$$\log P(\text{mm}) = 6.238 - \frac{689.39}{T(^\circ\text{C.}) + 206.44}$$

Trouton's constant and the heat of vaporization were 20.3 and 5.54 kcal/mole, respectively. The molecular weight found by gas density measurements is 148.5 (calcd, 149). The density of pentafluoroguanidine was found to be 1.51 g/ml at 0°.

The mass spectrum of pentafluoroguanidine showed a weak parent peak, relative intensity 0.88, at m/e 149. The major fragment, relative intensity 100, m/e 97, was assigned to $NF_2C{=}NF^+$ which results from loss of NF_2 from the parent molecule. Other major peaks with relative intensities greater than 10 were as follows (mass, ion, relative intensity): 14, N^+, 18; 26, CN^+, 16; 28, N_2^+, 23; 31, CF^+, 87; 33, NF^+, 70; 40, CN_2^+, 10; 45, CNF^+, 12; 50, CF_2^+, 12; 52, NF_2^+, 59; 59, CN_2F^+, 22; 64, CNF_2^+, 37; and 78, $CN_2F_2^+$, 76.

The infrared absorption spectrum of pentafluoroguanidine in the gas phase shows a weak intensity band at 6.15 assigned to $C{=}N$ stretch, a medium–weak band at 8.21, a medium band at 7.46, and strong bands at 10.10 and 11.03 μ assigned to the NF_2 groups. The 11.03 band has a shoulder at 10.65 μ.

The F^{19} nmr spectrum ($CFCl_3$ as reference) showed bands broadened by nitrogen coupling at ϕ -42.3, -46.9, and -20.2 in an area ratio of approximately $2{:}2{:}1$. The bands at ϕ -42.3 and -46.9 are attributed to the NF_2 groups syn and $anti$ to the $=NF$ at -20.2.

Pentafluoroguanidine is a very reactive compound. It reacts rapidly with mercury and must be handled in a mercury-free system. It hydrolyzes rapidly even at room temperature. Within 1 hr it partially hydrolyzes to form N_2F_4, CO_2, N_2, and HF. It may be stored, however, for long periods of time in dry glass containers without decomposition. On heating, pentafluoroguanidine began to undergo a slow exothermic decomposition at about 205° which became rapid at 265°. Pentafluoroguanidine is a very explosive material in the gas, liquid, or solid state. Explosions were readily initiated by shock and spark and sometimes by liquid–solid or solid–liquid phase transitions. When the material was exploded, the following reaction was shown to occur stoichiometrically.

$$(F_2N)_2C{=}NF \longrightarrow CF_4 + 1.5N_2 + 0.5F_2$$
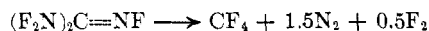
Experimental Section

Caution!—Pentafluoroguanidine is an extremely explosive compound in the gas, liquid, and solid state. It has been manipulated routinely in a mercury-free vacuum line with Freon-12 slush baths at -130 to -145°. Liquid nitrogen baths freeze the product and explosions often occurred during freezing and melting. It was standard practice to use adequate shielding and protective equipment and to keep the sample size below 0.5 g.

Preparation of $(F_2N)_2C{=}NF$.—Guanidine monohydrofluoride (5 g, 72 mmoles) was mixed with 50 g of sodium fluoride which had been dried at 110°. The mixture was charged into a three-necked, 1-l. monel flask fitted with a stirrer and gas inlet and outlet. The flask was immersed in an ice bath and stirred while 20–30% fluorine diluted with nitrogen was introduced into the flask at a total gas flow rate of 200 to 400 ml/min for 3 hr. The crude product was collected from the effluent stream in a glass U trap cooled to the range of -130 to -145° with a Freon-12 slush bath. When approximately 0.5 ml of crude product was collected in the U trap, the trap was removed and additional product was collected in a second and third trap, etc.

First-stage purification of the product to a 60–80% purity was achieved by codistillation[5] using a 10-mm copper column packed with fluorine-treated 40–60 mesh magnesium beads. Further purification to a 99+% purity was achieved either by repeated codistillation or by vapor phase chromatography using Dow Corning FS1265 fluorosilicone oil on a Chromosorb packed column. The yield of purified pentafluoroguanidine varied considerably from 10 to 25%.

Infrared Spectra.—The infrared data were obtained wth a Perkin-Elmer Model 137B spectrophotometer. The cell had a 2.5-cm path length and NaCl windows.

Mass Spectrum.—The mass spectrum was obtained on a Consolidated 21-103 spectrometer with inlet at room temperature and an ionizing voltage of 70 v.

Vapor Pressure.—The vapor pressure was measured in a mercury-free system from -80 to -2°.

Nmr Spectrum.—The nmr spectrum was obtained on an instrument described by Baker and Burd.[6]

Registry No.—Pentafluoroguanidine, 10051-06-6.

(5) G. H. Cady and D. P. Siegwarth, *Anal. Chem.*, **31**, 618 (1959).
(6) E. B. Baker and L. W. Burd, *Rev. Sci. Instr.*, **34**, 238 (1963); **28**, 313 (1957).

Chemiluminescent Reactions of Tetracyanoethylene and Trichloroacetyl Chloride with Hydrogen Peroxide. A Suggested Mechanistic Relationship

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While chemiluminescence has been observed from a considerable variety of chemical reactions,[1] only a few such reactions are known to provide moderate light intensities and emission lifetimes consistent with quantum yields above 1×10^{-2} einstein mole^{-1}.[2,3] The mechanism of light production is incompletely understood even in these relatively efficient chemiluminescent systems, but it has been recognized that such reactions require the presence or the formation of a fluorescent compound as well as the essentially
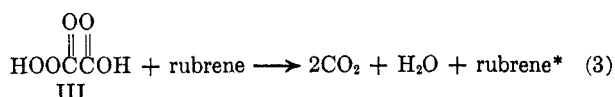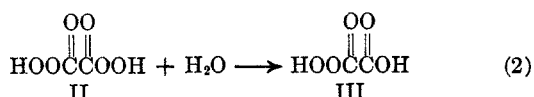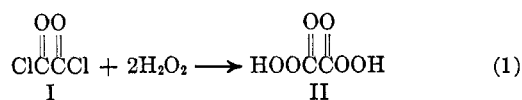
(1) E. N. Harvey, "A History of Luminescence," The American Philosophical Society, Philadelphia, Pa., 1957; R. S. Anderson, *Ann. N. Y. Acad. Sci.*, **49**, 337 (1948); K. D. Gundermann, *Angew. Chem., Intern. Ed. Engl.*, **4**, 566 (1965); E. J. Bowen, *Pure Appl. Chem.*, **9**, 473 (1964); R. J. Audeubert, *Trans. Faraday Soc.*, **35**, 197 (1939); H. D. K. Drew, *ibid.*, **35**, 207 (1939); R. F. Vasilev, *Opt. Spectry. USSR*, **18**, 234 (1965); J. Stauff, H. Schmidkunz, and G. Hartmann, *Nature*, **198**, 281 (1963); H. Linschitz and E. W. Abrahamson, *ibid.*, **172**, 909 (1953); R. T. Dufford, S. Calvert, and D. Nightingale, *J. Am. Chem. Soc.*, **45**, 2058 (1923); E. A. Chandross and F. I. Sonntag, *ibid.*, **86**, 3179 (1964); C. Dufraisse, L. Velluz, and L. Velluz, *Compt. Rend.*, **209**, 516 (1939).

(2) K. D. Gundermann and M. Drawert, *Chem. Ber.*, **95**, 2018 (1962); E. H. White and M. M. Bursey, *J. Am. Chem. Soc.*, **86**, 941 (1964); J. R. Totter, *Photochem. Photobiol.*, **3**, 231 (1964); K. D. Gundermann, W. Korstmann, and G. Bergmann, *Ann.*, **684**, 127 (1965); J. Lee and H. H. Seliger, *Photochem. Photobiol.*, **4**, 1015 (1965); M. M. Rauhut and A. M. Semsel, *J. Org. Chem.*, **30**, 3587 (1965); E. H. White and M. M. Bursey, *ibid.*, **31**, 1912 (1966); M. M. Rauhut, A. M. Semsel, and B. G. Roberts, *ibid.*, **31**, 2431 (1966).

(3) M. M. Rauhut, B. G. Roberts, and A. M. Semsel, *J. Am. Chem. Soc.*, **88**, 3604 (1966).

instantaneous release of 40 to 70 kcal mole^{-1} of energy needed to produce the singlet excited state of a fluorescer which emits in the visible region.[4]

Peroxide decomposition reactions, in general, are incapable of providing the necessary concerted energy release required for efficient chemiluminescence. The suggestion was recently put forward that the decomposition of certain peroxides which produce several stable products simultaneously through a "concerted multiple bond cleavage" mechanism, however, can accommodate the energy requirement and under favorable circumstances should be able to provide chemiluminescence in the presence of a fluorescer.[4] In terms of this concept the essential steps in the mechanism of the oxalyl chloride–hydrogen peroxide–fluorescer chemiluminescent reaction[5] were suggested by Rauhut, Roberts, and Semsel[3] to be as shown in eq 1–3.

$$\underset{I}{Cl\overset{OO}{\overset{\|\|}{CCCl}}} + 2H_2O_2 \longrightarrow \underset{II}{HOO\overset{OO}{\overset{\|\|}{CCOOH}}} \quad (1)$$

$$\underset{II}{HOO\overset{OO}{\overset{\|\|}{CCOOH}}} + H_2O \longrightarrow \underset{III}{HOO\overset{OO}{\overset{\|\|}{CCOH}}} \quad (2)$$

$$\underset{III}{HOO\overset{OO}{\overset{\|\|}{CCOH}}} + rubrene \longrightarrow 2CO_2 + H_2O + rubrene^* \quad (3)$$

In a search for new efficient chemiluminescent systems we have examined reactions of hydrogen peroxide with a series of potentially chemiluminescent compounds. The selected compounds when treated with hydrogen peroxide might, in principle, produce

TABLE I
COMPOUNDS SUCCESSFULLY TESTED FOR CHEMILUMINESCENCE[a]

Compd	Tests[b]		
	A	B	C
$(CN)_2C{=}C(CN)_2$	vw	ms	vw
$(CN)_2\overset{O}{\overset{/\backslash}{C}}{-}C(CN)_2$	vw	ms	vw
$NC\overset{O}{\overset{\|}{C}}CN$	vw	ms	vw
$Cl_3C\overset{O}{\overset{\|}{C}}CCl_3$	None	w	vw
$Cl_3C\overset{O}{\overset{\|}{C}}Cl$	ms	ms	None
$Cl_3C\overset{O}{\overset{\|}{C}}OCH_2CH_3$	None	w	None

[a] The qualitative chemiluminescent light intensities were evaluated in comparison to oxalyl chloride–hydrogen peroxide–9,10-diphenylanthracene system in 1,2-dimethoxyethane solvent by visual observation in a dark room. The oxalyl chloride system was defined as strong (s) in contrast to a chemiluminescent light barely visible described as very weak (vw). The intermediate intensities were classified as medium strong (ms), medium (m), and weak (w). [b] Tests are as follows: (A) approximately 3–5 mg of the compound to be tested was added to a 5-ml solution of 1 mg of 9,10-diphenylanthracene and 0.2 ml of 1 M anhydrous H_2O_2 in 1,2-dimethoxyethane at room temperature; (B) as in test A except the solution contained approximately 0.2 g of KOH; (C) as in test A except that the solution contained approximately 0.2 ml of methanesulfonic acid.

organic peroxides which through a concerted multiple bond cleavage process could release sufficient energy to produce chemiluminescence. Table I shows the successfully tested compounds.

Four of the test reactions produced moderately strong chemiluminescent light intensities. Thus tetracyanoethylene, tetracyanoethylene oxide, carbonyl cyanide, and trichloroacetyl chloride gave appreciable chemiluminescence when treated with alkaline hydrogen peroxide in 1,2-dimethoxyethane (DME) in the presence of fluorescers 9,10-diphenylanthracene (DPA) or rubrene. The trichloroacetyl chloride reaction alone provided appreciable chemiluminescence under neutral conditions, and none of the reactions was strongly chemiluminescent in the presence of methanesulfonic acid.

Principal products of the tetracyanoethylene reaction included cyanates, carbonates, and bicarbonates as identified by infrared spectroscopy. Products of the other reactions were not determined.

The chemiluminescence from the cyano compounds may be related through the eq 4–6.

$$\underset{IV}{(CN)_2C{=}C(CN)_2} + H_2O_2 \longrightarrow$$

$$\underset{V}{(CN)_2\overset{O}{\overset{/\backslash}{C}}{-}C(CN)_2} + H_2O \quad (4)$$

$$\underset{V}{(CN)_2{-}\overset{O}{\overset{/\backslash}{C}}{-}C{-}(CN)_2} + HO_2^- \longrightarrow$$

$$\underset{VI}{\left[(CN)_2{-}\overset{O^-}{\overset{\|}{C}}{-}C{-}(CN)_2\right]} \longrightarrow \underset{VII}{2(CN)_2C{=}O} + {}^-OH \quad (5)$$

$$\underset{VII}{(CN)_2C{=}O} + HO_2^- \xrightarrow{\text{rubrene}}$$

$$CO_3^{2-} + CNO^- + rubrene^* \quad (6)$$
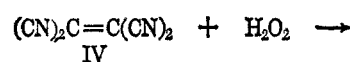
Thus, the reaction of IV with hydrogen peroxide is known to produce epoxide V;[6] similarly, VI has been reported to afford ketone VII in reactions with nucleophiles.[6a,c] Although the possibility of independent chemiluminescent processes has not been ruled out, the likelyhood of a carbonyl cyanide intermediate in reactions 4 and 5 is consistent with the observed chemiluminescence in reaction 6.

Chemiluminescence from carbonyl cyanide and trichloroacetyl chloride may be related in turn to peroxyoxalate chemiluminescence[3,5,7] perhaps in terms of diperoxyoxalic acid as a common intermediate (see Scheme I, eq 7–12).

Thus carbonyl cyanide (VII) would be expected first to produce peroxycyanoformic acid (VIII) in step 7 in analogy to the known reactions of VII with

(4) M. M. Rauhut, D. Sheehan, R. A. Clarke, and A. M. Semsel, paper presented at the Symposium on Chemiluminescence, U. S. Army Research Office, Durham, N. C., March 31 to April 2, 1965; also *Photochem. Photibiol.*, 4, 1097 (1965).
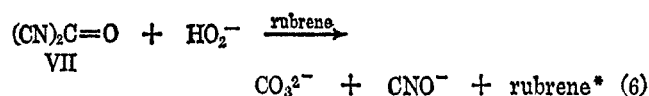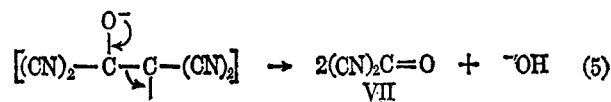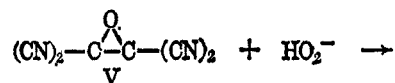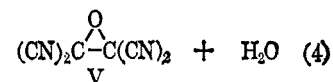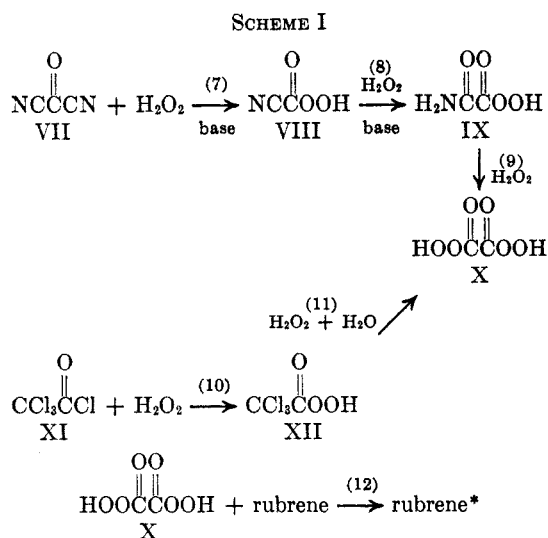
(5) E. A. Chandross, *Tetrahedron Letters*, 761 (1963).

(6) (a) W. J. Linn, O. W. Webster, and R. E. Benson, *J. Am. Chem. Soc.*, 87, 3651 (1965); (b) A. Rieche and P. Dietrich, *Chem. Ber.*, 96, 3044 (1963); (c) W. J. Linn, O. W. Webster, and R. E. Benson, *J. Am. Chem. Soc.*, 85, 2032 (1963); (d) W. J. Linn, U. S. Patent 3,115,517 (Dec. 24, 1963).
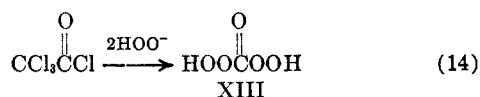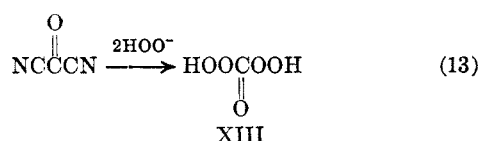
(7) L. J. Bollyky, R. H. Whitman, B. G. Roberts, and M. M. Rauhut, submitted for publication.

SCHEME I

$$NCCCN + H_2O_2 \xrightarrow[\text{base}]{(7)} NCCOOH \xrightarrow[\text{base}]{\overset{(8)}{H_2O_2}} H_2NCCOOH$$
$$\text{VII} \qquad\qquad \text{VIII} \qquad\qquad \text{IX}$$

$$\downarrow \overset{(9)}{H_2O_2}$$

$$HOOCCOOH$$
$$X$$

$$\overset{(11)}{H_2O_2 + H_2O} \nearrow$$

$$CCl_3CCl + H_2O_2 \xrightarrow{(10)} CCl_3COOH$$
$$\text{XI} \qquad\qquad\qquad \text{XII}$$

$$HOOCCOOH + \text{rubrene} \xrightarrow{(12)} \text{rubrene}^*$$
$$X$$

water or amines;[8] and the conversion of VIII to di-
peroxyoxalic acid is consistent with the rapid reaction
of nitriles with hydrogen peroxide to form amides[9]
and the ready hydrolysis of ketoamides to acids.[10]
Similarly, compound XI would be expected first to
produce peroxytrichloroacetic acid (XII) in step 10;[11]
then XII may be converted to X in reaction 11.[12]

Steps 9 and 11 respresent the hydrolysis of per acids
IX and XII in analogy to the hydrolysis of a keto-
amide $CH_3C(=O)C(=O)NH_2$[10] or dichlorophenoxy-
acetate $[Cl_2C(OR)C(=O)OR]$.[12] Per acids IX and
XII would be expected to hydrolyze with ease in alka-
line medium although the corresponding carboxylic
acid would not. Thus oxamide $[H_2NC(=O)C(=O)-$
$NH_2]$ is known to hydrolyze 30-fold faster than oxamic
acid $[H_2NC(=O)C(=O)OH]$[13] because the α-carboxyl-
ate anion decreases the hydrolytic reactivity of the
second amide group. It is thus reasonable that tri-
chloroacetyl chloride produces chemiluminescence,
whereas trichloroacetic acid fails to do so.

The possible alternate mechanisms (eq 13 or 14)
leading to the formation of carbonyl hydroperoxide are

$$NCCCN \xrightarrow{2HOO^-} HOOCOOH \qquad (13)$$
$$\text{XIII}$$

$$CCl_3CCl \xrightarrow{2HOO^-} HOOCOOH \qquad (14)$$
$$\text{XIII}$$

(8) R. Malachowski, L. Jurkiewicz, and J. Wojtowicz, *Chem. Ber.*, **70**, 1012 (1937); R. Malachowski and J. Jankiewicz-Wasowska, *Roczniki Chem.*, **25**, 35 (1951); *Chem. Abstr.*, **47**, 10483*f* (1951); R. Malachowski and L. Jurkiewicz, *Roczniki Chem.*, **24**, 88 (1950); *Chem. Abstr.*, **48**, 3914c (1950); R. Malachowski, *Roczniki Chem.*, **24**, 229 (1950); *Chem. Abstr.*, **47**, 8653*i* (1950).

(9) (a) B. Radziszewski, *Ber.*, **18**, 355 (1885); (b) K. B. Wieberg, *J. Am. Chem. Soc.*, **75**, 3961 (1953); (c) G. B. Payne, *J. Org. Chem.*, **26**, 663 (1961).

(10) (a) R. C. Thomas, C. H. Wang, and B. E. Christensen, *J. Am. Chem. Soc.*, **73**, 5914 (1951); (b) L. Claisen and J. S. Shadwell, *Ber.*, **11**, 620 (1878); (c) L. Claisen and E. Moritz, *ibid.*, **13**, 2121 (1880); (d) L. Claisen and O. Manasse, *ibid.*, **20**, 2194 (1887); (e) W. Tschelinzeff and W. Schmidt, *ibid.*, **62B**, 2210 (1929); (f) G. Gould, A. B. Hastings, C. B. Aufinsen, I. N. Rosenberg, A. K. Solomon, and Y. J. Topper, *J. Biol. Chem.*, **177**, 727 (1949).

(11) I. Ugi and F. Beck, *Chem. Ber.*, **94**, 1839 (1961); H. O. Pritchard and H. A. Skinner, *J. Chem. Soc.*, 272 (1950).

(12) Ya. N. Ivashchenko, V. P. Akkerman, and S. D. Moshchitskii, *J. Gen. Chem. USSR*, **33**, 3768 (1963).

(13) A. Bruylants and F. Kezdy, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **21**, 227 (1960); J. Packer, A. L. Thomson, and J. Vaughan, *J. Chem. Soc.*, 4516 (1952).

ruled out by the absence of chemiluminescence from
phosgene and hydrogen peroxide.[3] Moreover, it is
also unlikely that the recently discovered chemilumi-
nescent reaction of phenylacetonitrile with hydrogen
peroxide[14] is related mechanistically to the four new
chemiluminescent reactions reported here. These re-
actions produce chemiluminescent light emission several
orders of magnitude brighter than we obtained from the
phenylacetonitrile hydrogen peroxide reaction.

Experimental Section

Tetracyanoethylene, an Eastman Organic Chemicals reagent
grade compound, was recrystallized from benzene, mp 201–202°
(lit.[15] mp 198–200°).

Tetracyanoethylene oxide was prepared by the method of
Rieche and Dietrich.[6b]

Carbonyl cyanide was prepared by the method of Linn,[6d] and
characterized by the product of the dimethylaniline reaction, bis-
(4-dimethylaminophenyl)dicyanomethane, mp 195–197°, in
agreement with the reported value (lit.[6d] mp 194–196°)

Triphenylacetyl Chloride.—Triphenylacetic acid (Aldrich re-
agent grade, 4 g, 0.014 mole) was refluxed with 35 ml of thionyl
chloride for 3 hr. Boiling hexane was added until the solution
became cloudy. White crystals precipitated on cooling and were
filtered under nitrogen atmosphere, mp 127–129° (lit.[16] mp 127–
129°).

Bis(triphenylacetic) Carbonic Anhydride.—To a suspension of
1.63 g (0.005 mole) of potassium triphenylacetate in 50 ml of
1:1 benzene–1,2-dimethoxyethane, 0.25 g (0.0025 mole) of phos-
gene in 4 ml of benzene was added slowly with good stirring
under argon atmosphere. After 2 hr of stirring at 25° the re-
action mixture was filtered and evaporated to dryness to obtain
1.2 g (80%) of white crystals, which were recrystallized from
ether to obtain 0.8 g of product, mp 179–182°. Mixture melting
point and the infrared spectra indicated that the product was
not triphenylacetic anhydride.

Triphenylacetic Anhydride.—To a solution of 0.35 g (0.0014
mole) of triphenylacetyl chloride in 15 ml of anhydrous benzene,
0.115 ml (0.0014 mole) of triethylamine and 0.33 g (0.0014 mole)
of triphenylacetic acid were added. After 20 min of stirring the
solution was filtered, and the filtrate was evaporated to dryness.
The white solid residue was suspended in anhydrous ether,
stirred overnight, filtered, and washed with ether to obtain 0.48
g (75%) of white solid, mp 182–183°.

**Products of the Tetracyanoethylene (TCNE)–Hydrogen Per-
oxide Reaction.**—To a 250-ml DME solution of 0.7 g (5.5 ×
10^{-3} mole) of TCNE freshly crystallized from benzene, 3 ml of
50% anhydrous hydrogen peroxide in DME was added with
vigorous stirring. The temperature was kept at approximately
25° by cooling with water. To this solution 1.7 g (3 × 10^{-2}
mole) of solid KOH was added and the stirring was continued for
1 hr. Samples of the solution withdrawn showed moderately
strong chemiluminescence when DPA was added.

During the stirring, a white precipitate appeared in the solu-
tion. The reaction mixture was evaporated to dryness under
vacuum to obtain a white, water-soluble, solid residue which re-
acted with aqueous HCl with gas evolution. The infrared spec-
trum of this solid indicated the presence of bicarbonate (700,
825, 1400, 1640 cm^{-1}; ~40%), carbonate (875, 1400 cm^{-1};
~20%), isocyanate (2160 cm^{-1}; ~25%), and hydroxide and
cyanide (2100 cm^{-1}).

Qualitative Chemiluminescence Tests.—Several compounds not
listed in Table I were also tested for chemiluminescence. The
compounds, which produced very weak, barely visible light emis-
sion in test B but no visible light emission in tests A and C, in-
clude tetrachloroethylene and tetraphenylethylene. Compounds
that produced no visible light in any of the tests include those as
follow: ethylene oxide, tetramethylethylene oxide, dimethyl car-
bonate, phosgene, diacetyl, benzil, and triphenylacetyl chloride,

(14) E. McKeown and W. A. Waters, *Nature*, **203**, 1063 (1964).

(15) T. L. Cairns, R. A. Carboni, D. D. Coffman, V. A. Engelhardt, R. E. Heckert, E. L. Little, E. G. McGeer, B. C. McKusick, W. J. Middleton, R. M. Schribner, C. W. Theobald, and H. E. Winberg, *J. Am. Chem. Soc.*, **80**, 2775 (1958).

(16) L. W. Jones and C. D. Hurd, *ibid.*, **43**, 2422 (1921).

bis(triphenylacetic)carbonic anhydride, trifluoroacetic anhydride, and trichloroacetic acid.

A Convenient Synthesis of Dimethyl 4-Phenylacridinates[1,2]

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The reaction of α-amino ketones and dimethyl acetylenedicarboxylate to give an initial Michael adduct which then underwent dehydrative cyclization to pyrrole carboxylates has been described in the recent literature.[3,4] Mention was made[3] of the synthesis of a quinoline, 2,3-dicarbomethoxy-4-methylquinoline (dimethyl 4-methylacridinate) from 2-aminoacetophenone, but no experimental conditions or physical properties were given.

We have examined the analogous reaction of dimethyl acetylenedicarboxylate with a number of 2-aminobenzophenones and have found that dimethyl 4-phenylacridinates are formed directly without isolation of the intermediate Michael adducts. (See Table I.) Under the same reaction conditions, 2-aminoacetophenone yielded only the intermediate enamine adduct which, however, displayed *two* modes of cyclization. Upon heating under reflux in methanolic sodium methoxide it underwent dehydrative cyclization to the expected dimethyl 4-methylacridinate. On the other hand, pyrolysis generated the Conrad Limpach cyclization product, 8-acetyl-2-carbomethoxy-4(1H)-quinolone.

The observation that the Michael adduct of 2-aminoacetophenone required basic conditions for dehydrative cyclization, while the reaction of 2-aminobenzophenones and dimethyl acetylenedicarboxylate yielded the acridinates directly, undoubtedly reflects the greater electron deficiency at the ketone carbonyl in the Michael adducts formed from the benzophenones.

Dimethyl 6-nitro-4-phenylacridinate was obtained in low yield from dimethyl acetylenedicarboxylate and 5-nitro-2-aminobenzophenone. In this instance it seems probable that the diminished basicity of the aromatic amine decreases the facility with which the initial

Michael addition takes place. Efforts to effect an analogous cyclization with other acetylenic precursors such as diphenylacetylene, phenylacetylene, methyl propiolate, and ethyl phenylpropiolate were unsuccessful. Only starting materials were recovered in these cases.

In an attempt to prepare derivatives of 4-hydroxy-4-phenyl-1,2,3,4-tetrahydroacridinic acid, the possible photoenolization of several 2-aminobenzophenones was investigated. Yang and Rivas[5] have reported that 2-methylbenzophenone is inert to photopinacol formation in alcohol solution because it undergoes an internal hydrogen transfer to a transient dienic system which can be trapped by reaction with a suitable dienophile. 2-Aminobenzophenones are also inert to photoreduction, and the possibility that photoenolization occurs here as well has been suggested as a possible explanation.[6] We have examined the photolysis of a mixture of 5-chloro-2-aminobenzophenone and diethyl maleate in dry benzene but were unable to obtain any evidence for the formation of the photoenol.[7] Since the reaction of dimethyl acetylenedicarboxylate ("dark reaction") with 5-nitro-2-aminobenzophenone is very sluggish, as mentioned above, the possible reaction of these two components under photolysis conditions was also examined. There was no detectable formation of a quinoline product, and we thus conclude that no trappable photoenol is produced from 2-aminobenzophenones.

Experimental Section[8]

General Procedure for the Preparation of Dimethyl 4-Phenylacridinates.—A solution of 0.02 mole of the 2-aminobenzophenone[9] and 0.02 mole of dimethyl acetylenedicarboxylate in 100 ml of benzene was heated under reflux for 24 hr and evaporated to dryness under reduced pressure, and the residue was recrystallized from methanol. The analytical samples were conveniently prepared by sublimation at 100° (0.05 mm).

Dimethyl 4-Methylacridinate.—Treatment of 0.02 mole of 2-aminoacetophenone with 0.02 mole of dimethyl acetylenedicarboxylate under the conditions described above gave the intermediate enamine adduct, mp 95.5–97°, in 74% yield.

Anal. Calcd for C$_{14}$H$_{15}$NO$_5$: C, 60.65; H, 5.46; N, 5.06. Found: C, 60.45; H, 5.38; N, 5.09.

The nmr spectrum (DCCl$_3$) of this enamine adduct showed the acetyl methyl protons as a singlet at 2.62, the two ester methyl protons as singlets at 3.72 and 3.78, the single vinyl proton signal at 5.62,[10] an aromatic multiplet at 6.6–7.9, and the N–H proton as a singlet at 11.90 ppm (ratio 3:3:3:1:4:1).

A solution of 1.5 g of this enamine adduct in 50 ml of anhydrous methanol containing 0.08 g of sodium methoxide was heated under reflux for 4 hr, the methanol was removed under reduced pressure, the residual oil was taken up in hot benzene, and the

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(7) Even if a nonphotolytic Michael addition of 5-chloro-2-aminobenzophenone to diethyl maleate had taken place, the product would have been saturated and thus unable to undergo enamine addition to the carbonyl group. Thus the isolation of a 4-hydroxy-1,2,3,4-tetrahydroacridinic acid would have been direct evidence for photoenolization. Dimethyl acetylenedicarboxylate (as employed by Yang[5]) could not be used as a trapping dienophile, since the "dark reaction" gives rise to the same dimethyl 4-aryl-acridinate as Diels–Alder addition to the photoenol.

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(9) We are indebted to Dr. L. H. Sternbach of the Hoffmann-La Roche Research Laboratories, Nutley, N. J., for generous gifts of o-aminobenzophenone, 2-amino-5-chlorobenzophenone, and 2-amino-5-nitrobenzophenone.

(10) A single resonance signal in the vinyl region can be interpreted as evidence for the formation of a single geometric isomer from the amine-to-acetylene addition; see, for example, J. E. Dolfini, *J. Org. Chem.*, **30**, 1298 (1965); R. Huisgen, K. Herbig, A. Siegl, and H. Huber, *Chem. Ber.*, **99**, 2526 (1966), and references cited therein.