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Photo-induced 1,3-Dipolar Cycloaddition Reaction of Aziridinedicarboximide[1]

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Cycloaddition reaction of N-(*p*-methoxyphenyl)-1-benzyl-2,3-aziridinedicarboximide (**8**) with dimethyl acetylenedicarboxylate (**3**) was not effected thermally, but under irradiation it resulted in a formation of 1:1-cycloadducts, I (**9**), II (**17**), and III (**34**), and a 1:2-cycloadduct IV (**38**). The structural determination of these cycloadducts was made from their spectral data and chemical degradations. Further, mutual photochemical transformation of the cycloadducts was also verified.

Recently, many reports[3,4] have been published on reactions of substituted aziridines which proceed *via* a 1,3-dipole and/or its equivalent arising from thermally or photochemically induced C-C bond cleavage of the aziridine ring. These intermediates can subsequently be trapped by a suitably activated olefinic or acetylenic substrate to form substituted pyrrolidines or pyrrolines. In particular, Huisgen and his co-workers[4] studied thermal or photo-induced cycloaddition reaction of both dimethyl 1-(*p*-methoxyphenyl)-aziridine-*cis*-2,3-dicarboxylate (**1**) and its *trans* isomer (**2**) with dimethyl acetylenedicarboxylate (**3**) and found that this reaction proceeds with a high stereospecificity. Thermal cycloaddition of the *cis* compound (**1**) onto **3** led to the formation of the *trans* pyrroline derivative (**4**) and that of the *trans* isomer (**2**) yielded the corresponding *cis* pyrroline (**5**); on the other hand, photo-induced cycloaddition of **1** and **2** conversely gave **5** and **4**, respectively. These facts show that this cycloaddition proceeds through a dipolar intermediate, azomethine-ylide (**6** or **7**) produced by the initial aziridine ring opening, which is stereospecifically controlled as predicted by Woodward-Hoffmann postulates,[5] in parallel with a presumed mode of transformation of a cyclopropyl anion into an allyl anion. The present paper is concerned with the analogous cycloaddition of N-(*p*-methoxyphenyl)-1-benzyl-2,3-aziridinedicarboximide[6] (**8**) having a restricted bicyclic skeleton, which would offer with heating a poor condition for a conrotatory cycloaddition predicted, but with irradiation an ideal condition for a disrotatory cycloaddition.

A mixture of the aziridinedicarboximide (**8**) and two equivalent amount of dimethyl acetylenedicarboxylate (**3**) was irradiated in dioxane with a high-pressure Hanovia mercury lamp (550 W). Progress of the reaction was followed by thin-layer chromatography. Silica gel column chromatography of the product obtained by irradiation for two hours gave three kinds of cycloadducts, I, mp 122.5—124°, II, mp 159—160°, and III, mp 161—162°, in relative

1) Preliminary details of this work have been published: S. Oida and E. Ohki, *Chem. Pharm. Bull.* (Tokyo), **16**, 764 (1968).
2) Location: *Hiromachi, Shinagawa-ku, Tokyo.*
3) H.W. Heine and R.E. Peavy, *Tetrahedron Letters*, 3123 (1965); A. Padwa and L. Hamilton, *ibid.*, 4363 (1965); R. Huisgen, W. Scheer, G. Szemies, and H. Huber, *ibid.*, 397 (1966); H.W. Heine, R.E. Peavy, and A.J. Durbetaki, *J. Org. Chem.*, **31**, 3924 (1966); A. Padwa and L. Hamilton, *J. Heterocyclic Chem.*, **4**, 118 (1967); P.W. Woller and N.H. Cromwell, *ibid.*, **5**, 579 (1968); A. Padwa and W. Eisenhardt, *Chem. Commun.*, **7**, 380 (1968); H.W. Heine, A.B. Smith, III and J.D. Bower, *J. Org. Chem.*, 33, 1097 (1968).
4) R. Huisgen, W. Scheer, and H. Huber, *J. Am. Chem. Soc.*, **89**, 1753 (1967).
5) R.B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).
6) S. Oida and E. Ohki, *Chem. Pharm. Bull.* (Tokyo), **17**, 980 (1969).

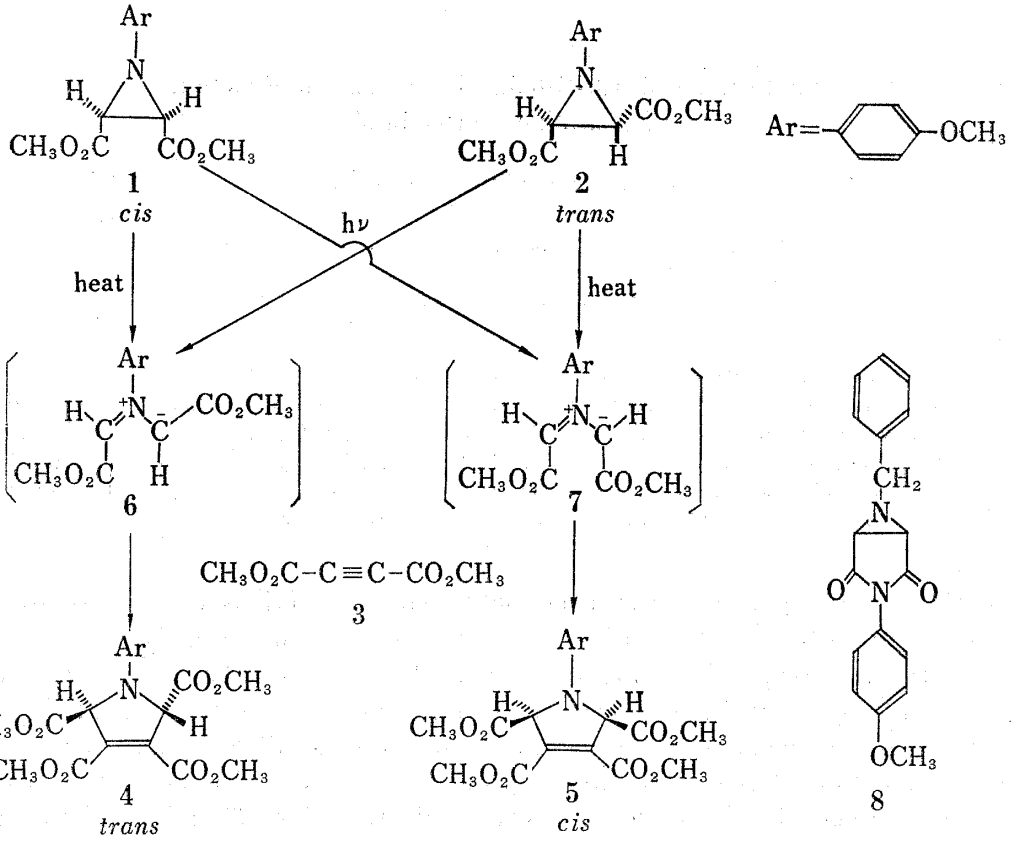
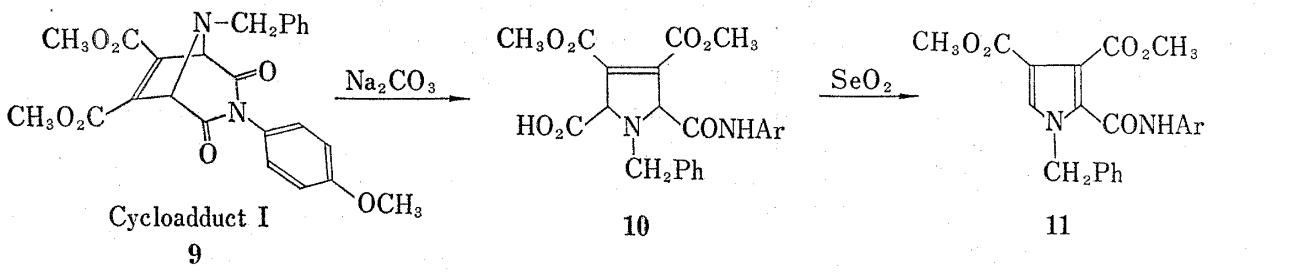
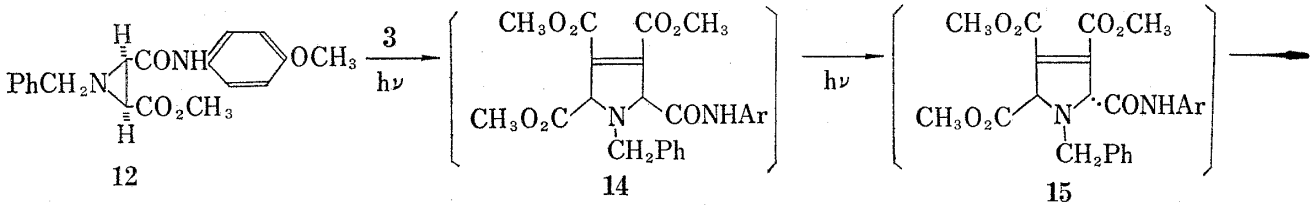


Chart 1





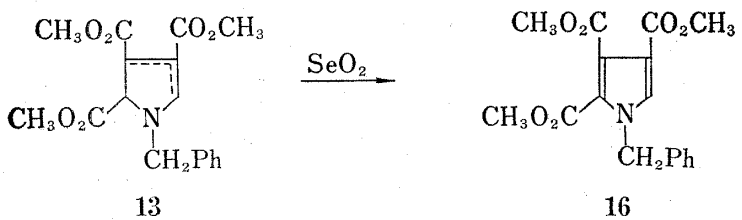


Chart 2

ratio of 1:6:2, and a small amount of cycloadduct IV, mp 267—269°, along with the unchanged material (18% recovery). The yield of a mixture of these cycloadducts was 50% based on the unrecovered **8**.

Elementary analysis and mass spectrometry of these cycloadducts showed that the cycloadducts I, II, and III are 1:1-adduct formed from **3** and **8**. The infrared (IR) spectrum of the cycloadduct I exhibited absorptions at 1751, 1733, and 1701 cm^{-1}, suggesting the presence of dicarboximide and ester groups. As shown in Fig. 1, the nuclear magnetic resonance (NMR) spectrum indicated singlet absorptions at 3.80, 3.84, 3.86, and 4.65 ppm in a relative ratio of 3:2:6:2 as peak areas, along with a multiplet of nine aromatic protons at 7—7.5 ppm. These absorptions would be due to methyl protons of methoxyl group, two protons at carbons bearing nitrogen, methyl protons of two methyl ester groups, and benzyl-methylene protons, respectively. Consequently, the NMR spectrum reflected the expected symmetrical and bicyclic structure (**9**). Further, mild saponification of the cycloadduct I with sodium carbonate gave an amorphous dimethyl ester of 3-pyrrolinetetracarboxylic acid derivative (**10**). Dehydrogenation of **10** with selenium dioxide in boiling dioxane was accompanied by decarboxylation and gave a pyrrole-2,3,4-tricarboxylic acid derivative (**11**), mp 152—153°, in good yield. These facts not only suggest that the cycloadduct I includes a substituted pyrroline structure, but also, together with the above-mentioned spectroscopic data, indicates that the cycloadduct I is 8-benzyl-6,7-bis(methoxycarbonyl)-3-(*p*-methoxyphenyl)-3,8-diazabicyclo[3.2.1]oct-6-ene-2,4-dione (**9**), which is a normal cycloadduct of **8** and **3**, just as predicted from the usual mode of the reaction.

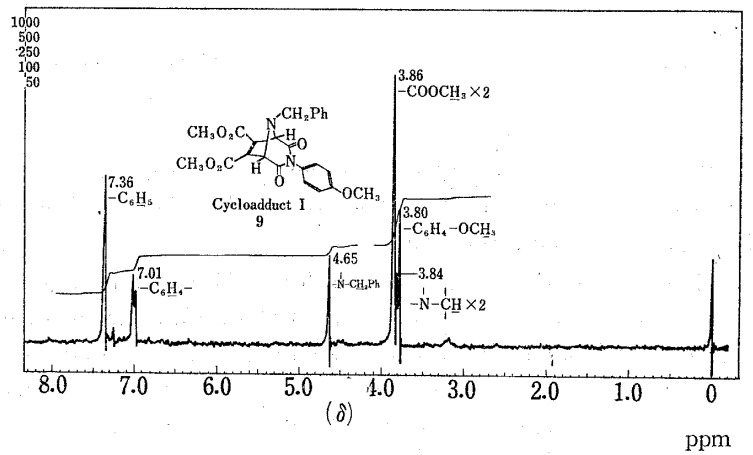


Fig. 1. NMR Spectrum of the Cycloadduct I (9) at 60 Mc in $CDCl_3$

Further, an alternate synthesis of the pyrroline derivative (**10**) was attempted to confirm its structure, and cycloaddition reaction of methyl 1-benzyl-*cis*-2-(*p*-methoxyphenylcarbamoyl)aziridine-3-carboxylate[6] (**12**),[7] which was prepared by saponification of **8** and successive esterification, with dimethyl acetylenedicarboxylate (**3**) was carried out under irradiation. However, it resulted unexpectedly in the formation of a complex mixture, from which only an amorphous trimethyl ester of pyrrolinetricarboxylic acid (**13**) was isolated in a low yield. The IR spectrum of **13** showed the absence of carbamoyl function, and only the presence of ester groups. Selenium dioxide oxidation of 13 in dioxane gave trimethyl 1-benzylpyrrole-2,3,4-tricarboxylate (**16**), mp 114—114.5°, in a fair yield. Although the final structural elucidation of **13** still remains, it may be well assumed that the cycloaddition reaction initially occurred to afford a pyrrolinetetracarboxylic acid derivative (**14**), but a photochemical release of the carbamoyl group from **14** successively progressed *via* a radical (**15**) to give **13**.

Structure of the cycloadduct II may be formulated as **17** based on the following facts. Its IR spectrum showed no NH or OH absorption, but exhibited absorptions corresponding to ester and dicarboximide groups at 1750, 1722, and 1692 cm^{-1}. Its NMR spectrum exhibited nine aromatic protons at 6.9—7.5 ppm, three O-methyl absorptions at 3.57, 3.67, and 3.80 ppm

7) Thermal cycloaddition reaction of 12 with 3 gave a resinous product, from which any simple adduct could not be isolated.

as singlets, and benzyl-methylene protons centering at 4.68 ppm as an AB-pattern quartet (J=15.5 cps), as shown in Fig. 2. The remaining two protons fell into 4.84 and 7.76 ppm as singlets. The latter absorption in the lower field would be assignable as a β-vinyl proton of β-aminoacryloyl group, –N–CH=C–CO–, which is consistent with the published data.[8] In addition, quite different from the case of the cycloadduct I, II had a characteristic ultraviolet (UV) absorption at 302 mμ (ε 15,700) which also supports the presence of the β-aminoacryloyl system. These spectral data conclusively indicate the presence of two methoxycarbonyl groups, dicarboximide group, N-benzyl group, and β-aminoacryloyl group in the molecule and collectively indicate that the cycloadduct II would be a hexahydropyrrolopyrrole derivative (**17**) or its possible alternate.

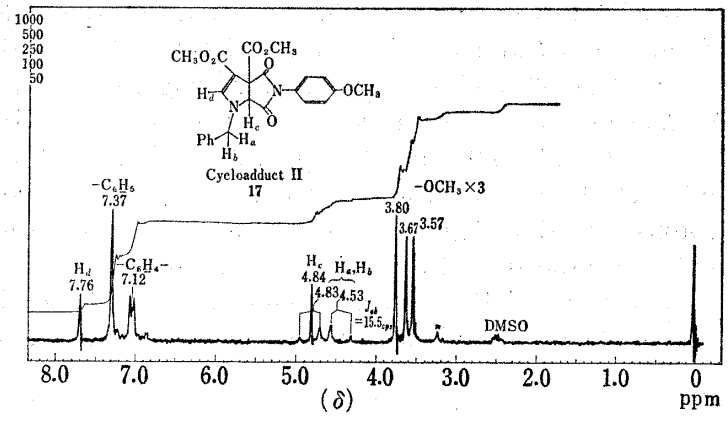


Fig. 2 NMR Spectrum of the Cycloadduct II (**17**) at 60 Mc in Me_2SO–d_6

It was found that the cycloadduct II resisted selenium dioxide oxidation, even under a drastic condition. Saponification of the adduct with sodium hydroxide at room temperature afforded an inseparable mixture of pyrrolinecarboxylic acids (**18** and **19**) whose structure will be discussed later. Treatment of this acid mixture with diazomethane gave a mixture of isomeric dimethyl esters of pyrrolinetricarboxylic acid derivatives (**20** and **21**), from which the major isomer (**20**) was separated as a colorless syrup by chromatography on silica gel. The IR spectrum of **20** did not show the absorption of dicarboximide group, but of a *p*-methoxyphenylcarbamoyl group at 3300, 1652, and 1552 cm^{-1}. Its UV spectrum also showed an absorption at 304 mμ (ε 15,900), suggesting that this saponification had no effect on the original chromophore system. The minor one (**21**) could not be characterized enough, giving no satisfactory result in elementary analysis, but its spectral data suggested that it is an isomer of **20**. Selenium dioxide oxidation of crude **21** in dioxane yielded the afore-mentioned pyrrole derivative (**11**) obtained from the cycloadduct I. On the other hand, analogous treatment of the major isomer (**20**) with selenium dioxide gave an isomeric pyrrole derivative (**22**), mp 129.5—130.5°. As the location of the *p*-methoxyphenylcarbamoyl group in **11** would be at the 2-position from its formation route, that of the isomer (**22**) should be at the 3-position. Based on these facts, the pyrroline derivatives would be assumed as **20** and **21**.

Formation of **20** and **21** from the cycloadduct II *via* **18** and **19** indicates that saponification of the cycloadduct II proceeds with the loss of one carbon by decarboxylation, suggesting that the adduct has a base-labile β-dicarboxylic acid function in the molecule. The NMR spectrum of **20** indicated that a broad doublet at 4.23 ppm is coupled both with a sharp doublet at 5.30 ppm, J=5 cps, and with a broad singlet at 7.13 ppm corresponding to the vinyl proton of the β-aminoacryloyl group, showing further the presence of the carbon sequence of –N–CH=C–CH–CH–. On the other hand, precise analysis, involving decoupling study, of the signals at 4.84 and 7.76 ppm in the NMR spectrum of the cycloadduct II did not show any possible mutual coupling predicted from the alternate formula (**23**). Thus, these facts rule out the formula (**23**) and show that the β-dicarboxylic acid function would be located at the 4-position

8) J.E. Dolfini, *J. Org. Chem.*, **30**, 1208 (1965).

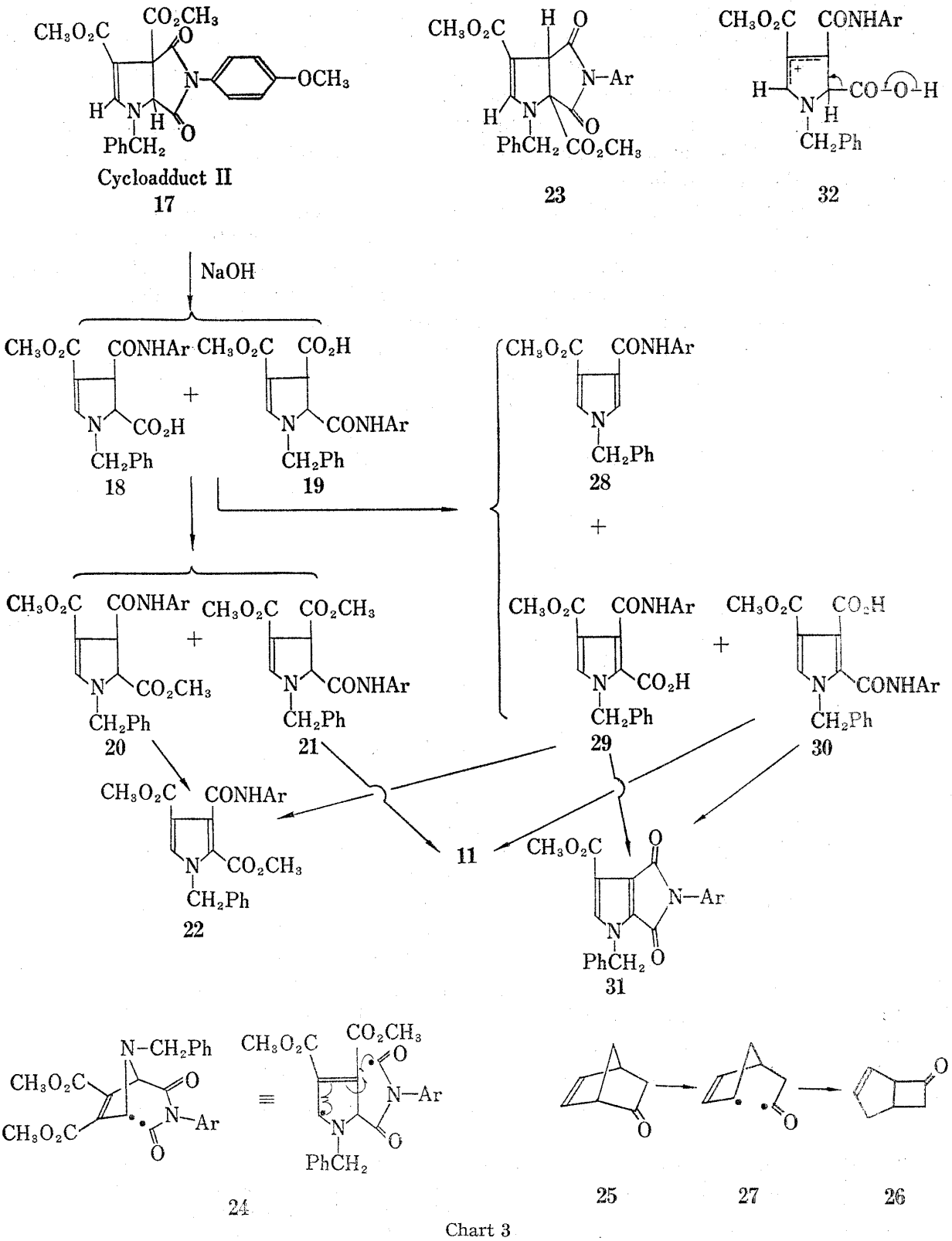


Chart 3

of the 2-pyrroline ring. Conclusively, the cycloadduct II was designated as 4-benzyl-6,6a-bis(methoxycarbonyl)-2-(*p*-methoxyphenyl)-1,2,3,3a,4,6a-hexahydropyrrolo[3,4-*b*]pyrrole-1,3-dione (**17**). The formation of **17** may be well explained in terms of photochemical rearrangement of the initially produced cycloadduct I (**9**) through a biradical intermediate (**24**) or the like, which may have arisen from I due to its highly strained bicyclic skeleton and its active carbonyl chromophore of the dicarboximide group. This phenomenon seems to parallel the

photochemical behavior of β,γ-unsaturated carbonyl system[9,10]; for example, UV irradiation of bicyclo[2.2.1]hept-5-en-2-one (**25**) affords bicyclo[3.2.0]hept-2-en-7-one (**26**) *via* a biradical intermediate[10] (**27**). As will be mentioned later, the cycloadduct I was found, in fact, to be transformed by irradition into the cycloadduct II.

For the stereochemistry of the cycloadduct II (**17**), any reliable result could not be obtained from these data. However, a *cis*-juncture of its hexahydropyrrolopyrrole ring is most plausible because of its higher stability.

Further, we would like to mention another degradation of **17**. A mixture of the pyrroline-tricarboxylic acid derivatives (**18** and **19**) obtained as above by saponification of **17** was directly treated with selenium dioxide and gave a pyrroledicarboxylic acid derivative (**28**), mp 147—148°, in 45% yield, accompanied with a pyrroletricarboxylic acid derivative (**29**), mp 213.5—214.5°, and its isomer (**30**), mp 181.5—182°. The structure of these products was determined from the fact that either **29** or **30** with acetic anhydride gave the same dicarboximide (**31**), mp 186—187°. Further, esterification of **29** with diazomethane gave **22**, while that of **30** gave **11**. The pyrroledicarboxylic acid derivative (**28**) obtained as a major product must have originated from the major acid derivative (**18**) (whose methyl ester (**20**) was obtained in 71% yield from **17** as mentioned earlier) and formed by its decarboxylation. Accordingly, the assigned structure (**28**) is more likely than its possible alternate formula, although there is no reliable chemical or spectral evidence to support this structure. Attempted preparation of **28** from **29** by treatment with selenium dioxide in boiling dioxane was not successful and resulted in the recovery of **29**. Therefore, it was presumed that the formation of **28** from **18** proceeds directly *via* an intermediate (**32**) formed by oxidation of **18** with selenium oxide.

The structure of the cycloadduct III was elucidated in the following way. The IR spectrum also exhibited ester and dicarboximide absorptions at 1746 and 1700 cm^{-1}. As shown in Fig. 3, different from the case of the cycloadduct I or II, absorptions arising from phenyl protons of the benzyl group disappear in the lower magnetic field of the NMR spectrum of the cycloadduct III and only an AA′BB′-pattern absorption due to aromatic protons of *p*-methoxyphenyl group is observed. Further, the spectrum indicates three singlets corresponding to O-methyl groups at 3.71, 3.73, and 3.78 ppm, an AB-pattern quartet corresponding to a methylene group centering at 3.26 ppm, $J=13$ cps, and two doublets due to bridgehead protons at 4.25 and 4.36 ppm with a mutual long-range coupling, $J=2$ cps. The remaining protons, which probably come from the disappeared five protons of phenyl group, fell into 5.1—6.3 ppm with peak area of four protons and around 3.1 ppm with peak area of one proton. The former absorption in the lower field suggests the presence of vinyl protons. On the other hand, the UV spectrum of the cycloadduct III exhibited a characteristic absorption at 272.5 mμ (ε 3,600), suggesting the presence of a homoannular conjugated diene chromophore. Treatment of the cycloadduct III with an active dienophile, tetracyanoethylene, in boiling dioxane afforded a 1:1-adduct (**33**), mp 262—264°, in a fair yield. The mass spectrum of **33** showed a molecular ion peak at *m/e* 576, supporting its structure.[11] Based on these facts, the cycloadduct III may be assigned as a pentacyclic compound (**34**) with a four-membered

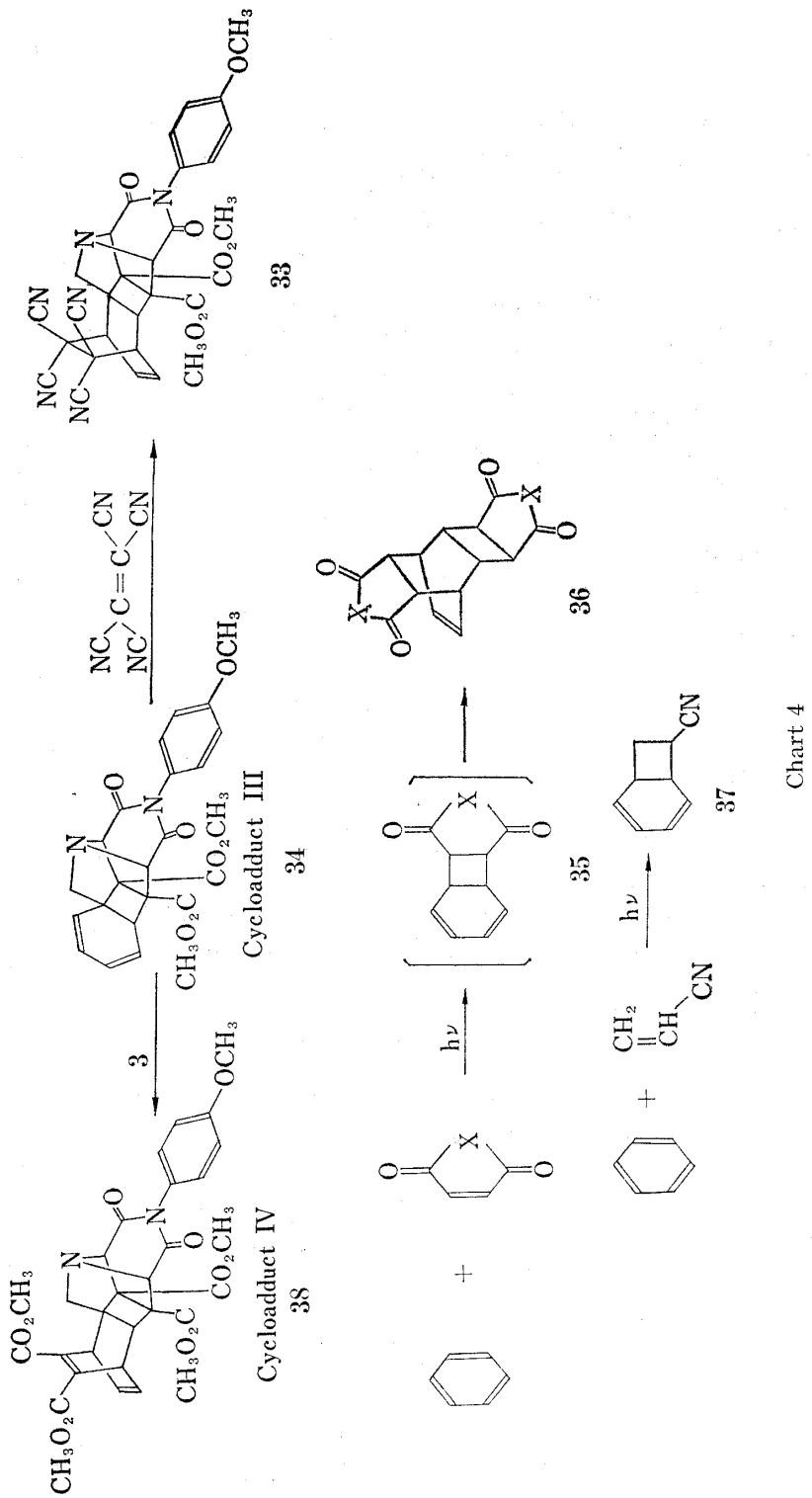
9) G.C. Schenck and R. Steinmetz, *Chem. Ber.*, **96**, 520 (1963); P.E. Eaton, *Tetrahedron Letters*, 3695 (1964); R.L. Cargill, M.E. Beckham, A.E. Siebert, and J. Dorn, *J. Org. Chem.*, **30**, 3647 (1965); E.F. Keifer and D.A. Carlson, *Tetrahedron Letters*, 1617 (1967); D.E. Bays and R.C. Cookson, *J. Chem. Soc.*, Sect. B, 226 (1967); W.F. Erman and H.C. Kretschman, *J. Am. Chem. Soc.*, **89**, 3842 (1967); L.A. Paquette and R.F. Eizember, *ibid.*, **89**, 6205 (1967); J.K. Crandall, J.P. Arrington, and J. Hen, *ibid.*, **89**, 6208 (1967); L.A. Paquette, R.F. Eizember, and O. Cox, *ibid.*, **90**, 5153 (1968); M. Fischer and B. Zeeh, *Chem. Ber.*, **101**, 2360 (1968).

10) D.I. Schuster, M. Axelrod, and J. Auerbach, *Tetrahedron Letters*, 1911 (1963).

11) There is no proof available for the stereochemistry of the adduct (**33**) or the cycloadduct IV (**38**). However, in consideration of its molecular model, the junction of tetracyanoethylene group or **3** from the rear side of two *cis*-methoxycarbonyl groups is more likely because of the steric hindrance of the latter groups.

ring system. Further, the mass spectrum of the cycloadduct III is almost superimposable on that of the cycloadduct I. Both of them indicated a base peak at *m/e* 91 corresponding to C_7H_7 with a strong intensity. These facts suggest that electron impact of the cycloadduct III may initially induce the cleavage of a four-membered ring and may form the same molecular ion as the cycloadduct I.

Formation of the cycloadduct III can be rationalized by an intramolecular photoaddition of the electrophilic olefin linkage bearing two methoxycarbonyl groups of the cycloadduct I



(**9**) with its phenyl group of the N-benzyl group. Actually, as will be shown later, UV irradiation of the adduct I gave the adduct III in a fair yield, along with the adduct II (**17**). Photoadducts (1:1) of dienophiles with benzene have been predicted[12] as a possible intermediate (**35**) in the course of formation of 2:1-photoadducts (**36**) by irradiation of maleimide or maleic anhydride in benzene. Recently, Job and Littlehailes[13] demonstrated that photoaddition reaction of acrylonitrile to benzene resulted in the formation of a 1:1-cycloadduct (**37**) in a trace amount (0.25%). In contrast to these observations, it is interesting that conversion of the cycloadduct I into III progressed in a fair yield. It may be ascribed to a spatial characteristics of the compound I involving a rigid bicyclic skeleton; it may enhance the possibility of an interaction between the benzene ring of N-benzyl moiety and the active olefinic bond, and may partly account for inertness of the resultant diene system of the cycloadduct III toward further reaction.

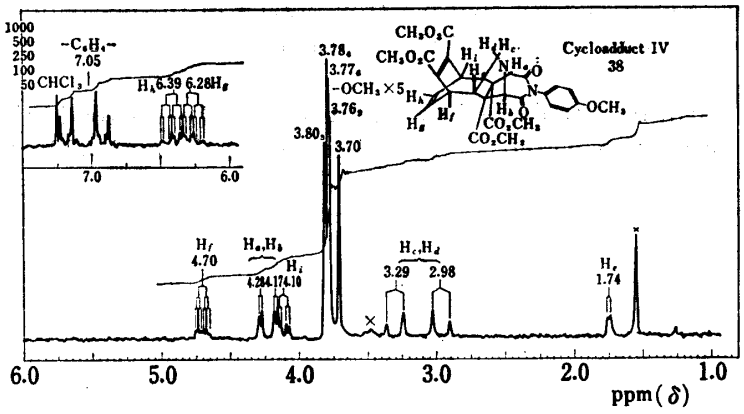


Fig. 3. NMR Spectrum of the Cycloadduct III (**34**) at 100 Mc in $CDCl_3$

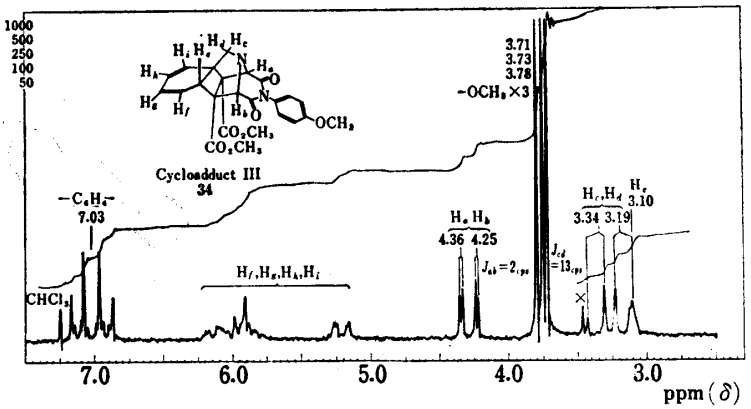


Fig. 4. NMR Spectrum of the Cycloadduct IV (38) at 100 Mc in $CDCl_3$
Coupling constants (cps): J_{ab}=2.1, J_{cd}=12.3, J_{ef}=2.0, J_{fi}=5.5, J_{fh}=2.1, J_{gh}=7.8, J_{gi}=2.0, J_{hi}=5.8.

The last and minor cycloadduct IV would be formulated as **38** in the following way.[11] Elementary analysis and mass spectrometry of this adduct indicated a composition of the 1:2-cycloadduct of **8** with **3**. As shown in Fig. 4, the NMR spectrum of the adduct IV reflected the structure of **38**; five O-methyl singlets, an AA'BB'-pattern absorption of *p*-methoxyphenyl group, a couple of AB-pattern absorptions centering at 3.13 ppm, J=12.3 cps, and 4.22 ppm, J=2 cps, which may be due to methylene protons bearing nitrogen, Hc and Hd, and two bridgehead protons, Ha and Hb, can be observed. These absorptions are quite similar to those of the cycloadduct III, suggesting the presence of a similar structure. The remaining five protons including two vinyl protons were analysed sufficiently as shown in Fig. 4 by a precise spin-decoupling study. Formation of the cycloadduct IV can be illustrated as the result of a further 1,4-cycloaddition reaction of dimethyl acetylenedicarboxylate (**3**) onto the diene system of the cycloadduct III (**36**). In fact, it was found that a mixture of **3** and the cycloadduct III treated in boiling dioxane gave the adduct IV in a fair yield. Thus, the formation of the cycloadducts III and IV in this reaction supports the mechanistic proposals[12] inferred by Bryce-Smith from his work on the formation of the 1:2-adduct (**36**) of benzene and maleic anhydride.

12) D. Bryce-Smith and J.E. Lodge, *J. Chem. Soc.*, 2675 (1962), and references cited therein.
13) B.E. Job and J.D. Littlehailes, *J. Chem. Soc.*, Sect C, 886 (1968). See also J.G. Atkinson, D.E. Ayer, G, Büchi, and E.W. Robb, *J. Am. Chem. Soc.*, **85**, 2257 (1963).

Finally, we would like to mention the process of this cycloaddition reaction under various conditions and also the mutual conversion of these cycloadducts. The yields of products formed at various time intervals are shown in Table I. These values were computed from the yield of crystalline mixtures of the cycloadducts separated by chromatography and from their NMR spectrometry as described in the experimental. Table I indicates that, under irradiation with a low-pressure mercury lamp, formation of the cycloadducts II and III, especially of II, increase with time, but formation of the cycloadduct I remains in an approximately constant level. This fact proves that the formation of the cycloadducts II or III proceeds *via* the cycloadduct I. When a high-pressure mercury lamp was used, formation of the adducts II and III was further accelerated but formation of I remained in a trace amount. The fact that irradiation with a Pyrex filter did not initiate this reaction is of interest: and it may suggest that UV ray of wave lengths shorter than 3000 Å is substantially necessary for the activation of aziridinedicarboximide (**8**) into a possible azomethine-ylide

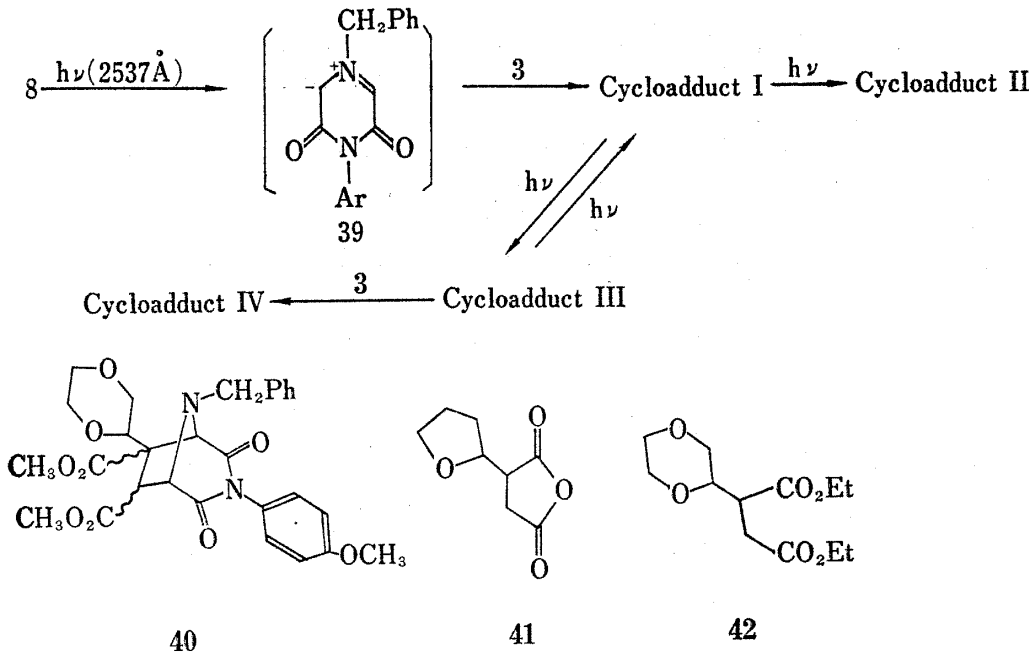


Chart 5

TABLE I. Percentage Composition Values for the Cycloaddition Reaction of **8** with **3** in Process of Time

UV source	Reaction time (hr)	Product (%)			
		Recovered **8**	I	II	III
Low-pressure mercury lamp (30 W)	3.5	57	21	—	2
	5.5	44	19	—	5
	7.5	26	17	12	10
	10.5	19	19	14	12
	15.0	8	17	23	17
High-pressure mercury lamp (450 W)	2.0	55	—	16	9
	3.0	41	4	23	7
	4.5	20	—	38	10
	6.0	11	1	43	—
	6.0[a]	94	—	—	—
	6.0[a,b]	90	—	—	—

a) A Pyrex filter was used.
b) The reaction mixture included 0.1—0.2M of acetophenone or benzophenone, 0.107M of **8** and 0.214M of **3**.

Table II. Percentage Composition Values for the Transformation of the Cycloadducts under Irradiation

UV source	Irradiated cycloadduct	Reaction time (hr)	Product (%) I	II	III
Low-pressure mercury lamp (30 W)	I	6 1/4	11	39	24
	II	6 1/4	—	95	—
	III	6 1/4	13	34	34
High-pressure mercury lamp (350 W)	I	3	—	60	—
	I[a)]	3	—	46	34
	II	5	—	77	—
	III	6 1/4	—	70	—

a) A Pyrex filter was used.

intermediate (**39**). Further, influence of sensitizers such as acetophenone and benzophenone with a Pyrex filter was examined but these compounds were found not to be effective for the progress of this reaction.

The mutual conversion of these cycloadducts is shown in Table II. Under irradiation of UV ray, the cycloadduct II was comparably stable, while the cycloadduct I was easily converted into the adducts II and III. This rearrangement seems to be effected by UV ray of both short and long wavelengths. The cycloadduct III was also converted into the cycloadducts I and II by irradiation, indicating that the reaction proceeds *via* a reversible transformation into the cycloadduct I which finally settles in the formation of II. Photolysis of the cycloadduct I in the presence of benzophenone in dioxane with a Pyrex filter was attempted but any formation of the cycloadduct II or III could not be observed. Chromatography of the reaction product yielded a 1:1-adduct of the cycloadduct I and dioxane, mp 207.5—209°, along with an unidentified mixture. Mass spectrometry of this adduct indicated a molecular ion peak at 538, and its structure may be formulated as **40** in consideration of analogous examples reported; *viz.* formation of a 1:1-adduct (**41**) by irradiation of maleic anhydride in tetrahydrofuran,[14)] or formation of **42** by irradiation of dimethyl maleate in dioxane in the presence of a sensitizer.[15)]

Moreover, when dichloroethane was used as a solvent in this cycloaddition in place of dioxane, the cycloadducts I and II were also obtained, but in a lower yield, as will be shown in the experimental part. Attempted cycloaddition reaction of **8** with another dienophile, tetracyanoethylene, under irradiation resulted in the formation of a complex resinous product.

In contrast to the photo-induced cycloaddition described above, thermal cycloaddition of **8** and **3** at 100° for 2 hr resulted in the recovery of a considerable amount of the starting materials. From the reaction product left after removal of the starting materials, none of the cycloadducts I, II, and III could be detected, but an isomeric 1:1-adduct, mp 179—181° (decomp.), was isolated in a low yield. Acetylation of this adduct gave a monoacetate, mp 180—185° (decomp.). Spectral data of these compounds did not give any information on their structures. Further study on this 1:1-adduct was abandoned because of the scarcity of the sample.

Experimental

Melting points are not corrected. IR spectra were determined on a Perkin-Elmer Model 221 or a Perkin-Elmer Infracord, UV spectra on a Beckman Model DK-2, and NMR spectra on a Varian A-60 or HA-100 spectrometer. Removal of solvent *in vacuo* was accomplished with a rotating flash evaporator

14) A. Ledwith and M. Sambhi, *J. Chem. Soc.*, Sect B, 670 (1966).
15) I. Rosenthal and D. Elad, *Tetrahedron*, **23**, 3193 (1967).

at 20—30 mmHg and usually at 35—50°. Plates for thin-layer chromatography were prepared with Silica Gel G (E. Merck AG) and visualization of spots was effected by spraying iodine or a solution of NH_4VO_3 in 50% H_2SO_4, followed by heating. The abbreviations used are as follows: s, singlet; d, doublet; q, quartet; m, multiplet; br, broad; sh, shoulder.

Cycloaddition Reaction of N-(*p*-Methoxyphenyl)-1-benzyl-2,3-aziridinedicarboximide (8) with Dimethyl Acetylenedicarboxylate (3) with Irradiation——Using a high-pressure Hanovia mercury lamp (550 W), a solution of 5.00 g of **8** and 5.00 g (*ca.* 2 equiv.) of **3** in 150 ml of dioxane was irradiated in a quartz immersion-well apparatus with stirring by bubbling dry N_2. The course of the reaction was followed by removing small aliquots at various intervals and examination of these by thin-layer chromatography. After 2 hr of irradiation, the reaction mixture was evaporated to dryness *in vacuo* and left *ca.* 11.5 g of an orange syrup which was chromatographed over 50 g of silica gel. Evaporation of the solvent from fractions eluted with benzene gave 1.6 g of a crystalline residue which was recrystallized fom MeOH, giving 887 mg (17.7%) of unchanged **8** as leaflets. The MeOH mother liquor was allowed to stand for a few hours, yielding a crystalline mass, mp 121—123.5°, which was recrystallized from MeOH to 325 mg (4.4%) of the cycloadduct I (**9**) as needles, mp 122.5—124°. IR ν_{max}^{Nujol} cm^{-1}: 1751, 1733, 1701. UV λ_{max}^{EtOH}: 265 mμ (ε 4100). Mass spectrum (75 eV) *m/e*: 450 (M^+), 359, 273, 242, 210, 166, 150, 134, 106, 91 (base peak), 65. *Anal.* Calcd. for $C_{24}H_{22}O_7N_2$: C, 63.99; H, 4.92; N, 6.22. Found: C, 64.33; H, 5.06; N, 6.12.

Further development of the chromatographic column with 10% (v/v) ether–benzene and evaporation of the solvent from fractions thus obtained afforded a syrup which yielded 2.645 g (36.3%) of a crystalline mixture of the cycloadducts II (**17**) and III (**34**), mp 147—157°, on trituration with MeOH. The NMR spectrum of the mixture indicated a relative ratio of **17** and **34** as *ca.* 3:1. Fractional recrystallization of the mixture from MeOH gave 1.470 g of the cycloadduct II (**17**) as prisms of mp 159—160° and 0.176 g of the cycloadduct III (**34**) as prisms of mp 161—162°. IR ν_{max}^{Nujol} cm^{-1} (for the cycloadduct II): 1795 (weak), 1750, 1722, 1692; (for the cycloadduct III): 1746, 1700. UV λ_{max}^{EtOH} mμ (ε) (for the cycloadduct II): 231 (17600), 302 (15700); (for the cycloadduct III): 225.5 (14000), 272.5 (3600), 279 (3400). Mass spectrum (75 eV) *m/e* (for the cycloadduct II): 450 (M^+), 359, 273, 242, 210, 166, 149, 134, 120, 106, 91 (base peak), 78, 65; (for the cycloadduct III): 450 (M^+), 359, 273, 242, 210, 166, 150, 134, 106, 91 (base peak), 65. *Anal.* Calcd. for $C_{24}H_{22}O_7N_2$: C, 63.99; H, 4.92; N, 6.22. Found (for the cycloadduct II): C, 63.90; H, 4.99; N, 6.03; (for the cycloadduct III): C, 63.89; H, 5.03; N, 6.10.

The MeOH mother liquor left after removal of the crude cycloadducts II and III was evaporated to dryness *in vacuo*. The residue was chromatographed on 20 g of silica gel. After elution of a small amount of the cycloadducts II and III with 10% (v/v) ether–benzene, further elution with the same solvent mixture and evaporation of the solvent from fractions obtained gave 75 mg of a syrup which crystallized on digestion with MeOH. The collected crystals were recrystallized from MeOH, yielding 53 mg of the cycloadduct IV (**38**) as fine prisms, mp 267—269°. IR ν_{max}^{Nujol} cm^{-1}: 1744, 1716, 1703. Mass spectrum (75 eV) *m/e*: 592 (M^+), 560, 397, 365 (base peak), 339, 217, 189, 163, 149, 134. *Anal.* Calcd. for $C_{30}H_{28}O_{11}N_2$: C, 60.81; H, 4.76; N, 4.73. Found: C, 60.67; H, 4.66; N, 4.99.

1-Benzyl-3,4-bis(methoxycarbonyl)-2-(*p*-methoxyphenylcarbamoyl)pyrrole (11)——i) A mixture of 200 mg of the cycloadduct I (**9**), 50 mg of Na_2CO_3, 3 ml of dioxane, and 2 ml of H_2O was stirred overnight at room temperature. The mixture was diluted with 30 ml of H_2O and washed with 20 ml of benzene. Evaporation of the solvent from the washings gave 65 mg of the unchanged **9** of mp 120—123°. The remaining aqueous layer was neutralized with dil. HCl and extracted with two 20 ml portions of benzene. The extract was dried (Na_2SO_4) and evaporated to dryness *in vacuo*, yielding the crude **10** as a yellow syrup (136 mg). The syrup was dissolved in 4 ml of dioxane and 100 mg of SeO_2 was added. This mixture was heated on a steam bath for 3 hr with stirring and, after cooling, was concentrated *in vacuo*. The resulting concentrate was dissolved in benzene and filtered. Evaporation of the solvent from the filtrate and recrystallization of the residual crystals from MeOH afforded 61 mg of **11** as fine prisms, mp 150.5—152°. Analytical sample was obtained by recrystallization from MeOH as prisms of mp 153—153.5°. IR ν_{max}^{Nujol} cm^{-1}: 3310, 3120, 1710 (sh.), 1692. UV ν_{max}^{EtOH}: 281 mμ (ε 13900). NMR ($CDCl_3$, 60 Mc) δppm: 3.80 (6H, s), 3.92 (3H, s), 5.63 (2H, s), 7.23 (4H, AA′BB′-pattern), 7.3 (6H, m,) 9.85 (1H, br.). *Anal.* Calcd. for $C_{23}H_{22}O_6N_2$: C, 65.39; H, 5.25; N, 6.63. Found: C, 65.26; H, 5.26; N, 6.91.

ii) A mixture of 95 mg of crude **21**, whose preparation will be described below, 150 mg of SeO_2, and 3 ml of dioxane was refluxed for 3 hr with stirring. The cooled mixture was diluted with H_2O and extracted with benzene. After drying, the extract was evaporated *in vacuo* and the residue was chromatographed on 3 g of silica gel. Evaporation of the solvent from fractions eluted with benzene and 5% (v/v) ether–benzene gave 22 mg of **11**, which was recrystallized from MeOH to 17 mg of prisms, mp 151.5—152.5°.

Cycloaddition Reaction of Methyl 1-Benzyl-*cis*-2-(*p*-methoxyphenylcarbamoyl)aziridine-3-carboxylate (12) with Dimethyl Acetylenedicarboxylate (3) under Irradiation——A solution of 1.93 g of **12** and 2.00 g of **3** in 150 ml of dioxane was irradiated with a high-pressure mercury lamp (550 W) for 2 hr in the same manner as described in the case of the reaction of **8** and **3**. Progress of the reaction was followed by withdrawal of small aliquots at various time intervals and examination of these by thin-layer chromatography. The reaction product (4.97 g) obtained by evaporation of the solvent was chromatographed on 50 g of silica gel. Evaporation of the solvent from fractions eluted with benzene gave 280 mg of **13** as a syrup which

was, without further purification, dissolved in 5 ml of dioxane and 300 mg of SeO_2 was added. The resulting mixture was warmed for 4 hr on a steam bath. After cooling and filtration, the mixture was evaporated *in vacuo* and the residue was chromatographed on 5 g of silica gel. Evaporation of the solvent from fractions eluted with benzene gave 150 mg of a syrup which crystallized on digestion with MeOH. Recrystallization from MeOH gave 76 mg of trimethyl 1-benzyl-2,3,4-pyrroletricarboxylate (**16**) as prisms, mp 114—114.5°. IR ν_{max}^{Nujol} cm^{-1}: 1747, 1723. UV λ_{max}^{EtOH} mμ (ε): 218 (33700), 262.5 (10600). NMR ($CDCl_3$, 60 Mc) δppm: 3.85 (6H, s), 3.99 (3H, s), 5.60 (2H, s), 7.39 (1H, s), 7.3 (5H, m). *Anal.* Calcd. for $C_{17}H_{17}O_6N$: C, 61.63; H, 5.17; N, 4.23. Found: C, 61.92; H, 5.01; N, 4.30.

Further elution of the chromatographic column gave an unidentified resinous mixture.

1-Benzyl-3,5-bis(methoxycarbonyl)-4-(*p*-methoxyphenylcarbamoyl)-2-pyrroline (20) and Its Isomer (21)——A mixture of 430 mg of the cycloadduct II (**17**), 300 mg of NaOH, 8 ml of dioxane, and 8 ml of H_2O was stirred for 2 hr at room temperature. The cooled mixture was acidified with dil. HCl and extracted twice with $CHCl_3$. The extract was dried (Na_2SO_4) and evaporated *in vacuo*. The residue was dissolved in 10 ml of ether and excess amount of CH_2N_2 etheral solution was added. Evaporation of the solvent gave 411 mg of a syrup which was chromatographed over 5 g of silica gel. Removal of the solvent from fractions eluted with benzene and 5% (v/v) ether–benzene gave 287 mg (71% from **17**) of **20** as a colorless syrup. IR $\nu_{max}^{liq.}$ cm^{-1}: 3300, 1750, 1688, 1652, 1552. UV λ_{max}^{EtOH} mμ (ε): 252.5 (16600), 304 (15900). NMR ($CDCl_3$, 60 Mc) δ ppm: 3.70 (3H, s), 3.75 (3H, s), 3.78 (3H, s), 4.23 (1H, br. d, J=5 cps), 4.52 (2H, br. s), 5.30 (1H, d, J=5 cps), 7.13 (1H, br. s), 7.17 (4H, AA'BB'-pattern), 7.35 (5H, m), 9.80 (1H, br.).

Further elution of the chromatographic column with 5% (v/v) MeOH–benzene and evaporation of the solvent gave 97 mg of crude **21** as a colorless syrup. Analytically pure samples of **20** and **21** were not obtained.

1-Benzyl-2,4-bis(methoxycarbonyl)-3-(*p*-methoxyphenylcarbamoyl)pyrrole (22)——A mixture of 230 mg of **20**, 300 mg of SeO_2, and 5 ml of dioxane was refluxed for 3 hr with stirring. The cooled mixture was diluted with H_2O and extracted twice with benzene. After drying, the extract was evaporated to dryness *in vacuo* and left a red syrup which crystallized on digestion with MeOH. Recrystallization of the collected crystals (186 mg), mp 126—127.5°, from MeOH gave **22** as prisms of mp 129—130.5°. IR ν_{max}^{Nujol} cm^{-1}: 3350, 1708, 1671, 1543. UV λ_{max}^{EtOH} 248 mμ (ε 23500). NMR ($CDCl_3$, 60 Mc) δppm: 3.79 (9H, s), 5.37 (2H, s), 7.24 (4H, AA'BB'-pattern), 7.3 (5H, m), 7.39 (1H, s). *Anal.* Calcd. for $C_{23}H_{22}O_6N_2$: C, 65.39; H, 5.25; N, 6.63. Found: C, 65.27; H, 5.26; N, 6.55.

1-Benzyl-3-methoxycarbonyl-4-(*p*-methoxyphenylcarbamoyl)pyrrole (28), 1-Benzyl-4-methoxycarbonyl-3-(*p*-methoxyphenylcarbamoyl)pyrrole-2-carboxylic Acid (29), and 1-Benzyl-4-methoxycarbonyl-2-(*p*-methoxyphenylcarbamoyl)pyrrole-3-carboxylic Acid (30)——A mixture of 500 mg of the cycloadduct II (**17**), 350 mg of NaOH, 9 ml of dioxane, and 9 ml of H_2O was stirred for 2 hr at room temperature. The mixture was acidified with dil. HCl and extracted twice with $CHCl_3$. The extract was dried and evaporated *in vacuo*. The residue (527 mg) was dissolved in 5 ml of dioxane and 0.5 g of SeO_2 was added. The resulting mixture was warmed on a steam bath for 2 hr. The cooled mixture was diluted with H_2O and extracted with benzene. The extract was washed with dil. Na_2CO_3 solution. The organic layer was evaporated *in vacuo* after drying and the residue (264 mg) was recrystallized from MeOH, yielding 181 mg (45% from **17**) of **28** as plates of mp 147—148°. IR ν_{max}^{Nujol} cm^{-1}: 3250 (br.), 3130, 3040, 1689, 1660, 1612, 1564. UV λ_{max}^{EtOH} mμ (ε): 243.5 (19800), 287.5 (16600). NMR ($CDCl_3$, 60 Mc) δppm: 3.77 (3H, s), 3.83 (3H, s), 5.02 (2H, s), 6.8—7.9 (11H, m), 11.73 (1H, br.). *Anal.* Calcd. for $C_{21}H_{20}O_4N_2$: C, 69.21; H, 5.53; N, 7.69. Found: C, 69.22; H, 5.64; N, 7.60.

The aqueous layer left after the extraction of **28** was acidified with dil. HCl and extracted twice with $CHCl_3$. Drying (Na_2SO_4) and evaporation of the solvent from the extract gave 160 mg of a semi-crystalline mass, which was washed with a small amount of MeOH–ether, leaving 57 mg of crude **29** as powder. Recrystallization from dioxane–benzene gave 28 mg of pure **29** as fine needles, mp 213.5—214.5°. IR ν_{max}^{Nujol} cm^{-1}: 1695, 1655, 1579. UV λ_{end}^{EtOH} 220 mμ (ε 33900). *Anal.* Calcd. for $C_{22}H_{20}O_6N_2$: C, 64.70; H, 4.94; N, 6.86. Found: C, 64.19; H, 4.92; N, 6.84.

Treatment of **29** with CH_2N_2 afforded **22**, mp 129—130.5°, which was identified with the sample obtained as above by IR and mixed mp.

The combined washings and the mother liquor of the recrystallization of **29** was concentrated *in vacuo* and the crystalline residue was washed with cold ether, leaving 31 mg of crystals, mp 175.5—179°, which was recrystallized from benzene–MeOH to **30** as needles, mp 181.5—182°. IR ν_{max}^{Nujol} cm^{-1}: 3300, 3130, 2680, 1735. NMR ($CDCl_3$, 60 Mc) δppm: 3.79 (3H, s), 3.92 (3H, s), 5.63 (2H, s), 7.53 (1H, s), 7.20 (4H, AA'BB'-pattern), 7.31 (5H, br. s), 11.30 (1H, br.), 14.5 (1H, br.). *Anal.* Calcd. for $C_{22}H_{20}O_6N_2$: C, 64.70; H, 4.94; N, 6.86. Found: C, 64.50; H, 4.93; N, 6.74.

Treatment of **30** with CH_2N_2 afforded **11**, mp 152—153°, which was identified with the sample obtained as above by IR and mixed mp.

1-Benzyl-3-methoxycarbonyl-5-(*p*-methoxyphenylcarbamoyl)-1,4,5,6-tetrahydropyrrolo[3,4-*b*]pyrrole-4,6-dione (31)——A mixture of 28 mg of **29**, 20 mg of AcONa and 150 mg of Ac_2O was warmed on a steam bath for 30 min. The cooled mixture was diluted with H_2O, the resulting crystalline mass was collected, and

washed with H_2O and MeOH. Recrystallization of the crystals (20 mg) thus obtained from $CHCl_3$–MeOH afforded 17 mg of **31** as pale yellow needles, mp 186—187°. IR ν_{max}^{Nujol} cm^{-1}: 1778, 1725 (sh.), 1718. UV λ_{end}^{EtOH} 220 mμ (ε 25500). *Anal.* Calcd. for $C_{22}H_{28}O_5N_2$: C, 67.68; H, 4.65; N, 7.18. Found: C, 67.33; H, 4.75; N, 7.33.

Working up described above, treatment of **30** with Ac_2O also yielded **31**. These samples were identical by IR and mixed mp.

1:1-Adduct (33) Obtained from the Cycloadduct III (34) and Tetracyanoethylene——A solution of 130 mg of **34** and 55 mg of tetracyanoethylene in 2 ml of dioxane was refluxed with stirring for 3—4 hr and the adduct (**33**) precipitated out. After further refluxing for 6 hr, the crystals were collected and washed with $CHCl_3$–hexane, giving 70 mg of **33** as leaflets, mp 262—264°. The sample was not easily soluble in organic solvent and analytically pure sample could not be obtained. IR ν_{max}^{Nujol} cm^{-1}: 1745, 1700. Mass spectrum (75 eV) *m/e*: 578 (M^+), 546, 450, 359, 273, 242, 210, 134, 128, 91 (base peak), 76.

Cycloaddition Reaction of the Cycloadduct III (34) with Dimethyl Acetylenedicarboxylate (3) to the Cycloadduct IV (38)——A solution of 50 mg of **34** and 100 mg of **3** in 0.5 ml of dioxane was refluxed for 10 hr. After evaporation of the solvent and excess of **3** *in vacuo*, the residue was chromatographed on 4 g of silica gel. Elution with benzene–ether (2:1, v/v) and removal of the solvent from the fractions gave 65 mg of a crystalline mass which was recrystallized from MeOH to yield 22 mg (33%) of **38**, mp 257—265°. Further recrystallization from $CHCl_3$–MeOH gave pure **38** as fine prisms, mp 265—269°, which was identified with the sample obtained as above by mixed mp, IR, and mass spectrometry.

Ratio of the Cycloadducts during the Reaction of 8 and 3, and Photochemical Interconversion of these Cycloadducts——A solution of 165 mg of **8** and 152 mg of **3** in 5 ml of dioxane was irradiated in a Vycor tube. After evaporation of the solvent *in vacuo*, the residue was chromatographed on 8 g of silica gel. Elution with 10:1 (v/v) benzene–ether, evaporation of the solvent from these fractions, and recrystallization of the residue from benzene–hexane gave a mixture of unchanged **8** and the cycloadduct I (**9**). Removal of the solvent from fractions eluted with 3:1 (v/v) benzene–ether and recrystallization of the residue from MeOH gave a mixture of the cycloadduct II (**17**) and III (**34**). Relative ratio of these products was determined by NMR spectra of these mixture thereby obtained in $CDCl_3$ and at 60 Mc, in comparison with that of the corresponding standard mixtures prepared from the pure samples. As key absorptions for this determination, 3.09 ppm (2H, s, $-\underline{N}-C\underline{H}_2-C_6H_5$) for **8**, 4.65 ppm (2H, s, $-\underline{N}-C\underline{H}_2-C_6H_5$) for the cycloadduct I, 3.80 ppm (3H, s, $C\underline{H}_3O-$) for the cycloadduct II, and 3.73 ppm (3H, s, $C\underline{H}_3O-$) for the cycloadduct III were available. The results were shown in Table I.

A solution of 100 mg of each cycloadduct in 5 ml of dioxane was irradiated in a Vycor tube. Relative ratio of products was also determined by NMR spectra of mixtures obtained by chromatography in the same manner as described above. The results are shown in Table II.

Moreover, in these experiments, the same result was obtained either in N_2 atmosphere or in air.

Irradiation of the Cycloadduct I (9) in the Presence of Benzophenone——A solution of 100 mg of the cycloadduct I and 137 mg of benzophenone in 5 ml of dioxane in a Vycor tube was irradiated with a high-pressure mercury lamp (450 W) through a Pyrex filter for 3 hr. The reaction product was chromatographed on 10 g of silica gel. After elution with 9:1 (v/v) benzene–ether and evaporation of some product (128 mg) arising from benzophenone, elution with 3:1 (v/v) benzene–ether and evaporation of the solvent from fractions thus obtained afforded 43 mg of crystalline mass which was recrystallized from MeOH, yielding 23 mg of a 1:1-adduct (**40**) of the cycloadduct I and dioxane, mp 208—209°. IR ν_{max}^{Nujol} cm^{-1}: 1741, 1701. NMR ($CDCl_3$, 100 Mc) δppm: 3.72 (6H, s), 3.81 (3H, s), 3.3—4.6 (12H, m), 6.97 (4H, s), 7.35 (5H, br. s). Mass spectrum (75 eV) *m/e*: 538 (M^+), 510, 452, 423, 361, 274, 242, 216, 170, 91 (base peak).

Cycloaddition Reaction of 8 with 3 in Dichloroethane——As described earlier, a mixture of 2 g of **8**, 3 g of **3**, and 150 ml of freshly-distilled dichloroethane was irradiated with a high-pressure mercury lamp (550 W) for 2 hr. After filtration of an unidentified solid (319 mg) containing halogen, mp 185° (decomp.), the mixture was evaporated to dryness *in vacuo*. The residue (6.7 g) was chromatographed on 30 g of silica gel. Evaporation of the solvent from fractions eluted with benzene afforded 1.37 g of a syrup containing the unchanged **3** and from fractions further eluted with the same solvent, 180 mg of a crystalline mass, from which 29 mg of dimethyl fumarate, mp 102.5—103.5°, was isolated by recrystallization from EtOH. Evaporation of the solvent from fractions eluted with 5% (v/v) ether–benzene gave 440 mg of a syrup, from which 70 mg (2.4%) of the cycloadduct I, mp 122—123.5°, was isolated, and fractions eluted with 50% ether–benzene gave 700 mg of a syrup from which 252 mg (8.6%) of the cycloadduct II, mp159—160°, was obtained.

Attempted Thermal Cycloaddition Reaction of 8 with 3——A mixture of 617 mg of **8** and 852 mg of **3** was heated at 100° for 3 hr in N_2 atmosphere with stirring. The resulting brown oil was dissolved in 2.5 ml of EtOH and stood with cooling, yielding 215 mg of unchanged **8**. After filtration of **8**, the mixture was evaporated *in vacuo* and the residue was chromatographed on 10 g of silica gel. After elution of the unchanged **3** with benzene, elution with 20:1 (v/v) benzene–ether and evaporation of the solvent from the fractions gave a syrup from which 33 mg of the unchanged **8** was further isolated. Further elution with 4:1 (v/v) benzene–ether (200 ml) followed by evaporation of the solvent gave 270 mg of a crystalline syrup,

whose recrystallization from AcOEt gave 124 mg of needles, mp 179—181° (decomp.). IR ν_{max}^{Nujol} cm^{-1}: 3180, 1720 (br.), 1675. UV λ_{max}^{EtOH} $m\mu$ (ε): 256.5 (16700), 307 (8300). NMR ($CDCl_3$, 60 Mc) δ ppm: 3.58 (3H, s), 3.74 (3H, s), 3.82 (3H, s), 4.7—7.8 (12—13H, complex absorption), 8.8 (1H, br.). *Anal.* Calcd. for $C_{24}H_{22}O_7N_2$: C, 63.99; H, 4.92; N, 6.22. Found: C, 63.91; H, 5.09; N, 6.35.

The 1:1-adduct (200 mg) thereby obtained was dissolved in 2 ml of pyridine, and 100 mg of Ac_2O was added. The mixture was stood for 1.5 hr at room temperature and poured into ice–water. The solution was extracted with benzene and evaporation of the solvent from the extract yielded a syrup which was chromatographed on 5 g of silica gel. After elution of some impurity (50 mg) with 20:1 (v/v) benzene–ether, elution with 4:1 (v/v) benzene–ether (150 ml) and evaporation of the solvent from these fractions gave a viscous syrup which crystallized on standing overnight. The crystals were collected and recrystallized from MeOH–ether, giving 80 mg of an acetate as prisms, mp 180—185° (decomp.). IR ν_{max}^{Nujol} cm^{-1}: 3190, 1772, 1733 (sh.), 1712. UV λ_{max}^{EtOH} $m\mu$ (ε): 253 (13100), 290 (8500, sh.). NMR ($CDCl_3$, 60 Mc) δppm: 1.4—2.4 (3H, br. s), 3.65 (3H, s), 3.79 (6H, s), 4.5—7.6 (11—12H, complex absorption), 10.18 (1H, br. s). *Anal.* Calcd. for $C_{26}H_{24}O_8N_2$: C, 63.41; H, 4.91; N, 5.69. Found: C, 63.53; H, 4.90; N, 5.72.

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