an internal standard and known thermal conductivity ratios showed II (42%) and IV (47%).

Compound IV did not show carbonyl absorption in the infrared. The mass spectrum of IV did not show a significant parent ion but did show intense ions at *m/e* 150 (M − C_3H_6O) and 135 [(M − C_3H_6O) − CH_3]. The nmr spectrum of IV shows an AB pattern (δ_A 5.72, δ_B 5.38, $^3J_{AB}$ = 10.3 Hz, olefinic protons), a complex four-proton multiplet (δ 1.2–2.2, methylene protons), and five singlets (δ 1.23, 6 H; 1.13, 3 H; 1.05, 3 H; 0.99, 3 H; 0.92, 3 H; six methyl groups).

Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.71; H, 11.76.

Compound II showed infrared carbonyl absorption at 5.83 μ. The nmr spectrum of II (CCl_4) showed an AB pattern (δ_A 2.57, δ_B 1.92, $^3J_{AB}$ = 15 Hz, bridgehead protons), a complex four-proton multiplet (δ 1.3–2.4, methylene protons), and six three-proton singlets (δ 0.90, 0.95, 1.02, 1.06, 1.13, and 1.19). In a separate experiment II was isolated in 42% yield by repeated chromatography on silica gel. An analytical sample prepared by distillation (67°, 0.07 mm) followed by sublimation (55° at 0.2 mm) had mp 38–39°.

Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.86; H, 11.47.

Isomerization of *trans*-5,5,7,7,8,8-Hexamethylbicyclo[4.2.0]-octan-2-one.—A solution of *trans*-5,5,7,7,8,8-hexamethylbicyclo-[4.2.0]octan-2-one in pentane was added to a column of basic alumina and left in contact with the basic alumina for 30 min. Elution with 1:1 ether–pentane gave *cis*-5,5,7,7,8,8-hexamethylbicyclo[4.2.0]octan-2-one, $\lambda_{\max}^{CCl_4}$ 5.91 μ. Distillation (120°, 15 mm) gave an analytical sample. The nmr spectrum (CCl_4) showed a complex six-proton multiplet (δ 1.0–2.5) and six methyl groups (δ 0.90, 3 H; 0.94, 3 H; 1.03, 9 H; 1.13, 3 H).

Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.97; H, 11.46.

Irradiation of *trans*-5,5,7,7,8,8-Hexamethylbicyclo[4.2.0]-octan-2-one in the Presence of Tetramethylethylene.—A solution of tetramethylethylene (2.27 g) and *trans*-5,5,7,7,8,8-hexamethylbicyclo[4.2.0]octan-2-one (0.46 g) in *t*-butyl alcohol (9 ml) was irradiated for 245 hr in a Pyrex vessel in a Rayonet reactor with 3500-Å lamps. Removal of the solvent and excess tetramethylethylene gave a crude mixture (0.72 g). Thin layer chromatography showed several products. Chromatography on silica gel gave two isomeric products (A and B). Recrystallization from pentane gave the pure products both having mp 53–55°. Neither product showed carbonyl absorption in the infrared, but both products showed double-bond absorption (A, $\lambda_{\max}^{CCl_4}$ 6.13 and 11.04 μ, and B, $\lambda_{\max}^{CCl_4}$ 6.13 and 10.99 μ). Both A and B showed parent ions at *m/e* 292. The nmr spectrum (CCl_4) of product A showed three olefinic protons as an ABC pattern (δ ~5.95, q, 1 H; 4.6–5.1, m, 2 H), three methine protons as an ABX pattern (δ 4.18, d, 1 H; 2.25, t, 1 H; 1.67, d, 1 H), and ten methyl groups (δ 0.82, 6 H; 0.87, 3 H; 0.98, 3 H; 1.03, 9 H; 1.08, 3 H; 1.12, 3 H; 1.18, 3 H). The nmr spectrum (CCl_4) of B showed three olefinic protons as an ABC pattern (δ ~5.85, q, 1 H; 4.6–5.1, m, 2 H) three methine protons (δ 4.22, d, 1 H; 2.18, t, 1 H; 2.65, d, 1 H), and ten methyl groups (δ 0.87, 3 H; 0.92, 6 H; 0.95, 3 H; 1.02, 6 H; 1.10, 6 H; 1.14, 3 H; 1.22, 3 H). The infrared spectra of A and B in solution were clearly differentiated, each containing bands not found in the other. The behavior of A and B on thin layer chromatography also differed significantly.

Anal. Calcd for $C_{20}H_{36}O$: C, 82.19; H, 12.33. Found for product A: C, 82.12; H, 12.18. Found for product B: C, 82.11; H, 12.37.

Treatment of either A or B with 2,4-dinitrophenylhydrazine in methanolic sulfuric acid gave the same 2,4-dinitrophenylhydrazone, mp 179–180°. The nmr spectrum ($CDCl_3$) of the derivative showed a broad N–H resonance (δ 11.0, lost on shaking with D_2O), three aromatic protons (δ 9.08, d; 8.28, q; 7.95, d), an aldimine proton (δ 7.48, d), three olefinic protons (δ 5.95, q, 1 H; 4.6–5.1, m, 2 H), two methine protons coupled to each other and one coupled to the aldimine proton (δ 2.92, q; 2.18, d), and six methyl groups (δ 0.96, 3 H; 1.00, 3 H; 1.03, 3 H; 1.07, 6 H; 1.10, 3 H).

Anal. Calcd for $C_{20}H_{28}N_4O_4$: C, 61.84; H, 7.27; N, 14.42. Found: C, 61.92; H, 7.20; N, 14.55.

Irradiation of *trans*-5,5,7,7,8,8-Hexamethylbicyclo[4.2.0]octan-2-one at Low Temperature.—A neat film of *trans*-5,5,7,7,8,8-hexamethylbicyclo[4.2.0]octan-2-one was irradiated in an Air Products low-temperature infrared cell at −180° with an unfiltered mercury lamp for 1110 min. No change in the infrared absorption of the sample was observed during this period. Similar irradiation at −40° produced significant new bands at 3090 (olefin C–H stretch), 2720 (aldehyde C–H stretch), 2110 (ketene), 1640 (C=C stretch), 1420 (C–H deformation), 1390 (aldehyde H-rock), 990 (*trans* C–H wag), and 910 cm^{-1} (=CH^2 wag).

Registry No.—I, 1073-13-8; II, 19018-67-8; IV, 19019-03-5; tetramethylethylene, 563-79-1; III, 19018-68-9.

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The Photolysis of Dihydro-1,2-oxazines

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Photolysis of nitrosobenzene-1,3-diene adducts (dihydro-1,2-oxazines) gives 1-phenylpyrroles. The reaction provides a convenient preparation for these compounds. Evidence for a mechanism involving intramolecular hydrogen abstraction and a γ-amino ketone intermediate is presented.

Recent articles have described photochemical transformations of heterocycles incorporating the N–O linkage. Thus isoxazoles[1,2] and 3-hydroxyisoxazoles[3] were found to rearrange to oxazole and oxazolone derivatives, oxaziranes[4] undergo fragmentation, and N-alkylisoxazolidines[5] ring expand to tetrahydro-1,3-oxazines. A common feature of these diverse photoprocesses is the cleavage of the endocyclic N–O bond.

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The present paper reports an additional example of this type in the six-membered ring series; a reaction that may also prove useful for synthesis.

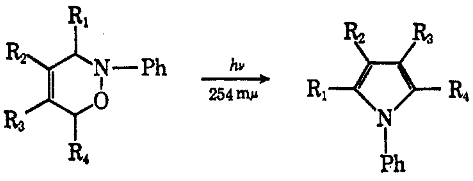
1,4 addition of nitrosobenzene to conjugated dienes produces 2-phenyl-3,6-dihydro-1,2-oxazines. To investigate their photochemical behavior, a series of substituted dihydrooxazines (Ia–g) was accordingly prepared. Unlike the bicyclic analogs,[6] the monocyclic dihydrooxazines employed in this work were thermally stable; they may be analyzed by vapor phase chromatography without decomposition. The ultraviolet spectra of these compounds showed maxima at 243–245 $m\mu$ ($\epsilon \sim 10^4$), which were insensitive to solvent polarity (ethanol, cyclohexane). On irradiation at 254 $m\mu$, solutions of the dihydrooxazines were efficiently converted to products. In each case, the major product was shown to be the corresponding 1-phenylpyrrole (II) (Table I). The identity of the products was established by comparison with authentic samples obtained by conventional procedures. With respect to both yield of pyrrole and convenience the dihydrooxazine photolysis compared favorably with the alternative syntheses employed. Hence the two-step sequence, nitrosobenzene plus diene, followed by photolysis, provides a useful preparative route for 1-arylpyrroles.

TABLE I

PHOTOLYSIS OF 2-PHENYL-3,6-DIHYDRO-1,2-OXAZINES[a]

Compd I	Yield of II, %[b]
a	68
b	86
c	90
d	48[c]
e	68
f	89
g	71

[a] 1–3% solutions in methanol. Irradiated 6–18 hr. [b] Vpc area %, uncalibrated. [c] Solvent: acetone–methanol (30:70). Product isolated by filtration.



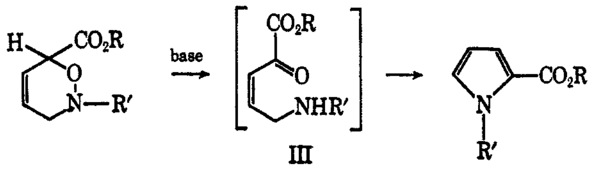
I II

a, $R_1 = R_2 = R_3 = R_4 = H$
b, $R_1 = R_4 = CH_3$; $R_2 = R_3 = H$
c, $R_1 = R_4 = H$; $R_2 = R_3 = CH_3$
d, $R_1 = R_4 = Ph$; $R_2 = R_3 = H$
e, $R_1 = R_2 = R_3 = H$; $R_4 = Ph$
f, $R_1 = R_2$ (or R_3) $= R_4 = H$; R_3 (or R_2) $= CH_3$
g, R_1 (or R_4) $= CH_3$; $R_2 = R_3 = R_4$ (or R_1) $= H$

Although photolysis to the pyrrole was observed in several solvents (cyclohexane, diethyl ether, tetrahydrofuran), methanol and ethanol were advantageous in eliminating wall deposits and in maintaining a homogeneous medium. Experiments with Ib showed that neither dissolved oxygen nor naphthalene were effective in quenching the rate of disappearance of the dihydrooxazine. However, appreciably cleaner, less colored product mixtures were obtained in deoxygenated solutions, indicating that oxygen participates in secondary reactions. Attempts to bring about the reaction by energy transfer from triphenylene and naphthalene were unsuccessful.

The unsubstituted compound, dihydrooxazine (Ia), photolyzed (254 $m\mu$, tetrahydrofuran) with a quantum yield of 0.76 ± 0.10. Competitive experiments, in which two substrates were simultaneously irradiated and their disappearance was followed by vapor phase chromatography, showed that the photoefficiencies of Ib and Ig were equal to that of Ia.[7]

In related systems, Kresze[6] has reported that thermal decomposition results in reversal to addends. On the other hand, 6-carbalkoxydihydrooxazines were transformed to 2-carbalkoxypyrroles by basic reagents, presumably through a transient α-keto-δ-amino ester intermediate (III).[8] Photoexcitation of I, however, might involve a transition of the "$\pi^* \rightarrow \sigma^*$" type, as suggested for peroxide and hydrazine photolyses.[9] Consequent homolysis of the N–O bond and intramolecular allylic hydrogen abstraction by the amino radical would produce a *cis*-γ-amino-α,β-unsaturated carbonyl compound, *e.g.*, IV (path A, Scheme I). Once formed, intermediate IV would be expected to cyclize and dehydrate to the pyrrole product. The quantum yield for dihydrooxazine formation (0.76) closely approximated that for pyrrole formation, indicating that cyclization *via* photoexcitation of the carbonyl group in IV, a two-photon process, is unlikely. The facile thermal conversion of compounds such as IV (generated *in situ*) to pyrroles has been noted previously.[10] The proposed major reaction path (A) is shown in Scheme I.



Although it is difficult to assess the relative reactivities of the amino and alkoxy radicals in this system, a reaction sequence (B) initiated by the alkoxy radical appeared possible. Allylic hydrogen abstraction by the latter would give IVa which could, in a manner analogous to IV, produce aniline and 2,5-dimethylfuran. Evidence for this minor path (B) was obtained by identifying these compounds in the product mixture from Ib. (Vpc peaks corresponding to small amounts of aniline were found with all the dihydrooxazines.) As a measure of the relative importance of paths A and B, the ratio of pyrrole to aniline was determined by vpc. In accord with Scheme I, the ratio from Ib (13.2) was constant throughout the reaction. A pyrrole to aniline ratio of 6.8, unchanged over a fourfold variation in initial concentration, was observed in the photolysis of Ic.

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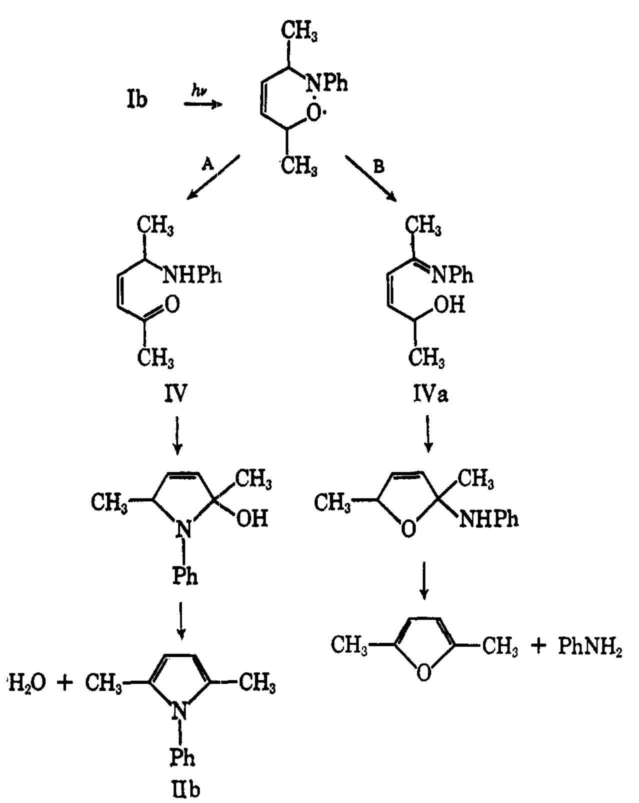
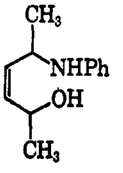
SCHEME I



In agreement with the experience of others,[8,10] intermediate IV was not detected when the photolysis was conducted at room temperature. Furthermore, oxidation of 5-phenylamino-*cis*-3-hexen-2-ol (V) with activated manganese dioxide, a selective oxidant of allylic alcohols,[11] gave none of the γ-amino ketone (IV). Rather, the isolated oxidation products from V were 2,5-dimethyl-1-phenylpyrrole (IIb) and aniline in the ratio *ca.* 14:1,[12] thus providing support for the proposed intermediacy of IV (and perhaps IVa) in the photolysis.



V

Direct evidence for the γ-amino ketone (IV) was obtained by irradiating Ib at $-180°$. At this temperature, an infrared peak developed at 1695 cm^{-1} which on warming above $-46°$ disappeared. The 1695-cm^{-1} peak was not regenerated on subsequent cooling without irradiation. Carbonyl absorptions for a series of α,β-unsaturated ketones structurally related to IV have been reported.[13] In the *s-cis* orientation, peaks were found at 1700–1687 cm^{-1}, while the *s-trans* isomers absorbed at 1690–1675 cm^{-1}. The *s-cis* orientation with the substitution pattern of IV gave a peak at 1697 cm^{-1} in good agreement with the 1695-cm^{-1} band observed.

Experimental Section

Infrared spectra were determined on chloroform solutions with a Perkin-Elmer Model 237, except for the low-temperature spectra which were determined with a Beckman IR-12. Ultraviolet spectra were obtained with a Cary Model 14 spectrophotometer, and vapor phase chromatography was carried out with an F & M Model 810, using helium as the carrier gas and a thermal conductivity detector.

Materials.—The dihydrooxazines were prepared from nitrosobenzene and the appropriate diene by previously described procedures: Ia,[14] Ib,[15] Ic,[16] Id,e,[17] If,[18] Ig.[19] Authentic samples of pyrroles IIb,[20] IId,[21] and IIe[22] were obtained by the literature methods. Oxidation of the corresponding 1-phenyl-3-pyrrolines with 1 equiv of chloranil in refluxing benzene for 20 hr afforded pyrroles IIc,[23] IIf,[23] and IIg.[24] Their properties were as reported. The 1-phenyl-3-pyrrolines were obtained from the dihydrooxazines by the method of Kojima.[18] 1-Phenylpyrrole was purchased from the Aldrich Chemical Co.

Photolyses.—For preparative runs, 1–3% solutions (methanol) of the dihydrooxazines were placed in cylindrical quartz tubes, purged with purified nitrogen for 30 min, and irradiated in a Rayonet chamber reactor with light from 16 low-pressure mercury lamps (84% of the emission at 254 mμ). Photolyses were carried out at 35°. Analysis by vapor phase chromatography (3-ft column, 10% Carbowax 20M on Chromosorb W, 160–220°) showed that under these conditions more than 90% of the starting material was transformed within 6–18 hr. The photolysis solutions were evaporated under reduced pressure and purified product was isolated by either recrystallization from methanol or vacuum sublimation at 0.1 mm. Pyrrole IIg, a liquid, was obtained by vapor phase chromatography, and IId precipitated during photolysis and was collected by filtration. The pyrrole products were identified by comparison of their physical properties, vpc retention times, and infrared spectra with authentic samples. The presence of aniline and 2,5-dimethylfuran was established by photolyzing Ib in diethyl ether and analyzing the product solution on two different columns: 3-ft 10% Carbowax 20M (70°, programmed to rise at 20°/min) and 10-ft 20% silicone rubber SE30 (100°, similar program). Peaks corresponding to aniline and 2,5-dimethylfuran were observed on both columns.

In a typical run, 0.500 g of If in 50 ml of methanol was irradiated for 6 hr. The solution, originally yellow, became more deeply colored. Analysis by vpc showed only aniline (11%) and 3-methyl-1-phenylpyrrole (89%); no starting material or other materials were detected. Evaporation of the solvent gave a brown solid which was transferred to a small sublimation apparatus. Sublimation resulted in the collection of 0.327 g (72%) of crystalline solid (IIf).

Quantum yields were determined by dissolving accurately weighed samples of Ia (12–15 mmol) and octadecane (internal standard) in 50 ml of tetrahydrofuran and irradiating with 254 mμ light from a low-pressure mercury lamp (Hanovia, 688A45). The water-jacketed quartz cell was completely blackened except for a 4.29-cm^2 window. Runs were made at 23° and the solution was vigorously stirred. The extent of reaction was estimated from the ratio of the integrated vpc peak areas. Measurements of the light flux were made before

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and after each run with the probe of a dual thermistor bolometer (YSI Model 65) placed inside the cell. Fluxes of *ca.* 3 × 10^4 ergs/cm^2 sec were employed.

Unsuccessful attempts to photosensitize the reaction were carried out on nitrogen-purged equimolar solutions of Ia and naphthalene or triphenylene in tetrahydrofuran. Pyrex-filtered light from a 550-W medium-pressure mercury lamp (Hanovia, Type A) was used.

5-Phenylamino-*cis*-3-hexen-2-ol (V).—Zinc dust, 7.5 g (0.12 mol), was added slowly to a stirred solution of 4.5 g (0.024 mol) of Ib in 40 ml of acetic acid. The temperature rose to 50° and stirring was continued overnight. The suspension was made basic with 28 g of sodium hydroxide in 100 ml of water and extracted with three 50-ml portions of benzene. The dried extracts were evaporated under reduced pressure to give 3.5 g of liquid. This material was distilled (short path, 0.1 mm) to give a pale yellow oil which was pure by vpc analysis. The analytical sample was collected from a 3-ft 10% Carbowax column at 220°.

Anal. Calcd for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.32. Found: C, 75.54; H, 9.07; N, 7.22.

Oxidation of V.—A suspension containing 1.0 g of V and 1.0 g of activated manganese dioxide[25] in 20 ml of benzene was refluxed for 17.5 hr. A sample was removed, filtered, and analyzed with a 3-ft Carbowax column. In addition to unreacted starting material, 2,5-dimethyl-1-phenylpyrrole and aniline (14:1) were the only products observed. The same reaction occurred more slowly at room temperature. Control experiments showed that aniline and 2,5-dimethyl-1-phenylpyrrole were essentially unchanged under the oxidation conditions.

Low-Temperature Photolysis of 3,6-Dimethyl-2-phenyl-3,6-dihydro-1,2-oxazine (Ib).—A film of Ib between sodium chloride plates was irradiated in an infrared cell cooled to −180° by liquid nitrogen. Light from an unfiltered 800-W Westinghouse mercury arc lamp was employed. After 25 min, a peak appeared at 1695 cm^{-1}. On warming above −46°, it disappeared. Cooling the sample back to −180° did not regenerate the 1695-cm^{-1} peak.

Registry No.—Ia, 19029-45-9; Ib, 19029-46-0; Ic, 19029-47-1; Id, 19029-48-2; Ie, 19029-49-3; V, 19029-97-1.

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Oxirane Radicals. The Thermal Decomposition of *t*-Butyl *cis*- and *trans*-α,β-Diphenylperglycidates[1]

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The di-*t*-butyl peroxide initiated decarbonylation reactions of 2,3-*cis*- and -*trans*-diphenyl-2,3-epoxypropanal and the thermal decomposition of *t*-butyl *cis*- and *trans*-α,β-diphenylperglycidates have been investigated as sources of isomeric oxirane radicals. The products obtained from the decarbonylation reactions are exclusively derived from opening of the oxirane ring. *t*-Butyl *cis*- and *trans*-α,β-diphenylperglycidates undergo thermal decomposition in cumene at 70° at identical rates and by a nonconcerted one-bond cleavage. The products (desoxybenzoin, *trans*-stilbene oxide, and 1,2,3,4-tetraphenyl-1,4-butanedione) formed are the same from either perester. The results indicate that the oxirane radical can abstract hydrogen but that rearrangement to the desyl radical is facile and accounts for the major proportion of products.

Theoretical arguments[3,4] predict that the most favorable hybridization for an alkyl radical is sp^3, although electron spin resonance investigations of methyl and other alkyl radicals are best interpreted by postulating a planar geometry.[5-7] It seems that the energy difference between planar and pyramidal conformations of free radicals are much smaller than the energy differences between the similar geometries of carbanions and carbonium ions. Support for this contention stems from studies on the configurational stabilities of vinyl radicals which indicate that these radicals equilibrate with great facility.[8-12] In contrast to the above, an electron pair in a trigonally hybridized orbital seems to be able to maintain its spatial configuration to a greater extent.[13]

The stereochemical fate of an electron in a nonbonding orbital that is part of a three-membered ring has also been studied.[14-18] Applequist concluded that the cyclopropyl radical is either planar or inverts its configuration very rapidly even though a large barrier, due to the extra I strain in the rehybridized state, exists.[14] This was demonstrated by showing that in the Hunsdiecker degradation of both *cis*- and *trans*-2-methylcyclopropanecarboxylic acid the identical mixture of *cis*- and *trans*-1-bromo-2-methylcyclopropane was obtained. Similar conclusions were reached by Walborsky from studies on the thermal decomposition of the diacyl peroxide of (+)(*R*)-1-methyl-2,2-diphenylcyclopropanecarboxylic acid in hydrogen donating solvents.[15,16] The formation of optically inactive

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