it has been assigned the structure 1-methylcyclopropane. The chemical shifts are reasonable on the basis of similar compounds: 1,3,3-trimethylcyclopropene,[1] vinyl hydrogen at 6.65 p.p.m. and allylic methyl at 2.00 p.p.m.; and cyclopropene,[2] methylene group at 0.92 p.p.m. No yield was determined accurately, but it was approximately 50%.



The reaction is probably related to the methods recently reported by Closs and co-workers,[1,3] namely, reaction of alkenyllithiums with methylene chloride, reaction of allylic halides with alkyllithium, reaction of 1,1-dihalo-2-alkenes with alkyllithium, and basic decomposition of α,β-unsaturated tosylhydrazones. All have in common an alkenylcarbene or alkenylcarbene-like intermediate[3] which closes to the cyclopropene. The present method, however, appears to complement the previous procedures, which have not been applied successfully to the preparation of cyclopropenes unsubstituted in the 3-position.

Closs,[3] *et al.*, have pointed out that cyclopropenes with hydrogens in the 3-position are quite unstable. 1-Methylcyclopropene, handled in a high-vacuum line, proved stable for at least 4 days in the gas phase or at liquid-nitrogen temperature. However, in carbon tetrachloride solution the material decomposed within 2 days at room temperature; the decomposition (probably some type of polymerization) was substantially complete after 1 week, no further change in the n.m.r. spectrum occurring after this time. Material stored in the liquid phase at −20° also decomposed within 2 weeks. No structure was assigned to the decomposition product.

Besides the reaction with Nessler's reagent, the only chemistry studied was the reaction of the cyclopropene with triphenylmethyl fluoroborate in acetic anhydride in an attempt to prepare methylcyclopropenium fluoroborate; no decoloration of the triphenylmethyl cation was noted.

Experimental[4]

1-Methylcyclopropene (II).—A solution of 25 ml. (23.1 g., 0.256 mole) of dry methallyl chloride in 50 ml. of anhydrous tetrahydrofuran was added dropwise to a slurry of 10.0 g. (0.256 mole) of sodamide in 50 ml. of anhydrous tetrahydrofuran. A slow stream of nitrogen was passed over the reaction mixture and then through a 6-in. column of $^3/_{32}$-in. glass helices, a washing bottle containing 200 ml. of 1 *N* sulfuric acid, a 6-in. column of calcium sulfate, and a Dry Ice trap. No noticeable gas evolution occurred at room temperature; the mixture was heated to gentle

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[1] G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **85**, 99 (1963).

[2] K. B. Wiberg and B. J. Nist, *ibid.*, **83**, 1226 (1961).

[3] G. L. Closs, L. E. Closs, and W. A. Böll, *ibid.*, **85**, 3796 (1963).

[4] For further details, including spectra, the Ph.D. Thesis of F. Fisher, University of Illinois, 1965, may be consulted.

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.

Acknowledgment.—This work was supported in part by National Science Foundation Grant GCP-166. The microanalysis was done by Mr. Josef Nemeth and his associates.

[5] N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1957, p. 480.

[6] H. J. Dauben, Jr., L. R. Honnen, and K. M. Harmon, *J. Org. Chem.*, **25**, 1442 (1960).

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

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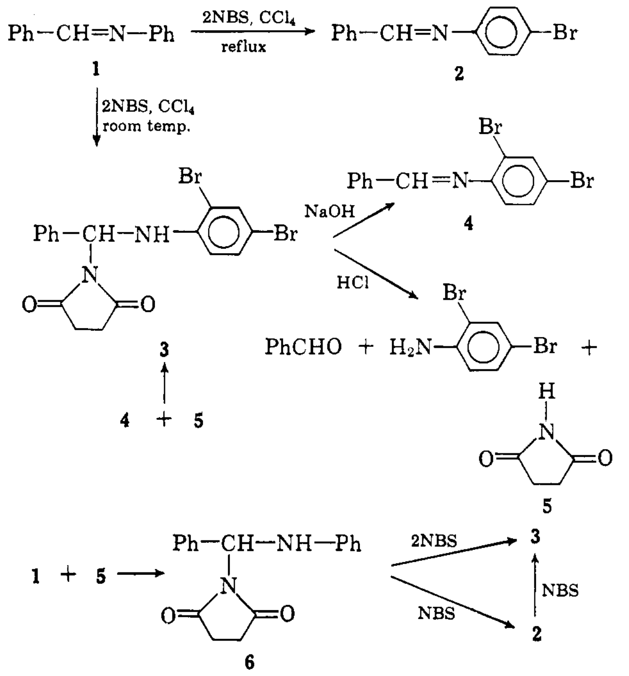
Various active hydrogen compounds have been known to add across the carbon–nitrogen double bond of Schiff bases.[2] *t*-Amyl hypochlorite also has been regarded as an addend in its reactions with Schiff bases.[3] The present study was undertaken to see if N-bromosuccinimide (NBS) would likewise undergo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

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

[2] R. W. Layer, *Chem. Rev.*, **63**, 489 (1963).

[3] R. Fusco and C. Musante, *Gazz. chim. ital.*, **66**, 258, 639 (1936); *Chem. Abstr.*, **31**, 1777, 3459 (1937).

[4] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 205, 249.

[5] C. D. Hurd and J. S. Strong, *J. Am. Chem. Soc.*, **72**, 4813 (1950).

[6] O. A. Moe and D. T. Warner, *ibid.*, **71**, 1251 (1949).