than a neutral molecule to which we limited discussion in this paper, see ref 18.

Since in the neutral molecule the five and six positions are not equivalent, tautomerism is possible. However, data to date[2] indicate that the five and six tautomers of 5- (or 6-) substituted benzimidazoles are thermodynamically nearly equivalent. Therefore deviations from linearity in the above correlations, though they may in part be attributed to tautomerism,[2,10d,19] appear in the main to be the result of experimental error and the approximate nature of LFER.

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# The Photochromism of 1-Aryl-2-nitroalkenes

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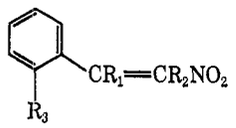
The photochromic properties of eight 1-aryl-2-nitroalkenes are reported. A *cis* relationship of nitro and phenyl groups is required for photochromism. Kinetic data from flash photolysis experiments are given for the dark fading reactions of the colored isomers in ethanol and cyclohexane. Thermodynamic properties of the dark reactions are also reported. The $\lambda_{max}$ obtained from spectra of the visible transients are listed.

In a previous paper[1] the photochromic behavior of 1-aryl-2-nitroalkenes in ethanol and cyclohexane solutions was reported. On irradiation with ultraviolet light, *trans*-α-methyl-β-nitrostyrene[2] was converted to the *cis* isomer, the isomer which exhibited photochromic properties. A preliminary examination of the kinetics of the color fading reaction of alcoholic solutions of *cis*-α-methyl-β-nitrostyrene and other arylnitroalkenes was reported. This paper presents a comprehensive kinetic study of compounds **1–8** listed in Table I.

TABLE I




| Compd | $R_1$ | $R_2$ | $R_3$ |
|---|---|---|---|
| 1 | H | H | H |
| 2 | Me | H | H |
| 3 | H | H | $OCH_3$ |
| 4 | H | $C_6H_5$ | H |
| 5 | $NO_2$ | $C_6H_5$ | H |
| 6 | $C_6H_5$ | H | H |
| 7 | $C_6H_5$ | $C_6H_5$ | H |
| 8 | $-CH_2CH_2CH_2CH_2-$ | | H |

## Results and Discussion

**Preparation and Configuration of the 1-Aryl-2-nitroalkenes.**—Only one geometrical configuration about the central double bond is possible in 1,1-diphenyl-2-nitroethylene (**6**), triphenylnitroethylene (**7**), and 1-phenyl-2-nitrocyclohexene (**8**); nitro and phenyl groups bear a *cis* relationship with respect to each other. When flash photolysis measurements of solutions of these compounds are carried out, a photochromic effect is observed on the first exposure to light. In contrast, β-nitrostyrene (**1**) and α-methyl-β-nitrostyrene (**2**) do not show photochromic behavior on the initial flash exposure. However, after either multiple exposures in the flash photolysis apparatus or a preliminary irradiation with ultraviolet light, solutions of these compounds become photochromic. The pure *cis* isomer of **2** shows the photochromic effect without preirradiation. The preliminary exposure to ultraviolet light apparently serves to convert these compounds from the *trans* configuration, obtained from the chemical preparations,[3,4] to the *cis* form.

The *cis* form of **2** was isolated from an ethanol solution following irradiation of the *trans* isomer. In the infrared spectra (neat) of the isomers the stretching absorption band associated with asymmetric $NO_2$ stretching in the conjugated nitroalkene structure, $C{=}CNO_2$, is at 1520 and 1524 $cm^{-1}$, respectively, for the *trans* and *cis* isomers. In the nmr spectrum (in $CCl_4$) of the *trans* isomer, the methyl group appears as a closely spaced doublet centered at 2.61 ppm (δ, TMS as an internal standard.) The nmr spectrum of the *cis* isomer shows this doublet shifted upfield to 2.03 ppm (δ). This shift is analogous to that observed for *trans*- and *cis*-α-methyl-β-bromostyrene.[5] The nmr spectra also show more splitting of the phenyl H's in the *cis* isomer.

*cis*-1,2-Dinitro-1,2-diphenylethylene (**5**) was obtained by passing nitric oxides through an ether solution of diphenylacetylene. Other workers[6–8] found that by using dinitrogen tetroxide a second isomer can also be isolated. By appropriate dipole moment measurements, Bergmann[9] assigned the geometrical configuration of these isomers. In accord with this assignment we found that solutions of **5** are photochromic without requiring preliminary irradiation.

1,2-Diphenyl-1-nitroethylene (**4**) was prepared by alkali treatment of 1,2-diphenyl-1,2-dinitroethane.[10] The *trans* isomer was isolated. Others[6,10,11] have pre-

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(2) The *cis* and *trans* designations in this paper relate to the orientation of the nitro and phenyl groups, with respect to each other.

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pared the *cis* isomer. Freeman and Stevens[11] based assignment of structure on the relationship of melting points and thermodynamic stability. Models show that the *trans* isomer (in which the phenyl groups are *cis* to each other) allows a closer approach to planarity, subjecting the reaction to steric control. As with the other *trans*-nitrostyrenes either several flashes or a preliminary irradiation with ultraviolet light is necessary before *trans* **4** shows photochromic behavior. *cis* **4** prepared photochemically from the *trans* isomer shows the photochromic effect on initial flash.[12]

1-*o*-Methoxyphenyl)-2-nitroethylene (**3**) was prepared by condensation of *o*-nitrobenzaldehyde and nitromethane.[13] Apparently the *trans* isomer was isolated. Compounds **3** and **1** show an infrared absorption band, before irradiation at 968 $cm^{-1}$, characteristic of the *trans* HC=CH entity.[14] The *cis* isomers have not been reported. When **3** is flashed there is no immediate effect. On continued flashing, however, photochromic behavior develops.

**Ultraviolet Spectra.**—Changes in the ultraviolet absorption spectra of solutions of these compounds when exposed to ultraviolet radiation were noted, but a detailed study of these characteristics was not carried out. After irradiation, the spectra of ethanol or cyclohexane solutions of the *trans* isomers of **1–4** show a shift to shorter wavelength and general decrease of absorption in the ultraviolet region. These same irradiated solutions exhibit photochromism, indicating some conversion to the *cis* forms. *trans*-$\alpha$-Methyl-$\beta$-nitrostyrene (**2**) in ethanol shows strong absorption at 290 m$\mu$. In the spectrum of the *cis* form, the 290-m$\mu$ band is no longer evident; there is a broad absorption which is not intense at about 210 m$\mu$. Campbell, Shavel and Campbell also noted an analogous hypsochromic shift in going from *trans* to *cis* **5**.[8] Similar behavior was observed for **4**.[12] These spectral shifts are attributed to greater deviations from planarity in the *cis* isomers arising from the juxtaposition of bulky nitro and phenyl groups. Steric crowding in stilbene derivatives has been shown to result in similar spectral changes.[15]

**Visible "Transient" Absorption Spectra.**—Spectra of the photochromic transients were determined in ethanol and cyclohexane. Only one absorption band is found in these compounds. Figure 1 shows the absorption curves of the colored transients in ethanol, and in Table II the $\lambda_{max}$ in ethanol and in cyclohexane at room temperature are listed. In Figure 2 the absorption curves of the transient of 1-phenyl-2-cyclohexane in different solutions are shown. The colored transients lie between 410 and 450 m$\mu$. There is no apparent relationship between solvent or structure and $\lambda_{max}$.

TABLE II

ABSORPTION MAXIMA FOR SOLUTIONS OF COLORED TRANSIENTS

| Compd | $\lambda_{max}$, m$\mu$ Ethanol | Cyclohexane |
|---|---|---|
| 1 | 430 | 420 |
| 2 | 425 | 420 |
| 3 | 435 | 430 |
| 4 | 430 | 430 |
| 5 | 440 | 440 |
| 6 | 430 | 450 |
| 7 | 420 | 420 |
| 8 | 410 | 420 |

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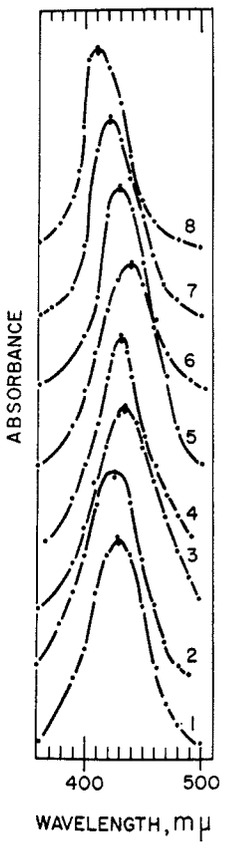



Figure 1.—Visible "transient" absorption spectra of **1–8** in ethanol.

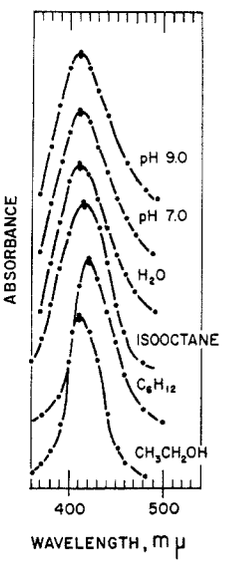



Figure 2.—Visible "transient" spectra of 1-phenyl-2-nitrocyclohexene (**8**) in various solvents.

**Kinetics.**—First-order kinetics is observed for the fading reaction of **1–8**. Although some decomposition occurs on extended irradiation, the rates obtained by flash photolysis do not appear to be affected. Flash exposures can be repeated several times on the same solution without changing the observed value of the first-order rate constant, $k$.

TABLE III

RATE PARAMETERS FOR THE THERMAL RELAXATION OF PHOTOCHROMIC SOLUTION OF 1-ARYL-2-NITROALKENES

| Compd | Solvent | Rate constant at 15.0°, $k$, sec$^{-1}$ × $10^{-2}$ | Half-life, $t^{1/2}$, sec | Preexponential factor, $A$, sec$^{-1}$ | Activation energy, $E_a$, kcal mole$^{-1}$ | Entropy of activation $\Delta S^*$, cal mol$^{-1}$ deg$^{-1}$ |
|---|---|---|---|---|---|---|
| 1 | Ethanol | 9.55 | $7.3 \times 10^{-4}$ | $3.3 \times 10^{11}$ | 11.3 | −7.8 |
| | Cyclohexane | 200 | $3.5 \times 10^{-4}$ | $8.1 \times 10^{11}$ | 11.4 | −6.1 |
| 2 | Ethanol | 47.3 | $1.5 \times 10^{-4}$ | $7.5 \times 10^{14}$ | 14.8 | +7.5 |
| | Cyclohexane | 94.4 | $7.3 \times 10^{-5}$ | $1.2 \times 10^{15}$ | 14.7 | +8.5 |
| 3 | Ethanol | 16.4 | $4.2 \times 10^{-4}$ | $5.4 \times 10^{13}$ | 13.9 | +2.3 |
| | Cyclohexane | 25.4 | $2.7 \times 10^{-4}$ | $4.9 \times 10^{13}$ | 13.6 | +2.1 |
| 4 | Ethanol | 0.243 | $2.9 \times 10^{-2}$ | $1.6 \times 10^{13}$ | 15.6 | −0.2 |
| | Cyclohexane | 0.422 | $1.6 \times 10^{-2}$ | $2.3 \times 10^{13}$ | 15.5 | +0.6 |
| 5 (air) | Ethanol | 0.210 | $3.2 \times 10^{-2}$ | $5.2 \times 10^{10}$ | 12.4 | −11.5 |
| | Cyclohexane | 0.150 | $4.6 \times 10^{-2}$ | $1.7 \times 10^{13}$ | 15.9 | −0.1 |
| 5 (argon) | Ethanol | 0.340 | $2.0 \times 10^{-2}$ | $9.6 \times 10^{10}$ | 12.4 | −10.3 |
| | Cyclohexane | 0.170 | $4.1 \times 10^{-2}$ | $1.3 \times 10^{13}$ | 15.7 | −0.6 |
| 6 | Ethanol | 131 | $5.3 \times 10^{-5}$ | $3.5 \times 10^{12}$ | 11.1 | −3.0 |
| | Cyclohexane | 255 | $2.7 \times 10^{-5}$ | $6.7 \times 10^{12}$ | 11.1 | −1.9 |
| 7 | Ethanol | 2.63 | $2.6 \times 10^{-3}$ | $5.7 \times 10^{11}$ | 12.3 | −6.8 |
| | Cyclohexane | 5.15 | $1.3 \times 10^{-3}$ | $1.2 \times 10^{12}$ | 12.3 | −5.3 |
| 8 | Ethanol | 2.62 | $2.6 \times 10^{-3}$ | $4.7 \times 10^{11}$ | 12.2 | −7.2 |
| | Cyclohexane | 6.10 | $1.1 \times 10^{-3}$ | $1.6 \times 10^{12}$ | 12.4 | −4.8 |

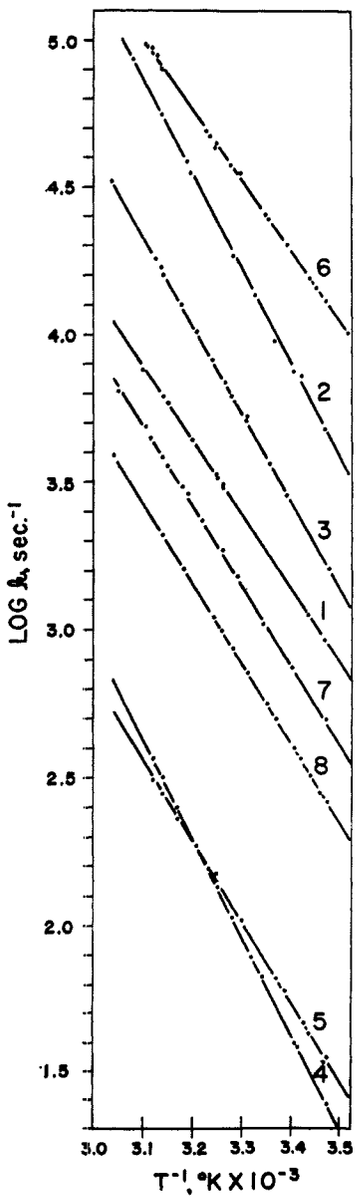


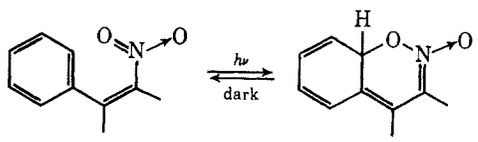

Figure 3.—Plots of log $k$ *vs.* $1/T$ for **1–8** in ethanol.

The rate parameters for ethanol and cyclohexane solutions are listed in Table III, and log $k$ values for ethanol solutions are given in Figure 3. With the exception of **5**, the value of $k$ observed for each compound is greater in cyclohexane than in ethanol. Activation energies appear to be unaffected by solvent change. Solvation effects are noted, however, by differences in entropy of activation values. Compound **5** is the least stable of the group and shows development of a yellow photoproduct after a few flash exposures in ethanol. When examined in deaerated solution and in an argon atmosphere, the visible decomposition is retarded. Exclusion of air, however, has little effect on the observed decay rate, which is greater in ethanol than in cyclohexane. For this compound, both the energy and entropy of activation are influenced by solvent change.

Activation energies fall in the range of 12–16 kcal mol$^{-1}$, probably indicating that the same mechanism is common in these compounds. The decay rate constant appears to be much smaller in the compounds which are 1,2-diphenyl substituted.

1-Phenyl-2-nitrocyclohexene (**8**) was studied in aqueous solutions also. The absorption maximum of the transient appears at 410 m$\mu$, as for the ethanol solution. The decay rate constants in deionized water (pH 4.8), phosphate buffer (pH 7.0), and borate buffer (pH 9.0), appear to be independent of the pH of the system.

**Structure and Photochromism.**—Apparently, in all of the 1-aryl-2-nitroalkenes investigated, the geometry is such that a prerequisite for photochromism is that the nitro and phenyl groups be *cis* with respect to each other. This suggests some form of intramolecular interaction between nitro and phenyl groups. The following mechanism is suggested for the formation of the colored transient. Substitution in one of the *o*-




phenyl positions does not affect photochromic behavior, *e.g.*, **3**. Photochromism could not be detected

in 1-(2,6-dichlorophenyl)-2-nitroethylene, although upon ultraviolet irradiation a hypsochromic shift in the ultraviolet spectrum is noted. Di-*ortho* substitution should not in itself prevent photochromism according to the above mechanism, but the size of the chloro group may present a steric barrier.

Formation of a four-membered ring by attack of a nitro oxygen on the $\beta$ carbon, analogous to the formation of $\beta$-lactones by irradiation of *cis*- or *trans*-acrylic acids,[16] seems unlikely since the $\beta$-lactones are formed more rapidly from the isomer in which the carboxyl and phenyl groups are *trans*. Also, the reaction occurs only with compounds which have a methyl or phenyl substituent on the carbon bearing the carboxyl group.

Studies on the scope and mechanism of this photochromic reaction are being continued in these laboratories.

## Experimental Section[17]

**$\beta$-Nitrostyrene** (1) was prepared by condensation of benzaldehyde and nitromethane according to the procedure of Worrall[3] and melted at 57–58° (lit.[3] 57–58°).

**$\alpha$-Methyl-$\beta$-nitrostyrene** (2).—$\alpha$-Methylstyrene was treated with nitric oxide according to the procedure of Burkhard and Brown[4] which yielded a mixture of *trans* 2 and $\alpha$-(nitromethyl)-styrene. It was not possible to separate the isomers by preparative vapor phase chromatography, which led to severance of the molecule at the ethylene linkage, or by chromatography on alumina with various solvents. Final separation was achieved by low-temperature crystallization from ethanol at −75°.[18] The *trans* isomer was liquid at room temperature and showed in the infrared spectrum the presence of the 1520-cm$^{-1}$ band associated with the asymmetric $NO_2$ stretching in conjugated nitroalkene structures, and absence of any band at 1558 cm$^{-1}$ due to nitroalkane.[19] The nmr spectrum shows the methyl group as a closely spaced doublet centered at 2.61 ppm ($\delta$, with respect to TMS as internal standard). Integration of the nmr spectrum showed the correct ratio of aromatic, unsaturated, and methyl protons. *Anal.* Calcd for $C_9H_9NO_2$: C, 66.24; H, 5.56; N, 8.59. Found: C, 66.39; H, 5.80; N, 8.55.

*cis* 2 was obtained by irradiating 0.5 g of *trans* 2 in 60 ml of ethanol for 48 hr in a Rayonet photochemical reactor fitted with 2537-Å lamps. The Pyrex reaction vessel was surrounded by a Pyrex jacket through which tap water was circulated. After evaporation of the solvent under reduced pressure, the residual liquor was distilled in a short-path creased tube. The distillate, collected at a pot temperature of 108–112° at 0.1 mm, was redistilled in the same manner. The infrared spectrum showed the conjugated nitroalkene absorption at 1524 cm$^{-1}$. In the nmr spectrum the methyl protons appeared at 2.03 ppm ($\delta$). *Anal.* Calcd for $C_9H_9NO_2$: C, 66.24; H, 5.56; N, 8.59; mol wt, 163.17. Found: C, 66.23; H, 5.67; N, 8.63; mol wt, 171 (vapor phase osmometry).

***trans*-1-(*o*-Methoxyphenyl)-2-nitroethylene** (3) was prepared by condensing *o*-methoxybenzaldehyde with nitromethane in the presence of triethylamine, according to the procedure of Worrall and Benington.[20] The yellow crystals, mp 50–51° (lit.[20] 50°), showed ir absorption bands at 968 (*trans*-CH=CH–) and 1509 cm$^{-1}$ (asymmetric $NO_2$ stretching in C=$CNO_2$).

**1,2-Diphenyl-1-nitroethylene** (4) was obtained as the *trans* isomer by alkali treatment of 1,2-diphenyl-1,2-dinitroethane according to the procedure of Meisenheimer and Heim.[10] The yellow crystals melted at 73–74° (lit.[10] 74–75°). The *cis* isomer has been reported to melt at 127–128°.[6,10,11] The infrared spectrum showed the conjugated nitroalkene structure at 1514 cm$^{-1}$.

***cis*-1,2-Dinitro-1,2-diphenylethylene** (5)[2] was prepared by passing nitric oxides through an ether solution of diphenylacetylene as described in the general procedure of Burkhard and Brown.[4] The light yellow crystals melted at 185–186° (lit. 186–187°,[6] 187–188°[11]).

**1,1-Diphenyl-2-nitroethylene** (6) was obtained by the procedure of Govindachari, Pai, and Rao,[21] and the straw yellow crystals melted at 87–88° (lit.[21] 92°).

**Triphenylnitroethylene** (7) was obtained by nitration of triphenylethylene in glacial acetic acid as prepared by Bergmann.[22] The yellow crystals melted at 172–173° (lit.[22] 172°).

**1-Phenyl-2-nitrocyclohexene** (8) was obtained by the procedure of Govindachari, *et al.*,[23] as a pale yellow liquid. The infrared spectrum showed the conjugated $NO_2$ band at 1523 cm$^{-1}$. *Anal.* Calcd for $C_{12}H_{13}NO_2$: C, 70.91; H, 6.44; N, 6.89. Found: C, 71.16; H, 6.83; N, 6.98.

**Kinetic Measurements.**—Samples for measurement were weighed in a darkened room. Solutions approximately $2 \times 10^{-4}$ *M* were prepared in "low actinity" volumetric flasks. Spectro grade ethanol or cyclohexane, dried by conventional methods, was used. Rate measurements in the temperature range 10–65° were carried out in a quartz reaction vessel with an optical path length of 20.0 cm, provided with an outer filter jacket. Aqueous $CuSO_4$ solution was circulated through the jacket and acted as a cut-off filter and also thermostated the solution. Measurements of temperature were made by a glass-enclosed copper-constantan thermocouple which dipped into the reaction solution at the cell neck. The flash photolysis measurements were made according to published techniques.[24] The optical transmission at $\lambda_{max}$ was recorded after flashing once with a flash energy of 1125 J. A fresh reaction solution was utilized for each flash exposure. In those cases (*trans* 1–4) where the original solution did not show any photochromism on flashing, the solution was preirradiated with a Hanovia quartz 125-W Hg lamp.

Values of the first-order specific rate constant, $k$, were calculated from the slope of the straight line in plots of log optical density *vs.* time. The reaction was followed for at least three half-lives. The Arrhenius activation energy, $E_{exp}$, was calculated from the slope of the straight line obtained in plots of log $k$ *vs.* $1/T$. The entropy of activation, $\Delta S^*$, was calculated using the following equation. The frequency factor, $A$, in the Arrhenius equation, $k = Ae^{-E_{exp}/RT}$, was calculated from the relationship, $A = ekT/he^{\Delta S^*/R}$.

$$k = e\bar{k}T/he^{\Delta S^*/R}e^{-E_{exp}/RT}$$

**Visible "Transient" Absorption Spectra.**—The sample solutions were placed in the quartz absorption cell at a constant temperature, then exposed to a single flash of reproducible intensity (constant C and V). The absorption spectrum of the short-lived species was obtained from plots of log (log $I_\infty/I_0$) *vs.* time. The process was repeated several times at each selected wavelength, with enough wavelengths chosen so that the entire visible absorption curve could be drawn, from which $\lambda_{max}$ was read.

**Registry No.**—1, 102-96-5; 2 (*cis*), 5670-65-5; 2 (*trans*), 15241-24-4; 3 (*trans*), 21298-69-1; 4 (*trans*), 18315-83-8; 5, 1796-05-0; 6, 5670-69-9; 7, 15795-67-2; 8, 5670-71-3.

**Acknowledgment.**—We express our thanks to Professor W. C. Price, King's College, University of London, London, Great Britain, for providing valuable discussion, space, and equipment for one of us (J. A. S.) during part of the period in which this work was carried out.

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(17) Melting points were taken in a Fisher-Johns block and are uncorrected.

(18) See A. Bluhm, *J. Chem. Educ.*, **35**, 200 (1958), for convenient apparatus for small-scale low-temperature recrystallizations.

(19) J. F. Brown, Jr., *J. Amer. Chem. Soc.*, **77**, 6341 (1951), reports these bands at 1513 and 1555 cm$^{-1}$, respectively.

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(21) T. R. Govindachari, B. R. Pai, and V. Rao, *Proc. Indian Acad. Sci.*, **48A**, 111 (1958).

(22) F. Bergmann, *J. Amer. Chem. Soc.*, **70**, 1618 (1948).

(23) T. R. Govindachari, K. Nagarajan, B. R. Pai, and N. Arumugam, *J. Chem. Soc.*, 4280 (1956).

(24) For an excellent review of flash photolysis, see G. Porter, "Technique of Organic Chemistry," Vol. VIII, Part II, Interscience Publishers, New York, N. Y., 1963, pp 1055–1101.