Communications TO THE EDITOR

Stable Oxonium Salts and Alkylation of Episulfides and Disulfides[1]

Sir:

Trialkyloxonium salts have been prepared by a variety of methods[2-5] since their discovery by Meerwein.[6,7] Their general utility has been somewhat limited by their instability, inconvenience of preparation, or hygroscopic nature. We now wish to report the synthesis of a stable, easily prepared oxonium salt, and its use in novel alkylations of an episulfide and disulfide.

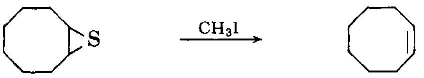
Trimethyloxonium 2,4,6-trinitrobenzenesulfonate was prepared by introducing diazomethane in gaseous methyl ether into a well stirred mixture of 2,4,6-trinitrobenzenesulfonic acid[8] in methyl ether at −35°. When a faint yellow color persisted, an equal volume of absolute ethyl acetate was added and the product was isolated by filtration, washed with petroleum ether, and dried in a vacuum desiccator. The yield was 70% from 0.010 mole of the acid. The product melted with effervescence at 115–120° (a nearly quantitative amount of methyl ether was liberated), resolidified immediately, and melted again at 181–183° (Calcd. for $C_9H_{11}N_3O_{10}S$: C, 30.60; H, 3.14; N, 11.90. Found: C, 30.88; H, 3.33; N, 12.06.). The same product could be obtained by adding a cold solution of trinitrobenzenesulfonic acid in acetonitrile to an equivalent amount of trimethyloxonium fluoborate[6] dissolved in nitromethane at 0–5°. The salt showed only slight decomposition after two weeks when stored in a closed container at 5–10°.

Triethyloxonium 2,4,6-trinitrobenzenesulfonate was prepared by mixing an ethyl acetate solution of the sulfonic acid with a nitromethane solution of triethyloxonium fluoborate[6] at 5°. The mixture was poured into an equal volume of absolute ether and the solid product was isolated and washed as described for the trimethyloxonium compound. The salt melted at 88–90° with effervescence, resolidified, and melted again at 142–144° (Calcd. for $C_{12}H_{17}N_3O_{10}S$: C, 36.45; H, 4.34; N, 10.63. Found: C, 36.82; H, 4.68; N, 10.58.).

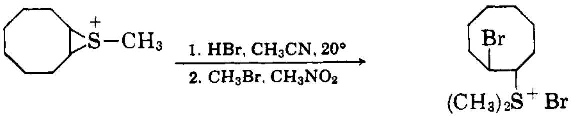
Thermal decomposition of trimethyloxonium 2,4,6-trinitrobenzenesulfonate led to methyl 2,4,6-trinitrobenzenesulfonate, m.p. 180–181° (Calcd. for $C_7H_5N_3O_9S$: C, 27.37; H, 1.64; N, 13.68. Found: C, 27.76; H, 1.94; N, 13.42.).

In continuing a study of alkylating agents,[9] the reaction of oxonium salts with sulfur-containing compounds has been investigated.

Cyclooctene sulfide was prepared by the reaction of cyclooctene with thiocyanogen,[10] followed by treatment of the crude 1,2-dithiocyanocyclooctane with sodium sulfide in methanol–water.[11] The yield of the sulfide, m.p. 25–26°, b.p. 71° (2 mm.), was 50% (Calcd. for $C_8H_{14}S$: C, 67.52; H, 9.92. Found: C, 67.33; H, 9.99.). Physical and chemical characterization was based on its infrared spectrum[12] (1038 cm.$^{-1}$, strong; 1140 cm.$^{-1}$, medium), ultraviolet spectrum[13] (λ_{max} 259 mμ), and desulfurization by methyl iodide.[9]



The reaction of 2-butene or cyclohexene sulfides with trimethyloxonium 2,4,6-trinitrobenzenesulfonate gave only dimeric or polymeric products. However, cyclooctene sulfide yielded a stable, easily purified solid whose physical and chemical properties were consistent with those expected for the cyclic sulfonium salt, m.p. 122–123° (Calcd. for $C_{15}H_{19}N_3O_9S_2$: C, 40.15; H, 4.26; N, 9.35. Found: C, 40.42; H, 4.50; N, 8.92.). The experimental molecule weight was 440[14] (Calcd.: 449.). The compound showed strong absorptiln bands at 1028 cm.$^{-1}$ and 1057 cm.$^{-1}$, indicative of ionic sulfonate, and a weak band at 3010 cm.$^{-1}$, characteristic of the C–H stretching frequency of a 3-membered ring. When the episulfonium salt was treated with hydrogen bromide and methyl bromide, the sulfonium salt that formed was identical (melting point, mixture melting point, and infrared spectrum) to the product of the reaction of cyclooctene sulfide with methyl bromide, m.p. 145–146° (Calcd. for $C_{10}H_{20}SBr_2$: C, 36.14; H, 6.07; Br, 48.14. Found: C, 36.32; H, 6.35; Br, 47.79.). Treatment of the episulfonium salt with sodium iodide in acetone resulted in rapid decomposition to cyclooctene, methyl disulfide, and iodine. This reaction, which is not characteristic of sulfonium salts in an unstrained ring



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(1) This investigation was supported by grant GM-8185 from the National Institutes of Health, U. S. Public Health Service.

(2) F. Klages and H. Meuresch, *Ber.*, **85**, 863 (1952).

(3) F. Klages and H. Meuresch, *ibid.*, **86**, 1322 (1953).

(4) H. Meerwein, V. Hederich, and K. Wunderlich, *Arch. Pharm.*, **291**, 541 (1958).

(5) H. Teichmann and G. Hilgetag, *Naturwissenshaften*, **47**, 39 (1960).

(6) H. Meerwin, G. Hinz, P. Hofmann, E. Kroning, and E. Pfeil, *J. prakt. Chem.*, **147**, 257 (1937).

(7) H. Meerwein, E. Battenberg, H. Gold, E. Pfeil, and G. Willfang, *ibid.*, **154**, 83 (1939).

(8) The acid was prepared by a procedure modified somewhat from that of C. Golumbic and M. Bergman, *J. Org. Chem.*, **11**, 519 (1946); no preliminary purification of the sodium salt was made, and the product was crystallized from acetone–chloroform.

(9) G. K. Helmkamp and D. J. Pettitt, *ibid.*, **25**, 1754 (1960).

(10) J. F. McGhie, W. A. Ross, F. J. Julietti, and B. E. Grimwood, *J. Chem. Soc.*, 4638 (1962).

(11) M. A. Youtz and P. P. Perkins, *J. Am. Chem. Soc.*, **51**, 3508 (1929).

(12) N. P. Neureiter and F. G. Bordwell, *ibid.*, **81**, 578 (1959).

(13) R. E. Davis, *J. Org. Chem.*, **23**, 216 (1958).

(14) The molecular weight was determined using a Mechrolab vapor pressure osmometer, Model 301A, with nitromethane solvent and trimethylsulfonium 2,4,6-trinitrobenzenesulfonate standard.

system,[15] excludes the possibility that a transannular product is involved.

When a small excess of methyl disulfide was added to trimethyloxonium 2,4,6-trinitrobenzenesulfonate in a small amount of nitromethane, an immediate reaction took place. The product, dimethylmethylthiosulfonium 2,4,6-trinitrobenzenesulfonate could be precipitated by the addition of ethyl ether. Crystallization from nitromethane–ether yielded a white, stable solid, m.p. 164–166° dec. (Calcd. for $C_9H_{11}N_3O_9S_3$: C, 26.92; H, 2.76; N, 10.46. Found: C, 27.20; H, 2.73; N, 10.61.). On treatment with aqueous sodium iodide, the salt yielded iodine in 85% yield and a 2:1 ratio of methyl sulfide to methyl disulfide. This corresponds stoichiometrically to the following process.

$$2\,(CH_3)_2{}^+SCH_3 + 2\,I^- \longrightarrow 2\,(CH_3)_2S + CH_3SSCH_3 + I_2$$

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[15] P. Mamalis and H. N. Rydon, *J. Chem. Soc.*, 1049 (1955).

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RECEIVED JUNE 12, 1963

Bis(phenylsulfonyl)diazomethane

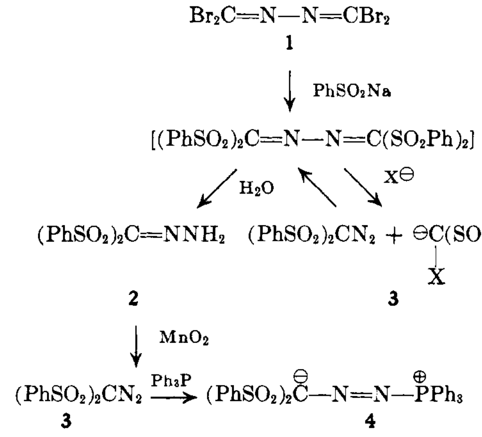
Sir:

Bis(phenylsulfonyl)diazomethane is of interest as a possible source of an exceptionally electrophilic carbene, bis(phenylsulfonyl)carbene. We have prepared and characterized bis(phenylsulfonyl)diazomethane **3** and studied its chemical properties. Bis(phenylsulfonyl)diazomethane has been alluded to,[1] but nothing has been published on its synthesis or properties.

Treatment of a solution of carbonyl bromide azine (**1**)[2] in dimethylformamide at 0° with four equivalents of sodium benzenesulfinate followed by addition of water gave bis(phenylsulfonyl)formaldehyde hydrazone (**2**),[3] m.p. 204° dec. Oxidation of a suspension of **2** in dichloromethane with active manganese dioxide or silver oxide gave bis(phenylsulfonyl)diazomethane (**3**) in 55% yield. Bis(phenylsulfonyl)methane, which apparently arises from a Wolff–Kishner-type reaction of **2**, was formed as a by-product.

Treatment of **1** with four equivalents of sodium benzenesulfinate under anhydrous conditions affords **3** directly. The intermediate azine apparently is very unstable to the nucleophiles present in the reaction mixture.

Purification of **3** is achieved by passing a benzene solution of crude **3** through neutral alumina. It can be recrystallized from a benzene–cyclohexane mixture to give long, yellow rods, m.p. 99–100° dec.; $\lambda_{max}^{CH_3CN}$ 232 mμ (ε 17,200), 375 (72); an infrared spectrum of **3** shows a strong band at 4.7 μ attributed to the diazo group. With triphenylphosphine **3** yields the stable phosphazine **4**, m.p. 194° dec.



Bis(phenylsulfonyl)carbene obtained by photolysis of **3** behaves as a strong electrophile. It can serve as both alkylating agent and oxidizing agent as exemplified by its reaction with methanol which gives rise to bis(phenylsulfonyl)methyl methyl ether and bis(phenylsulfonyl)methane. Diethyl ether is cleaved by bis(phenylsulfonyl)carbene with formation of bis(phenylsulfonyl)methyl ethyl ether and ethylene. Ionic and photolytic reactions of **3** and related bis(sulfonyl)diazomethanes will be reported in a future publication.

CONTRIBUTION NO. 887
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RECEIVED AUGUST 13, 1963

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[1] Abstract of a talk by F. Klages, *Angew. Chem., Intern. Ed. Engl.*, **1**, 603 (1962). The preparation of *p*-methoxybenzenesulfonyldiazomethane recently has been described by J. Strating and A. M. VanLeusen, *Rec. trav. chim.*, **81**, 966 (1962).

[2] J. Thiele, *Ann.*, **303**, 57 (1898).

[3] Satisfactory elemental analyses were obtained for all new compounds.

The Facile Isomerization of 2,4-Dimethyl-6-acylmethyl-*s*-triazines to 4-Acetamidopyrimidines[1]

Sir:

We are aware of only two reported examples of the isomerization of trisubstituted *s*-triazines to pyrimidines. Thus, 2,4,6-triethyl-*s*-triazine and 2,4,6-trimethyl-*s*-triazine have been isomerized to 4-amino-2,6-diethyl-5-methylpyrimidine (32%) and 4-amino-2,6-dimethylpyrimidine (12%), respectively, by reaction with methanolic ammonia under drastic conditions, *i.e.*, 150° at 8500 atmospheres for eighteen hours.[2]

We wish to report the synthesis of a new class of ketones containing the triazine ring (I) and their facile isomerization to 4-acetamidopyrimidines (II) under very mild conditions. The ketones (I, R = C_6H_5, *p*-ClC_6H_4, *p*-$CH_3OC_6H_4$, 2-pyridyl, 3-pyridyl, 2-furyl, and 2-thienyl) have been prepared in high yields by acylating 2,4,6-trimethyl-*s*-triazine with aromatic and heterocyclic esters using potassium amide in liquid ammonia as the condensing agent. When 2,4-dimethyl-6-phenacyl-*s*-triazine (I, R = C_6H_5) was heated in refluxing water for one hour, it was converted quantitatively from a yellow, crystalline solid, m.p. 69–72° (Calcd. for $C_{13}H_{13}N_3O$: C, 68.72; H, 5.73; N, 18.51.

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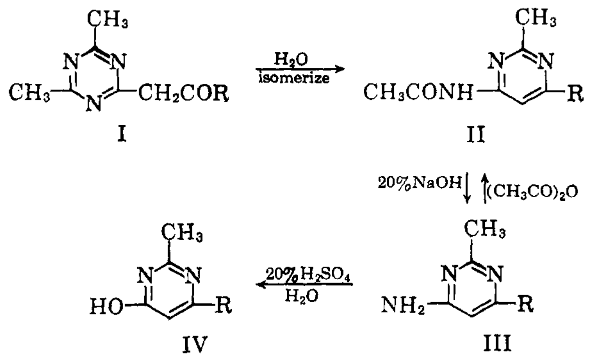
[1] This work was supported by a Grant-in-Aid from the Standard Oil Company of Ohio.

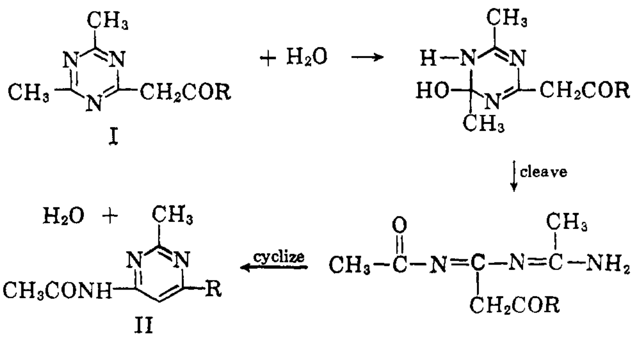
[2] T. L. Cairns, A. W. Larchar, and B. C. McKusick, *J. Am. Chem. Soc.*, **74**, 5633 (1952).



Found: C, 68.43; N, 5.47; N, 18.31.) to a sharp melting white, crystalline solid, m.p. 169–170°, whose analysis (Found: C, 68.93; H. 5.58; N, 18.29.) and molecular weight (Calcd. for $C_{13}H_{13}N_3O$: 227. Found: 227.7.) indicate that the product and 2,4-dimethyl-6-phenacyl-*s*-triazine are isomers. While I (R = C_6H_5) was cleaved by dilute acid to give a mixture of acetic acid (53%), benzoylacetic acid (71.5%), and ammonia and by dilute base to give a mixture of 2,4,6-trimethyl-*s*-triazine (83%) and benzoic acid (95%), the isomerized product was inert under these conditions. Cleavage of I (R = C_6H_5) by dilute base is not too surprising since this compound may be regarded to be structurally analogous to a 1,3-diketone, in which one carbonyl group is replaced by an azomethine function of the triazine ring, and such compounds are known to be cleaved by alkali.[3] In addition, while I (R = C_6H_5) forms both an oxime and a copper chelate, its isomer forms neither of these derivatives. It has been concluded that the product is 4-acetamido-2-methyl-6-phenylpyrimidine (II, R = C_6H_5), based on the following: (a) the fact that I (R = C_6H_5) loses its ketonic properties when it is isomerized; (b) an examination of the infrared spectrum of II (R= C_6H_5) which shows absorption at 1690 cm.$^{-1}$ (s) and 3350 cm.$^{-1}$ (m) characteristic of an amide function and does not show the strong, broad absorption characteristic of the triazine[4] ring at 1563 cm.$^{-1}$ [the last band is present in the infrared spectrum of I (R = C_6H_5)]; and (c) an examination of the n.m.r. spectra of the starting material and the isomerized product. The structure of this amide was confirmed by hydrolysis with 20% sodium hydroxide solution to the known 4-amino-2-methyl-6-phenylpyrimidine (III, R = C_6H_5, m.p. 164–165°[5]), whose ultraviolet absorption spectrum is identical with the reported spectrum[5] of an authentic sample. In addition, II (R = C_6H_5) is regenerated from III (R = C_6H_5) by reaction with acetic anhydride. Finally, III (R = C_6H_5) is quantitatively hydrolyzed to IV (R = C_6H_5), 4-hydroxy-2-methyl-6-phenylpyrimidine, m.p. 242°,[6] alone and when mixed with an authentic sample prepared by the reaction of ethyl benzoylacetate with acetamidine.[7]

All the triazinyl ketones (I) listed previously have been quantitatively isomerized to the corresponding 4-acetamidopyrimidines (II) which, in turn, have been quantitatively hydrolyzed to the corresponding 4-aminopyrimidines (III). The presently reported triazinyl ketone-4-acetamidopyrimidine isomerization is especially interesting because of the mild conditions which are employed and the quantitative yields which are obtained as contrasted with the low yields and drastic conditions which are necessary[2] to isomerize trialkyl-*s*-triazines to 4-amino-2,6-dialkylpyrimidines.

A possible scheme which rationalizes the isomerization of compounds I to compounds II is shown.



Further work is in progress to determine the scope and limitations of this isomerization and to shed more light on its mechanism with particular emphasis on determining the role of the substituent in the 6-position of the triazine ring on the course of the reaction. In addition, the participation of 2,4,6-trimethyl-*s*-triazine in alkylations and aldol-type condensations is being studied.

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RECEIVED JULY 15, 1963

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[3] C. R. Hauser, F. W. Swamer, and B. I. Ringler, *J. Am. Chem. Soc.*, **70**, 4023 (1948).

[4] W. M. Padgett, II, and W. F. Hammer, *ibid.*, **80**, 803 (1958).

[5] P. B. Russell, *J. Chem. Soc.*, 2951 (1954).

[6] G. Shaw and G. Sugowdz, *ibid.*, 665 (1954).

[7] A. Pinner, *Ber.*, **22**, 1618 (1889).

Photochemical Reactions of Peresters in the Presence of Copper Ions

Sir:

Since discovery[1,2] of the copper-catalyzed perester reaction, investigators in this field have used essentially the procedure first developed.[3] Namely, the perester is added to the substrate in the presence of a copper salt catalyst and the temperature of the mixture is maintained between 65 and 115°. The narrow temperature range is imposed mainly by the properties of commercially available peresters: *t*-butyl peracetate and *t*-butyl perbenzoate are stable at room temperature and undergo homolytic cleavage readily only at elevated temperatures. This temperature limitation causes several experimental inconveniences: low-boiling substrates must be treated under pressure and heat-sensitive acyloxy derivatives may undergo additional reactions before they are isolated.

It has now been found that a variety of substances readily react with peresters upon exposure to ultraviolet light in the presence of a trace amount of copper ions.

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[1] M. S. Kharasch and George Sosnovsky, *J. Am. Chem. Soc.*, **80**, 756 (1958).

[2] M. S. Kharasch and George Sosnovsky, Abstract of papers, 134th National Meeting of the American Chemical Society, Chicago, Ill., September, 1958, p. 7P.

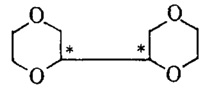
[3] M. S. Kharasch, George Sosnovsky, and N. C. Yang, *J. Am. Chem. Soc.*, **81**, 5819 (1959).

Irradiation with a Hanovia quartz lamp of a mixture of ethyl ether, *t*-butyl peracetate, and either cuprous bromide or cupric 2-ethyl hexoate at 35° produced 1-ethoxyethylacetate in 75% yield. The physical constants and the infrared spectra of this product agreed with those of the thermal reaction product. The values for the thermal reaction product were: b.p. 64–68° (68 mm.), $\gamma_{C=O}$ 1735 cm.$^{-1}$, $n^{25}_{\rm D}$ 1.3936. *Anal.* Calcd. for $C_6H_{12}O_3$: C, 54.53; H, 9.14. Found: C, 54.60; H, 9.23. Similarly, the reaction of ethyl ether with *t*-butyl perbenzoate produced 1-ethoxyethylbenzoate in 77% yield. The product was the same as the product of the thermal[4] reaction. The photochemical reaction of cyclohexene with *t*-butyl perbenzoate produced cyclohex-1-en-3-yl benzoate in 76% yield, and the product was also the same as that of the thermal[3] reaction.

Dimethylformamide reacted with *t*-butyl peracetate to form N-acetoxymethyl-N-methylformamide in 39% yield. The physical constants and the infrared spectra of the product agreed with those of the thermal reaction product. The values for the thermal reaction product were: b.p. 66° (0.1 mm.), $\gamma_{C=O}$ 1725 cm.$^{-1}$, $n^{25}_{\rm D}$ 1.4412. *Anal.* Calcd. for $C_5H_9O_3N$: C, 45.79; H, 6.92; N, 10.68. Found: C, 46.13; H, 7.27; N, 10.79.

The thermal reaction of tetrahydrofuran with *t*-butyl peracetate was shown previously to yield 2-*t*-butoxy tetrahydrofuran.[5-8] It has now been found that the photochemical reaction produced the 2-acetoxy derivative in 75% yield, b.p. 80° (22 mm.), $\gamma_{C=O}$ 1730 cm.$^{-1}$, $n^{25}_{\rm D}$ 1.4290. *Anal.* Calcd. for $C_6H_{10}O_3$: C, 55.37; H, 7.74. Found: C, 55.41; H, 7.88.

The photochemical reaction of 1,4-dioxane with peracetate produced dioxanyl acetate. This product also was identical with that of the thermal reaction product: b.p. 55–58° (0.1 mm.), $\gamma_{C=O}$ 1735 cm.$^{-1}$, $n^{25}_{\rm D}$ 1.4390. *Anal.* Calcd. for $C_6H_{10}O_4$: C, 49.35; H, 6.90. Found: C, 49.73; H, 6.98. In contrast, the photochemical reaction in the absence of copper ions yielded two products, m.p. 157 and 132°. Microanalyses and molecular weight determinations showed that one product is the *meso* and the other the *dl* form of the dioxane dimer (I).



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The reactions catalyzed by light only or copper ions only proceeded at a much slower rate than the reactions catalyzed by both light and copper ions. For example, while the copper-ion–light reaction of ethyl ether with *t*-butyl peracetate was completed in 91 hr., the reaction with copper or light alone was not completed after 400 and 240 hr., respectively. The combined effect of light and copper ions on the decomposition of peresters suggests the following mechanistic interpretation. The first step in the perester reaction is the formation of a complex between the copper ions and the perester. Since less energy is required to dissociate the O–O bond of the complexed perester than that of the uncomplexed perester, the copper ion-catalyzed reactions proceed at a faster rate.

The scope of the new photochemical reaction is currently being investigated, and the results will be reported at a later date.

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RECEIVED JULY 15, 1963

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[4] W. E. Cass, *J. Am. Chem. Soc.*, **69**, 500 (1947).

[5] George Sosnovsky, *J. Org. Chem.*, **25**, 874 (1960).

[6] S.-O. Lawesson, C. Berglund, and S. Grönwall, *Acta Chem. Scand.*, **14**, 944 (1960).

[7] George Sosnovsky, *Tetrahedron*, **13**, 241 (1961).

[8] S.-O. Lawesson and C. Berglund, *Arkiv Kemi*, **17**, 475 (1961).

Diborane Reduction of Aromatic Systems. Course of the Reduction–Elimination of Xanthone, Thioxanthone, and 9(10H)-Acridone to Their Corresponding Hydrocarbons

Sir:

In connection with our current synthetic interest in the system xanthene (**1**) ⇆ xanthydrol (**2**) ⇆ xanthone (**3**) a method was sought for the reduction of the xanthone system to xanthene under conditions less vigorous than lithium aluminum hydride or diphenylsilane.[1] This goal met with unexpected success when xanthone (**3**) was reduced quantitatively to xanthene (**1**) at 0° by the action of diborane in tetrahydrofuran solution.

Reflection as to the possible mechanisms of this reaction and the reducing potential of diborane[2] makes a hypothesis of direct hydrogenolysis of a borate ester of xanthydrol untenable. This belief was buttressed by the fact that we found benzophenone, fluorenone, 4,4′-dimethoxybenzophenone and 2-methoxybenzophenone give only their corresponding alcohols on diborane reduction.[3] Thus even in the case of a powerful electron-donating group such as *o*- or *p*-methoxy no hydrocarbon product was realized from the reduction. It is evident consequently that the xanthone (**3**) → xanthene (**1**) conversion involves an aromatic counterpart of the Thiele 1,4-elimination[4] reaction in which borate ion is the leaving group giving the resonance stabilized xanthonium ion (**5**). The aromatic species thus formed is then reduced by diborane involving hydride addition at C-9 with the heteroatom X serving as an electron sink. This thesis is supported by the inability of diborane to reduce either anthracene or phenanthrene under these experimental conditions.

2-Nitroxanthone is reduced only slowly at room temperature giving as an exclusive product 2-nitroxanthene[5] a fact that is in consort with the electron-withdrawing characteristic of the nitro group which would attenuate the rate of the elimination of the borate ester (step 2) as well as the rate of the reduction step 1 owing to the electrophilic nature of diborane.

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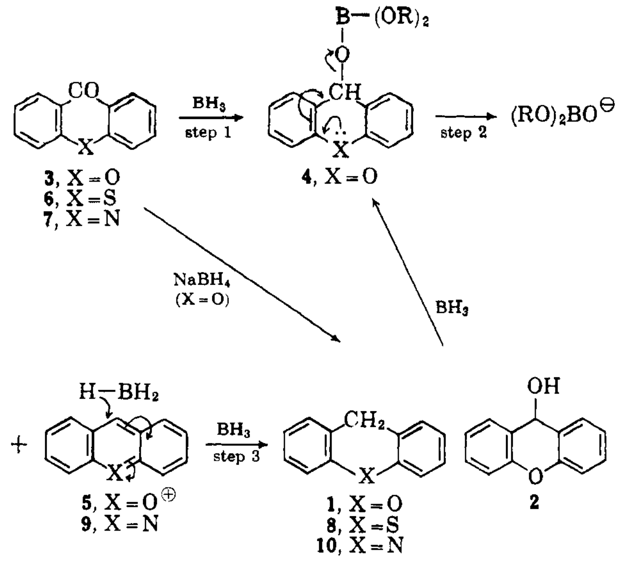
[1] Although it has been demonstrated that xanthone can be reduced to xanthene in 27.5% yield by the action of diphenyl silane at 270° [H. Gilman and J. Diehl, *J. Org. Chem.*, **26**, 4817 (1961)], these reaction conditions are too strenuous and afford low yields.

[2] H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1961, Chap. 17.

[3] At elevated temperatures and for protracted reaction times hydrocarbons can be produced; see G. P. Thakar and B. C. S. Rao, *J. Sci. Ind. Res.* (India), **21B**, 583 (1962).

[4] J. Thiele, *Ann.*, **306**, 333 (1899).

[5] This was characterized by CH analysis, infrared, ultraviolet, and n.m.r. spectra.

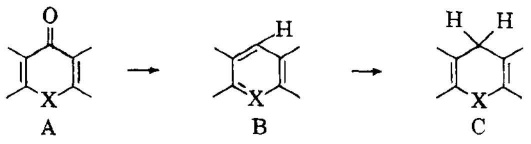


As heteroatoms both sulfur and nitrogen would be expected to participate in such a nucleophilic displacement (step 2). Thioxanthone (**6**) on treatment with diborane gave exclusively thioxanthene (**8**). 9(10H)-Acridone (**7**) being only slightly soluble in tetrahydrofuran gave a mixture of product consisting of starting material (**7**), acridine (**9**), and acridane (**10**). In this case the aromatic intermediate **9** was demonstrated clearly owing to its precipitation from the reaction media. In a separate experiment where the acridine (**9**) was in solution, it was reduced quantitatively to acridane (**10**).

In order to demonstrate that the ester **4** is indeed an intermediate in the reaction sequence, xanthydrol (**2**) was treated with diborane and the thus generated ester **4** yielded exclusively xanthene (**1**).

To establish that this reaction is restricted to the Lewis acid-type reducing agents such as diborane, xanthone (**3**) was reduced with sodium borohydride and gave only xanthydrol (**2**). Possibly the Lewis acid assists in the elimination of the borate ester.

It has been established, therefore, that an over-all hydrogenolysis of the system A to the system C can be carried out in high yield mediated by the reduction of the hetero double bond system B.



Subsequent to the completion of this work, two publications[6,7] have appeared in which the pyridinium ion has been reduced by sodium borohydride to a tetrahydropyridine. Such reactions are quite similar to step 3, preceding as is the demonstration by Brown and Bell[8] that borohydride can reduce stabilized carbonium ions.

The following reduction of xanthone is exemplary of the general experimental conditions employed. One gram of xanthone dissolved in 20 ml. of purified tetrahydrofuran is treated under nitrogen at 0° with 5 ml. of a stock solution of 1.9 *M* diborane in tetrahydrofuran. The mixture is stirred for one-half hour, after which the excess diborane is decomposed by the addition of small ice chips. The solution is diluted with an equal volume of water and the majority of the tetrahydrofuran removed under reduced pressure, whereupon pure xanthene crystallizes from the reaction mixture in quantitative yield, m.p. 100.5–101.5°. The homogeneity of samples was determined by thin layer chromatography on silica gel G.

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