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Compounds Related to Imido-Substituted Ethylenes. I.*
The Preparation of Diimido-Substituted Ethylenes

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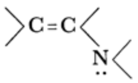
Methods for the preparation of *cis*-, *trans*-1, 2-diphthalimidoethylene, its nitro derivative, 1, 1-diphthalimido- and 1, 2-bis(*o*-sulfobenzimido)ethylene are described. In this connection, the thermal, irradiated and iodine-catalyzed isomerization of *cis*- and *trans*-1, 2-diphthalimidoethylene have also been studied in detail.

Unsaturated compounds I in which an unsaturated group is bonded with the nitrogen atom in an amino or imido group are expected to exhibit an interesting property under the influence of the unshared electron pair on the nitrogen atom.



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Particularly, it is presumed that the preparation of polyamino- or polyimido-substituted ethylenes becomes more difficult than that of mono-substituted ethylenes, and that the poly-substituted ethylenes exhibit an unusual reactivity under the influence both of the steric effect of the substituents and of the unshared electron pair on the nitrogen atom.

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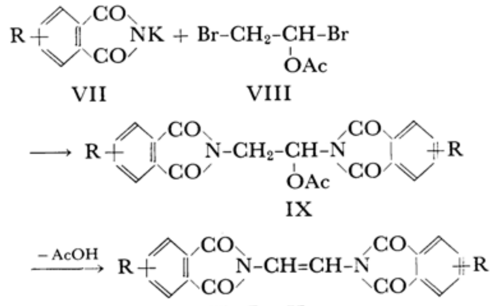
Although monoimido-substituted ethylenes such as *N*-vinyl-phthalimide have been well studied,[1] no information has been available regarding polyimido-substituted ethylenes.

Therefore, in this work, the preparation of 1, 2-diphthalimidoethylenes (II—IV), 1, 1-diphthalimido- (V) and 1, 2-bis-(*o*-sulfobenzimido)ethylene (VI) has been attempted in the expectation that the diimido-substituted ethylenes would exhibit an unexpected reactivity.[2] In this connection, the present paper will describe the results of our experiments with the *cis-trans* isomerization of II under various conditions.

Results and Discussion

The Preparation of 1, 2-Diphthalimidoethylenes (II—IV).—1, 2-Diphthalimidoethylenes (II—IV) were synthesized by the pyrolytic elimination of acetic acid at about 250°C from the corresponding 1, 2-diphthalimido-1-acetoxyethane (IX), which had been prepared by the condensation of the potassium phthalimide (VII) and 1, 2-dibromo-1-acetoxyethane (VIII)[3] in dimethylformamide (DMF).



II: R=H
III: R=3-NO$_2$
IV: R=4-NO$_2$

The crude II was recrystallized from DMF to give two compounds, whose solubilities in organic solvents were very small. The infrared spectrum of the more soluble, pale yellow needles (IIb) was in agreement with that of the crude II, but that of the less soluble, bright yellow grains or needles (IIa) was not.

As is shown in Fig. 1, the infrared spectra of IIa and IIb exhibit bands at 713 and 960 cm^{-1} which are to be ascribed to the –CH=CH– (*cis*) and –CH=CH– (*trans*) linkage respectively.[4] As no suitable solvent of II could be found, the measurement of the NMR spectrum or of the dipole moment was not carried out.

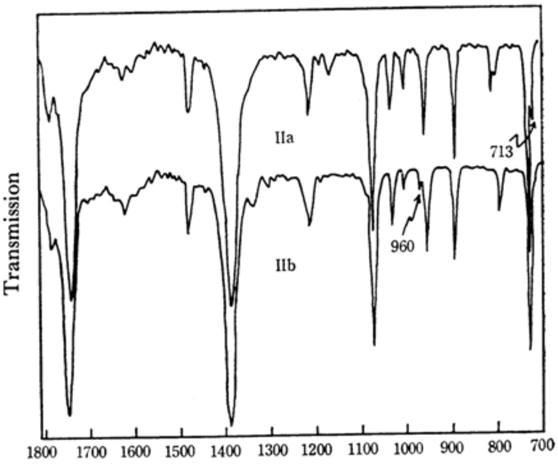


Fig. 1. Infrared spectra of IIa and IIb in KBr disks.

On the basis of the infrared spectra as well as of elemental analyses, however, IIa and IIb were assumed to be *cis-* and *trans*-form respectively. In view of this fact, it may be suggested that *cis-trans* isomerization took place during recrystallization.

Furthermore, the ultraviolet spectra of IIa and IIb were almost the same (Fig. 2), and the two

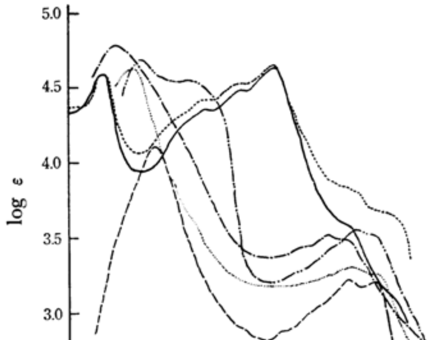


Fig. 2. Ultraviolet spectra of II, V and phthalimide derivatives.
---- IIa in tetrahydrofuran
—— IIb in tetrahydrofuran
—-— V in dioxane
— — — Phthalimide in dioxane
······ *N*-Ethylphthalimide in dioxane
–··–·· Diphthalimidoethane in dioxane

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[1] M. Bachstez, *Ber.*, **46**, 3087 (1913); K. Yanagi et al., *J. Org. Chem.*, **24**, 428, 1121 (1959), and other publications.

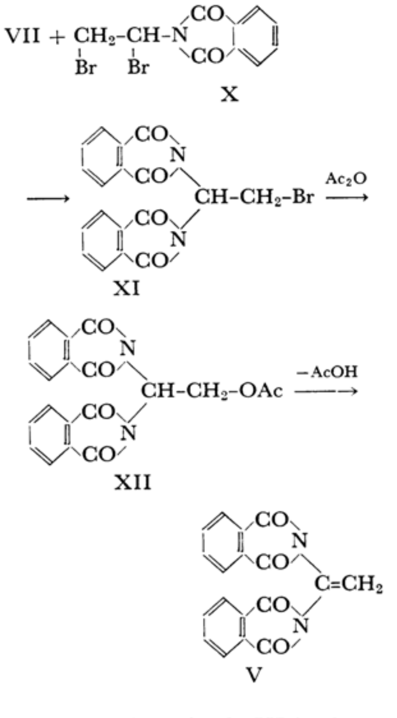
[2] For example, unusual phenomena were observed in addition reaction of bromine to II and V. (O. Tsuge, K. Yanagi and S. Fukuhara, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **69**, 932 (1966)).

[3] H. O. L. Fischer and L. Feldmann, *Ber.*, **62**, 862 (1929).

[4] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley & Sons. Inc., New York (1954), p. 40.

isomers have the same melting point; however, IIa does not exhibit its own melting point, because IIa is easily isomerized to IIb by irradiation with light and by heating, as will be mentioned below. The geometric isomerism of III and of IV is not yet clear.

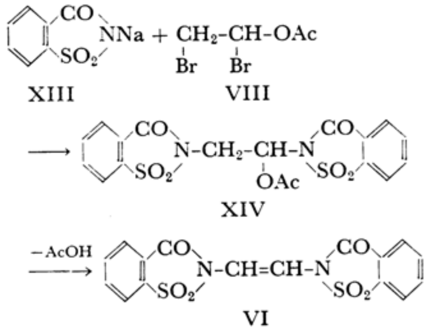
The Preparation of 1, 1-Diphthalimidoethylene (V).—1, 1-Diphthalimidoethylene (V) was synthesized by the pyrolytic elimination of acetic acid at 600°C from 1, 1-diphthalimido-2-acetoxyethane (XII) which had been prepared by the action of acetic anhydride on 1, 1-diphthalimido-2-bromoethane (XI), which had been obtained from VII and 1, 2-dibromo-1-phthalimidoethane (X)[1] in DMF.



The formation of only XI in the reaction of VII with X suggests that VII attacked selectively at the α-carbon atom of X. The structure of XI was proved by the fact that XII was different from the IX isomer (R=H) as well as by elemental analyses.

The ultraviolet spectrum of V is also shown in Fig. 2. The ultraviolet spectrum of II is different from those of phthalimide derivatives, but the spectrum of V is very similar to those of the latter. These observations indicate that the electronic state of II is quite different from that of the phthalimide because of the interaction between the π-electron in the carbon-carbon double bond and unshared electron pairs on the nitrogen atoms, and that the interaction mentioned above does not exist in V, since the two phthalimido groups and the carbon-carbon double bond are not in the same plane because of the steric effect of the bulky phthalimido group.

The Preparation of 1, 2-Bis(*o*-sulfobenzimido)ethylene (VI). — The similar pyrolytic elimination of acetic acid from 1-acetoxy-1, 2-bis(*o*-sulfobenzimido)ethane (XIV) which had been prepared by the treatment of sodium salt of *o*-sulfobenzimide (XIII) with VIII in DMF, afforded 1, 2-bis(*o*-sulfobenzimido)ethylene (VI).



The *cis-trans* Isomerization of IIa and IIb. —In order to obtain further information concerning the *cis-trans* isomerization of IIa and IIb, the isomerization reaction was carried out under various conditions.

The quantitative estimation of IIa and IIb in II was established by using the ratio method,[5] which was carried out by the measurement of the absorbances, A_1 and A_2, for the bands at 800 and 792 cm^{-1} respectively. Thus, samples of a mixture consisting of specified amounts of IIa and IIb in KBr were prepared and the absorbances, A_1 and A_2, were measured according to the respective baseline method. The calibration curves plotting

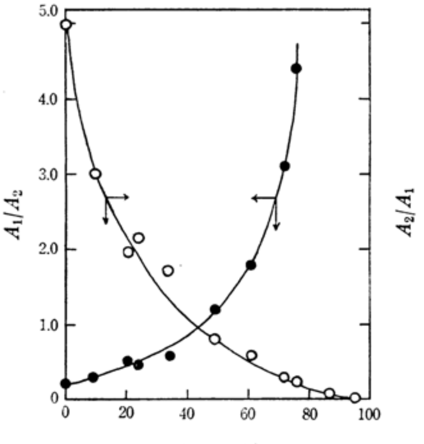


Fig. 3. Calibration curve.

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[5] S. Takagi, "Teiryō Bunseki no Jikken to Keisan (Experiment and Calculation of Quantitative Analyses)" (in Japanese), Vol. III, Kyoritsu, Tokyo (1961), p. 91.

the relationship between A_1/A_2 or A_2/A_1 and the concentration (wt. %) of IIb are shown in Fig. 3.

Thermal Isomerization.—The isomerization was observed on the recrystallization of II, as has been mentioned above; therefore, the thermal isomerization was examined in the solid state or in a solution.

The isomerization of IIa to IIb in the solid state was carried out in a sealed capillary tube under a nitrogen atmosphere. The results are shown in Table I.

TABLE I. THE THERMAL ISOMERIZATION OF IIa TO IIb

Temp. °C	Time min.	Degree of isomerization %	Temp. °C	Time min.	Degree of isomerization, %
100	60	0	200	5	12
100	180	4	250	5	100
150	30	0	300	5	100
150	60	4			

As is shown in Table I, the transition temperature from IIa to IIb in the solid state may be expected to be in the range from 200 to 250°C; hence, differential thermal analyses of IIa and IIb were carried out in order to establish the accurate transition temperature. The results are shown in Fig. 4. Although IIa showed a thermal abnormality at 220.5°C and melted at about 320°C, IIb showed no such anomalous curve and melted at about 320°C. Consequently, the transition temperature of IIa to IIb in the solid state may be concluded to be 220.5°C.

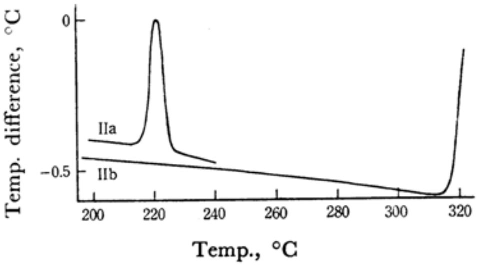

Fig. 4. Differential thermal analyses of IIa and IIb.

On the other hand, it was found that, in the isomerization in a solvent such as dioxane, tetrachloroethane, DMF or diethyleneglycol, IIb was isomerized to IIa in the range from 100 to 150°C, whereas IIa was isomerized to IIb above 150°C.

Iodine-Catalyzed Isomerization.—The isomerization under the influence of a catalytic amount of iodine was carried out in a tetrachloroethane solution at 20°C. The results are shown in Table II.

As Table II shows, the degree of isomerization of IIa to IIb in the presence of iodine increases with the increase in the reaction time, but in the absence of a catalyst neither form was isomerized.

TABLE II. IODINE-CATALYZED ISOMERIZATION[a)]

Reaction time, hr.	Yield, mg.	Degree of isomerization, %[b)]
i) From IIa to IIb		
1	30	65
3	31	78
6	32	83
24	31	100
24[c)]	31	0
ii) From IIb to IIa		
13	20	0
24	5	0
24[c)]	32	0

a) A solution of 40 mg. of the starting material in 50 ml. of tetrachloroethane was treated with 1 mg. of iodine in 10 ml. of tetrachloroethane.
b) The wt.% of IIb or IIa in the product.
c) In the absence of iodine.

While the recovered amount of IIb decreased as the iodine-catalyzed reaction time increased, the isomerization of IIb to IIa was not observed; the purple color of iodine and the yellow color of IIb disappeared after 24 hr., and an unidentified compound of colorless needles, m. p. 166—169°C, was formed. The same phenomenon was also observed in the treatment of IIa with iodine for a long while. The investigation of this side reaction is in progress and will be reported in the near future.

Isomerization by Irradiation with Light.—The isomerization by irradiation with light (3500—4000 Å) was carried out in a tetrachloroethane solution at 18—20°C. The isomerization of IIa to IIb was brought about, but that of IIb to IIa was not. As is shown in Fig. 2, the ultraviolet spectra of the two isomers are almost the same. This suggests either that both isomers are in nearly the same electronic state or that isomerization from one to another takes place during the measurement. In order to elucidate which of the alternatives is true, the isomerization was examined under the same conditions as when the spectrum was measured. As it was found that the *cis*-form was converted into the *trans*-form, the spectrum of IIa shown in Fig. 2 is that of the *trans*-form.

Experimental[6)]

1, 2-Diphthalimido-1-acetoxyethane (IX, R=H).—To a suspension of 185 g. of potassium phthalimide (VII, R=H)[7)] in DMF (450 ml.) 123 g. of 1, 2-dibromo-1-acetoxyethane (VIII)[3)] was slowly added, drop by drop, while the temperature was kept below 55°C with cooling. After the addition had been completed, the reaction mixture was stirred at room temperature for 2hr., and then water (4 l.) was poured into it. After a white precipitate had been collected by filtration, washed with water, and dried, recrystallization from glacial acetic acid gave colorless prisms. Yield, about 200 g.; m. p. 232—233°C.

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6) All melting points are uncorrected.
7) "Organic Syntheses," Coll. Vol. I, 119 (1948)

Found: C, 63.64; H, 3.73; N, 7.41. Calcd. for $C_{20}H_{14}O_6N_2$: C, 63.49; H, 3.73; N, 7.41%.

1, 2-Bis(3-nitrophthalimido)-1-acetoxyethane (IX, R=3-NO$_2$).—A mixture of 7.85 g. of potassium 3-nitrophthalimide (VII, R=3-NO$_2$)[8] and VIII (4.2 g.) in DMF (35 ml.) was heated at 100°C for 15 min., and then stirred at room temperature for another 5 hr. The reaction mixture was poured into ice water, and the precipitate was collected, washed with water, and dried. The acetic acid solution of the crude product was diluted with water, and the crystalline product was collected by filtration. Yield, 6.5 g. (81%); m. p. 115—116°C. The compound was not further refined.

1, 2-Bis(4-nitrophthalimido)-1-acetoxyethane (IX, R=4-NO$_2$).—A mixture of 4.6 g. of potassium 4-nitrophthalimide (VII, R=4-NO$_2$)[9] and VIII (2.46 g.) in DMF (30 ml.) was stirred at room temperature for 5 hr., and then the reaction mixture was poured into ice water (300 ml.). Recrystallization from glacial acetic acid gave IX (R=4-NO$_2$) as palely colored rods melting at 207—208.5°C; yield, 4.7 g. (48.5%).

Found: C, 51.45; H, 2.64; N, 12.15. Calcd. for $C_{20}H_{12}O_{10}N_4$: C, 51.29; H, 2.58; N, 11.96%.

1, 1-Diphthalimido-2-bromoethane (XI).—After a mixture of VII (11.12 g.) and 1, 2-dibromo-1-phthalimidoethane (X)[1] in DMF (70 ml.) had been stirred at room temperature for 9 hr., ice water (500 ml.) was added to the reaction mixture. The precipitate was collected by filtration; recrystallization from ethyl acetate gave XI as colorless grains melting at 206—207°C. Yield, 22.35 g. (93%).

Found: C, 54.14; H, 2.90; N, 7.19. Calcd. for $C_{18}H_{11}O_4N_2Br$: C, 54.16; H, 2.78; N, 7.02%.

1, 1-Diphthalimido-2-acetoxyethane (XII).—A mixture of XI (6.6 g.), fused potassium acetate (6.6 g.) and acetic anhydride (60 ml.) was heated under reflux for 9 hr. After it had then cooled, the mixture was poured into ice water (400 ml.) and allowed to stand overnight. The precipitate was collected and washed with water. Recrystallization from glacial acetic acid gave XII as colorless prismatic rods; m. p. 207—208°C. Yield, 4.0 g. (64%).

Found: C, 63.60; H, 3.74; N, 7.53. Calcd. for $C_{20}H_{14}O_6N_2$: C, 63.49; H, 3.73; N, 7.41%.

1-Acetoxy-1,2-bis(*o*-sulfobenzimido)ethane (XIV).—A mixture of 20.5 g. of sodium salt of commercial *o*-sulfobenzimide (XIII) and VIII (12.3 g.) in DMF (40 ml.) was heated for 1 hr. at 100°C, and then refluxed for another 2 hr. After the reaction mixture had cooled to room temperature, water (400 ml.) was added to it and the precipitate was collected and washed with water. Recrystallization from glacial acetic acid gave XIV as palely colored needles; yield, 15.03 g. (67%); m. p. 221.5—222.5°C.

Found: C, 47.97; H, 3.19; N, 6.24. Calcd. for $C_{18}H_{14}O_8N_2S_2$: C, 48.00; H, 3.13; N, 6.22%.

1, 2-Diphthalimidoethylene (II).—In a 500 ml. separable flask, 200 g. of IX (R=H) was heated at 250°C for 15 min. As acetic acid was eliminated, the reaction mixture was gradually solidified. The crude product was washed with alcohol and then with hot acetic acid to remove phthalimide and tarry material respectively. Recrystallization from DMF afforded yellow crystals, which were identified, by means of the infrared spectrum, as a mixture of *cis*- (IIa) and *trans*-form (IIb); yield, 118 g. (70%).

Pure *cis*-form (IIa), bright yellow grains or needles, was obtained quantitatively by heating the recrystallized product (10 g.) in dioxane (20 ml.) for 4—5 hr. at 100°C.

Found: C, 68.01; H, 3.26; N, 8.79. Calcd. for $C_{18}H_{10}O_4N_2$: C, 67.92; H, 3.17; N, 8.80%.

Pure *trans*-form (IIb) was prepared by heating a saturated DMF solution of the recrystallized product at 150°C, and by then rapidly cooling the solution to room temperature. Pale yellow needles; m. p. 318.5—319.5°C.

Found: C, 67.87; H, 3.23; N, 9.09. Calcd. for $C_{18}H_{10}O_4N_2$: C, 67.92; H, 3.17; N, 8.80%.

1, 2-Bis(3-nitrophthalimido)ethylene (III).—After 5 g. of IX (R=3-NO$_2$) had been heated by the procedure used to prepare II, recrystallization from DMF gave III as deep yellow needles melting at 344—344.5°C; yield, 1.3 g. (30%).

Found: C, 52.99; H, 2.02; N, 13.65. Calcd. for $C_{18}H_8O_8N_4$: C, 52.95; H, 1.98; N, 13.72%.

1, 2-Bis (4-nitrophthalimido)ethylene (IV).—After 1.7 g. of IX (R=4-NO$_2$) had been heated at 260°C for 15 min., recrystallization from DMF afforded 0.3 g. (20%) of IV as deep yellow needles; m. p. 334°C (decomp.).

Found: C, 53.21; H, 1.85; N, 13.80. Calcd. for $C_{18}H_8O_8N_4$: C, 52.95; H, 1.98; N, 13.72%.

From the filtrate, 1.17 g. (69%) of IX (R=4-NO$_2$) was recovered.

1, 1-Diphthalimidoethylene (V).—A solution of XII (30 g.) in acetone (700 ml.) was added, drop by drop, to a pyrolytic tube which had been placed in an electric furnace at 550°C. After about two-thirds of the acetone had been distilled out from the reaction mixture, which had been collected in the receiver, the residue was poured into water to separate the precipitate. The precipitate was collected by filtration and washed with water. Recrystallization from ethyl acetate gave V as palely-colored plates; m. p. 247—248°C. Yield, 5 g. (20%).

Found: C, 67.88; H, 3.17; N, 8.83. Calcd. for $C_{18}H_{10}O_4N_2$: C, 67.93; H, 3.17; N, 8.80%.

1, 2-Bis(*o*-sulfobenzimido)ethylene (VI).—After XIV (6.75 g.) had been heated at 250°C for 10 min. in a 10 ml. thin-walled flask, the reaction mixture was washed with 15 ml. of hot acetic acid. Recrystallization from DMF gave VI as pale brown grains; m. p. 283—284°C (decomp.). Yield, 5.3 g. (90%).

Found: C, 49.07; H, 2.54; N, 7.29. Calcd. for $C_{16}H_{10}O_6N_2S_2$: C, 49.23; H, 2.58; N, 7.18%.

Thermal Isomerization.—The thermal isomerization of *cis*- (IIa) and *trans*-form (IIb) in the solid state was carried out in a sealed tube under a nitrogen atmosphere. The effect of the reaction conditions on the isomerization is shown in Table I.

In this and in other isomerizations, the IIa and IIb in the reaction mixture were analyzed quantitatively by using the ratio method (Fig. 3).

Differential Thermal Analyses.—The differential thermal analyses were carried out by using the Rigaku Denki Type-V apparatus. Alumina was used as the reference compound, and the heating rate was kept

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[8] M. T. Bogert and V. J. Chambers, *J. Am. Chem. Soc.*, **27**, 652 (1905).

[9] M. T. Bogert and L. Boroschek, ibid., **23**, 755 (1901).

constant at 0.7°C/min. The temperature of the sample was higher than that of alumina throughout the run (Fig. 4). Perhaps this is caused by the difference in specific heat between sample and alumina.

Iodine-Catalyzed Isomerization.—To a solution of 40 mg. of IIa or IIb in tetrachloroethane (50 ml.), a solution of iodine (1 mg.) in tetrachloroethane (10 ml.) was added. After the reaction mixture had been allowed to stand at 20°C for a certain time, it was poured into petroleum ether (500 ml.). The precipitate was filtered and analyzed. The results are shown in Table II.

In a reaction of IIb with iodine, the reaction mixture was allowed to stand for a week, and then tetrachloroethane was distilled out in vacuo. The residue was recrystallized from dichloroethane to give colorless needles; m. p. 166—169°C.

Found: C, 64.55; H, 3.70; N, 9.09%.

Beilstein's test of the compound was negative, and its infrared spectrum exhibits the bands at 1770 and 1710 cm^{-1} ascribed to the phthalimido group. The investigation of this side reaction is now in progress; the structure of the compound will be described elsewhere in the near future.

Isomerization by Irradiation with Light.—Irradiations were carried out employing a 150 W., high-pressure mercury lamp with a water-cooled, quartz immersion well (Taika Kogyo, HLV-B Type). A solution of 400 mg. of IIa or IIb in tetrachloroethane (500 ml.) was irradiated with light (3500—4000 Å) under nitrogen at 18—20°C for 6 hr. The reaction mixture was poured into petroleum ether, and the precipitate was collected by filtration and then analyzed.