5-Bromo-2-dichloromethylenecyclopentanone (XIII).—Pyridinium bromide perbromide, 1.9 g(5 mmol) was added to a solution of 830 mg (5 mmol) of 2-dichloromethylenecyclopentanone in 15 ml of carbon tetrachloride. The mixture was stirred at ambient temperature for 15 min and filtered. The filtrate was treated with anhydrous sodium carbonate. Evaporation of the solvent left 1.2 g of an oil which solidified on cooling. Recrystallization from pentane gave white crystals: mp 63–64°; ir 5.80 and 6.30 μ; nmr 2.32 (m, 2), 2.95 (m, 2), and 4.40 ppm (q, 1, CHBr).

Anal. Calcd for $C_6H_5BrCl_2O$: C, 29.50; H, 2.05. Found: C, 29.01; H, 2.13.

2-Dichloromethylene-1-hydroxy-1-methylcyclopentane.—A mixture of 830 mg (5 mmol) of 2-dichloromethylenecyclopentanone and 8 mmol of methyllithium in ether was prepared at −70° and then kept at ambient temperature for 10 hr. After the addition of 10 ml of 3.7% hydrochloric acid, the mixture was extracted with methylene chloride. The solution was dried and the solvents were removed, leaving an oil. The oil was triturated with four 10-ml portions of pentane. The pentane solution was treated with Darco KB and the volume was reduced to *ca.* 3 ml. On cooling to −70° unreacted 2-dichloromethylenecyclopentanone crystallized. The solid was removed and the remaining solvent was evaporated, leaving 390 mg (43%) of an oil which solidified on standing. Sublimation *in vacuo* gave a pure sample of the alcohol: mp 45.5–46°; ir 2.98, 6.15, and 6.31 μ; nmr 1.52 (s, 3, CH_3CO) ,1.87 (m, 4), and 2.50 ppm (m, 3).

Anal. Calcd for $C_7H_{10}Cl_2O$: C, 46.45; H, 5.50; Cl, 39.25. Found: C, 46.50; H, 5.58; Cl, 39.24.

3-Dichloromethylene-2-methylcyclopentene.—A mixture of 300 mg of 2-dichloromethylene-1-hydroxy-1-methylcyclopentane, 10 ml of 10% sulfuric acid, and 10 ml of methanol was stirred for 4 hr. The mixture was made basic with 10% sodium hydroxide solution and extracted with methylene chloride. After drying, the solvent was evaporated to leave 284 mg of an oil. Purification by vpc gave a colorless liquid: ir 5.80 (w), 6.17, 6.22, and 11.30 μ; $\lambda_{\max}^{\mathrm{EtOH}}$ 230 mμ (ϵ 7280); nmr 2.08 (m, 3), 2.35 (m, 2), 2.70 (m, 2), and 5.98 ppm (br s, 1).

Anal. Calcd for $C_7H_8Cl_2$: C, 51.55; H, 4.90. Found: C, 51.50; H, 4.91.

3-Dichloromethylene-2-phenylcyclopentene.—A solution of phenyllithium in ether, prepared from 1.18 g of bromobenzene and 105 mg of lithium, was added to a Dry Ice cooled solution of 2-dichloromethylenecyclopentanone in tetrahydrofuran. The reaction was worked up in the usual manner to give 1.08 g of an oil whose ir spectrum indicated the presence of a mixture of alcohol and starting ketone. A 243-mg portion of this oil was stirred for 2 hr at 25° with 0.5 ml of boron trifluoride etherate in 10 ml of ether. The ether solution was washed with sodium bicarbonate solution, dried, and evaporated to leave 201 mg of an oil. The oil was placed on a short alumina column and eluted with hexane to give 150 mg of diene. An analytical sample was prepared by evaporative distillation: ir 3.20, 6.24, 6.70, and 11.20 μ; nmr 2.60 (m, 2), 2.90 (m, 2), 6.15 (t, 1, HC=C), and 7.22 ppm (s, 5, ArH).

Anal. Calcd for $C_{12}H_{10}Cl_2$: C, 64.00; H, 4.44. Found: C, 64.20; H, 4.38.

Registry No.—I, 10412-35-8; II, 13017-26-0; 2,4-dinitrophenylhydrazone derivative of II, 23231-13-2; phenylhydrazone of 2-dichloromethylene-3-pentanone, 23231-14-3; oxime of 2-dichloromethylene-3-pentanone, 23231-15-4; 2,4-dinitrophenylhydrazone derivative of 2-dichloromethylenecyclopentanone, 23231-16-5; phenylhydrazone derivative of 2-dichloromethylenecyclopentanone, 23231-17-6; oxime of 2-dichloromethylenecyclopentanone, 23231-18-7; 2-dichloromethylenecyclohexanone, 10412-36-9; oxime of 2-dichloromethylenecyclohexanone, 23231-20-1; phenylhydrazone derivative of 2-dichloromethylenecyclohexanone, 23231-21-2; IV, 23231-22-3; V, 23231-23-4; VI, 23231-24-5; 2-diisopropylaminomethylenecyclopentanone, 23231-25-6; 2-di-*n*-butylaminomethylenecyclopentanone, 23231-26-7; 2-dipyrrolidinomethylenecyclopentanone, 23263-81-2; IX, 23231-27-8; X, 23231-28-9; XIII, 23240-69-9; 2-dichloromethylene-1-hydroxy-1-methylcyclopentane, 23240-70-2; 3-dichloromethylene-2-methylcyclopentene, 23240-71-3; 3-dichloromethylene-2-phenylcyclopentene, 23240-72-4.

Intermediates in Nucleophilic Aromatic Substitution. III.[1] Visible Absorption Spectra of the Acid and Basic Form of the 1,3,5-Trinitrobenzene–Piperidine Meisenheimer Complex in 10% Dioxane–90% Water

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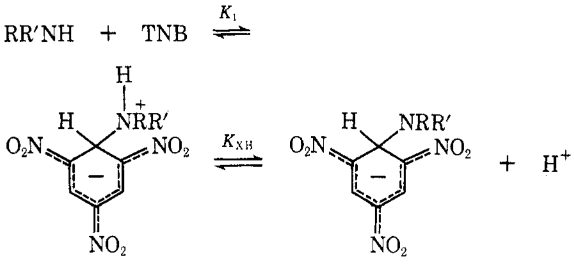
There exist a number of reports on the absorption spectra of the Meisenheimer complexes produced by the interaction of 1,3,5-trinitrobenzene (TNB) with aliphatic amines in a variety of solvents.[2–7] With primary and secondary amines, equilibrium 1 has



(1)

XH X⁻

R′ = Alkyl or H

consistently been found to strongly favor X⁻ over XH, so that the spectra always referred to the basic form X⁻. We wish now to report the spectrum of the zwitterionic form XH of the piperidine–TNB complex in 10% dioxane–90% water at 25°.

Figure 1 shows spectra of TNB in two different piperidine–piperidine hydrochloride buffer solutions, at different pH[8] but equal ionic strength. Knowledge of the equlibrium constants K_1 and K_{XH} and of the easily obtained spectrum of pure X⁻ would allow one to dissect the respective contributions of both species to the overall spectrum and thus to find the spectrum of pure XH by difference. The matter is, however, more complex for two reasons. (1) TNB and piperidine undergo another interaction to form the oxyhydroxylamine YH and its conjugate anion Y⁻;[1] though YH and Y⁻ do not contribute to the visible spectrum, they appreciably reduce the equilibrium concentrations of XH and X⁻. (2) There is also some concurrent for-

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[1] Part II: C. F. Bernasconi, *J. Amer. Chem. Soc.*, **92**, 129 (1970).

[2] R. E. Miller and W. F. K. Wynne-Jones, *J. Chem. Soc.*, 2375 (1959).

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[5] (a) R. Foster and R. K. Mackie, *Tetrahedron*, **16**, 119 (1961); (b) R. Foster and R. K. Mackie, *ibid.*, **22**, 1831 (1966).

[6] J. Osugi and M. Sasaki, *Rev. Phys. Chem. Jap.*, **37**, 43 (1967).

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[8] For our definition of pH in 10% dioxane–90% water, see ref 1.

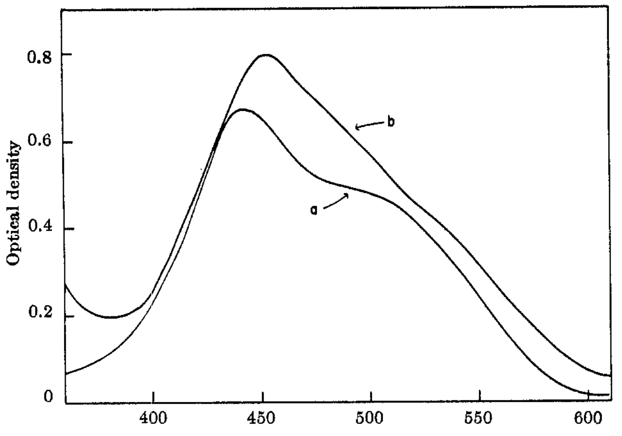
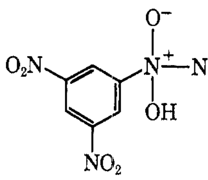
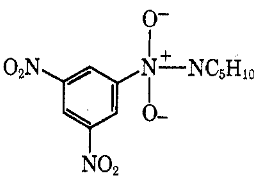


Figure 1.—Absorption spectra of TNB in the presence of a piperidine–piperidine hydrochloride buffer in 10% dioxane–90% water at 25°: a, [Pip] = 0.045 *M*, [Pip HCl] = 0.005 *M*, [NaCl] = 0.49 *M*, $[TNB]_0 = 1.60 \times 10^{-4}$ *M*, pH 12.02; b, [Pip] = 0.10 *M*, [Pip HCl] = 0.50 *M*, $[TNB]_0 = 1.20 \times 10^{-3}$ *M;* pH 10.65.

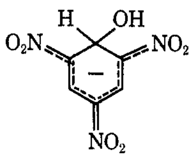
mation of a Meisenheimer complex (Z^-) between TNB and the hydroxide ion, which significantly contributes to the spectra in Figure 1.



YH



Y^-



Z^-

A kinetic analysis of all relevant equilibria has been reported in the preceding paper[1] of this series. It yielded the following results: $K_1 = 0.20 \pm 0.04$ l. M^{-1}; $K_{XH} = 1.5 \pm 0.2 \times 10^{-11}$ *M* l.$^{-1}$; K_2 (formation of YH form piperidine and TNB) = 4.3 ± 1.3 l. M^{-1}; K_{YH} (acid dissociation constant of HY to produce Y^-) = $2.5 \pm 0.3 \times 10^{-12}$ *M* l.$^{-1}$; K_3 (formation of Z^- from OH^- and TNB) = 5.0 ± 0.2 l. M^{-1}. These data allow the calculation of the concentrations of XH, X^-, and Z^- by use of eq 2–4; $[TNB]_0$ stands for the stoichiometric concentration of TNB.

$$[XH] = \frac{K_1[Pip][TNB]_0}{D} \qquad (2)$$

$$[X^-] = \frac{K_1(K_{XH}/[H^+])[Pip][TNB]_0}{D} \qquad (3)$$

$$[Z^-] = \frac{K_3[OH^-][TNB]_0}{D} \qquad (4)$$

$$D = 1 + \left(K_1 + K_1\frac{K_{XH}}{[H^+]} + K_2 + K_2\frac{K_Y}{[H^+]}\right)[Pip] + K_3[OH^-]$$

For the solution giving rise to spectrum a in Figure 1 ([Pip] = 0.045 *M*, [Pip HCl] = 0.005 *M*, [NaCl] = 0.49 *M*, $[TNB]_0 = 1.60 \times 10^{-4}$ *M*, pH 12.02), the following complex concentrations were computed: $[XH] = 8.22 \times 10^{-7}$ *M;* $[X^-] = 1.28 \times 10^{-5}$ *M;* $[Z^-] = 4.75 \times 10^{-6}$ *M*. Spectrum a is made up by the combined contribution of XH, X^-, and Z^- in the proportion of their respective concentrations and extinction coefficients. In a first approximation, XH can be neglected owing to its low concentration. Hence, to find the spectrum of pure X^-, the contribution of Z^- has to be substracted from spectrum a in Figure 1. This has been done using a spectrum of pure Z^- (not shown); the result is spectrum a in Figure 2, with λ_{max} 445 mμ.

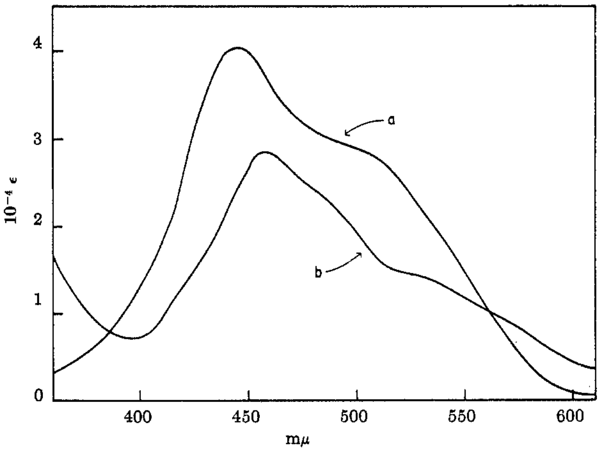


Figure 2.—Spectra of piperidine–TNB Meisenheimer complexes: a, X^-; b, XH.

The solution producing spectrum b in Figure 1 {[Pip] = 0.10 *M*, [Pip HCl] = 0.50 *M*, $(TNB)_0 = 1.20 \times 10^{-3}$ *M*, pH 10.65} contains the following complex concentrations: $[XH] = 1.38 \times 10^{-5}$ *M;* $[X^-] = 0.93 \times 10^{-5}$ *M;* $[Z^-] = 1.55 \times 10^{-6}$ *M*.[9] By subtracting from this spectrum the contributions of X^- and Z^- in the appropriate manner, one ends up with spectrum b in Figure 2, which is for pure XH and has λ_{max} 458 mμ.

The equilibrium constants not being known with high enough accuracy, particularly at high piperidine hydrochloride concentration, the uncertainty in actual complex concentrations and thus in the quantitative aspect of the foregoing procedure is considerable and may be *ca.* ±25%. Furthermore, the spectra of piperidine–TNB solutions, changing rather rapidly with time owing to decomposition of TNB,[1] had to be extrapolated to zero time, which is an additional source of error.

Nevertheless the following statements can be made. (1) The shape of the absorption spectrum of X^- is probably precise within ±4% at all wavelengths; it may well be, however, that all extinction coefficients are too high by some constant factor. The basis of this supposition is that in acetonitrile, ε of the same complex at 444 mμ is 33,000,[4] whereas here it is 40,500. The possibility of a solvent effect on ε cannot be excluded, however; solvent-dependent extinction coefficients of other Meisenheimer complexes are well documented.[10] (2) Insofar as all extinction coefficients of X^- may be too high by *ca.* 20%, the extinction coefficients of XH in Figure 2 may have come out too

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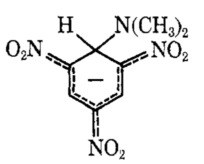
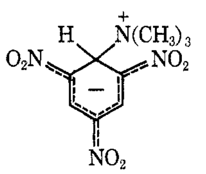
[9] These concentrations were calculated by using K_2 and K_{YH} values which are 50% higher than the ones listed above. This is a conservative estimate of the expected increase of those constants owing to the effect of the high piperidine hydrochloride concentration.[1]

[10] R. Foster and C. A. Fyfe, *Rev. Pure Appl. Chem.*, **16**, 61 (1966).

low. The shape should not be affected drastically by this possible error, however. Thus there can be no doubt that the general character of the spectrum of XH is definitely different from that of X^-; for obvious reasons we do not attach importance to the lower extinction coefficient at the absorption maximum. (3) It is interesting that the effect of attaching a proton to the amine nitrogen on X^- brings about a bathochromic shift of *ca.* 13 mμ. An analogous creation of a positive charge through addition of a methyl or ethyl group either does not change the absorption maximum or shifts it slightly to *shorter* wavelengths, as seen by comparing I and II[5a] or the ethyl analog.[2] This may be related to the capability of forming an intramolecular hydrogen bond to the *ortho* nitro group in the present case and the lack of this possibility when the nitrogen bears three alkyl groups. Other evidence for such intramolecular hydrogen bonding has been discussed.[1]



I



II

(4) The fact that the calculation of spectra based on complex concentrations derived from kinetic equilibrium data gives satisfactory extinction coefficients shows convincingly that Y^- and YH do not significantly absorb in the visible, an observation which had been used as partial evidence in assigning the structure of YH and Y^-.[1] However, the experimental uncertainties in this system are too large to allow complete exclusion of the possibility of a fourth interaction of CT[11]-complex formation.[4] If a fourth complex were formed with a small equilibrium constant, an additional term would need to be added to D in eq 2–4; if it were small enough (*e.g.*, *ca.* 0.5 l. M^{-1} as in acetonitrile[4]) so as not to alter D significantly, it would escape unnoticed.

Registry No.—Piperidine–TNB complex (XH), 12402-43-6; piperidine–TNB complex (X^-), 12402-42-5; 1,3,5-trinitrobenzene, 99-35-4.

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[11] Charge transfer.

1,2 Cycloaddition of Singlet Oxygen to 9,9′-Bifluorenylidene

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Typically the reactions of singlet oxygen with olefins has been studied with olefins possessing allylic hydrogen atoms.[1] The resulting allylic hydroperoxides were suggested to arise by an "ene"-type mechanism.[2] In contrast, there are few reports of 1,2 cycloadditions of singlet oxygen to olefins. Cycloaddition of singlet oxygen to olefins is suggested when nitrogen is conjugated with the olefinic site. Thus, enamines[1a,3] and 10,10′-dimethyl-9,9′-biacridylidene[4] undergo cleavage of the double bond with singlet oxygen, a result expected from decomposition of the 1,2-dioxetane intermediate produced by cycloaddition. It can be noted that tetraaminoethylenes give analogous products, ureas, with ground-state triplet oxygen.[5] Recently, cycloaddition of singlet oxygen to indene and methylated indenes was demonstrated[6] even though allylic hydrogen atoms were present. This is to be contrasted with the lack of reaction of norbornene with singlet oxygen.[1e] The bridgehead location of the allylic hydrogens voids the "ene"-type reaction which would lead to a bridgehead double bond, but the possibility of 1,2 cycloaddition exists. We report here some of our results in the search for 1,2 cycloaddition of singlet oxygen to olefins.

Our interest in 1,2-dioxetane intermediates[7] led us to investigate the possible intervention of this intermediate in the reaction of singlet oxygen with an olefin devoid of allylic hydrogens and heteroatoms. For this purpose we chose to study the reaction of 9,9′-bifluorenylidene (I) with singlet oxygen, which is generated both chemically and photochemically. A 1,2-dioxetane intermediate, resulting from a cycloaddition reaction between I and singlet oxygen, will give fluorenone by analogy to the decomposition of other such intermediates.[7,8]

Singlet oxygen was generated chemically from hydrogen peroxide and sodium hypochlorite[9] as well as photochemically from oxygen with methylene blue sensitizer.[9b] Competitive oxidations with mixtures of I and 2-methyl-2-butene (II) were carried out. Chemical generation of singlet oxidation gave fluorenone in 44% yield from I and 41% reaction of II. Fluorenone was isolated and characterized from a reaction where II was excluded. Photosensitized oxidation of the olefin mixture gave fluorenone in 91% yield along with 66% reaction of II. To verify that fluorenone was generated from singlet oxygen, which in turn was produced from the sensitizer, a control reaction was crrried out under the conditions of the sensitized oxygenation, but without the sensitizer. The yield of fluorenone was reduced

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[1] (a) C. S. Foote, *Accounts Chem. Res.*, **1**, 104 (1968); (b) K. Gollnick, *Advan. Photochem.*, **6**, 1 (1968); (c) K. Gollnick, "Oxidation of Organic Compounds," Vol. III, Advances in Chemistry Series, No. 77, American Chemical Society, Washington, D. C., 1968, p 78; (d) R. Higgins, C. S. Foote, and H. Cheng, ref 1c, p 102; (e) F. A. Litt and A. Nickon, ref 1c, p 118; (f) S. J. Arnold, M. Kubo, and E. A. Ogryzlo, ref 1c, p 133; (g) A. U. Khan and D. R. Kearns, ref 1c, p 143.

[2] (a) A. Nickon and J. F. Bagli, *J. Amer. Chem. Soc.*, **83**, 1498 (1961); (b) C. S. Foote, S. Wexler, and W. Ando, *Tetrahedron Lett.*, 4111 (1965).

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