Photochemical and Thermal 1,2- and 1,4-Cycloaddition Reactions of Azodicarbonyl Compounds with Monoolefins

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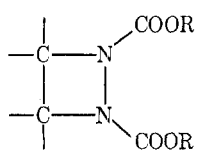
Dialkyl azodiformates form dihydrooxadiazines with indene, dihydro-1,4-dioxine, vinylene carbonate, *cis*- and *trans*-1,2-dimethoxyethylene, and vinyl acetate by 1,4 addition; 1,2 addition yielding diazetidines is observed with vinyl ethers. Diazetidines also result from the addition of 4-phenyl-Δ^1-1,2,4-triazoline-3,5-dione (PTD) to indene and dihydro-1,4-dioxine. Dihydrooxadiazines are formed in a concerted Diels–Alder reaction with *inverse electron demand*, the diazetidines *via* dipolar intermediates. The acceleration of azodiformate addition by illumination is due to the photochemical production of *cis* azodiformates, which show increased thermal reaction rates compared with the *trans* isomers.

The thermal reaction of azodicarbonyl compounds (*e.g.*, diethyl azodiformate) with monoolefins normally results in substitution, which may be combined with an obligatory shift of the double bond following a concerted[5-8] or free-radical path,[7c,9] or consists of a formal insertion into a =CH bond.[5,10]

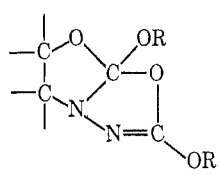
Of the variety of conceivable cycloaddition reactions the following four appear as the most plausible.

1,2 addition



1

1,3 addition



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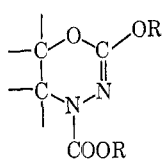
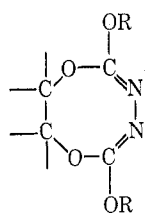
1,4 addition



3

1,6 addition



4

Only a few instances have been reported of 1,2-cycloaddition reactions[11-16] leading to diazetidines **1**, and of 1,4-cycloaddition reactions[16-18] with formation of dihydrooxadiazines **3**. 1,3 addition has been proposed for the reaction of $(CH_3)_3CCON{=}NCOC(CH_3)_3$ with diphenyl ketene.[19] To our knowledge no examples of 1,6 addition have been reported.

The mechanisms of these cycloaddition reactions have not yet been explored, and the factors governing the different paths are unknown. In this paper we wish (a) to present spectral and chemical evidence which allows one to distinguish between the different products, (b) to contribute to the understanding of the mechanisms of the 1,2- and 1,4-cycloaddition reactions, and (c) to discuss the photochemical acceleration of the two latter processes.

Results

Dihydrooxadiazines.—1,2-Disubstituted olefins without easily abstractable allylic hydrogen should undergo cycloaddition reactions with azodicarbonyl compounds. The two ring protons should have identical environments in **1** and **4**, but different ones in **2** and **3**, thus allowing a distinction by nmr.

Dihydro-1,4-dioxine, vinylene carbonate, and *trans*-1,2-dimethoxyethylene gave the 1:1 adducts **5**–**7** with dimethyl azodiformate (DMAD). The nmr data (Table I) show the two ring protons to be different; therefore **1** and **4** can be ruled out as structural possibilities.[20] The distinction between **2** and **3** should be possible by ir: two valence vibrations (C=O and C=N) are

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(2) Department of Chemistry, Boston College.

(3) Taken in part from the Ph.D. thesis D. V. White, Boston College, May 1969.

(4) Taken in part from the doctoral dissertation B. Kim, Göttingen University, 1966.

(5) R. Huisgen and H. Pohl, *Chem. Ber.*, **93**, 527 (1960).

(6) B. T. Gillis and P. E. Beck, *J. Org. Chem.*, **27**, 1947 (1962); **28**, 3177 (1963).

(7) (a) B. Franzus and J. H. Surridge, *ibid.*, **27**, 1951 (1962); (b) B. Franzus, *ibid.*, **28**, 2954 (1963); (c) W. A. Thaler and B. Franzus, *ibid.*, **29**, 2226 (1964).

(8) J. M. Cinnamon and K. Weiss, *ibid.*, **26**, 2644 (1961); G. O. Schenck, E. Koerner von Gustorf, B. Kim, G. von Bünau, and G. Pfundt, *Angew. Chem.*, **74**, 510 (1962).

(9) R. Huisgen and F. Jakob, *Justus Liebigs Ann. Chem.*, **590**, 37 (1954).

(10) K. Alder and H. Niklas, *ibid.*, **585**, 97 (1954).

(11) J. C. Kauer and A. K. Schneider, *J. Amer. Chem. Soc.*, **82**, 852 (1960); W. D. Phillips in "Determination of Organic Structures by Physical Methods," Vol. II, F. C. Nachod and W. D. Phillips, Ed., Academic Press Inc., New York, N. Y., 1962, p 452; W. H. Knoth and D. D. Coffman, *J. Amer. Chem. Soc.*, **82**, 3873 (1960).

(12) E. Koerner von Gustorf and B. Kim, *Angew. Chem.*, **76**, 592 (1964).

(13) R. W. Hoffmann and H. Häuser, *ibid.*, **76**, 346 (1964); R. W. Hoffmann, *ibid.*, **80**, 823 (1968).

(14) O. L. Chapman and S. J. Dominianni, *J. Org. Chem.*, **31**, 3862 (1966); E. Fahr, *et al.*, *Angew. Chem.*, **79**, 154 (1967).

(15) J. Firl and S. Sommer, *Tetrahedron Lett.* 1133, 1137 (1969).

(16) E. Fahr and H. Lind, *Angew. Chem.*, **78**, 376 (1966), and references therein.

(17) J. J. Tufariello, T. F. Mich, and P. S. Miller, *Tetrahedron Lett.*, 2293 (1966).

(18) G. Ahlgren and B. Akermark, *Acta Chem. Scand.*, **21**, 2910 (1967).

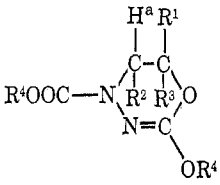
(19) E. Fahr and J. Markert, DECHEMA Colloquium, Frankfurt/Main, Germany, 1969. Detailed discussions with Professor Fahr prior to publication are gratefully appreciated. J. Markert and E. Fahr, *Tetrahedron Lett.*, 769 (1970).

(20) It could be argued that hindered rotation about the N–COOR bonds in **1** could possibly make the ring protons different. However, the nmr spectra of **5**–**7** remained unchanged at 70°, that is, far beyond the coalescence temperature for such processes.[21]

(21) J. C. Breliere and J. M. Lehn, *Chem. Commun.*, 426 (1965); C. H. Bushweller, *ibid.*, 80 (1966); G. J. Bishop, B. J. Price, and I. O. Sutherland, *ibid.*, 672 (1967); E. L. Allred, C. L. Anderson, R. L. Miller, and A. L. Johnson, *Tetrahedron Lett.*, 525 (1967); R. M. Moriarty, M. R. Murphy, S. J. Druck, and L. May, *ibid.*, 1603 (1967); J. E. Anderson and J. M. Lehn, *Tetrahedron*, **24**, 123 (1968); **24**, 137 (1968). Dr. J. E. Anderson kindly provided us with a copy of his manuscript prior to publication.

TABLE I

NMR DATA OF DIHYDROOXADIAZINES[a]



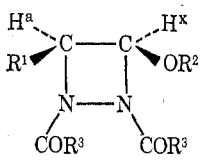
Compd	τ					Cps			Solvent
	H^a	R^1	R^2	R^3	R^4	J_{ax}	J_{bx}	J_{ab}	
5	4.51 (d)[b]	5.17 (d)[b]	6.9 (m)		6.44 (s); 6.48 (s)	1.9			C_6D_6
6	3.23 (d)[b]	3.68 (d)[b]			6.05 (s); 6.07 (s)	6.1			$CDCl_3$
7	4.45 (d)	6.97 (s)	6.73 (s)	5.10 (d)	6.42 (s)	1.4			C_6D_6
8	4.40 (d)	5.33 (d)	6.63 (s)[b]	6.72 (s)[b]	6.30 (s); 6.35 (s)	1.8			C_6D_6
9	6.55 (q)	7.90 (s)	6.0 (q)	3.51 (t)	5.82 (q); 8.70 (t)	2.5	2.5	13.5	CCl_4

	Substituent			
5	H^x	OCH_2CH_2O		CH_3
6	H^x	OCO (=O)		CH_3
7	OCH_3	OCH_3	H^x	CH_3
8	H^x	OCH_3	OCH_3	CH_3
9	$-O-C(=O)-CH_3$	H^b	H^x	C_2H_5

[a] The nmr spectra were recorded with a Varian A-60 A and HA-100; the letter abbreviations used follow: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, o = octet, m = multiplet, b = broad; tetramethylsilane was used as internal standard. [b] Reversed assignment possible.

TABLE II

NMR DATA OF DIAZETIDINES[a]



Compd	τ					Cps			Solvent
	H^a	H^x	R^1	R^2	R^3	J_{ab}	J_{ax}	J_{bx}	
10	5.57 (q)	4.77 (q)	5.99 (q)	6.51 (s)	6.17 (s); 6.19 (s)	9.5	6	4	$CDCl_3$
11	Under $R^2 + R^3$	4.80 (q)	Under $R^2 + R^3$	Obsc. (m); 8.78 (t)	5.82 (q); 8.74 (t)		6	4	CCl_4
12	5.55 (q)	4.67 (q)	5.95 (q)	~6.2 (m); 8.73 (t)	6.17 (s); 6.19 (s)	9.5	6	4	$CDCl_3$
12-D_1	5.55 (d)	4.62 (d)		~6.3 (m); 8.74 (t)	6.17 (s); 6.19 (s)		6		$CDCl_3$
13	4.78 (s)	= H^a	6.50 (s)	= R^1	6.44 (s)				C_6D_6
14	5.17 (s)	= H^a	6.26 (m)	= R^1	2.61 (m)				CD_3CN

	Substituent		
10	H^b	CH_3	OCH_3
11	H^b	C_2H_5	OC_2H_5
12	H^b	C_2H_5	OCH_3
12-D_1	D	C_2H_5	OCH_3
13	OCH_3	CH_3	OCH_3

[a] See footnote *a*, Table I.

expected for **3**, one (C=N) for **2** in the 1600–1800-cm^{-1} region. However, all three adducts display three bands in this area, *e.g.*, **7** at 1678, 1714, and 1750 cm^{-1} (in CCl_4). While this observation appears incompatible with the structural type **2**, it easily can be reconciled with the dihydrooxadiazine structure **3**: two conformers with different overlap between the C=O π-orbital and the nitrogen nonbonding orbital result from hindered rotation about the N–COOR bond. This process has been demonstrated in a detailed nmr study published elsewhere,[22] and the ratio of the two conformers from nmr corresponds to the ratio of intensities of the 1714- and 1750-cm^{-1} bands in **7**. Therefore, these bands are assigned to the C=O vibrations and the 1678-cm^{-1} band to the C=N group.[23]

The dihydrooxadiazine **7** is formed in quantitative yield, but from *cis*-1,2-dimethoxy-ethylene and DMAD we obtained the dihydrooxadiazine **8** (Table I) and the diazetidine **13** (Table II) in a 4:1 ratio according to nmr. Vinyl acetate gave the dihydrooxadiazine **9** with diethyl azodiformate (DEAD); the structural assignment rests on the band at 1675 cm^{-1} (C=N).[24]

(22) E. Koerner von Gustorf, D. V. White, and J. Leitich, *Tetrahedron Lett.*, 3109 (1969).

(23) Cyclic C=N groups are known to cause strong absorption in the 1630–1680-cm^{-1} region: E. Fahr, K. Königsdorfer, and F. Scheckenbach, *Justus Liebigs Ann. Chem.*, **690**, 138 (1965); A. I. Meyers, *J. Org. Chem.*, **26**, 218 (1961).

(24) An earlier assignment[4,12] of a diazetidine structure to **9** is herewith revised.

TABLE III
NMR DATA OF INDENE ADDUCTS[a]

Compd	τ					Cps				
	H^a	H^b	H^x	H^y	R	J_{ab}	J_{ax}	J_{bx}	J_{xy}	Solvent
30a	6.9 (o)		5.17 (o)	4.78 (d)	5.82 (q) 5.88 (q) 8.72 (t) 8.77 (t)	16	9	7.5	5	CCl_4
30b	6.83 (o)		5.06 (o)	4.65 (d)	6.14 (s) 6.18 (s)	16	9	7.5	5	$CDCl_3$
21	6.78 (q)	6.08 (q)	4.61 (o)	4.07 (d)		18.8	6.6	1.1	5.6	$CDCl_3$
24	6.85 (q)	7.12 (d)	7.30 (t)	6.39 (d)		16.5	7	≦1.0	5.5	CD_3COCD_3

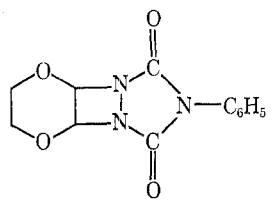
[a] See footnote *a*, Table I.

All dihydrooxadiazines failed to undergo catalytic hydrogenation at room temperature and normal pressure.

Diazetidines.—DMAD and DEAD form 1:1 adducts **10–12** with methyl and ethyl vinyl ether.[12,15] Compounds **10–12** (Table II) showed two bands at >1700 cm^{-1} in the 1600–1800-cm^{-1} region. The only structure compatible therewith is that of a diazetidine **1**. Compound **11** underwent ring opening to **15** on catalytic hydrogenation.

4-Phenyl-Δ^1-1,2,4-triazoline-3,5-dione[25] (PTD) is a *cis*-locked azodicarbonyl compound and a very electrophilic cyclophile: of the different modes of cycloaddition (**1–4**) only **1** is possible in this case.

The diazetidine **14** (Table II) was obtained from PTD and dihydro-1,4-dioxine besides some polymeric material and showed identical ring protons as expected. Catalytic hydrogenation of **14** gave **16**.



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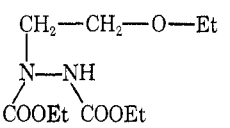

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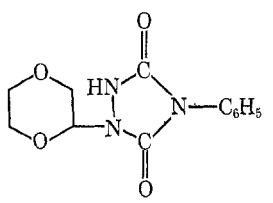


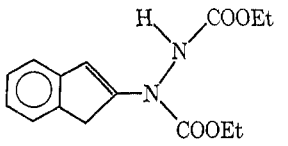
16

Azodiformate and PTD Adducts of Indene.—DEAD and indene form a 1:1 adduct at room temperature (80% yield after 1 month),[26] for which structures **17** and **18** have been suggested. Alder, *et al.*[10] showed a preference for **17**, since 2-indanone resulted from alkaline hydrolysis, and **29** was obtained by catalytic hydrogenation of the adduct. We recently ruled out **17** on the basis of spectral data and suggested[4,12] **18**; independently, Huebner, *et al.*,[27] reached the same conclusion.

(25) J. Sauer and B. Schröder, *Chem. Ber.*, **100**, 678 (1967). We are grateful to Professor Sauer for detailed information about his procedure prior to publication, and for a generous sample of PTD. R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, *J. Chem. Soc., C*, 1905 (1967).

(26) O. Diels and K. Alder, *Justus Liebigs Ann. Chem.*, **450**, 237 (1926).

(27) C. F. Huebner, *et al.*, *J. Org. Chem.*, **32**, 1126 (1967).



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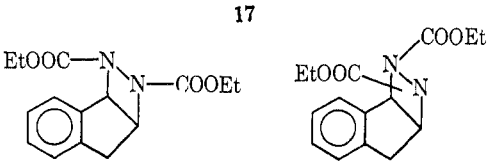

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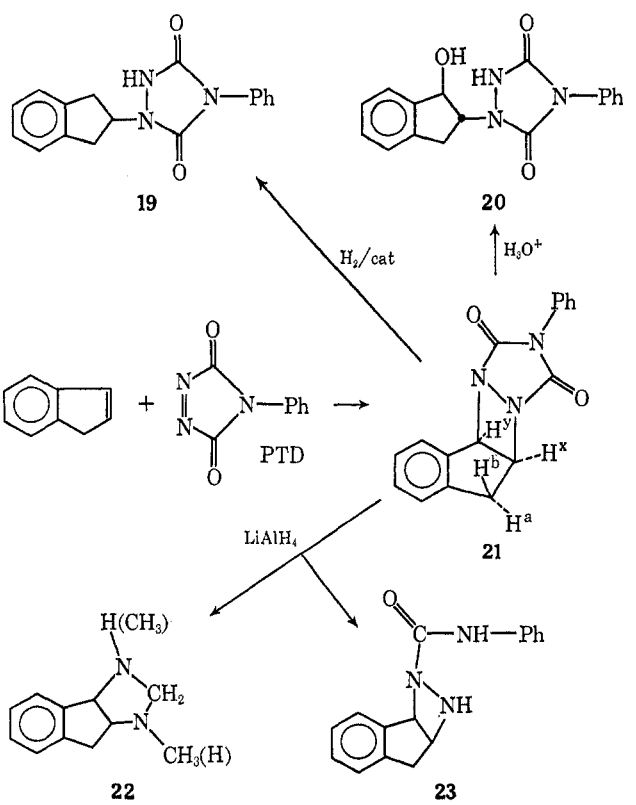
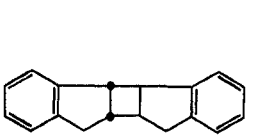
This structure has also to be revised on the basis of the following data. The reaction of indene with PTD gives the diazetidine **21**. The structure of **21** is based on its ir spectrum (>C=O at 1712 and 1782 cm^{-1} in KBr, no >NH), mass spectrum and nmr data (Table III); almost identical ABXY systems reveal the structural similarities of **21** (Scheme I) with the adduct (**25**) of indene and phthalazine-1,4-dione.[14]

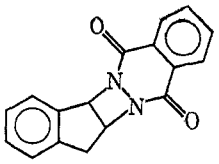
The formation of **19** by ring cleavage in the benzylic

SCHEME I





24

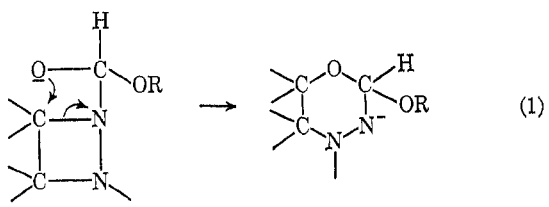


25

position on catalytic hydrogenation, and the proton-catalyzed attack of water leading to **20** are also in accord with **21**. A *trans* configuration has been assigned to **20** without further proof, since this should result from both SN2- or SN1-type attack of water on **21**.

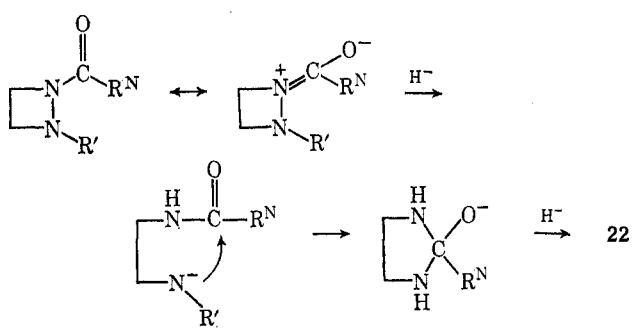
The reduction of **21** with $LiAlH_4$ yields N-methylaniline, aniline, N-N-dimethylaniline, indene, and large amounts of tarry materials. As further products only traces of the imidazole derivative **22** and of the diazetidine **23** could be isolated; their structures have been assigned tentatively on the basis of spectral evidence.[28] No alcoholic product was detected in the $LiAlH_4$ reduction of **21**.

A comparison of the reactions of **21** (Scheme I) with those of the adduct of indene and diethyl azodiformate (Scheme II) shows that hydrogenation[32] and hydrolysis lead to the analogous products **29** and **30**, whose structures are indicated by their spectra. However, with the formation of **28** in high yields with $LiAlH_4$ a basic difference between the two indene adducts becomes apparent. According to the results with **21** the OH in **28** does not stem from an attack by water on a diazacyclobutane system in the course of the work-up procedure. A formation of **28** *via* a rearrangement of **18** by AlH_4^- (eq 1) seems very unlikely.[34]

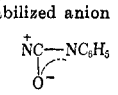


(1)

(28) The reduction of $NCONR_2 \rightarrow NCH_3$ in **22** parallels the behavior of carbamates[29] and diethyl tetrahydropyridazine-1.2-dicarboxylates[30] toward $LiAlH_4$; the mechanism of the rearrangement observed in the formation of **22** could be pictured as follows.



The carbonyl group in **23** is protected from further reduction, probably by formation of the resonance stabilized anion



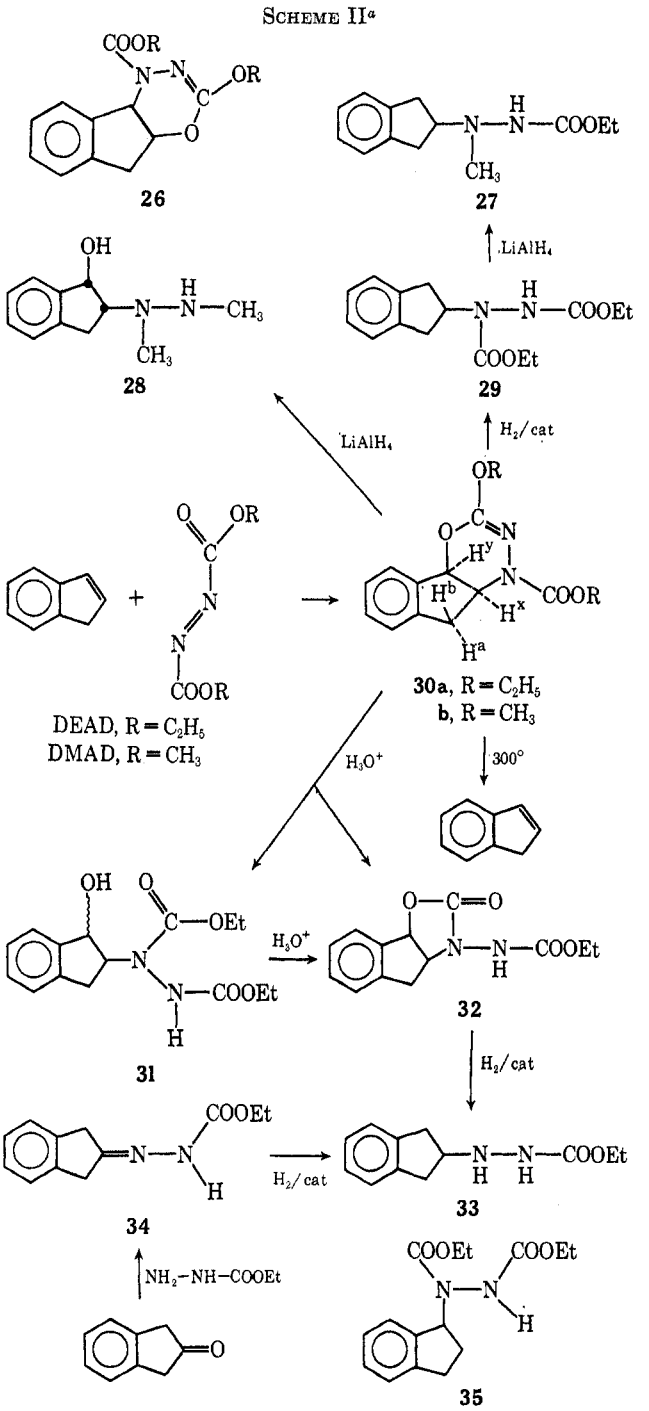
as postulated in a similar case.[31]

(29) N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956, p 636; B. Weiss, *J. Org. Chem.*, **30**, 2483 (1965).

(30) H. R. Snyder and J. G. Michels, *ibid.*, **28**, 1144 (1963).

(31) R. Huisgen, F. Jakob, W. Siegel, and A. Cadus, *Justus Liebigs Ann. Chem.*, **590**, 1 (1954).

SCHEME II[a]



[a] All reactions shown in this scheme have been carried out with **30a**.

Therefore, the predominant formation of **28** suggests that this indene adduct is correctly represented by the dihydrooxadiazine[36] structure **30** and not by the

(32) As it turned out later, **30** is the only dihydrooxadiazine, so far, which undergoes catalytic hydrogenation. This can be explained by the activation of the benzylic position, which is also responsible for the easy cleavage of benzyl ethers and esters on hydrogenation.[33]

(33) R. C. Fuson, "Advanced Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1953, p 261.

(34) Such a rearrangement would be analogous to that of, *e.g.*, N-benzoylaziridines to 2-oxazolines[35] by I^-. However, I^- did not have any effect on the indene azodiformate adduct, but rearranged[3] the diazetidine **10**.

(35) H. W. Heine, *Angew. Chem.*, **74**, 772 (1962).

(36) C. F. Huebner, E. M. Donoghue, C. J. Novak, L. Dorfman, and E. Wenkert, *J. Org. Chem.*, **35**, 1149 (1970), have also demonstrated the correctness of **30** by $LiAlH_4$ reduction to **28**, and have proven *cis* configuration for **28** by chemical means. Correspondence with Dr. Huebner, who kindly postponed the publication of his paper to allow the simultaneous appearance of our work is gratefully appreciated.

TABLE IV
IR DATA OF 30a AND 30b

Compd	Solvent	C=N (cm⁻¹)	C=O (cm⁻¹)	C=O (cm⁻¹)
30a[a]	CH_3CN	1674	1700	1736
	CH_3NO_2	1672	1698	1732
	$C_6H_5NO_2$	1674	1699	1737
	C_6H_5N	1674	1698	1738
	C_6H_6	1675	1700	1743
	Dioxane	1675	1699	1743
	CCl_4	1674	1700	1743
	CH_2Cl_2	1672	1699 (sh)	1733
	$CHCl_3$	1671	1697 (sh)	1727
	$CHBr_3$	1667		1724
	C_2H_5OH	1667		1724
	KBr	1658	1683	1690
30b	$C_6H_5CH_3$	1675	1703	1745
	$CHCl_3$	1670	~1700 (sh)	1730

[a] See ref 39.

diazetidine structure **18**. A discussion of the nmr and ir data lends further support to this structural assignment.

The coupling constants in the nmr spectrum (Table III) of **21** closely resemble those in the cyclobutadiindene[37] **24**. Both compounds possess the same rigid arrangement of a four-membered ring fused to the five-membered ring of the indene moiety. J_{ax} and J_{bx} in the indene azodiformate adduct **30** are completely different from those in **21** and **24**. Inspection of molecular models reveals a dihedral angle close to 90° of H^bC–CH^x in **21**, thus explaining[38] the very small value of J_{bx}; the corresponding angle in **30** is much larger.

The ir spectrum of **30** shows three bands in the 1600–1800-cm^{-1} region whose positions have been studied in a variety of solvents (Table IV).[39] While the polarity of the solvent does not have a strong effect on these bands, their position is shifted to lower wavenumbers in those solvents which are capable of hydrogen bonding. Hydrogen bonding with chloroform could be demonstrated: the intensity of the C-D stretching vibration in $CDCl_3$ at 2254 cm^{-1} is strongly increased[40] by the presence of **30**. According to these solvent effects all three bands have to be attributed to >C=O or >C=N valence vibrations.

Up to four (possibly overlapping) >C=O bands could be expected[41] for the two possible configurational isomers of **18** by vibrational coupling.[42] However, according to our experience tetrahydropyridazine derivates resulting from the addition of azodiformates to dienes[43] show >C=O bands only at ≧1700 cm^{-1}. Three bands at the observed positions can be easily explained with the dihydrooxadiazine structure **30** on the basis of the experience with **5**–**8** as being due to the existence of two conformers (hindered rotation about the N–COOR bond). This conformational process can be directly observed by low temperature nmr.[22]

The chemical reactions carried out with **30** are compiled in Scheme II. The structures of the compounds shown are based on spectral evidence. The proposed[10] nonidentity of **29** and **35** (obtained from indan and DEAD) was confirmed by nmr.[44]

Attention should be drawn to the fact, that there is no evidence for any formation of the isomeric adduct **26**.

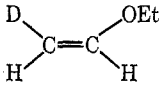
The formation of **30** at 20° is accelerated by several orders of magnitude, if mixtures of indene and azodiformates are irradiated with light of ≧350 mμ. The photochemical preparation of **30** gives very good yields of analytically pure material. Illumination has also been used for the preparation of **5** and **6**.

Mechanistic Considerations

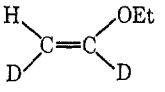
Thermal Reactions.—The reaction constants listed in Table V show no considerable influence of solvent polarity on the rates of the addition of DEAD to indene (dihydrooxadiazine formation) and to vinyl ethyl ether, and of PTD to indene (diazetidine formation).

Retention of configuration (within the limits of detectability by nmr) was observed for the formation of the dihydrooxadiazines **7** and **8**, and excess *trans*- or *cis*-1,2-dimethoxy-ethylene is not isomerized in these reactions.[45,46]

The formation of only one diazetidine **13** from *cis*-1,2-dimethoxyethylene is not unequivocal, since no diazetidine was obtained with *trans*-1,2-dimethoxyethylene. DMAD and **36** gave **12**-D_1 under retention (see Table II) of configuration (stereospecificity > 90 % by nmr). The configuration of **37** remains unchanged in the addition of DMAD.



36



37

Are the dihydrooxadiazines and the diazetidines formed in one- or two-step reactions?

The following criteria are considered important for this distinction.[47] (1) Isolation, spectroscopic and kinetic detection, or scavenging with additives of an intermediate give positive proof for a two-step cycloaddition. (2) Stereospecificity is a necessary requirement for one-step cycloaddition. Stereoequilibration proves a two-step reaction.[45,48] However, several stereospecific two-step cycloadditions are known.[47,49] (3) Effects of substituents (orientation phenomena) are observed in one- and two-step reactions. A con-

(37) G. O. Schenck, W. Hartmann, S. P. Mannsfeld, W. Metzner, and C. H. Krauch, *Chem. Ber.*, **95**, 1642 (1962); A. G. Anastassiou and G. W. Griffin, *J. Org. Chem.*, **33**, 3441 (1968).

(38) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

(39) We are grateful to Mr. R. E. Sacher, U. S. Army Natick Laboratories, for measuring these spectra on a Beckman IR-12.

(40) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, p 197.

(41) Helpful discussions of this problem with Professor M. K. Wilson, Tufts University, are gratefully acknowledged.

(42) C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy," Academic Press Inc., New York, N. Y., 1963, p 265.

(43) B. T. Gillis, in "1,4-Cycloaddition Reactions," J. Hamer, Ed., Academic Press Inc., New York, N. Y., 1967, p 143.

(44) We are indebted to Dr. H. Niklas for a sample of **35**.

(45) E. Koerner von Gustorf and J. Leitich, *Tetrahedron Lett.*, 4689 (1968).

(46) E. Koerner von Gustorf, *ibid.*, 4693 (1968).

(47) R. Gompper, *Angew. Chem.* **81**, 348 (1969); *Angew. Chem. Int. Ed. Engl.*, **8**, 312 (1969); valuable discussions with Professor Gompper, who kindly provided a manuscript prior to publication, are gratefully appreciated.

(48) P. D. Bartlett, C. J. Dempster, L. K. Montgomery, K. E. Schueller, and E. H. Wallbillich, *J. Amer. Chem. Soc.*, **91**, 405 (1969).

(49) S. Proskow, H. E. Simmons, and T. L. Cairns, *ibid.*, **88**, 5254 (1966).

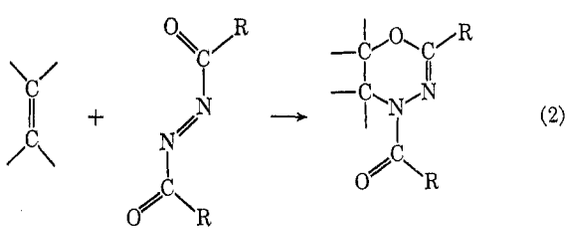
TABLE V

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE ADDITION OF DEAD TO INDENE AND ETHYL VINYL ETHER, AND OF PTD TO INDENE

System	Solvent	Temp, °C	k (1/mol sec)	$\Delta H^{\pm}$ (kcal/mol)	$\Delta S^{\pm}$, eu
DEAD + indene	Acetonitrile	40	1.3×10^{-6}		
	Acetic anhydride	40	1.1×10^{-6}		
	Benzene	40	3.2×10^{-7}		
	Ethyl acetate	40	2.1×10^{-7}		
	Indene	20	4.2×10^{-7}	12.8 ± 0.4	-44 ± 2
	Indene	40	1.8×10^{-6}		
	Indene	60	6.6×10^{-6}		
DEAD + ethyl vinyl ether	Acetonitrile	20	2.0×10^{-5}		
	Acetic anhydride	20	1.7×10^{-5}		
	Benzene	20	6.0×10^{-6}		
	Ethyl acetate	20	4.4×10^{-6}		
	Ethyl vinyl ether	20	3.5×10^{-6}	11.0 ± 0.8	-46 ± 3
	Ethyl vinyl ether	25	4.6×10^{-6}		
	Ethyl vinyl ether	30	6.6×10^{-6}		
PTD + indene	Acetonitrile	20	1.5		
	Acetonitrile (+ 1.5 % H_2O)	20	4.9		
	Chlorobenzene	20	1.0		
	Acetone (dry)	20	1.6×10^{-1}		
	Acetone (+ 1.5% H_2O)	20	4.1×10^{-1}		
	Benzene	20	2.3×10^{-1}	7.2 ± 0.5	-36 ± 4
	Benzene	25	3.0×10^{-1}		
	Benzene	30	3.5×10^{-1}		
PTD + H_2O	Acetone (1.5% H_2O)	20	7.8×10^{-3}		

clusion (that it is a one-step reaction) is only possible if the orientation is contrary to the polarity of the substituents.[47] (4) Solvent effects are meaningful only (proving two-step cycloaddition), if rate constants increase several orders of magnitude going from an unpolar (*e.g.*, cyclohexane) to a polar (*e.g.*, acetonitrile) solvent.[47,49] Missing solvent effects (a requirement for one-step reactions) have been reported for several dipolar cycloaddition reactions.[47] (5) A small enthalpy of activation ($\Delta H^{\pm}$ 25 kcal/mol) and a highly negative activation entropy ($\Delta S^{\pm} \approx -35$ eu) are typical activation parameters of one-step cycloaddition (*e.g.*, Diels–Alder) reactions.[50,51] However, dipolar cycloadditions with similar data are known.[47] (6) Kinetic secondary isotope effects[52] allow an empiric distinction between one- and two-step cycloadditions.[50a,53,54]

The selection rules of Woodward and Hoffman[55,56] allow concerted oxadiazine formation (eq 2) by $\pi^4s + \pi^2s$ addition. Water (which can add to dipolar intermediates) did not affect the formation of **30**. Therefore, the experimental criteria 1–5 are fulfilled for an one-step formation (eq 2) of dihydrooxadiazines.[57] Criterion 6 has not been checked for this reaction as yet.



(2)

Oxadiazine formation by addition of an electron-rich C=C bond (dienophile) to the electron-poor "diene" N=NC=O can be looked upon as a Diels–Alder reaction with inverse electron demand;[50,59] in accord with this, all attempted 1,4-additions failed with electron-poor olefins. The observed regiospecific[60] addition of indene suggests control by orientation phenomena possibly due to a slight polarity of the transition state.[47]

A concerted $\pi^2s + \pi^2s$ diazetidine formation (eq 3) is forbidden by the Woodward–Hoffmann rules,[55,56] and it, indeed, proceeds in a different fashion. A dipolar intermediate **38** was trapped with water[61] in the reaction[62] of PTD with indene yielding **20**. A study[54] of the secondary α-deuterium kinetic isotope effect in the addition of DMAD to ethyl vinyl ether revealed an unsymmetric transition state: change of

(50) (a) J. Sauer, *Angew. Chem.*, **79**, 76 (1967); (b) R. Huisgen, R. Grashey, and J. Sauer, in "The Chemistry of Alkenes," S. Patai, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 739.

(51) R. Huisgen, *Angew. Chem.*, **75**, 742 (1963).

(52) E. A. Halevi, *Progr. Phys. Org. Chem.*, **1**, 109 (1963).

(53) W. R. Dolbier and S.-H. Dai, *J. Amer. Chem. Soc.*, **90**, 5029 (1968).

(54) E. Koerner von Gustorf, D. V. White, J. Leitich, and D. Henneberg, *Tetrahedron Lett.*, 3113 (1969), and references therein.

(55) R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 2046 (1965).

(56) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968); R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969).

(57) With the *reservatio mentalis* that rotation in a (improbable) biradical intermediate should be fast as compared with ring closure.[48-51, 58]

(58) P. D. Bartlett, R. Helgeson, and O. A. Wersel, *J. Appl. Chem.* (London), **16**, 187 (1968).

(59) W. E. Bachmann and N. C. Deno, *J. Amer. Chem. Soc.*, **71**, 3062 (1949).

(60) A. Hassner, *J. Org. Chem.*, **33**, 2684 (1968).

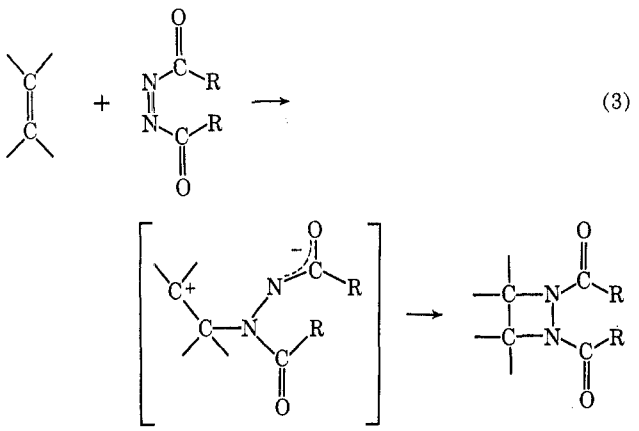
(61) It could be argued, that water changes the mechanism of this reaction. This appears very unlikely, since the ratios of the reaction constants in acetone and in acetonitrile are very similar with and without water.

(62) E. Fahr, and J. Flemming, as well as C. F. Huebner and his collaborators, have obtained **20** from indene and PTD in acetone according to private communications, but were unable to isolate **21**. We are grateful to Professor Fahr for a copy of the thesis of J. Flemming, Würzburg University, 1967. NOTE ADDED IN PROOF.—Compound **21** was obtained also by H. Helfert, Thesis, Würzburg University, 1969.

hybridization in the direction $sp^2 \rightarrow sp^3$ had occurred at $=CH_2$ but not at $=CH(OR)$.

Criteria 2–5 would have been in accord with a one-step process; an explanation could be "that, in certain stepwise cycloadditions by way of a dipolar ion, a coulombic orienting force in the first step eliminates or greatly diminishes this period in which the system searches for a favorable orientation for ring closure."[48]

It may appear surprising that the orbital symmetry-allowed concerted 1,4 addition (eq 2) of azodiformates to olefins can be completely overcome by the disconcerted 1,2 addition (eq 3). However, there are precedents;[63,64] there is no reason why the activation energy of the 1,2 addition should not be the lower one.



(3)

38

What factors are responsible for low activation energies of 1,2 cycloaddition? High polarity and polarizability of the olefin and high polarizing power of the cyclophile should facilitate the formation of a dipolar intermediate. Table VI shows that the electron polarizability[65] of the C=C bond of mono- and 1,2-disubstituted olefins indicates whether 1,2 or 1,4 addition of azodiformates has to be expected, increased polarizability favoring 1,2 addition. More data are needed to check possible predictions. The role of polarity, *e.g.*, in the reactions of 1,1-disubstituted olefins with azodiformates,[5,10,15,66] will be discussed elsewhere.

If the coulombic forces between the developing charge-carrying centers exceed repulsion early on the way from educt to product, the formation times of the two new bonds of a diazetidine may overlap to some extent (*e.g.*, ethyl vinyl ether + azodiformates). A fully developed two-step mechanism may be one extreme on a continuous scale with a completely symmetrical transition state as the other extreme.

Photochemical Reactions.—Illumination $\lambda \geqq 300$ mμ of the normally *trans*-configurated[67] azodiformates in inert solvents results in a partial conversion to *cis*-azodiformates;[68] the composition of the photoequilibrated mixtures depends on the wavelength used. *cis* Azodiformates are much more reactive in thermal cycloaddition reactions than the *trans*-configurated isomers;[68] even the products obtained may be different.[69] Therefore, the thermal reaction constants of the two geometrical isomers with an olefin and the composition of the photostationary state have to be known to allow a distinction, whether the acceleration is due to the photochemical formation of the *cis* isomer and its subsequent fast thermal reaction with the substrate, or whether it consists in a direct reaction of electronically excited azodiformate.

TABLE VI

EFFECT OF OLEFIN POLARIZABILITY ON CYCLOADDITION OF AZODIFORMATES

Olefin	Polarizability[a]	Cycloaddition
Ethyl vinyl ether	2.9	1.2
cis-1,2-Dimethoxyethylene	2.3	1.4 and 1.2
Vinyl acetate	2.1	1.4
Indene	2.1[b]	1.4
trans-1,2-Dimethoxyethylene	1.7	1.4
Dihydro-1,4-dioxine	1.2	1.4
Vinylene carbonate	1.1	1.4

[a] See ref 65. [b] Comparability with other values can be accidental.

The rate constants[68] for the thermal reactions of *cis*- and *trans*-DEAD with indene and ethyl vinyl ether are listed in Table VII; the photochemical acceleration (P) of the disappearance of DEAD achieved under conditions ($\lambda \geqq 370$ mμ) where only 2–4% *cis*-DEAD was present in the photostationary state has been compared with the value (for 3% *cis*-DEAD) calculated according to the following expression.

$$P = \frac{k_{cis}[cis\text{-DEAD}]}{k_{trans}\,[\text{DEAD}]} + 0.97$$

The intensity of illumination was sufficient to ensure that the formation of *cis*-DEAD was fast compared with its consumption.

According to the data given there is no necessity to postulate a direct reaction of electronically excited azodiformate in both cases.

Compound **30a** is obtained from indene and diethyl azodiformate in the dark, from the illumination of the mixture of both reactants, and from adding indene (16%) in the dark to a solution of DEAD, 16% of which had been transformed before into *cis*-DEAD by appropriate illumination. In this instance *cis*- and *trans*-DEAD yield the same product. The higher reactivity of *cis*-DEAD in comparison with the *trans* isomer toward indene can be attributed not only to its higher ground state energy, but also to a higher population of the cisoid conformations of the N=N-C=O system, owing to steric interactions of the OR groups in the transoid conformations as revealed by an inspection of molecular models. In this respect the azodiformates parallel other dienes, whose re-

(63) P. D. Bartlett and K. E. Schueller, *J. Amer. Chem. Soc.*, **90**, 6077 (1968).

(64) R. Huisgen and P. Otto, *Tetrahedron Lett.*, 4491 (1968); G. Binsch, L. A. Feiler, and R. Huisgen, *ibid.*, 4497 (1968).

(65) Difference between the experimentally determined molecular refraction and the calculated molecular refraction (using atomic refraction constants but omitting the C=C increment). For a detailed discussion of this experimental measure of the C=C bond polarizability see C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 119.

(66) 1,1-Dimethoxyethylene undergoes substitution with azodiformates; E. Koerner von Gustorf and D. V. White (1969), unpublished results.

(67) C. G. LeFévre, R. J. W. LeFévre, and W. T. Oh, *Aust. J. Chem.* **10**, 218 (1957); R. J. W. LeFévre, W. T. Oh, I. H. Reece, R. Roper, and R. L. Werner, *ibid.*, **11**, 92 (1958); A. Simon and H. Wagner, *Naturwissenschaften* **47**, 540 (1960).

(68) G. O. Schenck, H. R. Kopp, B. Kim, and E. Koerner von Gustorf, *Z. Naturforsch. B*, **20**, 637 (1965); E. Koerner von Gustorf and D. Hess, to be published, obtained *cis*-di-*t*-butyl azodiformate (95+ %) mp 32–34°.

(69) R. Askani, *Chem. Ber.*, **98**, 2551 (1965).

TABLE VII

PHOTOCHEMICAL ACCELERATION P OF THE ADDITION OF DEAD TO INDENE AND ETHYL VINYL ETHER

	$k_{cis(20°)}$, M^{-1} sec^{-1}	$k_{trans,(20°)}$, M^{-1} sec^{-1}	P_{obsd}[a]	P_{calcd}
DEAD + indene	1.0×10^{-3}	4.2×10^{-7}	76	75
DEAD + ethyl vinyl ether	6.2×10^{-4}	3.5×10^{-6}	3	6.5

[a] Ratio of the disappearance of DEAD (1.4×10^{-2} M in the neat olefins) under illumination (20 and 25 min; xenon high pressure lamp OSRAM XBO 2001 with UVG filter Spiegelglas AG Weilheim) to the dark reaction at 20 and 22.5°.

activity in Diels–Alder reactions increases with increasing population of the cisoid conformations.[46,50,70]

While **11** is formed from *trans*-DEAD and ethyl vinyl ether, the reaction of the latter with *cis*-DEAD in the dark, as well as with DEAD under illumination, yields similar mixtures of products resulting from hydrogen abstraction reactions, as demonstrated by NH absorption in ir; the structures of these products are currently being investigated.

We have not been able to observe any considerable acceleration of the addition of PTD to indene by illumination ($\lambda \geqq 500$ mμ). This finding points against a biradical intermediate in the corresponding thermal cycloaddition reaction; it also suggests the formation of *cis*-DEAD as being responsible for the photochemical acceleration of the reactions discussed above.

The photochemical observations are in accord with a concerted nature of the dihydrooxadiazine formation. The photochemical *cis–trans* isomerization of the azodiformates seems to be a much more important process than the addition of any electronically excited species to the unsaturated substrate in the systems investigated. A precedent is the photochemical addition of azobenzene to ketene, which consists of the photochemical formation of *cis*-azobenzene and its thermal addition to ketene; the thermal addition of pure *cis*-azobenzene to ketene is even slowed by illumination owing to the photochemical formation of the unreactive *trans*-azobenzene.[71]

Finally it should be noted that instances for reactions of electronically excited azodiformates with unsaturated substrates are known, *e.g.*, with cycloheptatriene[4,72] or cyclohexene;[73] in the former case it has been established that the thermal reaction follows a concerted path, but that the photochemical reaction proceeds in two steps.

Experimental Section[74]

Methyl 4a,6,7,8a-Tetrahydro-2-methoxy-4H-*p*-dioxino[2,3-*e*]-1,3,4-oxadiazine-4-carboxylate (5).—Dioxene[75] (0.71 g, 8.2 mmol) and 1.0 g (6.9 mmol) of DMAD in 12 ml of benzene were illuminated (3500 Å) for 67 hr in a Rayonet photochemical chamber reactor at 20°. Removal of the solvent from the colorless reaction mixture gave 1.6 g of solid material, mp 120–131°. Recrystallization from benzene–pentane yielded 0.35 g of pure **5**: mp 133–136°; mol wt 240 (232 mass spectrum); ir (CCl_4): no NH; 1723, 1755 cm^{-1} (C=O); 1681 cm^{-1} (C=N).

Anal. Calcd for $C_8H_{12}N_2O_6$ (232.2): C, 41.38; H, 5.21; N, 12.06. Found: C, 41.59; H, 5.35; N, 11.93.

Attempts to hydrogenate **5** catalytically in the presence of Raney Ni or Pd–$BaSO_4$ in ethyl acetate failed, and the starting material could be recovered.

Methyl 5,6-Dihydro-5,6-carbonato-2-methoxy-4H-1,3,4-oxadiazine-4-carboxylate (6).—Vinylene carbonate (0.69 g, 8.0 mmol) and 1.0 g (6.9 mmol) of DMAD in 12 ml of benzene were illuminated (as above) for 185 hr. Removal of the solvent and of polymeric material gave 0.069 g of **6**, mp 114–116°, after tedious recrystallization from chloroform and toluene: mol wt 232 (mass spectrum); ir ($CHCl_3$): no NH; 1840, 1762, 1730 cm^{-1} (C=O); 1680 cm^{-1} (C=N).

Anal. Calcd for $C_7H_8N_2O_7$ (232.2): C, 36.22; H, 3.47; N, 12.07. Found: C, 36.10; H, 3.60; N, 12.00.

Methyl *trans*-5,6-Dihydro-2,5,6-trimethoxy-4H-1,3,4-oxadiazine-4-carboxylate (7).—A solution of 1.25 g (8.5 mmol) of DMAD in 3 ml of C_6D_6 was added dropwise at 20° to 1.0 g (11 mmol) of *trans*-1,2-dimethoxy-ethylene[76] (98+% by preparative glpc) in 3 ml of C_6D_6. The reaction mixture was almost colorless after 30 min. On standing overnight a precipitate appeared. All volatile material was removed *in vacuo;* according to nmr analysis the C_6D_6 contained exclusively *trans*-1,2-dimethoxyethylene. The residue (2.0 g, 8.5 mmol), mp 126–128°, was pure (within the limits of nmr) **7** (recrystallization from benzene–*n*-hexane raised the melting point to 128–130°): mol wt 227; mass spectrum:[77] *m/e* (rel intensity) 234 (19), 235 (2), 203 (10), 175 (1), 159 (2), 149 (2), 118 (17), 89 (6), 88 (100), 86 (5), 85 (7), 75 (10), 73 (18), 70 (4); ir (KBr): no NH, 1727, 1688 cm^{-1} (C=O); 1660 cm^{-1} (C=N).

Anal. Calcd for $C_8H_{14}N_2O_6$ (234.2): C, 41.03; H, 6.03; N, 11.96. Found: C, 41.20; H, 6.16; N, 11.98.

Attempted catalytic hydrogenation of **7** with Raney Ni in ethyl acetate failed, and the starting material was recovered.

Methyl *cis*-5,6-Dihydro-2,5,6-trimethoxy-4H-1,3,4-oxadiazine-4-carboxylate (8) and Dimethyl *cis*-3,4-Dimethoxy-1,2-diazetidine 1,2-dicarboxylate (13).—DMAD (0.31 g, 2.1 mmol) in 1 ml of C_6D_6 was added to 0.26 g (2.4 mmol) of *cis*-1,2-dimethoxyethylene[76] (98+% by preparative glpc) in 1 ml of C_6D_6. Decolorization of the mixture took overnight. All volatile material was removed *in vacuo;* according to nmr analysis the C_6D_6 contained exclusively *cis*-1,2-dimethoxyethylene. The residue, a colorless oil (0.52 g, 2.2 mmol), was a 4:1 mixture of **8** and **13** according to nmr. Separation of these two compounds has not been achieved as yet: mol wt 260 (234 mass spectrum); ir ($CHCl_3$): no NH; 1725, 1705 cm^{-1} (C=O); 1665 cm^{-1} (b) (C=N).

Anal. Calcd for $C_8H_{14}N_2O_6$ (234.2): C, 41.03; H, 6.03; N, 11.96. Found: C, 40.87; H, 5.93; N, 11.78.

Ethyl 6-Acetoxy-2-ethoxy-5,6-dihydro-4H-1,3,4-oxadiazine-4-carboxylate (9).—DEAD (5.9 g, 34 mmol) and 28 g (0.33 mol) of vinyl acetate were refluxed under argon for 65 hr. The residue left after solvent removal was extracted with petroleum ether, 6.5 g remaining undissolved. The extract gave 3.2 g of a material, whose recrystallization from benzene–petroleum ether yielded 2.2 g (8.5 mmol) of **9**: mp 60–62°; mol wt 237; ir (CCl_4): no NH; 1770, 1750 (sh), 1705 cm^{-1} (C=O); 1675 cm^{-1} (C=N).

Anal. Calcd for $C_{10}H_{16}N_2O_6$ (260.3): C, 46.15; H, 6.20; N, 10.76. Found: C, 46.07; H, 6.23; N, 10.78.

(70) D. Craig, J. J. Shipman, and R. B. Fowler, *J. Amer. Chem. Soc.*, **83**, 2885 (1961).

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(74) Melting points are uncorrected. Ir spectra were taken with a grating spectrometer MH-2, SEM Brückl, Munich, and with a Beckman IR-12. The nmr spectra (τ) were recorded with a Varian A-60A and HA-100; the letter abbreviations used follow: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, o = octet, m = multiplet, b = broad; tetramethylsilane was used as internal standard. Molecular weights were determined cryoscopically or osmometrically (Mechrolab) in benzene. Indene, DEAD, and DMAD (all supplied by Aldrich) were purified by distillation. Illumination techniques have been described by G. O. Schenck, in A. Schönberg "Präparative Organische Photochemie," Springer-Verlag, Heidelberg, 1958, p 210.

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Attempted catalytic hydrogenation of **9** with PtO_2 or Raney Ni in ethyl acetate failed; the starting material was recovered.

Dimethyl 3-Methoxy-1,2-diazetidine-1,2-dicarboxylate (10).—A solution of 2.0 g (14 mmol) of DMAD and 82 g (1.4 mol) of methyl vinyl ether (J. T. Baker Chemical Co.) in 100 ml of benzene was decolorized after 4 days at room temperature. After solvent removal 2.7 g of an oil remained, which was purified by short-path distillation at 40–50° and 10^{-5} mm, yielding 0.79 g (4 mmol) of **10** as a colorless oil: mol wt 208; mass spectrum: *m/e* (rel intensity) 204 (98), 205 (11), 173 (17), 172 (26), 145 (55), 130 (11), 128 (18), 118 (21), 113 (14), 101 (31), 86 (31), 85 (17), 75 (100), 71 (12); ir (CCl_4): no NH, 1725, 1735, and 1760 cm^{-1} (C=O).

Anal. Calcd for $C_7H_{12}N_2O_5$ (204.2): C, 41.18; H, 5.92; N, 13.72. Found: C, 41.43; H, 6.17; N, 13.35.

Dimethyl 3-Ethoxy-1,2-diazetidine-1,2-dicarboxylate (12).—A solution of 2.0 g (14 mmol) of DMAD and 5.0 g (70 mmol) of ethyl vinyl ether (Fluka) became colorless after 2 days at room temperature. The solvent was removed, and 2.4 g (11 mmol) of an oil remained, comprising pure **12** according to ir. A part of the material was short-path distilled at 10^{-5} Torr and 40–54°: mol wt 240; mass spectrum: *m/e* (rel intensity) 218 (100), 186 (16), 159 (21), 145 (37), 104 (16), 89 (57), 86 (26), 85 (30), 84 (42), 72 (62), 71 (22), 61 (21); ir (CCl_4): no NH, 1727, 1764 cm^{-1} (C=O).

Anal. Calcd for $C_8H_{14}N_2O_5$ (218.2): C, 44.03; H, 6.47; N, 12.84. Found: C, 43.90; H, 6.34; N, 12.72.

Diethyl 3-Ethoxy-1,2-diazetidine-1,2-dicarboxylate (11).—A solution of 12.0 g (69 mmol) of DEAD in 50.6 g (0.7 mol) of vinyl ethyl ether (Fluka) became colorless after 18 hr at room temperature. After removal of excess ethyl vinyl ether 16.6 g of an oil was left, whose distillation at 130° yielded 5.3 g (21 mmol) of **11**: bp 108° (3×10^{-5} mm); $n^{20}D$ 1.4581; mol wt 246; ir (CCl_4): no NH; 1715, 1760 cm^{-1} (C=O).

Anal. Calcd for $C_{10}H_{18}N_2O_5$ (246.3): C, 48.77; H, 7.37; N, 11.38. Found: C, 48.64; H, 7.22; N, 11.32.

Since 7.9 g of a brown resin was obtained as residue from the vacuum distillation, decomposition of the undistilled oil (11.1 g, 45 mmol) obtained from the reaction of 7.8 g (45 mmol) of DEAD and 22.0 g (0.31 mol) of ethyl vinyl ether showed this to be pure **11** according to ir and elemental analysis, mol wt 219.

Anal. Found: C, 48.69; H, 7.32; N, 11.48.

Diethyl N-(2-Ethoxy-1-ethyl)-bicarbamate (15).—Compound **11** (3.7 g, 15 mmol) in 120 ml of ethyl acetate took up 1 mol of H_2/mol in 7 hr on shaking with H_2–PtO_2. Filtration and solvent removal gave 3.4 g of colorless oil, distillation of which at 150° yielded 1.9 g (7.7 mmol) of **15**: bp 115° (0.5 mm); $n^{20}D$ 1.4468; mol wt 251; ir (CCl_4): 3410, 3300 cm^{-1} (NH); 1720, 1755 cm^{-1} (C=O); nmr (CCl_4): 2.40 (s, 1 H); 5.85 (q, 4 H), J = 7 cps; 6.4 (m), 6.51 (q), J = 7 cps, (6 H); 8.74 (t), J = 7 cps, 8.84 (t), J = 7 cps (9 H).

Anal. Calcd for $C_{10}H_{20}N_2O_5$ (248.3) C, 48.38; H, 8.12; N, 11.28. Found: C, 48.35; H, 7.90; N, 11.97.

***cis*-1-Deuterio-2-ethoxyethylene (36).**—Ethoxydeuterioacetylene was obtained with an isotopic purity of 80% (mass spectrum) by using D_2O instead of H_2O in the slightly modified standard procedure.[78]

Ethoxydeuterioacetylene (4.1 g, 58 mmol) in 50 ml of methyl benzoate took up 1 mol of H_2/mol in 45 min on shaking with 5 g of aged Raney Ni–H_2. Immediate filtration and distillation gave 2.4 g (33 mmol) of a product, bp 29–36°, which contained **36** and *trans*-1-deuterio-2-ethoxyethylene (T) in a 5.1:1 ratio, besides ~27% undeuterated ethyl vinyl ether (U), according to the gravimetric determination of the area underneath the $C{=}C(O)H^x$ signals in the expanded nmr spectrum (neat). **36**: 3.54 (t), 3.65 (t), J_{ax} = 7 cps, J_{Dx} = 2.2 cps. T: 3.48 (obsc), 3.72 (obsc). U: 3.41, 3.52, 3.64, 3.76, J_{ax} = 7 cps, J_{bx} = 14 cps.

A solution of 0.56 g (7.8 mmol) **36** and 0.25 g (1.7 mmol) of DMAD in 12 ml of benzene became colorless in 4 days at room temperature and yielded 0.39 g (1.8 mmol) of adduct after solvent removal. This adduct contained according to nmr analysis (as above) **12**-D_1, the corresponding *trans* adduct in a 5.5:1 ratio, and **12**.

(*cis*-1,2-Dideuterio)-2-ethoxyethylene (37).—A solution of 4.4 g (63 mmol) of ethoxyacetylene in 50 ml of methyl benzoate was shaken with D_2–Raney Ni up to a consumption of 1 mol of D_2/mol. Distillation after filtration gave 1.7 g of product, bp 31–34°, which consisted mainly of **37**: nmr (neat) 1 olefinic H at 5.90 (t), J_{DH} = 2.2 cps.

The reaction of 1.0 g (13 mmol) of **37** with 0.25 g (1.7 mmol) of DMAD in 10 ml of benzene gave after 2 days at room temperature 0.36 g of adduct, with 1 H (four-membered ring) at 5.94 ($CDCl_3$).

2,3,4a,5,6,6a-Hexahydrodiazeto[3,4-*b*]dioxindicarboxylic Acid N-Phenylimide (14).—Solutions of 1.0 g (12 mmol) of dioxene in 80 ml of toluene and of 2.32 g of PTD (13 mmol) in 250 ml of toluene were both added dropwise to 100 ml of toluene with magnetic stirring at −40 to −60° over a period of 5 days. A white precipitate (1.76 g) was separated by filtration. Extraction of the material with $CHCl_3$ left 0.54 g (2.1 mmol) of **14** undissolved: mp 208–212°; mol wt (acetone) 279; mass spectrum: *m/e* (rel intensity) 261 (11), 149 (4), 142 (4), 120 (9), 119 (59), 92 (15), 91 (22), 87 (11), 86 (100), 85 (46), 83 (69), 78 (22); ir (KBr): no NH; 1702, 1729, and 1790 cm^{-1} (C=O).

Anal. Calcd for $C_{12}H_{11}N_3O_4$ (261.2): C, 55.17; H, 4.24; N, 16.08. Found: C, 54.84; H, 4.25; N, 15.98.

1-(1,4-Dioxan-2-yl)-4-phenyl-1,2,4-triazolidine-3,5-dione (16).—Compound **14** (0.22 g, 0.8 mmol) in ethyl acetate was shaken for 8 hr with H_2–Raney Ni. Cumbersome recrystallization of the residue, after filtration and solvent removal, gave 15 mg of **16**: mp 155–158° (from benzene–$CHCl_3$–*n*-hexane); mass spectrum: *m/e* (rel intensity) 263 (28), 228 (10), 177 (43), 168 (13), 149 (31), 119 (61), 91 (37), 88 (61), 87 (98), 86 (100), 84 (35), 77 (31), 73 (47), 69 (33); ir (KBr): 3300 cm^{-1} (NH); 1695–1720, 1788 cm^{-1} (C=O).

Anal. Calcd for $C_{12}H_{13}N_3O_4$ (263): C, 54.75; H, 4.98; N, 15.96. Found: C, 54.90; H, 5.60; N, 16.19.

1,2,2a,7b-Tetrahydro-3H-indeno[2,1-*c*]1,2-diazete-1,2-dicarboxylic Acid N-Phenylimide (21).—A solution of 5.0 g (29 mmol) of PTD[25] in 350 ml of benzene was added dropwise at 5–10° to 34 g (0.29 mol) of indene under an argon atmosphere. Compound **21** (2.88 g, 10 mmol) precipitated overnight on standing at ≦10°: mp 166–167.5° (from $CHCl_3$); mol wt 281; mass spectrum: *m/e* (rel intensity) 291 (23), 177 (27), 130 (10), 129 (43), 120 (18), 119 (100), 115 (14), 91 (42), 78 (15), 77 (17), 64 (29).

Anal. Calcd for $C_{17}H_{13}N_3O_2$ (291.3): C, 70.09; H, 4.50; N, 14.42. Found: C, 69.85; H, 4.61; N, 14.18.

1-(2-Indanyl)-4-phenyl-1,2,4-triazolidine-3,5-dione (19).—Compound **21** (1.03 g, 3.4 mmol) in ethyl acetate yielded 0.93 g (3.2 mmol) of **19** on shaking with H_2–Raney Ni: mp 166.5–168° (from benzene–*n*-hexane); mass spectrum: *m/e* (rel intensity) 293 (3), 179 (4), 178 (36), 177 (14), 149 (5), 119 (4), 118 (4), 117 (41), 116 (100), 115 (18), 103 (4), 91 (11), 78 (9), 77 (5); ir (KBr): 3060, 3160 cm^{-1} (NH); 1675, 1770 cm^{-1} (C=O); nmr ($CDCl_3$): 2.57 (s, 5 H); 2.76 (b s, 1 H); 2.85 (s, 4 H); 4.95 (qui, 1 H), J = 7.7 cps; 6.83 (q, 4 H).

Anal. Calcd for $C_{17}H_{15}N_3O_2$ (293.3): C, 69.61; H, 5.15; N, 14.33. Found: C, 69.39; H, 5.21; N, 14.33.

1-(1-Hydroxy-2-indanyl)-4-phenyl-1,2,4-triazolidine-3,5-dione (20).—Compound **21** (0.50 g, 1.7 mmol) was dissolved in 43 ml of acetone containing 1.5 ml of concentrated aqueous HCl, and kept for 5 days at room temperature. After solvent evaporation and extraction with benzene 0.19 g (0.6 mmol) of benzene-insoluble **20** remained: mp 205–207° (from $CHCl_3$); mol wt (in $CHCl_3$) 312; mass spectrum: *m/e* (rel intensity) 309 (2), 291 (18), 178 (11), 133 (12), 132 (90), 119 (21), 117 (10), 116 (100), 115 (17), 91 (15), 83 (14); ir (KBr): 3450 cm^{-1} (OH); 3060, 3140 cm^{-1} (NH); 1685, 1710, 1768 cm^{-1} (C=O); nmr [$(CD_3)_2$-CO]: 2.6 (m, 10 H); 4.45 (d, 1 H) J = 8 cps; 5.28 (b, q, 1 H); 6.77 (b, d, 2 H); 7.2 (b, 1 H).

Anal. Calcd for $C_{17}H_{15}N_3O_3$ (309.3): C, 66.01; H, 4.89; N, 13.58. Found: C, 65.52; H, 4.90; N, 12.92.

Reaction of PTD with Indene in the Presence of Water.—A solution of 1.0 g (5.7 mmol) of PTD in 50 ml of dry acetone was added dropwise to a solution of 0.70 g (6.0 mmol) of indene in 50 ml of acetone containing 3% water. After 1 hr the solvent was removed and 0.53 g (1.7 mmol) of benzene insoluble **20** remained (mp 206–208° from $CHCl_3$–*n*-hexane). Its identity with the product fron the acid hydrolysis was proven by melting point and ir.

Anal. Calcd for $C_{17}H_{15}N_3O_3$ (309.3): C, 66.01; H, 4.89; N, 13.58. Found: C, 65.71; H, 4.93; N, 13.41.

In a control experiment 0.50 g (1.7 mmol) **21** was dissolved in 50 ml of acetone containing 3% water, and kept for 6 hr at room

(78) E. R. H. Jones, G. Eglinton, M. C. Whiting, and B. L. Shaw, *Org. Syn.*, **34**, 46 (1954). We extracted the crude ethoxyacetylene from the reaction mixture with *n*-butyl ether instead of distilling it at 100°.

temperature. Extraction with benzene after solvent removal did not yield any insoluble material; from the benzene solution 0.49 g of **21**, mp 166–168°, identical with the starting material according to ir, was recovered.

$LiAlH_4$ Reduction of 21.—Compound **21** (4.15 g, 14 mmol) in 300 ml of benzene was added dropwise to 10.8 g (0.3 mol) of $LiAlH_4$ in 500 ml of anhydrous ether. After refluxing for 1 hr excess $LiAlH_4$ was destroyed with water; the filtrate, dried over Na_2SO_4, yielded 2.06 g of a brown oil after solvent removal. A colorless liquid (0.73 g) could be separated from this oil by short-path distillation at room temperature and 10^{-2} mm in an apparatus equipped with a liquid N_2 cooled finger; glpc showed it to be a mixture of N-methylaniline (93%), indene (4.1 %), aniline (1.7 %), and N,N-dimethylaniline (<0.5 %). The residue from this distillation was separated by extraction into a pentane-soluble fraction (a) and a pentane-insoluble fraction (b).

Very cumbersome recrystallization of tarry fraction a gave 3 mg of colorless **1,2,3,3a,4,8b-hexahydro-1-(or 3)-methylindeno[2,1-*d*]imidazole (22)**, mp 75–85° dec (from pentane). Attempted purification by tlc was inadequate owing to decomposition: mass spectrum: *m/e* (rel intensity) 174 (26), 173 (42), 145 (69), 144 (100), 132 (24), 131 (28), 130 (50), 116 (21), 115 (33), 78 (20), 77 (22); ir (KBr): 3220 cm^{-1} (NH); 2780, 2840 cm^{-1} (NCH_3, NCH_2); no C=O; nmr ($CDCl_3$, microcell): 2.7 (m, 4 H); 5.2 (d, 1 H), $J \approx 6$–7 cps; 6.2 (m, 1 H); 6.7 (m), 6.95 (b, s, 4 H); 7.6 (s), 7.7 (b, 4 H).

From the pentane-insoluble dark brown oil (b) ~30 mg of colorless **1,2,2a,7b-tetrahydro-3H-indeno[2,1-*c*]1,2-diazete-1-carboxanilide (23)** could be separated by crystallization at <10°; it was purified by washing with benzene: mp 137–139°; mass spectrum:[79] *m/e* (rel intensity) 265 (2), 130 (32), 129 (43), 119 (47), 117 (28), 116 (100), 115 (44), 102 (23), 93 (31), 91 (28), 78 (15), 77 (15), 64 (19), 63 (17); calcd for $C_{16}H_{15}N_3O$: *m/e* 265.1215; found: *m/e* 265.1212 and 265.1215; ir (KBr): 3300, 3180 cm^{-1} (NH); 1662 cm^{-1} (C=O); 1515 cm^{-1} (amide II band); nmr ($CDCl_3$): 2.07 (b, 1 H); 2.6 (m, 9 H); 4.15 (d, 1 H) $J = 5.5$ cps; 5.0 (b, m, ~2 H); 6.75 (m, 2 H).

Photochemical Formation of 4a,9b-Dihydro-2-ethoxy-4H-indeno[2,1-*c*]-1,3,4-oxadiazine-4-carboxylic Acid Ethyl Ester (30a).—DEAD (20.1 g, 0.116 mol) and 40.0 g (0.345 mol) of indene were irradiated for 28 hr at room temperature using a high pressure xenon lamp Osram XBO-2001 placed in a Friesecke and Hoepfner cinema projector FH-X-66. The colorless reaction mixture yielded 30.5 g (0.105 mol) of **30a**, mp 105–106.5°, on trituration with pentane: mol wt 305; mass spectrum: *m/e* (rel intensity) 290 (23), 291 (4), 171 (3), 149 (4), 130 (3), 129 (3), 117 (17), 116 (100), 115 (16), 105 (3), 78 (3); ir (Table IV): no NH; uv_{max} (CH_3OH): 36930 cm^{-1} (ϵ 758), 37900 (850), 39000 (820).

Anal. Calcd for $C_{15}H_{18}O_4N_2$ (290.3): C, 62.06; H, 6.25; N, 9.65. Found: C, 62.10; H, 6.30; N, 9.59.

Photochemical Formation of 4a,9b-Dihydro-2-methoxy-4H-indeno[2,1-*e*]-1,3,4-oxadiazine-4-carboxylic Acid Methyl Ester (30b).—Illumination of 12.9 g (89 mmol) of DMAD and 158 g (1.36 mol) of indene for 48 hr with an immersed high pressure mercury lamp HPK 125 W (Solidex filter) at 20° gave 24 g of residue after removal of indene at 100° *in vacuo*. Extraction of the residue with 800 ml of pentane yielded 7.0 g (27 mmol) of **30b**: mp 110–112° (from CCl_4–pentane); mol wt 259; mass spectrum: *m/e* (rel intensity) 262 (27), 263 (5), 149 (6), 129 (6), 117 (14), 116 (100), 115 (21), 103 (2), 91 (2), 77 (2), 65 (2); ir (Table IV): no NH.

Anal. Calcd for $C_{13}H_{14}N_2O_4$ (262.3): C, 59.54; H, 5.38; N, 10.68. Found: C, 59.30; H, 5.29; N, 10.71.

Addition of Diethyl *cis*-Azodiformate (*cis*-DEAD) to Indene.—Illumination (40 hr, 3500 Å; Rayonet preparative photochemical reactor RPR-208) of 6.0 g (34 mmol) of DEAD in 500 ml of benzene at 20° afforded 0.64 g (3.7 mmol) of *cis*-DEAD according to titration with cyclopentadiene.[68] Reaction of this solution with 1.0 g (8.6 mmol) of indene in the dark yielded 1.0 g (3.5 mmol) of **30a**, mp 104–105.5°, its ir was identical with that of the photochemically prepared material.

Pyrolysis of 30a.—Compound **30a** (2.1 g, 7.3 mmol) was heated *in vacuo* to 300° with a bunsen burner. The reaction products were collected from the trap and the flask by rinsing with pentane; besides 0.42 g (1.4 mmol) of unreacted **30a** 0.48 g (4.1 mmol) of indene (identified by glpc) was obtained.

(79) High-resolution mass spectrum performed on a MS-9 through the courtesy of Dr. G. Schaden.

Diethyl-(2-Indanyl)bicarbamate (29).—Compound **30a** (8.7 g, 30 mmol) in 300 ml of ethyl acetate gave quantitatively **29** on shaking with H_2–PtO_2: mp 68–74°; mol wt 291; mass spectrum: *m/e* (rel intensity) 292 (0.4), 177 (9), 176 (16), 150 (5), 130 (13), 117 (25), 116 (100), 115 (8), 104 (14), 103 (6), 91 (5); ir (KBr): 3285 cm^{-1} (NH); 1710, 1750 cm^{-1} (C=O); 1517 cm^{-1} (amide II band); nmr (CCl_4): 2.97 (s), 3.1 (b, 4 H); 4.97 (qui, 1 H), $J = 8$ cps; 5.88 (q), 5.95 (q, 4 H); 6.98 (d, 2 H), $J = 8$ cps; 8.79 (t), 8.82 (t, 6 H).

Anal. Calcd for $C_{15}H_{20}N_2O_4$ (292.3): C, 61.63; H, 6.90; N, 9.58; 1 act H, 0.34. Found: C, 61.45; H, 7.02; N, 9.29; act H, 0.44.

Ethyl 3-(2-Indanyl)-3-methylcarbazate (27).—Compound **29** (1.29 g, 4.4 mmol) in 15 ml of benzene and 50 ml of ether were added to 0.75 g (20 mmol) of $LiAlH_4$ in 80 ml of ether. Refluxing for 2 hr, destruction of excess $LiAlH_4$ with water, filtration, and drying over K_2CO_3 gave 0.77 g (3.3 mmol) of **27**: mp 79–80° (from benzene–pentane); mol wt 231; ir (CCl_4): 3460, 3270 cm^{-1} (NH); 1750, 1735, 1705 cm^{-1} (C=O), 1500 cm^{-1} (amide II band); nmr (CCl_4): 3.00 (s, 4 H); 3.40 (b, s, 1 H); 5.95 (q, 2 H), $J = 7$ cps; 6.25 (m, 1 H); 7.11 (b, d, 4 H), $J = 7.5$ cps; 7.41 (s, 3 H); 8.81 (t, 3 H), $J = 7$ cps.

Anal. Calcd for $C_{13}H_{18}N_2O_2$ (234.3): C, 66.64; H, 7.74; N, 11.96. Found: C, 66.95; H, 7.95; N, 11.95.

2-(1,2-Dimethylhydrazino)-1-indanol (28).—Compound **30a** (5.85 g, 20 mmol) in 40 ml of benzene and 100 ml of ether was added to 3.90 g (0.1 mol) of $LiAlH_4$ in 150 ml of ether. After 2 hr refluxing, work-up with water, drying over K_2CO_3, and solvent removal 3.05 g (16 mmol) of **28** remained: mp 67–75° (from benzene–pentane); mol wt 186; mass spectrum: *m/e* (rel intensity) 192 (86), 193 (12), 162 (15), 144 (11), 133 (16), 132 (12), 119 (18), 117 (14), 116 (100), 115 (18), 105 (18), 103 (16), 91 (30), 77 (23), 73 (98); ir (CCl_4): 3430 cm^{-1} (OH); 3200 cm^{-1} (NH); 2780, 2830 cm^{-1} (NCH_3); nmr (CCl_4): 2.9 (m, 4 H); 5.14 (d, 1 H), $J = 4.5$ cps; 6.9 (m, 2 H); 7.1 (m, 3 H); 7.51 (s, 3 H); 7.54 (s, 3 H).

Anal. Calcd for $C_{11}H_{16}N_2O$ (192.3): C, 68.72; H, 8.39; N, 14.57; 2 act H, 1.04. Found: C, 68.50; H, 8.60; N, 14.48; act H, 1.03.

Diethyl (1-Hydroxy-2-indanyl)bicarbamate (31) and Ethyl 3-(2,3,3a,8b-Tetrahydro-2-oxo-4H-indeno[2,1-*d*]oxazolyl)carbamate (32).—Finely powdered **30a** (4.9 g, 17 mmol) was added with stirring over a period of 30 min to 27.5 ml of concentrated H_2SO_4, kept in an ice bath. After 20 more min the dark red solution was slowly poured into 650 g of ice–water. The mixture was allowed to warm up to room temperature and 0.3 g of a slimy precipitate was removed by filtration. Two fractions of crystals separated from the clear filtrate during 6 days at room temperature: (a) 0.42 g, mp 115–130°, on the surface of the solution, and (b) 1.74 g, mp 105–125°, on the bottom of the flask. Recrystallization of a from benzene–*n*-hexane gave **31**: mp 123–126°; mol wt 310; mass spectrum: *m/e* (rel intensity) 308 (4), 290 (8), 218 (11), 177 (29), 176 (94), 150 (40), 149 (12), 145 (12), 132 (71), 130 (37), 116 (49), 115 (43), 104 (26), 91 (12), 84 (100), 69 (23); ir (KBr): 3400 cm^{-1} (OH); 3230 cm^{-1} (NH); 1755, 1687 cm^{-1} (C=O); 1550 cm^{-1} (amide II); nmr ($CDCl_3$): 2.7 (m, 5 H); 4.70 (b, d, 1 H), $J = 8$–9 cps; 5.23 (m, 1 H); 5.76 (q, 4 H), $J = 7$ cps; 6.05 (b, ~1 H); 6.97 (m, 2 H); 8.72 (t 6 H), $J = 7$ cps.

Anal. Calcd for $C_{15}H_{20}N_2O_5$ (308.3): C, 58.43; H, 6.54; N, 9.09. Found: C, 58.25; H, 6.51; N, 9.02.

Recrystallization of fraction b from benzene–*n*-hexane yielded 1.14 g (4.4 mmol) of **32**: mp 131–132°; mol wt 275; mass spectrum: *m/e* (rel intensity) 262 (6), 218 (59), 145 (12), 130 (31), 129 (41), 126 (21), 117 (22), 116 (44), 115 (29), 113 (11), 84 (100), 69 (18); ir (KBr): 3250 cm^{-1} (NH); 1760–1770, 1722–1733 cm^{-1} (C=O); 1535 cm^{-1} (amide II band); nmr ($CDCl_3$): 2.6 (m, 4 H); 2.9 (b, s, 1 H); 4.12 (d, 1 H), $J = 7.5$ cps; 5.23 (m, 1 H); 5.77 (q, 2 H), $J = 7$ cps; 6.8 (m, 2 H); 8.75 (t, 3 H), $J = 7$ cps.

Anal. Calcd for $C_{13}H_{14}N_2O_4$ (262.3): C, 59.54; H, 5.38; N, 10.68. Found: C, 59.70; H, 5.20; N, 10.67.

Acid-Catalyzed Transformation 31 → 32.—Compound **31** (1.0 g, 3.2 mmol) was added over a 10-min period to 4.9 ml of concentrated H_2SO_4, kept in an ice bath. The solution was poured into 125 g of ice–water, and filtered. After 6 days at room temperature 0.23 g (0.9 mmol) of **32**, mp 129–131°, had precipitated, showing ir data as given above.

Ethyl 3-(2-Indanyl)carbazate (33).—Compound **32** (1.0 g, 3.8 mmol) in 150 ml of ethyl acetate yielded on 1.5-hr shaking with

H_2–Pd–$BaSO_4$, after filtration and solvent removal, 0.84 g (3.8 mmol) of **33**: mp 121–122° (from benzene–*n*-hexane); mol wt 224; ir (KBr): 3310, 3250 cm^{-1} (NH); 1700 cm^{-1} (C=O); 1508 cm^{-1} (amide II); nmr ($CDCl_3$): 2.86 (s, 4 H); 3.46 (b, 1 H); 5.83 (q) J = 7 cps, 6.1 (m, 4 H); 7.08 (m, 4 H); 8.75 (t, 3 H), J = 7 cps.

Anal. Calcd for $C_{12}H_{16}N_2O_2$ (220.3): C, 65.43; H, 7.32; N, 12.72. Found: C, 65.42; H, 7.24; N, 12.75.

Synthesis[80] of Ethyl 3-(2-Indanyl)carbazate (33).—Addition of 0.5 ml of glacial acetic to a solution of 5.0 g (38 mmol) of 2-indanone[81] and 4.3 g (41 mmol) of ethyl carbazate (purum Fluka) in 75 ml of ethanol (95%) at 50° gave the precipitation of 6.0 g (28 mmol) of 2-indanone-N-carbethoxyhydrazone (**34**) in 5 min: mp 176–177° (from benzene–acetone–*n*-hexane), lit.[80] mp 168–169.5°; mol wt (acetone) 215; ir (KBr): 3200, 3120 cm^{-1} (NH); 1700, 1655 cm^{-1} (C=O, C=N); nmr ($CDCl_3$): 2.0 (b, 1 H); 2.79 (s, 4 H); 5.70 (q, 2 H), J = 7 cps; 6.25 (m, 4 H); 8.67 (t, 3 H), J = 7 cps.

Anal. Calcd for $C_{12}H_{14}N_2O_2$ (218.3): C, 66.04; H, 6.47; N, 12.84. Found: C, 65.83; H, 6.47; N, 12.57.

Compound **34** (1.0 g, 4.6 mmol) in 75 ml of ethanol and 25 ml of glacial acetic acid was shaken with H_2–Pt–charcoal for 3.5 hr. Filtration, solvent removal *in vacuo*, and recrystallization of the remaining product from benzene–*n*-hexane afforded 0.38 g (1.7 mmol) of **33**: mp 121–122°, lit.[80] mp 120–120.5°; mol wt 227.

Anal. Calcd for $C_{12}H_{16}N_2O_2$ (220.3): C, 65.43; H, 7.32; N, 12.72. Found: C, 65.10; H, 7.07; N, 12.78.

Compound **33**, synthesized following this procedure, was identical with the product from the catalytic hydrogenation of **32** according to ir, nmr, and mixture melting point.

Kinetic Measurements.—Absorption spectroscopy (uv) at 24400–24700 cm^{-1} (DEAD) and 18400 cm^{-1} (PTD) was used to monitor the concentrations of DEAD and PTD in all the kinetic runs. The measurements were carried out with a Zeiss spectrophotometer PMQ II in 1-cm water-jacketted cells. Temperature was controlled to ±0.1° with a Haake ultrathermostat. The following initial concentrations were used in various solvents (Table V): system DEAD–indene, 2×10^{-2} *M* DEAD–1.4 *M* indene; system DEAD–ethyl vinyl ether, 2×10^{-2} *M* DEAD–1.4 *M* ethyl vinyl ether; system PTD–indene, 7×10^{-3} *M* PTD–7×10^{-3} *M* indene. All runs were at least duplicated.

Standard equations and graphic methods were applied to determine the orders of reaction, rate constants, and activation parameters. The maximum error observed for the rate constants was ± 7%; it was only exceeded for PTD + indene in acetonitrile (±16%).

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3,4-Disubstituted and Fused 1,2,5-Thiadiazole N-Oxides

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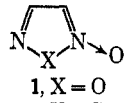
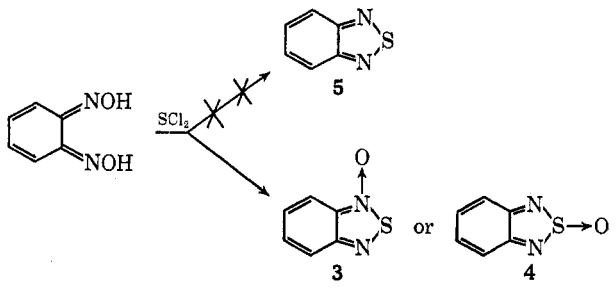
Acyclic and cyclic compounds containing the α-dioxime grouping are converted into mixtures of 3,4-disubstituted and fused 1,2,5-thiadiazoles and the corresponding N-oxides by reaction with sulfur dichloride.

Although furoxans (**1**) have been known for a long time, the corresponding 1,2,5-thiadiazole N-oxides (**2**) have not been definitely recognized. The reaction of



1, X = O
2, X = S

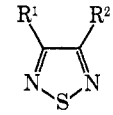
o-benzoquinone dioxime with sulfur dichloride has been reported,[1] but the structure of the reaction product was not determined unequivocally; the structures that were proposed are that of an N-oxide (**3**) and S-oxide (**4**); formation of 2,1,3-benzothiadiazole (**5**) was not observed.



5

3 **4**

Previous investigations of the action of sulfur monochloride and sulfur dichloride on aliphatic compounds containing an NCCN grouping also involved oximes and α-dioximes. α-Isonitrosocyanoacetamide and α-isonitrosophenylacetonitrile were converted into 3-cyano-4-hydroxy-1,2,5-thiadiazole[2] (**6**) and 3-chloro-4-phenyl-1,2,5-thiadiazole,[3] (**7**), respectively, while glyoxime and



6, R^1 = CN; R^2 = OH
7, R^1 = Cl; R^2 = C_6H_5
8, R^1 = R^2 = H and/or Cl
9, R^1 = R^2 = CH_3

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