CO_2CH_3), 6.3–7.55 (m, 4, aromatic); mass spectrum, *m/e* 313 (M^+, 5), 171 (100, base peak); UV (λ_{max}, nm (log ϵ), 95% EtOH) 249 (3.68), 304 (3.18), 438 (2.88).

(d) 10,11-Bis(methoxycarbonyl)-7-methyl-8,9-benzo-7-azatricyclo[4.3.2.0]undeca-8,10-diene (VIId). Sensitized irradiation of 1.50 g (8.11×10^{-3} M) of Id and 2.50 g (1.76×10^{-2} M) of DMAD gives 1.78 g (5.44×10^{-3} mol) of VIId (82% yield, based on recovered starting material).

VIId: blood-red liquid: ^1H NMR (δ, $CDCl_3$) 1.28–2.66 (m, 8, C(2)–C(5)H_2), 2.96 (s, 3, N–CH_3), 3.87 (s, 6, C(10)– and C(11)–CO_2CH_3), 6.35–7.45 (m, 4, aromatic); UV (λ_{max}, nm, 95% EtOH) 250, 302, 432.

(e) 5-*tert*-Butyl-6,7-bis(methoxycarbonyl)-2-methyl-3,4-benzo-2-azabicyclo[3.2.0]hepta-3,6-diene (VIIe). Sensitized irradiation of 1.50 g (8.02×10^{-3} M) of Ie and 2.50 g (1.76×10^{-2} M) of DMAD gives 1.32 g (4.01×10^{-3} mol) of VIIe (77% yield, based on recovered starting materials).

VIIe: red liquid; ^1H NMR (δ, $CDCl_3$) 1.11 (s, 9 C(5)-*tert*-butyl), 3.02 (s, 3, N–CH_3), 3.79, 3.83 (s, 6, C(6)– and C(7)–CO_2CH_3), 4.52 (s, 1, C(1)–H), 6.4–7.6 (m, 4, aromatic); mass spectrum, *m/e* 329 (M^+, base peak), 187 (90); UV (λ_{max}, nm (log ϵ), 95% EtOH) 252 (3.62), 295 (3.21), 411 (2.81).

(f) 2,5-Di-*tert*-butyl-6,7-bis(methoxycarbonyl)-3,4-benzo-2-azabicyclo[3.2.0]hepta-3,6-diene (VIIf). Sensitized irradiation of 1.50 g (6.55×10^{-3} M) of If and 2.50 g (1.76×10^{-2} M) of DMAD gives 480 mg of a mixture containing 75% VIIf (15% yield, not based on recovered starting material).

VIIf: deep orange liquid; ^1H NMR (δ, $CDCl_3$) 1.08 (s, 9, C-(5)-*tert*-butyl), 1.50 (s, 9, *N*-*tert*-butyl), 3.80 (s, 6, C(6)– and C(7)–CO_2CH_3), 4.88 (s, 1, C(1)–H, 6.3–7.5 (m, ?, aromatic); UV (λ_{max}, nm) 408 (CT absorption).

Photochemical Ring Closure of Some Substituted 3,4-Bis(methoxycarbonyl)-1-methyl-6,7-benz-1-azepines. (a) IIa $\xrightarrow{h\nu}$ VIIa. Under the direct irradiation of 1.10 g (4.02×10^{-3} M) of IIa, ^1H NMR indicates a 30% conversion to VIIa, and 205 mg (18%) of Va is isolated by preparative TLC. The temperature is carefully kept below 15 °C at *all* times during workup and isolation. The original crude reaction mixture contains not less than 5% (by NMR) Ia (TLC corroborates this observation).

(b) IIb $\xrightarrow{h\nu}$ VIIb. Direct irradiation of 300 mg of IIb (1.05×10^{-3} M) for 9 h indicates a 45% conversion to VIIb by NMR. VIIb (126 mg, 42%) is isolated by preparative TLC (10% ether–petroleum ether, three elutions). Less than 5% cycloreversion to Ib can be detected by NMR (and TLC).

Diimide Reduction of VIIc to *exo*-and *endo*-9,10-Bis(methoxycarbonyl)-2-methyl-3,4-benzo-2-azatricyclo[3.3.2.0]deca-3-ene (*exo*- and *endo*-X). To 10 mL of tetrahydrofuran containing 0.500 g (1.16 mol) of the red VIIc are added 3.10 mL (64 mmol) of hydrazine hydrate (97%), 6 drops of saturated copper sulfate solution, and 6 drops of glacial acetic acid; this solution is added dropwise to a solution of 1.71 g of sodium metaperiodate in 16 mL of water (2.5 h).[20] The reaction mixture is added to 50 mL of water and extracted 3 × 25 mL with ether, and the ether extracts are dried over $MgSO_4$ and removed at reduced pressure, leaving a pale yellow residual oil. Preparative TLC of the reaction mixture (20% ether–petroleum ether) indicates the presence of at least four distinct bands, two with relatively large R_f values. The first gives 50 mg of Id, 1-methyl-2,3-trimethyleneindole, followed by 120 mg of a colorless oil, a mixture of *exo*- and *endo*-VIId-red: ^1H NMR (δ, $CDCl_3$) 1.60 (d, 1), 1.5–2.5 (m, 6), 2.73, 2.78 (s, 3), 3.59, 3.66, 3.72 (s, 6) 6.22–7.54 (m, 5); mass spectrum, *m/e* 315 (M^+, 7), 171 (100, base peak); UV (λ_{max}, nm, 95% EtOH) 235, 255, 290. By NMR the mixture contains 50% of each isomer, exo and endo. The slow moving bands are not fully characterized, but they have molecular ions at *m/e* 385 in the mass spectrum and puzzling and complicated NMR spectra.

Photochemical Ring Opening of 2-Acetyl-6-(methoxycarbonyl)-5-piperidino-3,4-benzo-2-azabicyclo[3.2.0]hepta-3,6-diene. 2-Acetyl-6-(methoxycarbonyl)-5-piperidino-3,4-benzo-2-azabicyclo[3.2.0]hepta-3,6-diene is prepared by the procedure of Lin and Snieckus,[15] but it cannot be triturated, and it required preparative TLC separation from the thermally ring-opened product prior to purification. The bicycloheptadiene (115 mg) is irradiated in 6 mL of benzene solution for 4 days at 10 °C (no thermal ring is observed in the dark experiment). ^1H NMR shows a quantitative conversion to 1-acetyl-4-(methoxycarbonyl)-5-piperidino-6,7-benzo-1-azepine.

Acknowledgment. This work was supported by the National Institutes of Health (1-TO1 NS 14883-01) and the Petroleum Research Fund, administered by the American Chemical Society. The authors are grateful for these funds. Fruitful discussions with Drs. Roger Card and A. H. A. Tinnemans, as well as with Professors J. C. Dalton and T. H. Kinstle, are also acknowledged.

Registry No. Ia, 603-76-9; Ib, 875-79-6; Ic, 52751-31-2; Id, 6303-88-4; Ie, 46270-99-9; If, 28864-80-4; IIa, 34132-46-2; IIb, 69496-54-4; IV, 27150-56-7; VIIa, 69496-49-7; VIIb, 69496-50-0; VIIc, 69594-36-1; VIId, 69594-37-2; VIIe, 69496-52-2; VIIf, 69496-53-3; *endo*-X, 72121-26-7; *exo*-X, 72151-26-9; indole, 120-72-9; 2-methylindole, 95-20-5; 3-*tert*-butylindole, 19013-51-5; 2,3-trimethyleneindole, 2047-91-8; 6,7,8,9-tetrahydro-9*H*-carbazole, 942-01-8; DMAD, 762-42-5; 1-acetyl-4-(methoxycarbonyl)-5-piperidino-6,7-benzo-1-azepine, 27150-47-6.

Photocycloaddition of Dimethyl Acetylenedicarboxylate to 1,3-Dimethylindole

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Received October 5, 1979

In contrast to the clean photoaddition of activated indoles to dimethyl acetylenedicarboxylate (DMAD) reported in the previous paper,[1] the reaction of 1,3-dimethylindole produces seven different products. In this paper the structures of these seven products are reported, and mechanistic considerations of the photocycloaddition of dimethyl acetylenedicarboxylate to activated indoles are discussed.

Background

In addition to the predominant (2 + 2) reaction of DMAD with a variety of activated indoles,[1] we have identified six other products, several of which present interesting structure elucidation problems from reaction of 1,3-dimethylindole with DMAD. In this paper we discuss the reaction of 1,3-dimethylindole with DMAD, the products formed, and the mechanistic information the reaction provides about the photochemical reaction of

(1) Davis, P. D.; Neckers, D. C. *J. Org. Chem.*, preceeding paper in this issue.

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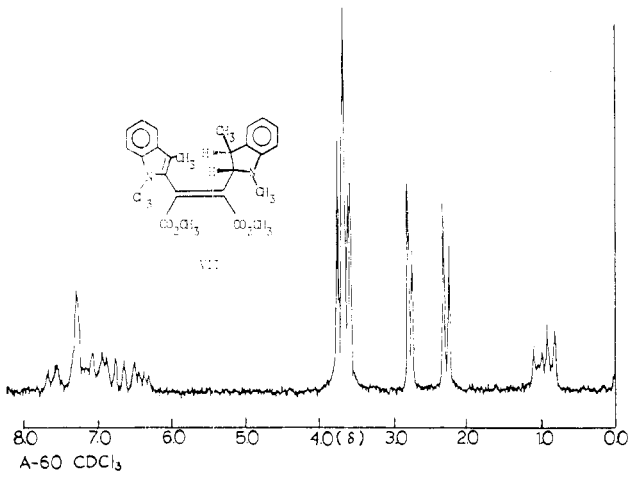


Figure 1. The ^1H NMR spectrum of dimethyl 2-(1,3-dimethylindol-2-yl)-3-(*trans*-2,3-dihydro-1,3-dimethylindol-2-yl)-maleate (VII) in $CDCl_3$.

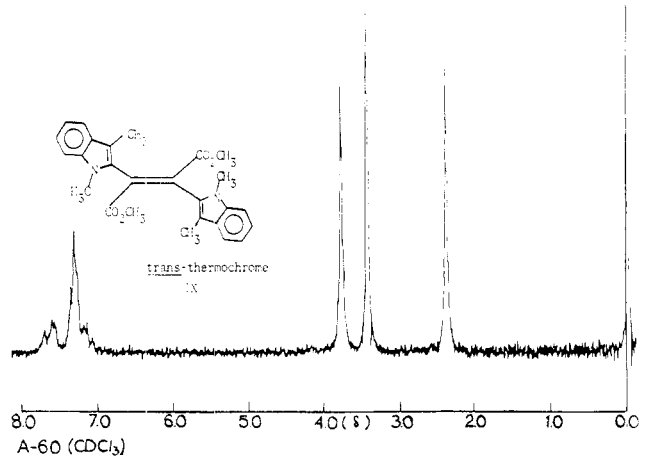
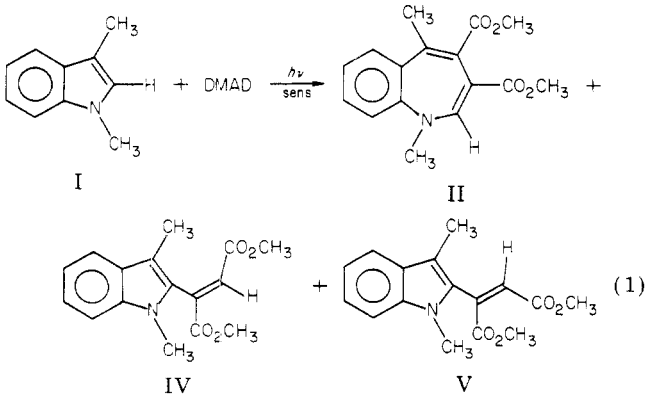


Figure 2. The ^1H NMR spectrum of dimethyl 2,3-bis(1,3-dimethylindol-2-yl)fumarate (IX).

activated indoles with acetylene esters.

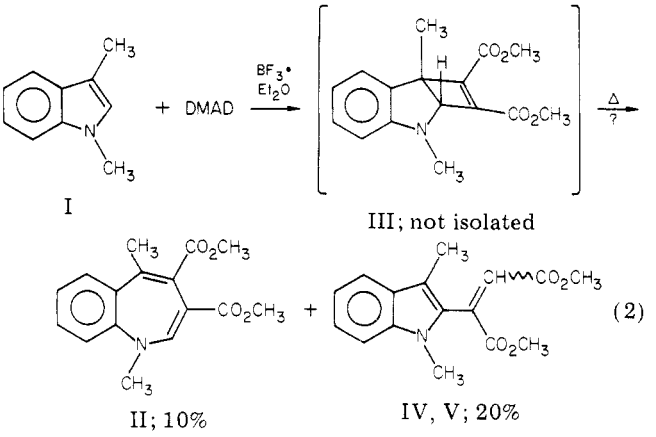
Results

1,3-Dimethylindole (I) was irradiated with DMAD in different solvents as previously reported.[1] Immediately identified were the benzazepine (II) and the previously known fumarate (IV) and maleate (V) esters (eq 1).[2]



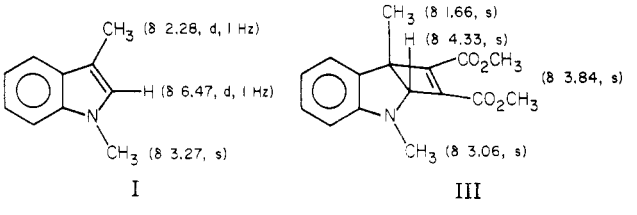
(1)

That the cyclobutene III was also present in the reaction mixture and that it was the precursor to II were shown as follows: Fried, Taylor, and Westwood[3] had reported that in the BF_3-Et_2O catalyzed reaction of I and DMAD a thermally unstable intermediate, suggested to be 6,7-bis(methoxycarbonyl)-2,5-dimethyl-3,4-benzo-2-azabicyclo[3.2.0]hepta-3,6-diene (III), was detected in a three-component mixture. When the reaction mixture was heated, the unstable intermediate gave the benzazepine II. Other components remained unchanged; "*however, attempts to isolate the cyclobutene were unsuccessful*".[3] This is summarized in eq 2.

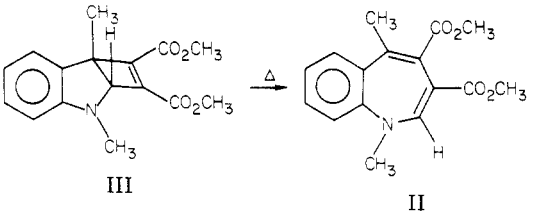


(2)

When this reaction was repeated, the temperature was carefully controlled (<15 °C) throughout, and a red product having a larger R_f value than that of either IV or V and identified as the cyclobutene (III) was isolated. Heating the crude reaction mixture shows that III is converted to benzazepine II. The chemical shifts of starting material and cyclobutene are compared below:



The expected upfield chemical shifts of the *N*-methyl, C(3)-methyl and C(2)-H absorptions are observed, with the latter two absorptions no longer coupled in III. An unexpected thermal lability is demonstrated by III, it being smoothly converted to II at 58 °C (eq 3) with a $\tau_{1/2}$ of 1 h.



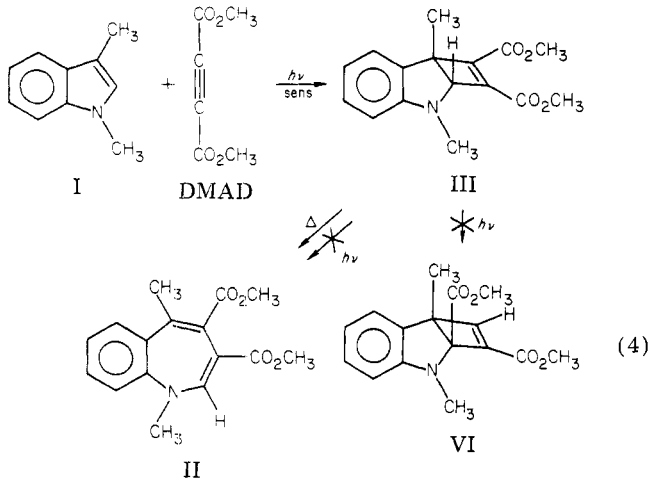
(3)

In the photochemical reaction of I + DMAD under normal conditions, i.e., slight excess of indole, formation of III is accompanied by the formation of six other products. When a twofold excess of DMAD is used, however, and the temperature held at 10 °C, III predominates and no II is formed, though II rather than III is isolated when the reaction is carried out at ambient temperature. *This suggests that the primary photochemical process in the addition of 1,3-dimethylindole to DMAD is the formation*

(2) Acheson, R. M.; Bridson, J. N.; Cameron, T. S. *J. Chem. Soc., Perkin Trans. 1* **1972**, 968.

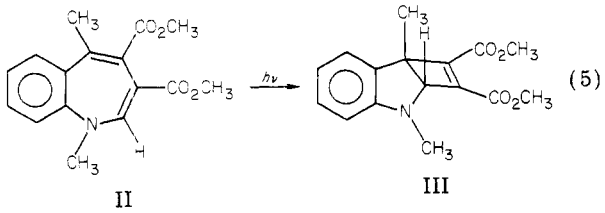
(3) Fried, F.; Taylor, J. B.; Westwood, R. *J. Chem. Soc. D* **1971**, 1226.
(4) Johnson, D. C. Ph.D. Thesis, University of Minnesota *Diss. Abstr.* **1962**, *23*, 834.

of the (2 + 2) cycloadduct followed by a thermal, not photochemical, ring opening. An allylic rearrangement to VI is not an observed secondary photochemical process (eq 4).[1]



I DMAD III II VI (4)

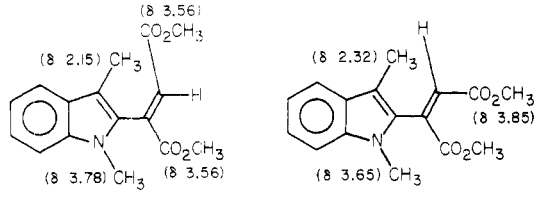
General [2 + 2] Photocycloaddition: Physical and Chemical Characteristics. Photocyclization of the benzazepine II to the cyclobutene III is also observed (eq 5).[1] When II is photolyzed in benzene at 10 °C, the yield



II III (5)

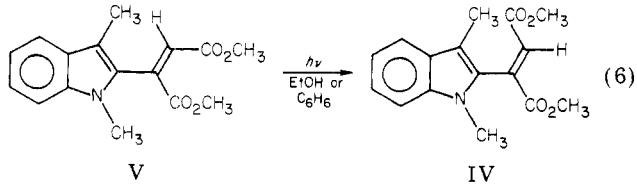
of III is 71%. If temperature is controlled, the cyclobutene (III) and not the benzazepine (II) is the primary photochemical product.

The relative yields of IV and V depend on the irradiation



IV V

time. Only at irradiation times of less than 24 h can V be detected, and at times of less than 2 h V is the predominant product (60–70% vs. IV). Independent direct irradiation of V in benzene or 95% ethanol shows that the photostationary state favors IV by greater than 98% (eq 6).



V IV (6)

Structural analysis of the remaining four products indicates all are 2:1 adducts of 1,3-dimethylindole to DMAD. Using excess 1,3-dimethylindole with DMAD, VII, which melts sharply at 195–196 °C, is the major product. Its UV spectrum is similar to that of the maleate and fumarate substitution products, and its mass spectrum indicates a molecular ion (M^+) at m/e 432. Chemical analysis confirms the molecular formula, $C_{26}H_{28}N_2O_4$.

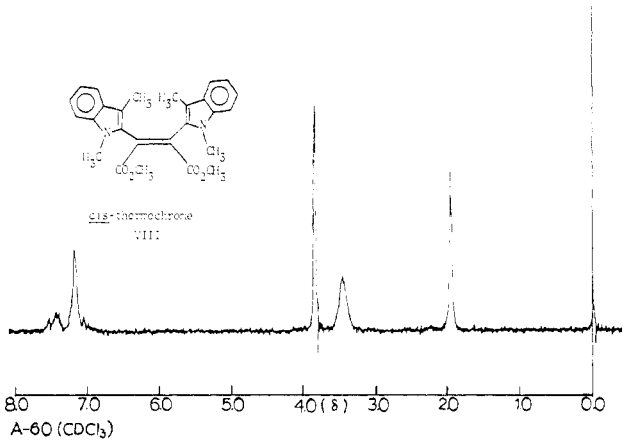
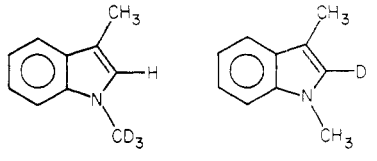


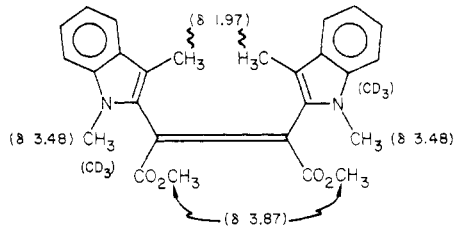
Figure 3. The ^1H NMR spectrum of dimethyl 2,3-bis(1,3-dimethylindol-2-yl)maleate (VIII).

The ^1H NMR spectrum (Figure 1) suggests at least two isomers in $CDCl_3$. The spectrum is characterized by two three-proton doublets centered at δ 0.90, CH_3–CR_2H; two three-proton singlets at δ 2.3, the approximate chemical shift of the C(3)–methyl in 1,3-dimethylindole; two three-proton singlets at δ 2.8, a chemical shift similar to that of most indoline *N*-methyls; and a series of singlets between δ 3.6 and 4.0 (11 H). In benzene-d_6, solvent effects allow the observation of six three-proton singlets and a two-proton multiplet. The aromatic region integrates as eight protons. Assignments of the N–CH_3 and C(2)–H from I in the product were made by carrying out the irradiation with I-d_3 and I-*d* (see Experimental Section) under similar conditions. (The NMR spectra of IX and VIII are given in Figures 2 and 3.)

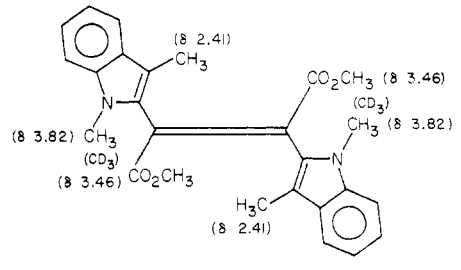


I-d_3 I-*d*

VII-d_6 from the irradiation of I-d_3 contained two N–CD_3's, and its NMR spectrum was identical with that of VII except for the absence of singlets centered at δ 2.8 and two singlets in the low field region at δ 3.25 and 3.38 (C_6D_6). This suggests the presence of both indole and indoline type N–CH_3 moieties in VII.



VIII, *cis*-thermochrome



IX, *trans*-thermochrome

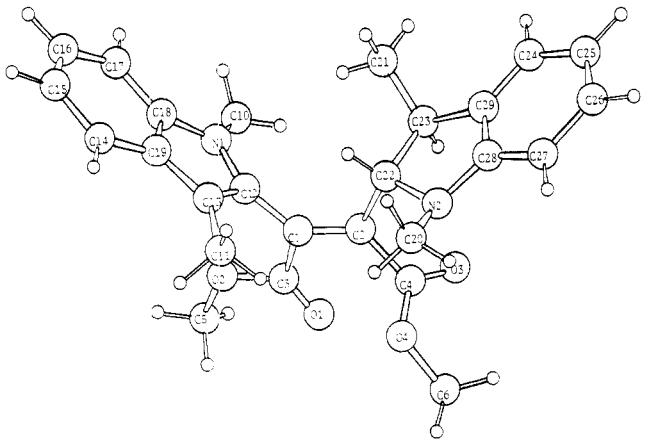
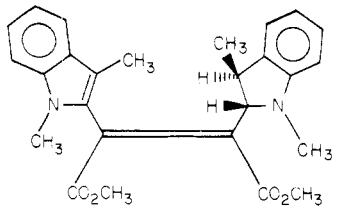


Figure 4. X-ray crystal structure of dimethyl 2-(1,3-dimethylindol-2-yl)-3-(2,3-*trans*-dihydro-1,3-dimethylindol-2-yl)maleate (VII).

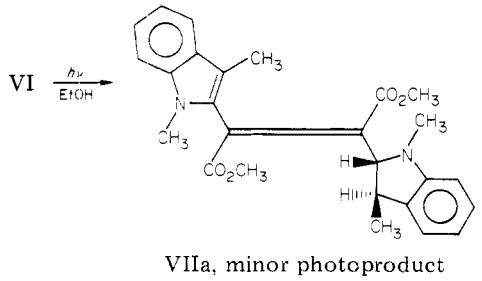
If the stereochemical assignment of the double bond in VIII is correct, then this suggests that olefinic stereochemistry of the 2:1 dimethylindole adduct, VII, must also be cis. X-ray analysis confirmed this assignment and further shows that the major product of the reaction of 1,3-dimethylindole with DMAD is dimethyl 2-(1,3-dimethylindol-2-yl)-3-(2,3-*trans*-dihydro-1,3-dimethylindole-2-yl)maleate (Figure 4).



VII

Understanding of the ^{1}H NMR data for VII is possible if one considers the existence of rotational isomers which interconvert slowly on the NMR time scale. This is confirmed at variable high-temperature NMR; thus, raising the temperature of Me_2SO-d_6 solution containing the 2:1 adduct, VII, showed the expected coalescence of all but the highest field absorptions ($\delta > 2.3$), which approach coalescence at the highest temperature studied, 187 °C. (See Experimental Section for spectral details.) The free energy of activation for rotation is calculated to be between 26.0 and 26.2 kcal/mol.

A minor component of the original reaction was the isomer VIIa, with trans stereochemistry about the double bond. VII undergoes more extensive cis–trans photoisomerization in 95% EtOH (eq 7).



(7)

VIIa, minor photoproduct

To prove that products VII and IX are not secondary photoproducts, III and IV were individually irradiated in the presence of I (direct and sensitized). In each case no reaction was observed.

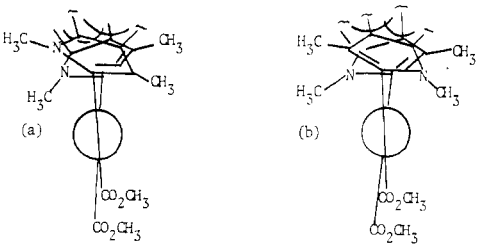
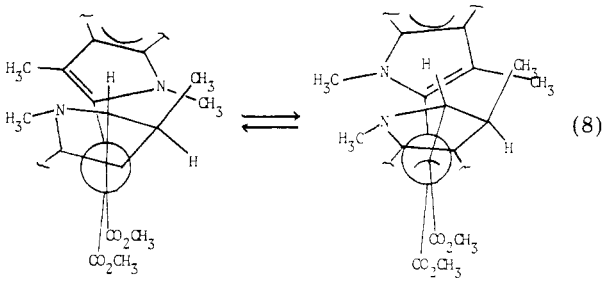


Figure 5. Potential rotational conformers for VIII.

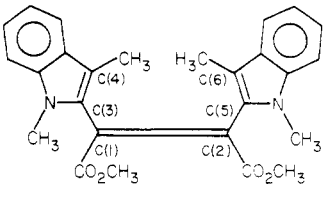
Conformational Analysis of VII. Variable high-temperature ^{1}H NMR has shown the presence of detectable rotational isomerism in VII. Integration of the resolved doublets at high field, δ 0.85, in benzene-d_6 suggests the presence of two approximately equally populated conformations. The situation appears to be somewhat more complex in $CDCl_3$ and Me_2SO-d_6. The X-ray analysis suggests but one of the stable conformers. We suggest that the other rotamer has the indolyl substituent rotated approximately as shown in eq 8. Alternative rotation of the



(8)

indolinyl substituent places its aromatic ring in too close proximity to the pyrrole portion of the indolyl substituent to be favored, a deduction drawn from molecular models. Calculations based on k_c and T_c provide a value of $\Delta G^{\ddagger}$ = 26.1 kcal/mol as the barrier to rotation in Me_2SO-d_6.

A relatively high barrier to rotation is implicated in the *cis*-thermochrome, VIII. Its stable conformer can be distinguished on the NMR time scale at room temperature in Me_2SO-d_6; however, the coalescence temperature in $CDCl_3$, the solvent in which the spectrum of VIII was initially taken, is well below the ambient probe temperature. In Me_2SO-d_6 the free energy of activation for the rotational process is calculated to be 16.6 kcal/mol.



VIII

Using the numbering scheme shown above for VIII, conformations which contain the torsional angles ∠C(4)–C(3)–C(1)–C(2)–∠C(1)–C(2)–C(5)–C(6), 0°–0°, shown for IX above, and ∠C(4)–C(3)–C(1)–C(2)–∠C(1)–C(2)–C(5)–C(6), 0°–180°, seem unlikely since molecular models indicate that the C(4)–CH_3 and C(6)–CH_3, and C(4)–CH_3 and N–CH_3 substituent positions, respectively, would lead to overlap of the various atoms, an energetically unlikely situation.

The low-temperature ^{1}H NMR spectra of VIII indicate the presence of one stable conformer, in which the four C–CH_3's and N–CH_3's are nonequivalent. This would be the case in conformers such as VIIIa (not VIIIb) in Figure 5 or if the torsion angles are close to ∠C(4)–C(3)–C(1)–C-

(2)-∠C(1)-C(2)-C(5)-C(6), 0-180°. The reasons for this particular conformational preference are not clear.

A summary of the photoproducts derived from 1,3-dimethylindole and DMAD appears in Chart I.

Mechanistic Considerations. Potential mechanisms explaining the complex reaction of 1,3-dimethylindole with DMAD and by analogy the reaction of other activated indoles with DMAD are indicated in Scheme I. The mechanism is supported by a number of previous results for the cycloadditions of multiple bonds.

Scheme I

$$^3\text{indole}^* + \text{DMAD} \rightarrow {}^3\text{exciplex}^* \quad \text{(i)}$$

$$^3\text{indole}^* + \text{DMAD} \rightarrow \text{indole}^{+\cdot} - \text{DMAD}^{-\cdot} \quad \text{(ii)}$$

$$^3\text{exciplex}^* \rightarrow \text{indole}^{+\cdot} - \text{DMAD}^{-\cdot} \quad \text{(iii)}$$

$$^3\text{exciplex}^* \rightarrow {}^3\text{1,4-biradical} \quad \text{(iv)}$$

$$^3\text{exciplex}^* \xrightarrow{H^+ \text{ transfer}} \text{diradical} \quad \text{(v)}$$

$$\text{indole}^{+\cdot} - \text{DMAD}^{-\cdot} \rightarrow {}^3\text{1,4-biradical} \quad \text{(vi)}$$

$$\text{indole}^{+\cdot} - \text{DMAD}^{+\cdot} \xrightarrow{H^+ \text{ transfer}} \text{diradical} \quad \text{(vii)}$$

$$^3\text{1,4-biradical} \rightarrow {}^1\text{1,4-biradical} \quad \text{(viii)}$$

$$\text{1,4-biradical} \rightarrow 2 + 2 \text{ cycloadduct} \quad \text{(ix)}$$

$$\text{diradical} \rightarrow \text{substitution products} \quad \text{(x)}$$

In laser photolysis experiments Wilkinson and Garner[5] have shown that quenching of the triplet state of acetophenone by *N*-methylindole gives rise to a short-lived transient absorbing at 460 nm and assigned as the *N*-methylindole triplet. This transient is quenched by naphthalene and oxygen, giving rise to triplet naphthalene and singlet oxygen, respectively. The rate constant for *N*-methylindole quenching of acetophenone is 4.7×10^9 M^{-1} s^{-1}. The first-order rate constant for triplet decay in *N*-methylindole is $5.6 \pm 1 \times 10^5$ s^{-1}. The lifetime is therefore 1.8×10^{-6} s. We assume the triplet energy of DMAD to be greater than 73 kcal/mol, the triplet energy of acetophenone. The photochemical process following population of the acetophenone triplet state is presumably one of energy transfer to the 1,3-dimethylindole triplet. Naphthalene completely quenches the formation of all products.

Lewis[6] used the order of magnitude decrease in efficiency of (2 + 2) adduct formation in going from a relatively nonpolar solvent, benzene, to the polar solvent, acetonitrile, to implicate the presence of a triplet exciplex. This decrease is suggested to be due to an increase in the rate of radical ion formation in Scheme I. Radical ion pair annihilation leads either to back-transfer of electrons or to singlet- or triplet-state excitation. In the present study, the ratio of efficiency for product formation in these respective solvents is 4.05. Our solvent effects are interpreted to suggest the absence of a zwitterion intermediate, where rate differences are expected to be between 2.8×10^3 and 6.5×10^4, favoring the more polar acetonitrile in favor of a biradical intermediate.[7]

Substitution products such as IV and V, observed in photocycloaddition reactions, have been rationalized as occurring via either H^+ transfer in an exciplex in aprotic solvents or exciplex protonation in protic solvents. For example, Saito and co-workers,[8] in the photochemical reaction of acrylonitrile with 1,2-dimethylindole where 3- and 4-substituted products are observed, have rationalized their formation by a similar mechanism. They observe singlet exciplex emission in acetonitrile. McCullough,[9] in his studies of the photocycloaddition of naphthalene and acrylonitrile, observed a solvent dependence on the ratio of cyclobutanes to substituted naphthalenes. He also finds that if methanol-*O*-*d* or deuterium acetate is used as a solvent, the substitution products contain one deuterium atom in the methyl group. It is not clear whether all of the substitution products contain a deuterium atom.

In the present study, changing solvents from the aprotic solvent benzene or acetonitrile to the protic solvent methanol causes a dramatic increase in the ratio of substitution products, IV and V, to all other products. Hence this quenching effect probably precedes biradical formation. In methanol-*O*-*d*, the fumarate, IV, contains greater than 59% d_1. This suggests competitive protonation (deuteration) and/or proton transfer within an interme-

Chart I

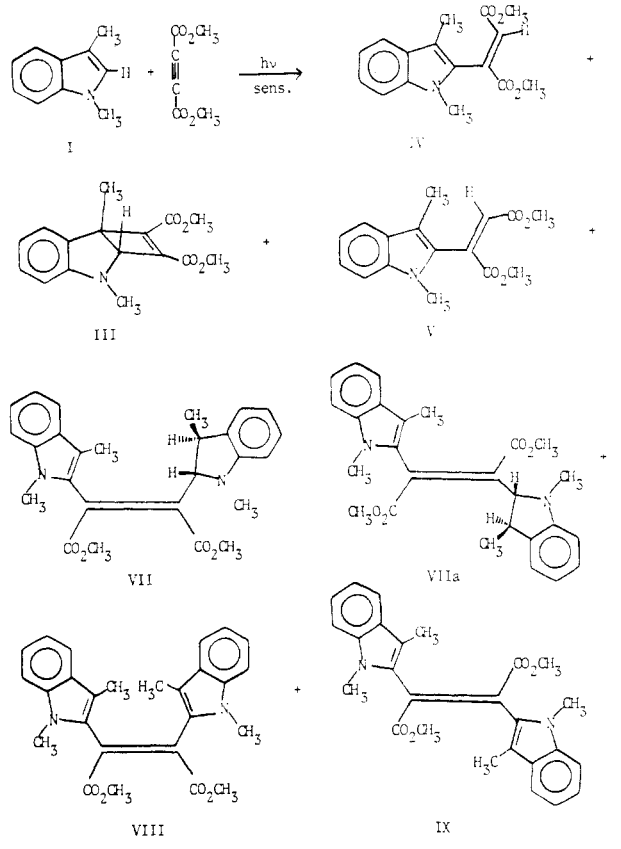


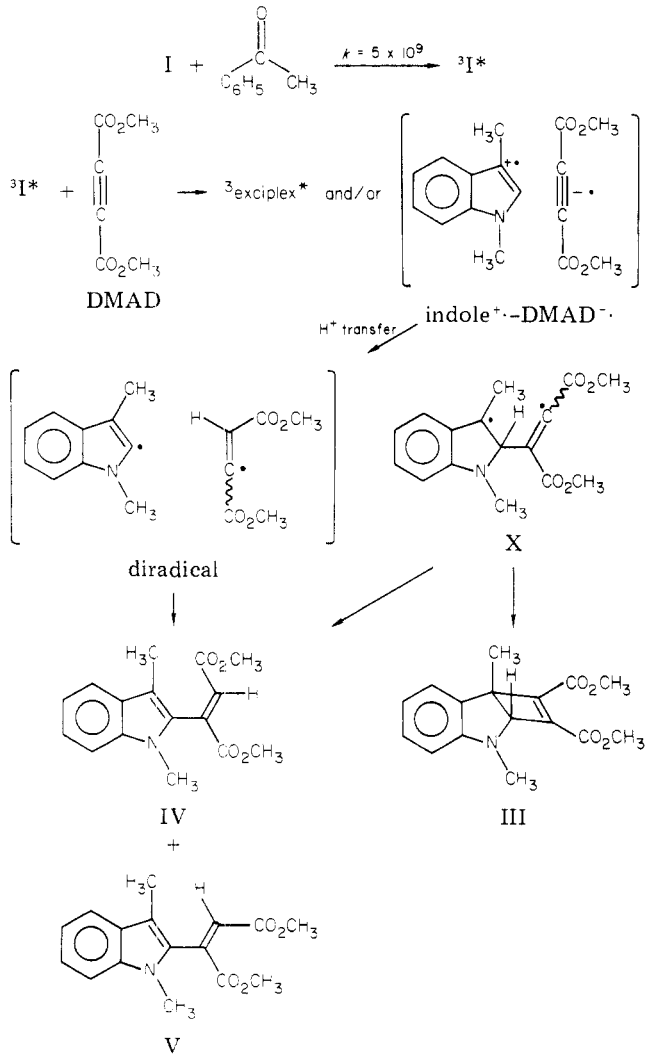
Table I. Effects of the Relative Concentrations of 1,3-DMI, I, and Dimethyl Acetylenedicarboxylate on the Ratio of Products[a]

[I], M	% substitution, IV and V	% cyclobutene, III	% 2:1 thermochromes, VII, VIII, IX
0.030	28.7	50.1	21.2
0.060	20.1	41.2	38.5
0.120	11.5	23.8	64.7
0.240	7.0	12.5	80.5
0.480	5.7	4.7	89.6
0.960	7.4	<2.2	90.4

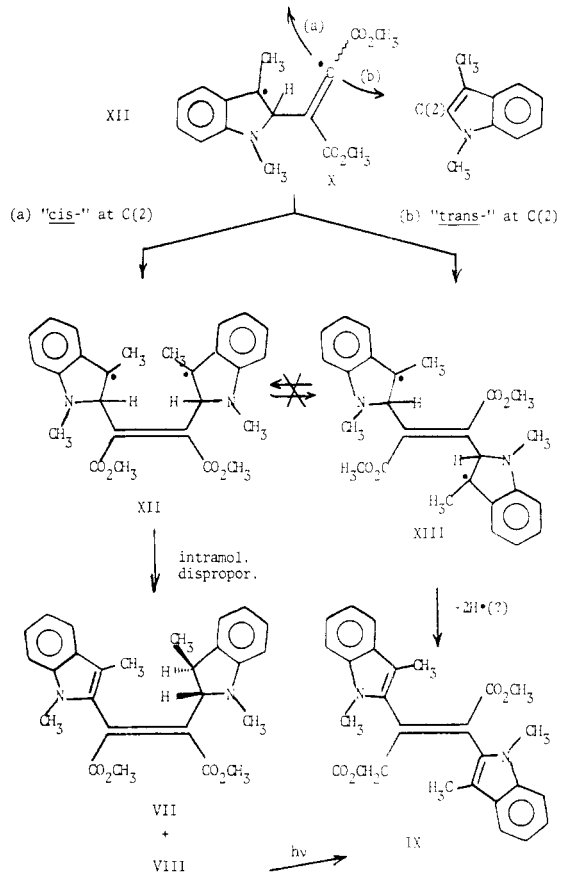
[a] Concentration of DMAD = concentration of acetophenone = 0.035 M; solvent = benzene.

(5) Wilkinson, F.; Garner, A. *J. Chem. Soc., Faraday Trans. 2* **1977**, 222.
(6) Lewis, F. D.; Hoyle, C. S. *J. Am. Chem. Soc.* **1976**, *98*, 4338.
(7) Huisgen, R. *Acc. Chem. Res.* **1977**, *10*, 117, and references therein.
(8) Yamasaki, K.; Matsuura, T.; Saito, I. *J. Chem. Soc., Chem. Commun.* **1974**, 944.
(9) Bowman, R. M.; Chamberlain, T. R.; Huang, C. W.; McCullough, J. J. *J. Am. Chem. Soc.* **1974**, *96*, 692.

Scheme II



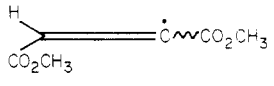
Scheme III



diate which precedes the biradical. We have no evidence to distinguish these processes as occurring in an exciplex and/or a radical ion pair, e.g., v or vii.

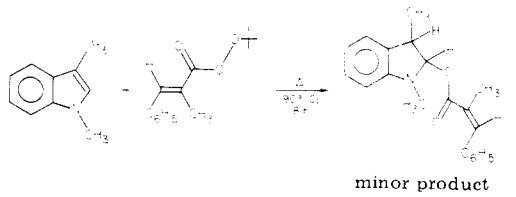
The ratios of products are dependent on the relative concentrations of starting materials. As the concentration of 1,3-dimethylindole is increased, there is an increase in the relative amounts of VII, VIII and IX and a corresponding decrease and disappearance in III, the cycloadduct, as well as decreases in IV and V. Table I summarizes these results. Qualitatively we interpret this to mean that an intermediate, probably a 1,4-biradical, X, which gives both the substitution product and cyclobutene, is being trapped by 1,3-dimethylindole to give VII, VIII, and IX. At high concentrations of I, the cyclobutene is completely quenched with only a partial quenching of the substitution products, indicating to us competing pathways for 1:1 substitution product formation. Many biradicals have been trapped;[10] however, *our trapping of a biradical with another molecule of starting material is unique.* Scheme II outlines our proposed mechanism for formation of III, IV, and V.

We propose Scheme III to rationalize the formation of VII (and isomer), VIII, and IX. The 1,4-biradical, X, is an intramolecular unknown benzylic and vinylic biradical. ESR studies of the model vinyl radical, XI, have suggested



XI

both a linear and rapidly equilibrating (10^{12}) nonlinear species.[11] The vinylic radical portion of X is then proposed to react with the indole to give two incipient 1,6-biradicals, XII and XIII. Attack by the biradical XI at C(2) in 1,3-substituted indoles is expected on the basis of work by us[12] and others.[13] For example, Waters[13a] ob-



minor product

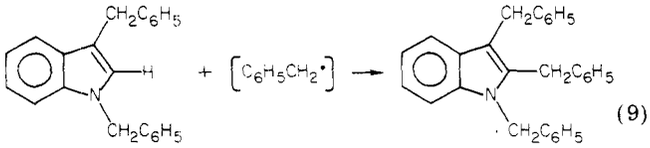
(10) (a) Wagner, P. J. *Adv. Photochem.* **1971**, *4*, 168 and references therein. (b) Hammond, G. S.; Turro, N. J.; Fischer, A. *J. Am. Chem. Soc.* **1961**, *83*, 4674. (c) Caldwell, R. A. *Ibid* **1973**, *95*, 1690. (d) Wilson, R. M.; Wunderly, S. *Ibid.* **1974**, *96*, 7350. (e) Wagner, P. J.; Lin, K. C. *Ibid.* **1974**, *96*, 5952. (f) O'Neal, H. E.; Miller, R. G.; Gunderson, E. *Ibid.* **1974**, *96*, 3351. (g) Wagner, P. J.; Zepp, R. G. *Ibid.* **1972**, *94*, 287. (h) Farid, S. *J. Chem. Soc., Chem. Comm.* **1971**, 73.

(11) (a) Neilson, G. W.; Symons, M. C. B. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1405. (b) Bonazzola, L.; Fenistein, S.; Marx, R. *Mol. Phys.* **1971**, *22*, 689. (c) Iwasaki, M.; Eda, B. *J. Chem. Phys.* **1970**, *52*, 3837. (d) Neta, P.; Fessenden, R. W. *J. Phys. Chem.* **1972**, *76*, 1957.

(12) Davis, P. D.; Neckers, D. C., unpublished results. Our own preliminary model studies on the thermal decomposition of *tert*-butyl β-methylpercinnamates in the presence of 1,3-dimethylindole have indicated that addition at the 2-position of the indole is the predominant non-hydrogen-abstracting process. It is well-known that the hydrogens on the C(3)-CH_3 are very easily abstracted by most radicals, and this would probably be the case for the vinylic or carboxy radical.

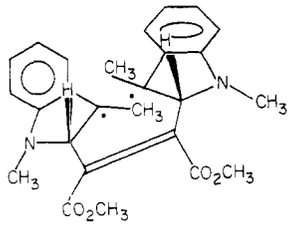
(13) (a) Hutton, J.; Waters, W. A. *J. Chem. Soc.* **1965**, 4253. (b) Matsuo, T.; Mihara, S.; Ueda, I. *Tetrahedron Lett.* **1976**, 4581. (c) Saito, I.; Ito, S.; Matsuura, T. *J. Am. Chem. Soc.* **1978**, *100*, 2901. (d) A similar preference for attack at the 2-position of *N*-methyl- and 1,3-dimethylindole is observed in the anodic cyanation where an electron-transfer process is believed involved: Yoshida, K. *J. Am. Chem. Soc.* **1979**, *101*, 2116.

served the formation of 1,2,3-tribenzylindole in the reaction of benzyl radical with 1,3-dibenzylindole (eq 9). We have observed a model reaction to stop at the addition step.[12]



(9)

XIII is expected to lead to *trans*-thermochrome, IX. The nature of this process is unknown. A similar addition process in the biradical XII leads to the stereospecific formation of VII, which is only expected via an intramolecular disproportionation. The only sterically feasible transition state suggests the trans stereospecificity in this reaction.[14]



The biradical trapping in the photochemistry of I/DMAD would hint at a similar fate for the biradicals expected as intermediates for the other indoles. At approximately the same relative concentrations of 3-*tert*-butyl-1-methylindole and 1-methyl-3-phenylindole with respect to DMAD and very high concentrations of 1-methylindole, there is strong evidence for the formation of similar 2:1 adducts.[15] The determining factors are probably biradical reactivity or stability in the competing intermolecular and intramolecular processes. Intermolecular biradical trapping is proposed to be increasingly competitive with biradical ring closure to the cyclobutene as the "benzylic" radical is stabilized by methyl, *tert*-butyl, or phenyl substituents. If this portion of the biradical is not stabilized, the intramolecular ring closure is preferred (in addition to low concentrations of indole). No attempt was made to look for 2:1 adduct formation from 1,2-dimethylindole where the C(2) position is now blocked with a methyl group, and comparable hydrogen abstraction cannot subsequently take place. Under comparable conditions, with 3-methylbenzo[*b*]thiophene and DMAD no 2:1 adducts are detected.[1]

Conclusion

In conclusion we have chemically trapped a 1,4-biradical in the (2 + 2) cycloaddition of 1,3-dimethylindole (I) with DMAD. Products isolated include four 2:1 adducts, as well as substitution and (2 + 2) cycloaddition products. Work in this and related systems is continuing in our laboratory.

Experimental Section

General. ^1H and ^{13}C NMR spectra were recorded on Varian A-60 and CFT-20 spectrometers. Unless otherwise indicated, $CDCl_3$ was used as the solvent with Me_4Si (tetramethylsilane) as the internal standard; coupling constants (J) are in hertz and chemical shifts are in δ values. Infrared (IR) spectra were obtained on a Perkin-Elmer 337 spectrophotometer, mass spectra on a Varian MAT CH7 spectrometer, and ultraviolet (UV) spectra on a Beckman Acta IV spectrophotometer. Vapor phase chromatography (GC) was carried out on a Hewlett-Packard Model 5710A chromatograph equipped with dual columns and a flame ionization detector (analytical) and on a Varian Model 90-P chromatograph with a thermal conductivity detector (preparative). A 6 ft × 0.25 in. column packed with 10% SE-30 adsorbed on Chromosorb W was used for both analytical and preparative purposes. Chromatograms were recorded on either a Houston Instruments Omniscribe Model A-5213-15 or a Hewlett-Packard Model 33805 integrator. Melting points were taken on a Thomas–Hoover capillary melting point apparatus and are uncorrected. 3-Methylindole (skatole) and dimethyl acetylenedicarboxylate (DMAD) were purchased from Aldrich Chemical Co. 1,3-Dimethylindole and 1-(methyl-d_3)-3-methylindole were prepared as previously described[1] using CH_3I and CD_3I, respectively.

1,3-Dimethylindole (I): liquid at room temperature; ^1H NMR (δ, $CDCl_3$) 2.32 (d, J = 1 Hz, 3, C(3)–CH_3), 3.26 (s, 3, N–CH_3), 6.74 (d, J = 1 Hz, 1, C(2)–H), 6.91–7.72 (m, 4, aromatic); mass spectrum, m/e 145 (M^+); UV (λ_{max} nm (log ϵ) 95% EtOH) 282 (3.74), 292 (3.74).

1-(Methyl-d_3)-3-methylindole (I-d_3): ^1H NMR (δ, $CDCl_3$) 2.28 (d, J = 1 Hz, 3, C(3)–CH_3), 6.53 (br s, 1, C(2)–H), 6.93–7.72 (m, 4, aromatic); mass spectrum, m/e 148 (M^+), 100% d_3.

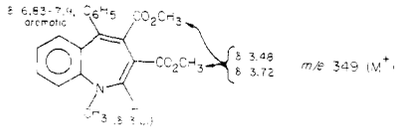
Synthesis of 2-Deuterio-1,3-dimethylindole (I-d_1). To 25 mL of dry ether under N_2 and containing 6.0 g (0.041 mol) of 1,3-dimethylindole (I) is added 0.16 mol of *n*-butyllithium, and the solution is refluxed for 8 h. The solution is cooled to 0 °C in an ice bath followed by the careful, but rapid, addition of a large excess of D_2O. Addition of 100 mL of H_2O, ether extraction (3 × 50 mL), washing with H_2O, and drying over $MgSO_4$ give 5.7 g (94%) of a colorless liquid (crystallizes only when cooled in the refrigerator). Deuterium incorporation is determined by ^1H NMR integration, by comparing the integrated area of the C(2)–H (δ 6.74, d, J = 1 Hz) doublet of any unreacted or recovered undeuterated I with the C(3)–CH_3 singlet from the deuterated product (δ 2.31, s, 3). It is found to be 99.7% monodeuterated and is confirmed by mass spectral analysis.

2-Deuterio-1,3-dimethylindole (I-d): ^1H NMR (δ, $CDCl_3$) 2.28 (d, J = 1 Hz, 3, C(3)–CH_3), 3.52 (s, 3, N–CH_3), 7.02–7.83 (m, 4, aromatic); mass spectrum, m/e 146 (M^+), 99.7% d_1.

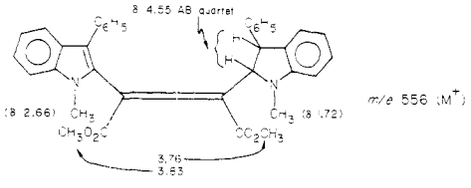
Isolation of 6,7-Bis(methoxycarbonyl)-2,5-dimethyl-3,4-benzo-2-azabicyclo[3.2.0]hepta-3,6-diene (III), the First Cyclobutene from an Activated Indole–Dimethyl Acetylenedicarboxylate Cycloaddition. To 50 mL of anhydrous ether containing 10 g (0.069 mol) of 1,3-dimethylindole and 10 g (0.070 mol) of DMAD is added approximately 20 mL of BF_3·Et_2O

(14) The 1,6-biradical, XII, is expected to disproportionate intramolecularly in either direction. If, however, one direction is favored, this preference cannot be detected in the products since they will be identical. Using the unsymmetrical methyl propiolate as the reacting acetylene, we have shown that no preference is observed.

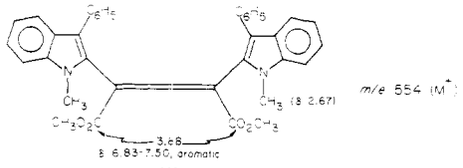
(15) (a) 3-*tert*-Butyl-1-methylindole: We have not isolated any 2:1 adducts; however, we have observed two major components on the GC trace with retention times expected for these products. Work is under way to identify these components. (b) 1-Methyl-3-phenylindole: Three products have been identified and are shown below with their NMR and mass spectral data:



i



ii



iii

(c) 1-Methylindole: A GC collected mixture (unresolved) was shown by mass spectral analysis (temperature dependence of M^+) to contain components with molecular ions at m/e 402 and 404. These are consistent with both types of 2:1 adducts. Very high relative concentrations of 1-methylindole were required to obtain even detectable amounts of these products.

(Aldrich) and the mixture stirred at 15 °C for 24 h. An additional 100 mL of ether is added, washed with 50-mL portions of water until they are colorless, and then dried with $MgSO_4$. The ether is then evaporated under reduced pressure (<15 °C). Preparative thick layer chromatography (20 × 20 cm × 2 mm) in 10% ether–petroleum ether of 500 mg of the reaction mixture gives three poorly resolved bands, identified as IV (120 mg), V (85 mg), and VI (54 mg) in order of decreasing R_f values. IV when heated is converted cleanly (100%) to II (which has the smallest R_f value by comparison).

(a) III: blood-red oil; ^1H NMR (δ, $CDCl_3$), 1.66 (s, 3, C(5)–CH_3), 3.06 (s, 3, N–CH_3), 3.84 (s, 6, C(6) and C(7) CO_2H_3), 4.33 (s, 1, C(1)–H), 6.4–7.4 (m, 4, aromatic); UV (λ_{max} nm (log ϵ), 95% EtOH) 2.51 (3.61), 302 (3.14), 435 (2.97).

(b) 2-(1,3-Dimethylindol-2-yl)fumarate (IV): red crystals, mp 103–105 °C; ^1H NMR (δ, $CDCl_3$) 2.16 (s, 3, C(3)–CH_3), 3.65 (s, 3, N–CH_3), 3.81, 3.85 (singlets, 6, $2CO_2CH_3$), 7.34 (s, 1, vinyl), 6.95–9.75 (m, 4, aromatic); mass spectrum, m/e 287 (M^+); UV (λ_{max} nm (log ϵ) 95% EtOH), 228 (4.56), 296 (3.79), plateau absorption to >400 nm.

(c) 2-(1,3-Dimethylindol-2-yl)maleate (V): yellow crystals, mp 189–191 °C; ^1H NMR (δ, $CDCl_3$) 2.32 (s, 3, C(3)–CH_3), 3.53, 3.56, 3.76 (oil, 9, N–CH_3, $2CO_2CH_3$), 6.12 (s, 1, vinylic), 6.95–7.75 (m, 4, aromatic); mass spectrum, m/e 287 (M^+); UV (λ_{max} nm (log ϵ) 95% EtOH) 227 (0.452), 259 (3.82), 277 (3.76), 340 (3.86).

(d) 3,4-Bis(methoxycarbonyl)-5-methyl-6,7-benz-1-azepine (II): yellow cubes, mp 83–86 °C (lit.[16] 87–89 °C); ^1H NMR (δ, $CDCl_3$) 2.36 (s, 3, C(5)–CH_3), 3.16 (s, 3, N–CH_3), 3.73, 3.83 (singlets, 6, C(3)– and C(4)–CO_2CH_3), 6.7–7.4 (m, 5, aromatic and C(2)–H); mass spectrum, m/e 287 (M^+); UV (λ_{max} nm (log ϵ), 95% EtOH) 245 (4.23), 283 (3.86), 312 (3.65).

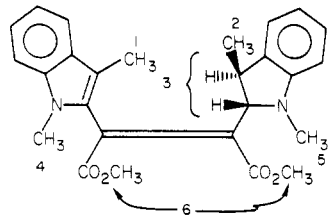
Sensitized Irradiation of 1,3-Dimethylindole (I) and Dimethyl Acetylenedicarboxylate. Small-scale photochemical reactions are carried out in 13 × 100 mm culture tubes sealed with Teflon-lined screw caps following N_2 purging. Each tube contains 6 mL of solution with benzene as solvent. The results outlined in Table I, which shows the concentration dependence of the products, are obtained by syringing the required amounts of 1,3-dimethylindole (I) [26 mg (0.030 M), 52 mg (0.060 M), 104 mg (0.090 M), 208 mg (0.180 M), 416 mg (0.360 M), 832 mg (0.960 M)] and constant amounts of DMAD [30 mg (0.035 M)] and acetophenone [25 mg (0.035 M)] into benzene to give 6.0 mL of solution. Each sample is irradiated for 24 h in a merry-go-round apparatus immersed in a constant temperature bath (10 °C). The relative amounts of the seven products observed are analyzed by GC, following removal of solvent and dilution of 1.0 mL in CH_2Cl_2, on a 6 ft × 0.25 in. 10% SE-30 column at 250 °C (oven temperature).

(a) Low Relative Concentration of I to DMAD. Preparative Scale. The irradiation of 2.0 g of I (1.38 × 10^{-2} M), 3.5 g of DMAD (2.46 × 10^{-2} M), and 750 mg of acetophenone is carried out under N_2 for 12 h in benzene solvent and in the constant temperature bath (10 °C). Benzene is removed under reduced pressure while the temperature is carefully kept below 15 °C. GC analysis shows a predominance of the three short-retention-time products. Small amounts of the higher molecular weight compounds are also detectable. Starting materials are removed as described previously,[1] and the products are separated by preparative TLC. From 500 mg of crude product applied, 235 mg of red III (confirmed by NMR) and 130 mg of a mixture containing both IV and V (76 and 24%, respectively, by NMR) are isolated. IV and V are interconverted by the methods of Johnson applied to the substituting products obtained thermally with DMAD in the *N*-methyl- and 1,2-dimethylindole systems.

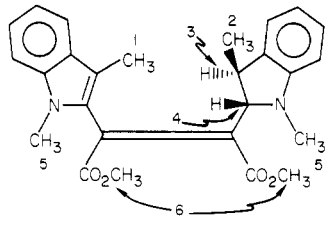
(b) High Relative Concentration of I to DMAD. Preparative Scale. 1,3-Dimethylindole (I) [30.0 g (0.207 M)], 2.0 g of DMAD (0.014 M), and 1.00 g of acetophenone are irradiated under a constant flow of N_2 for 36 h at ambient temperatures. Benzene is removed under reduced pressure with a hot water bath. GC analysis of the crude product mixture indicates a predominance of two products of longer retention times. Starting materials are separated as before; however, because of the large quantity of excess I, special care is taken in its removal. Successive 6 g applications are made to the same 45 × 2.5 cm chromatography column. Each application is allowed to be adsorbed completely before the next is made. With petroleum ether as eluent, all unreacted I is removed before DMAD and acetophenone are removed with 2–5% ether–petroleum ether, followed by products; 4.28 g. Preparative TLC (1.4 g per 20 × 20 cm × 2 mm plate) with 15% ether–petroleum ether (3 elutions) gives primarily two bands. The fastest band, a dark brown, contains IX and some IV, and the second, a very broad and pale yellow band, contains primarily VII. Following the same irradiation procedure as above for a shorter irradiation period (<12 h), a third band, which is orange and has a smaller R_f value, is observed in the preparative TLC and contains VIII. IX (220 mg) can be triturated from a concentrated $CHCl_3$ solution with methanol (or alternatively, freeze (–78 °C)–heating cycles with small amounts of methanol induced crystallization). Yellow crystalline VII (2.52 g) is obtained similarly. In the shorter irradiation, 35 mg of VIII is crystallized from the third TLC band. If a mixture of VII and IX is obtained, care must be taken to prevent cocrystallization of IX with VII or VII with IX.

Dimethyl 2-(1,3-dimethylindol-2-yl)-3-(*trans*-2,3-dihydro-1,3-dimethylindol-2-yl)maleate (VII): yellow crystals, mp 195–196 °C; ^1H NMR (δ, $CDCl_3$) 0.90 (d, J = 6.5 Hz, 3), 1.07 (d, 6.5 Hz, 3), 2.24 (s, 3), 2.31 (s, 3), 2.74 (s, 3), 2.78 (s, 3), 3.58, 3.61, 3.68, 3.74 (singlets, 11), 6.25–7.64 (m, 8); ^1H NMR (δ, C_6D_6) 0.73 (d, J = 6.5 Hz, 3), 0.96 (d, J = 6.5 Hz, 3), 2.28 (s, 3), 2.32 (s, 3), 2.62 (s, 3), 2.73 (s, 3), 3.24 (s, 3), 3.29 (s, 3), 2.32 (s, 3), 3.40 (s, 3), 3.48 (s, 3), 3.59 (s, 3), 3.65–4.13 (m, 2), 6.25–7.80 (m, 8); ^{13}C NMR (δ, $CDCl_3$) 9.77 (q), 9.86 (q), 17.43 (q), 18.75 (q), 30.85 (q), 34.13 (q), 35.20 (q), 41.51 (d), 41.79 (d), 52.00 (q), 52.22 (q), 52.60 (q), 74.59 (d), 75.67 (d), 106.59, 104.24, 108.64, 109.08, 109.30, 111.62, 118.07, 118.35, 119.05, 119.28, 119.57, 122.22, 122.41, 122.60, 122.79, 125.54, 127.68, 127.92, 128.10, 128.76, 129.39, 133.20 (s), 133.59 (s), 127.41 (s), 150.83 (s), 151.55 (s), 152.93 (s), 165.58 (s), 165.72 (s), 167.59 (s), 167.66 (s); mass spectrum, m/e 433 (M + 1, 31.5), 432 (M, 100), 418 (6), 403 (7), 387 (9), 374 (31), 360 (11), 359 (9), 343 (11), 314 (15), 313 (22), 299 (14), 298 (10), 297 (10), 287 (16), 254 (10), 253 (7), 227 (14), 146 (12), 145 (15); UV (λ_{max} nm (log ϵ), 95% EtOH) 309 (3.66), 350 (shoulder) (3.23).

Anal. Calcd: C, 72.22; H, 6.48; N, 6.48. Found: C, 71.88; H, 6.46; N, 6.45.



1, δ, 2.28, 2.32
2, δ, 0.73 (d), 0.96 (d)
3, δ, 3.65–4.13 (m)
4, δ, 3.24, 3.40
5, δ, 2.62, 2.73
6, δ, 3.29, 3.32, 3.48, 3.59



1, δ, 9.77, 9.86
2, δ, 17.43, 18.75
3, δ, 41.51, 41.79
4, δ, 74.59, 75.67
5, δ, 30.85, 34.13, 35.20
6, δ, 52.00, 52.22, 52.60

Dimethyl 2-(1,3-dimethylindol-2-yl)-3-(*trans*-2,3-dideuterio-1,3-dimethylindol-2-yl)maleate (VII-d_2): yellow crystals, mp 193–195 °C; ^1H NMR (δ, C_6D_6) identical with VII (above) except the absorptions 0.73 (s, 3) and 0.96 (s, 3) are singlets and the 3.65–4.13 multiplet has disappeared; mass spectrum, m/e 434 (M^+, 100).

Dimethyl 2-(1-methyl-d_3-3-methylindol-2-yl)-3-(*trans*-2,3-dihydro-1-methyl-d_3-3-methylindol-2-yl)maleate (VII-d_6): yellow crystals, mp 195–197 °C; ^1H NMR (δ, C_6D_6) identical with VII except for the disappearance of singlets at 2.62, 2.73, 3.24, and 3.40; mass spectrum, m/e 438 (M^+, 100).

Dimethyl 2,3-bis(1,3-dimethylindol-2-yl)fumarate (IX): red-brown crystals, mp 238–239 °C; ^1H NMR (δ, $CDCl_3$) 2.41 (s, 6), 3.46 (s, 6), 3.82 (s, 6); ^{13}C NMR (δ, $CDCl_3$) 9.36, 30.81, 52.87, 108.47, 109.27, 118.44, 118.69, 119.23, 119.48, 123.06, 127.91, 137.93, 167.81; mass spectrum, m/e 430 (m, 100), 371 (31); UV (λ_{max} nm (log ϵ), 95% EtOH) 303 (3.71), 359 (3.73), tails to 580.

(16) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* 1971, *27*, 368.

Table II. Bond Angles (degrees) in VII[a]

C(3)-9(2)-C(5)	116.3	C(15)-C(14)-C(19)	117.8
C(4)-O(4)-C(6)	115.7	C(14)-C(15)-C(16)	120.9
C(10)-N(1)-C(12)	127.3	C(15)-C(16)-C(17)	122.2
C(10)-N(1)-C(18)	125.6	C(16)-C(17)-C(18)	118.1
C(12)-N(1)-C(18)	106.9	N(1)-C(18)-C(17)	131.5
C(20)-N(2)-C(22)	117.3	N(1)-C(18)-C(19)	108.4
C(20)-N(2)-C(28)	119.0	C(17)-C(18)-C(19)	120.1
C(22)-N(2)-C(28)	107.0	C(13)-C(19)-C(14)	132.2
C(2)-C(1)-C(3)	118.8	C(13)-C(19)-C(18)	107.0
C(2)-C(1)-C(12)	122.0	C(14)-C(19)-C(18)	120.8
C(3)-C(1)-C(12)	118.2	N(2)-C(22)-C(2)	110.6
C(1)-C(2)-C(4)	122.0	N(2)-C(22)-C(23)	104.7
C(1)-C(2)-C(22)	124.3	C(2)-C(22)-C(23)	111.3
C(4)-C(2)-C(22)	113.6	C(21)-C(23)-C(22)	113.5
O(1)-C(3)-O(2)	122.9	C(21)-C(23)-C(29)	114.0
O(1)-C(3)-C(1)	126.6	C(22)-C(23)-C(29)	102.7
O(2)-C(3)-C(1)	110.5	C(25)-C(24)-C(29)	117.2
O(3)-C(4)-O(4)	125.8	C(24)-C(25)-C(26)	121.0
O(3)-C(4)-C(2)	124.3	C(25)-C(26)-C(27)	122.2
O(4)-C(4)-C(2)	109.7	C(26)-C(27)-C(28)	116.8
N(1)-C(12)-C(1)	124.7	N(2)-C(28)-C(27)	127.0
N(1)-C(12)-C(13)	109.9	N(2)-C(28)-C(29)	111.6
C(1)-C(12)-C(13)	124.9	C(27)-C(28)-C(29)	121.3
C(11)-C(13)-C(12)	127.2	C(23)-C(29)-C(24)	129.0
C(11)-C(13)-C(19)	124.9	C(23)-C(29)-C(28)	109.4
C(12)-C(13)-C(19)	107.8	C(24)-C(29)-C(28)	121.5

[a] Estimated standard deviation for a typical C-C-C bond angle is 0.5°. Refer to Figure 4, for the atom-numbering scheme.

Anal. Calcd: C, 72.56; H, 6.05; N, 6.51. Found: C, 72.38; H, 6.06; N, 6.41.

Dimethyl 2,3-bis[(1-methyl-d_3)-3-methylindol-2-yl]fumarate (IX-d_6): red-brown crystals, mp 239–240 °C; ^{1}H NMR (δ, $CDCl_3$) identical with IX except for the disappearance of the singlet at 3.82; mass spectrum, m/e 436 (M^+, 100).

Dimethyl 2,3-bis(1,3-dimethylindol-2-yl)maleate (VIII): orange needles, mp 205–208 °C; ^{1}H NMR (δ, $CDCl_3$) 1.97 (s, 6), 3.48 (bs, 6), 3.87 (s, 6); ^{13}C NMR (δ, $CDCl_3$) 9.40, 30.82, 52.55, 109.27, 118.01, 118.32, 119.10, 119.42, 121.56, 122.67, 128.12, 137.82, 156.50; mass spectrum, m/e 430 (M^+, 100); UV (λ_{max} nm (log ϵ) 95% EtOH) 301 (3.86), 333 (3.96), 388–398 (3.93), tails to 560.

Dimethyl 2,3-bis[(1-methyl-d_3)-3-methylindol-2-yl]maleate (VIII-d_6): orange oil; ^{1}H NMR (δ, $CDCl_3$) identical with VIII except for the disappearance of a broad singlet at 3.48; mass spectrum, m/e 436 (M^+, 100).

X-Ray Analysis of VII. Crystals of VII ($C_{26}H_{28}N_2O_4$, M_r 432.52) are monoclinic, space group $P2_1/n$, with a = 10.732 (4), b = 13.99 (5), c = 16.569 (5) Å, α,β = 99.40 (2)°, and d_{calcd} = 1.240 g cm^{-3} for Z = 4. The intensity data were measured on a Hilger–Watts diffractiometer (Ni-filtered Cu Kα radiation, θ–2θ scans, pulse height discrimination). A crystal measuring approximately 0.25 × 0.25 × 0.5 mm was used for data collection; the data were not corrected for absorption (μ = 6.9 cm^{-1}). A total of 3114 reflections were measured for θ < 57°, of which 2501 were considered to be observed [$I > 2.5\sigma(I)$]. The structure was solved by a multiple solution procedure[12] and was refined by full-matrix least-squares refinement. In the final refinement anisotropic thermal parameters were used for the heavier atoms, and isotropic temperature factors were used for the hydrogen atoms. The hydrogen atoms were included in the structure factor calculations, but their parameters were not refined. The final discrepancy indices are R = 0.70 and wR = 0.084 for the 2501 observed reflections. The final difference map has no peaks greater than ±0.2 e A^{-3}. Tables II, III, and IV summarize the various bond angles, bond lengths, and some important torsional angles.

Photochemical Cis-Trans Isomerization of VIII to IX. VIII in 50 mL of benzene (2.33 × 10^{-3} M) is irradiated in a Rayonet photochemical reactor at 300 nm for 30 h. GC and NMR analysis indicate a quantitative conversion to IX.

Oxidation of VII to VIII with 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). V (300 mg, 0.694 mmol) and DDQ (Aldrich) (170 mg, 0.750 mmol) are refluxed in 25 mL of xylene for 8 h. The cooled solution is filtered, washed with 3 × 10 mL of water, and dried. Preparative TLC yields 252 mg of IX (83% yield) as the exclusive product. This is confirmed by melting point, NMR, and GC comparison with an authentic sample of IX.

Table III. Bond Lengths (angstroms) in VII[a]

O(1)-C(3)	1.181	C(12)-C(13)	1.355
O(2)-C(3)	1.338	C(13)-C(19)	1.416
O(2)-C(5)	1.448	C(14)-C(15)	1.391
O(3)-C(4)	1.194	C(14)-C(19)	1.386
O(4)-C(4)	1.326	C(15)-C(16)	1.373
O(4)-C(6)	1.443	C(16)-C(17)	1.358
N(1)-C(10)	1.471	C(17)-C(18)	1.402
N(1)-C(12)	1.394	C(18)-C(19)	1.398
N(1)-C(18)	1.393	C(21)-C(23)	1.520
N(2)-C(20)	1.438	C(22)-C(23)	1.546
N(2)-C(22)	1.485	C(23)-C(29)	1.501
N(2)-C(28)	1.407	C(24)-C(25)	1.413
C(1)-C(2)	1.357	C(24)-C(29)	1.383
C(1)-C(3)	1.498	C(25)-C(26)	1.354
C(1)-C(12)	1.475	C(26)-C(27)	1.398
C(2)-C(4)	1.510	C(27)-C(28)	1.396
C(2)-C(22)	1.511	C(28)-C(29)	1.379
C(11)-C(13)	1.473		

[a] Estimated standard deviation for a typical C-C bond length is 0.007 Å.

Table IV. Torsion Angles (degrees) in VII[a]

C(19)-C(13)-C(12)-C(1)	−172.7
C(13)-C(12)-C(1)-C(2)	−76.8
C(12)-C(1)-C(2)-C(4)	170.1
C(1)-C(2)-C(4)-O(4)	−77.2
C(2)-C(4)-O(4)-C(6)	−179.0
C(5)-O(2)-C(3)-C(1)	−197.0
O(2)-C(3)-C(1)-C(2)	177.6
C(3)-C(1)-C(2)-C(22)	171.9
N(2)-C(28)-C(29)-C(23)	1.5
C(28)-C(29)-C(23)-C(22)	11.5
C(29)-C(23)-C(22)-N(2)	−19.3
C(23)-C(22)-N(2)-C(28)	21.0
C(22)-N(2)-C(28)-C(29)	−14.6

[a] Estimated standard deviation for a typical C-C-C-C torsion angle is 0.6°.

Photochemical Cis-Trans Isomerization of VII In Ethanol. Irradiation of VII in benzene at 300 nm produces essentially no isomerization; however, the irradiation of 150 mg of VII in 95% EtOH (9.14 × 10^{-4} M) for 12 h shows a 65% conversion to another product(s). Separation by preparative TLC gives two bands; the slower is VII and the faster, a yellow oil, is assigned to its trans isomer, VIIa, on the basis of the ^{1}H NMR spectrum. By NMR there appears to be some impurity (or another compound), 30%. The retention time of this fast-moving component corresponds with that of a product in the original photochemical reaction mixture.

Dimethyl 2-(1,3-dimethylindol-2-yl)-3-(*trans*-2,3-dihydro-1,3-dimethylindol-2-yl)fumarate (VIIa): bright yellow oil; ^{1}H (δ, $CDCl_3$) 1.48 (d, J = 6.5 Hz, 3), 2.29 (s, 3), 2.83 (s, 3), 3.36 (s, 3), 3.69 (s, 3), 6.3–7.5 (m, 4), indoline hydrogens (?).

Solvent Effects of the Photochemical Efficiency of Product Formation from I and DMAD. Samples containing I (104 mg), DMAD (30 mg), and acetophenone (25 mg) in 6 mL of benzene and acetonitrile solutions are irradiated for 2 h (shortest time in which measurable amounts of product can be detected conveniently). The respective solvents were removed and each sample is diluted to 1.00 mL with CH_2Cl_2 in a volumetric flask. The areas of the peaks obtained for VII, VIII, and IX are averaged for three 5.0-μL GC injections from each solution. The ratio of the average areas of benzene to acetonitrile, 4.05, is taken as the ratio of product formation efficiencies. The short retention time products show the same trend, but are not conveniently measured quantitatively.

Direct and Sensitized Photolysis of III. (i) III, 1.0 (3.48 × 10^{-3} M), is irradiated in the presence (250 mg) and absence of acetophenone sensitizer for 15 h. The amounts of cycloreversion to I and DMAD are <13 and <25%, respectively, by NMR.

(ii) The same experiments carried out in the presence of I (2 equiv excess) show qualitatively (by GC and NMR) a greater

tendency to form 2:1 adducts. (Note: This presumably is a result of cycloreversion and not product formation directly from III.) Qualitatively the product formation is considerably slower (in 15 h, 10% by NMR) than from I and DMAD directly.

The Sensitized Irradiation of I and DMAD in Methanol-*O*-*d*. Six samples each containing 100, 50, and 25 mg of DMAD, I, and acetophenone, respectively, in 6 mL of CH_3OD solution are irradiated for 36 h. The solvent is removed at reduced pressure with a hot water bath. Preparative TLC is used to isolate III. Further purification is carried out by preparative GC, followed by mass spectral analysis of the isolated product. Comparison with an authentic sample of IV shows that the IV obtained in methanol-*O*-*d* is a mixture of IV-d_0 (41%) and IV-d_1 (59%).

Variable-Temperature ^{1}H NMR. The variable-high-temperature ^{1}H NMR experiments on compounds IX and VII are carried out on a Varian CFT-20 spectrometer equipped with a variable temperature controller (Varian V6040 controller) and using Me_2SO-d_6 as solvent. The temperature calibrations are made by using an ethylene glycol standard and are performed at each temperature studied. The solvent used is a 50:50 $CDCl_3$ Me_2SO-d_6 mixture. At the lowest temperatures (cooled in dry ice–acetone and warmed in probe) observed $\Delta\nu$ is constant for VIII at 11.0 Hz.

The free energies of activation are determined by using eq 10 and 11. The values of $\Delta\nu$ are determined from the "low" temperature spectra. The values of $\Delta\nu$ are, for VIII, 11 Hz (J = 0 Hz) at δ 1.94 and, for VII, 4.4 Hz (J = 0 Hz) at δ 2.23 and 10.6 Hz (J = 7.0 Hz) at δ 0.91. The coalescence temperature, T_c, for VIII at δ 1.97 (45 °C) is determined directly, while the T_c's for VII at δ 0.91 and δ 2.23 are extrapolated to 200 and 220 °C, respectively. The free energies of activation, $\Delta G^{\ddagger}$, obtained are 16.6 kcal/mol for VIII and 26.2 and 26.0 kcal/mol for VII.

$$k_c = (\Delta\nu^2 + 6J^2)^{1/2}/2 \quad (10)$$

$$\Delta G^{\ddagger} = RT_c\,(\ln (R/Nh) + \ln (T_c/k_c)) \quad (11)$$

Acknowledgment. This work was supported by the National Institutes of Health (1 RO1 NS 14883-01). It was taken, in part, from the Ph.D. thesis of Paul D. Davis, submitted to the Graduate School of the University of Toledo. Helpful discussions with Dr. Roger Card and Professor J. C. Dalton are hereby acknowledged.

Registry No. I, 875-30-9; I-d_3, 72206-02-1; I-*d*, 72206-03-2; II, 34187-47-8; III, 69496-51-1; IV, 34203-07-1; V, 34219-44-8; VII, 72206-04-3; VII-d_2, 72206-05-4; VII-d_6, 72214-05-2; VIIa, 72206-06-5; VIII, 72206-07-6; VIII-d_6, 72206-08-7; IX, 72206-09-8; IX-d_6, 72206-10-1; DMAD, 762-42-5; 3-*tert*-butyl-1-methylindole, 46270-99-9; 1-methyl-3-phenylindole, 30020-98-5; 1-methylindole, 603-76-9; i, 72206-11-2; ii, 72206-12-3; iii, 72206-13-4.

Stability of Carbon-Bonded Anionic σ Complexes. 3.[1,2] Decomposition in Aqueous Acidic Media

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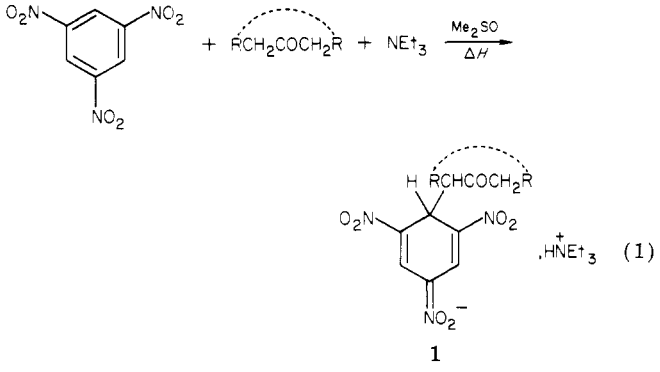
Received August 6, 1979

Kinetic data for the acid-catalyzed and uncatalyzed decomposition of anionic σ complexes of 1,3,5-trinitrobenzene and simple ketones are discussed. The ^{13}C NMR spectral characteristics of certain complexes are presented, and chemical shifts of the carbonyl carbon in the complexes are correlated with structure and rates of decomposition in aqueous media.

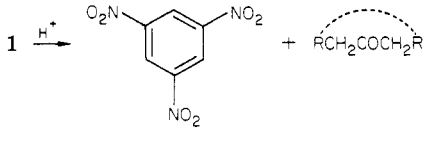
For some time we have been interested in the factors which contribute to the stability, in aqueous media, of anionic σ complexes (Meisenheimer complexes) formed from simple enolates and *sym*-trinitrobenzene (TNB). We have previously reported relative thermodynamic heats of formation for a series of such complexes formed from simple acyclic and cyclic ketones in Me_2SO, initiated by triethylamine (eq 1).[1,2] These relative heats of formation do not provide a direct measure of complex stability but do allow comparisons which are of interest. For example, the very large heat of formation found for the cyclopentanone complex provided a qualitative rationale for its unusual stability, even in 0.1 M acid. We have previously commented on possible explanations for this large heat of formation.[2]



(1)

1

We report here kinetic data for the decomposition of complexes like 1 in acidic solution from pH 0 to pH 6. The complexes were prepared from acetone, diethyl ketone, cyclopentanone, cyclohexanone, cycloheptanone, acetophenone, *p*-methoxyacetophenone, *p*-cyanoacetophenone, and *p*-nitroacetophenone. These kinetic data, especially those obtained for the para-substituted acetophenones, allow characterization of the mechanism of decomposition (eq 2) in more detail than has previously been possible.



(2)

Methods of Procedure

The complexes were all prepared, with minor variations (see Experimental Section), by dissolving 1 equiv of TNB

(1) M. J. Strauss, R. M. Murphy, and C. A. Wulff, *J. Am. Chem. Soc.*, **96**, 2678 (1974).
(2) C. A. Wulff, R. M. Murphy, and M. J. Strauss, *J. Org. Chem.*, **40**, 1499 (1975).

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