The more rapidly eluted product proved to be 15, ir $\nu_{max}^{CCl_4}$ 1706 cm^{-1}; the second substance was identified as 16, ir $\nu_{max}^{CCl_4}$ 1715 cm^{-1}.

Irradiation of 4-Methyl-N-carbomethoxyazepine (17).—A solution of 1.50 g (9.1 mmol) of 17[9] in 350 ml of methanol was irradiated as described for 10 for 12 hr. The reaction mixture was concentrated and samples of 18 (60%, ir $\nu_{max}^{CCl_4}$ 1712 cm^{-1}) and 19 (40%, ir $\nu_{max}^{CCl_4}$ 1712 cm^{-1}) were collected by gas chromatography[14] at 110°.

Unsaturated Heterocyclic Systems. LV. Cycloaddition Reactions of Derivatives of 1H-Azepine[1]

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The cycloadditions of N-substituted azepines to various dienophiles and dienes have been studied. With tetracyanoethylene, the azepines add as 1,4-dienes without prior valence bond isomerization; however, a directional specificity is observed with the monomethyl ring substituted examples. With N-phenylmaleimide, there is again evidenced 1,4 addition to the seven-membered ring, the stereochemical outcome (*endo*) being in agreement with orbital symmetry considerations. In the case of isobenzofurans, $(4 + 2)\pi$ cycloaddition to the 4,5 bond of the azepines occurs. Significantly, the stereochemistry of these reactions is likewise *endo*. 2,5-Dimethyl-3,4-diphenylcyclopentadienone functions in a similar fashion. Therefore, this kinetic preference for addition to the double bond of the azepine ring most remote from the nitrogen atom does not appear to be dependent on the electronic characteristics of the 4π donor. These results indicate that the 1H-azepine nucleus is unique in its capability to undergo thermally induced cycloaddition reactions without recourse to prior valence tautomerism.

A common and fundamental property of conjugated medium-ring polyenes is their capability for cycloaddition. Frequently, however, addition of a dienophile to a cyclic polyolefin eventuates in Diels–Alder [$(4 + 2) \pi$] reaction with the valence tautomer of the triene or tetraene system. Thus, cyclooctatetraenes (1), azacyclooctatetraenes (2), cycloheptatrienes (3), and oxepins (4) yield tricyclic adducts formally derived from bicyclo[4.2.0]octatriene,[3] 7-azabicyclo[4.2.0]octatriene,[4] norcaradiene,[5] and benzene oxide[6] intermediates, respectively. The reported exceptions to this general trend appear to be tropone (5),[7] certain tropolones and their ethers,[7] and 1H-azepines (6).[8] This difference in behavior is understandable in view of the facility with which 1–4 equilibrate with their valence tautomers and the contrasting difficulty presumably experienced by 5[9]

and 6[10] to attain a similar rapid equilibrium with their bicyclic forms. Cycloaddition to the diene tautomers is kinetically preferred because of the favorable increase in coplanarity of the four participating π orbitals in these structures.

More recently, several reports concerning the cycloaddition of cyclic trienes to suitable dienes in a $(6 + 4)\pi$ reaction have appeared. Thus, tropone (5) condenses readily with cyclopentadiene to give 7,[11] whereas both

7

8a, R = O
b, R = H₂
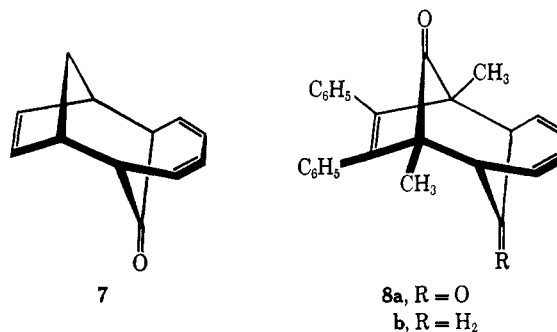
5 and cycloheptatriene add to 2,5-dimethyl-3,4-diphenylcyclopentadienone to afford 8a and 8b, respectively.[12] Orbital symmetry considerations indicate that such reactions, if effected with heat, may be concerted and should exhibit a preference for *exo* addition

(1) For previous paper, see L. A. Paquette and D. E. Kuhla, *J. Org. Chem.*, **34**, 2885 (1969).

(2) National Institutes of Health Predoctoral Fellow, 1965–1968.

(3) For a review, consult G. Schröder, "Cyclooctatetraene," Verlag Chemie, Weinheim/Bergstr., Germany, 1965.

(4) L. A. Paquette and T. Kakihana, *J. Amer. Chem. Soc.*, **90**, 3897 (1968).

(5) (a) K. Alder and G. Jacobs, *Chem. Ber.*, **86**, 1528 (1953); (b) M. J. Goldstein and A. H. Gervitz, *Tetrahedron Lett.*, 4417 (1965); (c) G. H. Wahl, Jr., *J. Org. Chem.*, **33**, 2158 (1968).

(6) (a) E. Vogel, R. Schubart, and W. A. Böll, *Angew. Chem. Intern. Ed. Engl.*, **3**, 510 (1964); (b) E. Vogel, E. A. Böll, and H. Günther, *Tetrahedron Lett.*, 609 (1965).

(7) (a) T. Nozoe, T. Mukai, K. Takase, and T. Nagase, *Proc. Jap. Acad.*, **28**, 477 (1962); *Chem. Abstr.*, **48**, 2678 (1954); (b) J. Meinwald, S. L. Emerson, N. C. Yang, and G. Buchi, *J. Amer. Chem. Soc.*, **77**, 4400 (1955); (c) O. L. Chapman and D. J. Pasto, *ibid.*, **81**, 3696 (1959); (d) T. Nozoe, T. Mukai, T. Nagase, and Y. Toyooka, *Bull. Chem. Soc. Jap.*, **33**, 1147 (1960); (e) J. Ciabattoni, J. E. Crowley, and A. S. Kende, *J. Amer. Chem. Soc.*, **89**, 2778 (1967); (f) Y. Kitahara, I. Murata, and T. Nitta, *Tetrahedron Lett.*, 3003 (1967); (g) S. Ito, H. Takeshita, Y. Shoji, Y. Toyooka, and T. Nozoe, *ibid.*, 3215 (1968).

(8) (a) J. E. Baldwin and R. A. Smith, *J. Amer. Chem. Soc.*, **87**, 4819 (1965); (b) A. S. Kende, P. T. Izzo, and J. E. Lancaster, *ibid.*, **87**, 5044 (1965).

(9) Valence tautomerism of a tropone or tropolone would lead to an energetically unfavorable cyclopropanone derivative.

(10) (a) L. A. Paquette, D. E. Kuhla, J. H. Barrett, and R. J. Haluska, *J. Org. Chem.*, **34**, 2866 (1969); (b) L. A. Paquette, D. E. Kuhla, and J. H. Barrett, *ibid.*, **34**, 2879 (1969); (c) L. A. Paquette, J. H. Barrett, and D. E. Kuhla, *J. Amer. Chem. Soc.*, **91**, 3231 (1969).

(11) (a) R. C. Cookson, B. V. Drake, J. Hudec, and A. Morrison, *Chem. Commun.*, 15 (1966); (b) S. Ito, Y. Fujise, T. Okuda, and Y. Inoue, *Bull. Chem. Soc. Jap.*, **39**, 1951 (1966).

(12) R. B. Woodward and K. Houk, unpublished work cited by R. B. Woodward, "Aromaticity," Special Publication No. 21, Chemical Society (London), 1967, pp 242–246.

(observed in the cases of **7** and **8**) if symmetry factors are dominant.[13]

Earlier, the kinetically controlled dimerization of 1-carbalkoxy-1H-azepines was shown to be the result of a similar $(6 + 4)\pi$ combination with *exo* orientation,[10c] in which the azepine molecules play the rather unique bifunctional role of 6π- and 4π-electron donors. We now report a more detailed investigation of the characteristics of these 8π heterocycles in a variety of cycloaddition reactions.

Tetracyanoethylene.—Only recently have the structures of the adducts produced by reaction of N-carbethoxy- and N-carbomethoxyazepines with tetracyanoethylene (TCNE) been rigorously established as **9a** and **9b**, respectively.[8,14] Kende and Baldwin combined an evaluation of spectral parameters, chemical transformations, and X-ray analysis[15] to demonstrate that the cycloadditions resulted from bonding directly to the nonrearranged seven-membered ring. The reaction of TCNE with a mixture of 1-carbomethoxy-bromoazepines to give **10** and **11** has been described.[8a,16]


9a, R = C₂H₅
b, R = CH₃
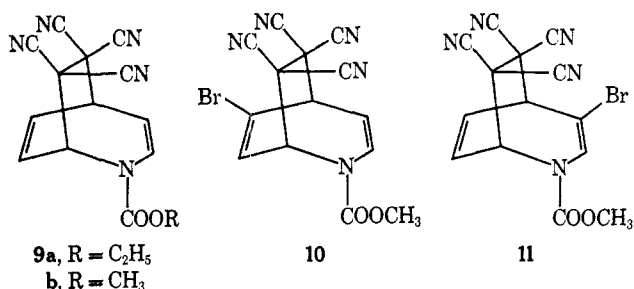
We have investigated the reaction of TCNE with the three isomerically pure methyl N-carbomethoxyazepines. The 4-methyl isomer (**12**) was found to react readily with TCNE in refluxing toluene solution to produce in 65% yield the previously characterized[8a] $(4 + 2)\pi$ adduct **13**. There was no evidence that any of the isomeric possibility (**14**) had formed.
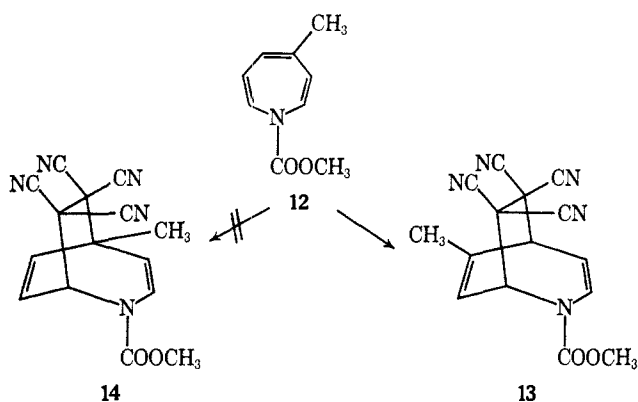

2-Methyl-N-carbomethoxyazepine (**15**) under identical conditions gave **16**, but only in 2.5% yield. The

(13) R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 4388 (1965).

(14) For a previous erroneous structural assignment, see K. Hafner, *Angew. Chem.*, **75**, 1041 (1963); *Angew. Chem. Intern. Ed. Engl.*, **3**, 165 (1964).

(15) J. H. van den Hende and A. S. Kende, *Chem. Commun.*, 384 (1965).

(16) I. C. Paul, J. E. Baldwin, and R. A. Smith, *J. Amer. Chem. Soc.*, **88**, 3653 (1966); R. A. Smith, J. E. Baldwin, and I. C. Paul, *J. Chem. Soc.*, *B*, 112 (1967).

nmr spectrum of **16** in DMSO-d_6 displayed a multiplet at δ 6.28–6.91 characteristic of H₆ and H₇, a one-proton
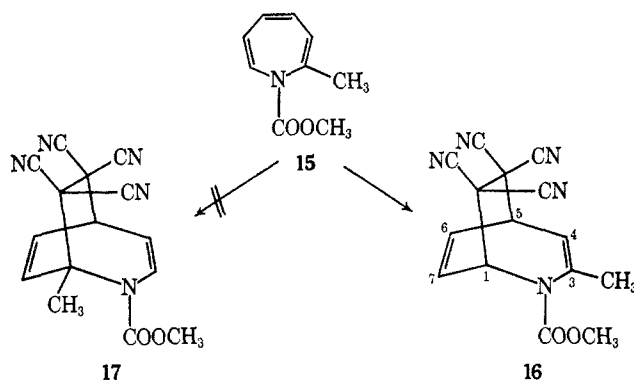
doublet of doublets centered at 6.04 ($J_{16} = 1.4$ Hz, $J_{17} = 7.5$ Hz), multiplets at 5.08–5.31 and 3.85–4.15 (H₄ and H₅, respectively), and C-methyl absorption (d, $J = 1.5$ Hz) at 2.15. The appearance of the very characteristic pair of doublets at δ 6.04 assignable to H₁ serves to rule out the possibility that the adduct was actually **17**, which bears a methyl group at that position. No indication was ever obtained that **17** was present in the crude reaction mixtures. The only other characterizable product was 2-methyl-N-carbomethoxy-aniline (5% yield) which presumably arose from rearrangement of **15**.[10b] The major portion of the reaction mixture was intractable black tar.

Refluxing 3-methyl-N-carbomethoxyazepine (**18**) with TCNE in toluene led to the formation of a mixture of adducts **19** and **20** in 66% yield. The two substances
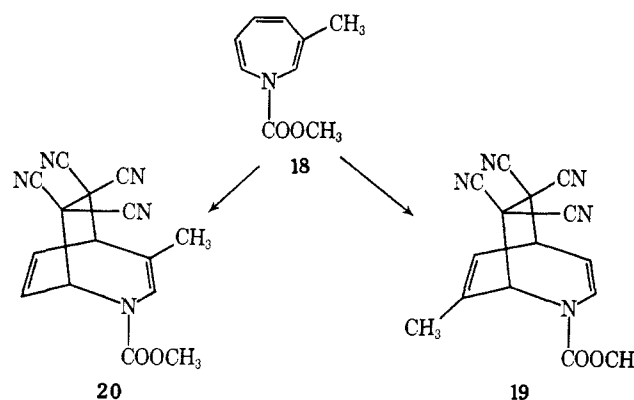
could not be separated by preparative thin layer or column chromatography. However, when the yellowish oil was treated with a seed crystal of **13**, a white crystalline solid, mp 146 5–148.5°, was deposited. The nmr spectrum of this material (in DMSO-d_6) showed significant absorptions centered at δ 6.45 (two-proton multiplet, H₃ and H₆), 5.76 (broad singlet, H₁), 5.43 (multiplet, H₄), ca. 3.81 (multiplet, H₅), and 2.15 (slightly broadened three-proton singlet, C-methyl). The appearance of a signal at δ 5.43, which has a chemical shift assignable to H₄, permitted the assignment of structure **19** to the crystalline product. Other indications that the solid was the 7-methyl derivative were found in the absence of a low field absorption due to H₇, the simplification of the H₁ signal, since spin–spin

coupling to H_6 is not possible, and the high field position of the methyl resonance.[17]

The filtrates from the above crystallization could not be sufficiently enriched in **20** to permit isolation of this adduct in a pure state. However, by careful integration of the C-methyl signals assignable to **19** (δ 2.15) and **20** (δ 2.77) in the nmr spectrum of the crude reaction mixture, the approximate product ratio was determined to be 55:45 in favor of **19**.

These results once again demonstrate the importance of steric effects on 1H-azepine reactivity. The 4-methyl isomer (**12**) gave only that adduct in which the methyl substituent does not occupy a bridgehead position. The same positional selectivity is observed in the case of 2-methyl-N-carbomethoxyazepine (**15**). Since neither of the adducts derivable from the 3-methyl derivative (**18**) has a methyl group at a bridgehead position, substantial quantities of both adducts are formed.

The earlier data of Baldwin and Smith[8a] can now be examined in more quantitative fashion. The isolation of adducts derived principally from 4-substituted N-carbomethoxyazepines seems to be a reflection of their more favorable reactivity with TCNE, the high positional selectivity of the cycloaddition, and the high crystallinity (in a qualitative sense) of these adducts.[18] Since only a 15% yield of **13** was actually isolated from toluene by these workers, interpretation of their results in terms of carbomethoxynitrene selectivity necessarily must remain tentative.[19]

Attempts to form tetracyanoethylene adducts of annelated azepines **21** and **22** afforded only intractable black tars.[20]

N-Phenylmaleimide.—N-Carbalkoxyazepines are rather inert to dienophiles such as maleic anhydride and dimethyl acetylenedicarboxylate, even at elevated temperatures in the absence of solvent.[8b] In our hands, N-carbethoxyazepine did, however, undergo

reaction with N-phenylmaleimide when heated in toluene at reflux for 16 hr. A crystalline 1:1 adduct was obtained in 25% yield. The complexity of its nmr spectrum (Figure 1) suggested that symmetrical structures such as **23** and **24** could be removed from further consideration. Identification of the structure of the adduct as **25** was achieved through detailed analysis of its spectral properties.
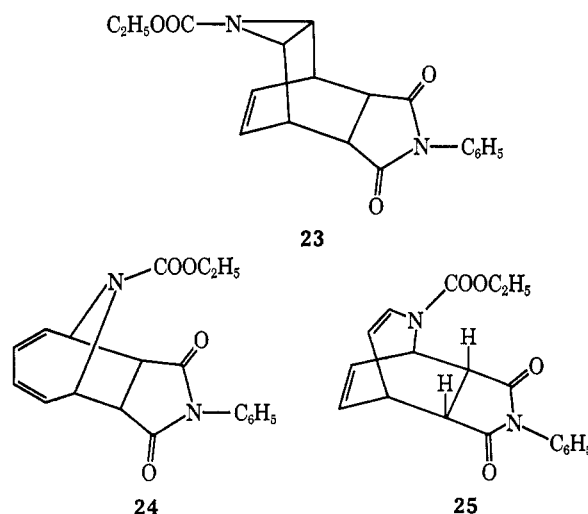
Thus, the infrared spectrum of **25** exhibited, in addition to a carbonyl peak at 1715 cm^{-1}, an intense absorption at 1650 cm^{-1} characteristic of an α,β-unsaturated carbamate double bond.[21] The ultraviolet spectrum of this adduct [$\lambda^{C_2H_5OH}_{max}$ 215 (ϵ 15,700) and 248 sh mμ (ϵ 7700)] lies in good agreement with the absorption previously reported for the $>$C$=$CNHCOCH$_3$ chromophore.[22] The nmr spectrum of **25** is illustrated in Figure 1 and the chemical-shift parameters and coupling constants are listed in Table I. The assignments for
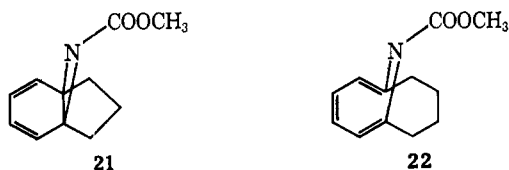
TABLE I

NUCLEAR MAGNETIC RESONANCE DATA FOR COMPOUND **25**

Proton label	Chemical shift, δ ppm	Principal coupling constants, Hz
A	1.30	$J_{AD} = 7.0$
B	3.10	$J_{BE} = 8.0, J_{BH} = 8.8$
C	3.58	$J_{CF}, J_{BC} = <1.0$
D	4.25	$J_{AD} = 7.0$
E	5.11	$J_{BE} = 8.0, J_{EI} = 9.5$
F	5.50	$J_{FG} = 8.0$
G	5.97	$J_{GH} = 8.7, J_{FG} = 8.0$
H	6.51	$J_{GH} = 8.7, J_{BH} = 8.8$
I	6.67	$J_{EI} = 9.5$
J	7.35	

the spin–spin coupling interactions were tested through double-resonance experiments,[23] which revealed that the "triplets" representing protons B, E, G, and H were truly doublets of doublets. The bridgehead proton B is split by vicinal hydrogens E and H approximately equally. Vinyl protons E and I split one another, a situation which is duplicated with protons G and H; G is also coupled to F. Additionally, the spectrum of **25** bears many similarities to the spectrum of the N-

(17) In their analysis of the nmr spectrum of i, Baldwin and Smith[8a] noted a significant difference in the chemical shifts of the C_4 and C_7 methyl substituents.

i
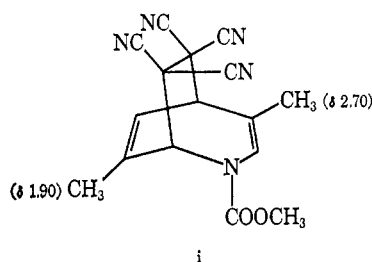
(18) This statement is based on a comparative examination of the crystallinities of **13**, **16**, and **19**.

(19) The fact that carbomethoxynitrene displays no appreciable selectivity in reactions with toluene has recently been confirmed: J. A. Baldwin and R. A. Smith, *J. Org. Chem.*, **32**, 3511 (1967); K. Hafner, personal communication.

(20) The thermal sensitivity of **21**[10b] precluded the use of solvents with boiling points higher than that of benzene. Although the propensity for rearrangement exhibited by **22** was a less serious problem, the application of

21   22

forcing conditions to any cycloaddition invariably resulted in skeletal rearrangement.[10b]

(21) See footnote 10a for a discussion of this point.

(22) G. Rosenkranz, O. Mancera, F. Sondheimer, and C. Djerassi, *J. Org. Chem.*, **21**, 520 (1956).
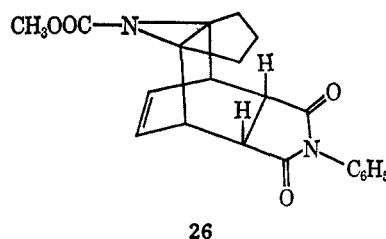
(23) J. D. Baldeschwieler and E. W. Randall, *Chem. Rev.*, **63**, 81 (1963).
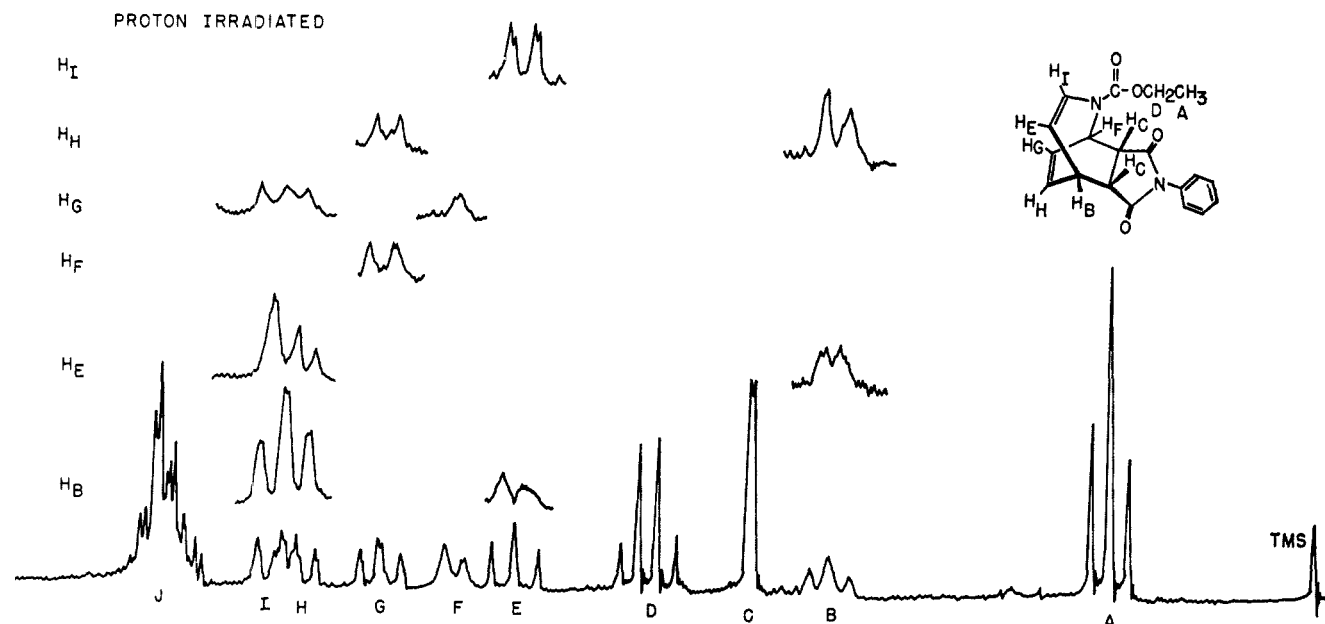
Figure 1.—Proton nmr spectrum of 25 (CDCl₃ solution) at 60 MHz.

carbethoxyazepine–TCNE adduct[8b] as it should, since the six carbon atoms of the azepine ring are in quite comparable chemical environments.
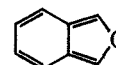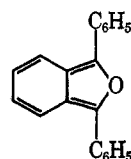
A significant final observation on the spectrum of **25** concerns the magnitude of the J_{BC} and J_{CF} coupling constants (<1.0 Hz). That the bridgehead hydrogens are not significantly coupled with the neighboring α-carbonyl protons is a phenomenon that can best be accommodated by an *endo* orientation for the succinimide ring. The relevant dihedral angles are seen from Dreiding models to be approximately 82° for the *endo* isomer and 48° for the *exo* counterpart.[24] Therefore, from expectations based on the Karplus correlation,[25] spin–spin coupling constants of ∼1.0 and ∼4.0 Hz should be observed for the respective two isomers.[26] The *endo* mode of addition is therefore indicated; the over-all reaction is then a $(4 + 2)\pi$ cycloaddition to the unrearranged azepine nucleus with *endo* stereochemistry, in agreement with the Woodward–Hoffmann rules for such processes.[27]

Interestingly, addition of N-phenylmaleimide to **21** proceeded smoothly in refluxing benzene during several hours to give a colorless crystalline substance in high yield. Assignment of structure **26** to this adduct is based on the uniquely symmetrical features of its nmr spectrum which establishes, *inter alia*, the presence of two vinyl protons (multiplet centered at δ 6.35), two α-carbonyl protons (broadened multiplet at 3.62), two allylic bridgehead protons (slightly split band at 3.38),

(24) As nearly as can be determined from molecular models, the dihedral angles between the two H$_C$ atoms and their adjacent bridgehead neighbors, H$_B$ and H$_F$, are equivalent.

(25) M. Karplus, *J. Amer. Chem. Soc.*, **85**, 2870 (1963); *J. Chem. Phys.*, **30**, 11 (1959).

(26) Stereochemical analysis of a bicyclo[3.2.2]nonadiene system in this fashion gives results which are diametrically opposed to the geometric conclusions derivable from a bicyclo[2.2.1]heptane, or norbornene, framework. In this latter structural type, the "pinching effect" exerted by the single atom bridge causes the relevant dihedral angles between *endo* and bridgehead protons to approach 90°. Lack of coupling in such molecules is then generally construed as an indication of *exo* substitution. Consult, for example, L. A. Paquette, *J. Org. Chem.*, **30**, 629 (1965); see particularly footnote 16.

(27) R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 4388 (1965).

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and the trimethylene chain (broad six-proton absorption in the 1.16–2.31 region). The imide ring in **26** is assigned *syn* to the double bond for reasons of preferred steric accessibility by the dienophile, in accordance with established precedence,[28] and maintenance of favorable secondary orbital interactions throughout the bond-forming procedure.[27] Especially noteworthy is the fact that **26** represents the lone example at this time of a Diels–Alder addition to the azanorcaradiene tautomer of a 1H-azepine.[29]

Isobenzofurans.—In an attempt to obtain information concerning the possible intermolecular 6π donor capability of 1H-azepines, the addition of two reactive dienes,[30] isobenzofurans **27** and **28**, to these heterocycles has been examined.

27   **28**

When a solution of **27** and N-carbethoxyazepine in benzene was refluxed under nitrogen for 72 hr, a single reaction product was obtained in 52% yield. The substance exhibited ir bands at 1720 (urethan carbonyl),

(28) L. A. Paquette and J. C. Philips, *ibid.*, **90**, 3898 (1968).

(29) Azepine **22** was found to be unreactive toward N-phenylmaleimide in refluxing benzene for periods of time up to 8 hr.[30]

(30) See, for example, (a) M. S. Newman, *J. Org. Chem.*, **26**, 2630 (1961); (b) L. F. Fieser and M. J. Haddadin, *J. Amer. Chem. Soc.*, **86**, 2081 (1964); *Can. J. Chem.*, **43**, 1599 (1965); (c) L. A. Paquette, *J. Org. Chem.*, **30**, 629 (1965); L. A. Paquette and T. R. Phillips, *ibid.*, **30**, 3883 (1965).

TABLE II

SPECTRAL PARAMETERS FOR THE AZEPINE–ISOBENZOFURAN ADDUCTS

		$\delta_{TMS}^{CDCl_4}$, multiplicity, J			
Compd	$\lambda_{max}^{C_2H_5OH}$, mμ (ε)	Bridgehead protons	β-Vinyl protons	α-Vinyl protons	H—C—O—C—H
30	235 (12,700)	3.62, m	6.42, d, 10Hz	4.77, d, 10Hz	. . .
31	234 (15,100)	3.60, m	6.30, d, 10Hz	4.98, d, 10Hz	. . .
32	Strong end absorption	3.63, m	6.20, d, 10Hz	4.92, d, 10Hz	. . .
36a	232 (15,000)	3.24, m	6.42, d, 10Hz	4.77, d, 10Hz	5.58, m
36b	230 (19,200)	3.17, m	6.20, d, 10Hz	4.68, d, 10Hz	5.12, m
36c	251 (10,700)	3.24, m	6.33, d, 10Hz	4.92, d, 10Hz	5.23, m
36d	235 (3,100)	3.23, m	6.16, d, 10Hz	4.72, d, 10Hz	5.12, m

1680, and 1600 cm^{-1} (olefinic bonds), and uv absorption at 235 mμ (ε 12,700). The nmr spectrum was compatible only with a symmetrical structure such as 29 or 30, since
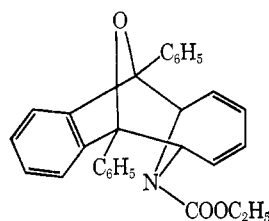
29
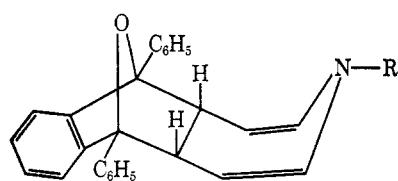
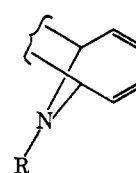30, R = COOC$_2$H$_5$
31, R = COOCH$_3$
32, R = SO$_2$CH$_3$

it displayed, inter alia, two equivalent pairs of vinyl protons as doublets (J = 10.0 Hz) centered at δ 6.42 and 4.77 and two bridgehead protons as a multiplet at δ 3.62.[31]

Before considering the structure of the above adduct, it is significant to note that this cycloaddition is apparently entirely general in nature. Thus, N-carbomethoxy- and N-methanesulfonylazepine were found to condense with 27 to form analogous adducts (Table II). Likewise, in situ generation of isobenzofuran (28)[30b] in the presence of a number of N-substituted azepines resulted in the formation of a structurally related addition product in each instance. Comparison of the spectral properties (Table II) leaves no doubt that the series of adducts derived from the two isobenzofurans have the same fundamental structure. The nmr spectrum of the adduct from isobenzofuran and N-carbethoxyazepine was identical with that of the diphenylisobenzofuran adduct except for the appearance of a doublet of doublets at δ 5.58 assignable to the protons on carbon bonded to the bridgehead oxygen atom.

The appreciable difference in chemical shift (1.28–1.65 ppm) between the pairs of vinyl protons in these adducts is not to be expected from a diene component such as that found in structure 29. Rather, in those

compounds where the moiety defined by 33 is found, the vinyl proton absorption corresponds to a pseudo-singlet or a slightly broadened multiplet.[21,32] Con-

33

versely, in a structure such as 30, the two vinyl protons β to the nitrogen atom would be expected to be diamagnetically shifted relative to the α protons.[10a,33] Furthermore, the chemical shifts of these protons should be affected by changes in the electronegativity of the nitrogen substituent, and this is observed (Table II). In addition, the infrared and ultraviolet parameters correspond well with the spectral characteristics of homoazepines 34a[33a] [ν_{max}^{film} 1725 and 1670 cm^{-1}; $\lambda_{max}^{C_2H_5OH}$ 231 mμ (ε 11,430)] and 34b[33b] [ν_{max}^{film} 1725 and 1665 cm^{-1}; λ_{max}^{hexane} 232 mμ (ε 13,000)]. As expected from structures 30–32, the position of the ultraviolet maximum is dependent on the nature of the
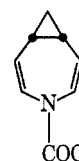
34a, R = CH$_3$
b, R = C$_2$H$_5$

nitrogen substituent because of the direct involvement of the nitrogen atom in the chromophoric group. This would not be the case with 29, where the nitrogen center is effectively insulated from the diene component.

These data suggested that the cycloadducts have the gross stuctures 30–32 and 36. In order to confirm these assignments, 36b was hydrogenated. Two equivalents of hydrogen were consumed and a tetrahydro derivative (37) was produced which, when dehydrated with polyphosphoric acid, was readily converted to the disubsti-

(31) The possibility of accidental coincidence of nmr signals from differently oriented protons in an unsymmetrical structure was eliminated by alteration of the nmr solvent (benzene, etc.) and the electronic characteristics of the nitrogen substituent (see ensuing discussion). A symmetrical pattern remained apparent in all instances.

(32) (a) L. A. Paquette and J. H. Barrett, J. Amer. Chem. Soc., 88, 2590 (1966); (b) A. L. Johnson and H. E. Simmons, ibid., 88, 2591 (1966); 89, 3191 (1967); (c) K. Hafner and J. Mondt, Angew. Chem., 78, 822 (1966); Angew. Chem. Intern Ed. Engl., 5, 839 (1966); (d) W. S. Murphy and J. P. McCarthy, Chem. Commun., 1155 (1968).

(33) (a) L. A. Paquette and R. J. Haluska, ibid., 1370 (1968); (b) W. H. Okamura, W. H. Snider, and T. J. Katz, Tetrahedron Lett., 3367 (1968); (c) E. L. Stogryn and S. J. Brois, J. Org. Chem., 30, 88 (1965).

35

36a, R = COOC$_2$H$_5$ **c**, R = COCH$_3$
b, R = COOCH$_3$ **d**, R = SO$_2$CH$_3$

37

38
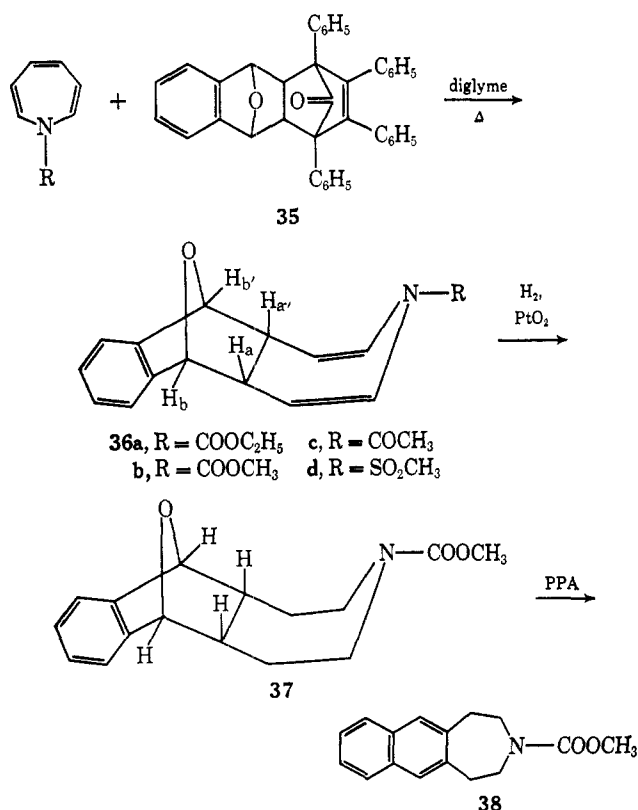
tuted naphthalene **38**. The ultraviolet spectrum of **38** (see Experimental Section) is unequivocally that of a naphthalene.[34] The 2,3 disubstitution pattern on the aromatic system was clearly evident from the aryl proton region of the nmr spectrum, which exhibited an absorption pattern identical to that found in 2,3-dimethylnaphthalene.[35] The eight methylene protons are easily recognizable as an A$_2$B$_2$ system, the inherent symmetry of which can only be rationalized in terms of structure **38**.

At this point, the stereochemistry of **30–32** and **36** remained to be determined. Molecular models of **36** established that the dihedral angle between H$_a$ and H$_b$ (or H$_a'$ and H$_b'$) is approximately 45°. In the related *exo* isomer, the dihedral angle is 90°. On the basis of the Karplus relationship,[25,26] J_{ab} (or $J_{a'b'}$) coupling constants of 4 Hz and 0 Hz should be found in the *endo* and *exo* isomers, respectively. Analysis of the doublet of doublets pattern exhibited by H$_a$ and H$_a'$ in **36a** shows that two coupling constants of 3.0 and 1.5 Hz exist. A spin-decoupling analysis of the upfield portion of the spectrum indicated that $J_{ab} = J_{a'b'} = 3.0$ Hz, while the smaller coupling (1.5 Hz) was the result of long range spin–spin interaction between H$_a$ and H$_b'$ and H$_a'$ and H$_b$. In actuality, the geometry of the bonds linking these protons is seen to correspond exactly to a W-plan coplanar arrangement, a general requirement for coupling across four single bonds.[36] It should be pointed out that the geometrical features required for such long range spin–spin interaction are not present in a structure such as **39** or its *endo* isomer.

From the magnitude of J_{ab} (or $J_{a'b'}$), the *endo* stereochemistry was indicated. Additional confirmation of this assignment came from an unexpected source. The nmr spectrum of **37** displays a two-proton multiplet at exceptionally high field (δ 0.57), signifying that two of the methylene protons occupy positions which are subject to remarkably increased shielding. Examination of Dreiding models of this tetrahydro derivative indicated that the protons labeled H$_c$ (see **40**) are held rigidly below the plane of the benzene ring in the preferred boat conformation. Measurement of the distances from these protons to the center of the aromatic ring in the manner of Johnson and Bovey[37] gives $A = 6$ cm and $B = 3$ cm, which is predicted to result in a diamagnetic shift of approximately 120 Hz, in good agreement with the observed value. Such a ring current effect gives excellent support to the *endo* formulation and additionally verifies the gross structural assignments.

39   **40**
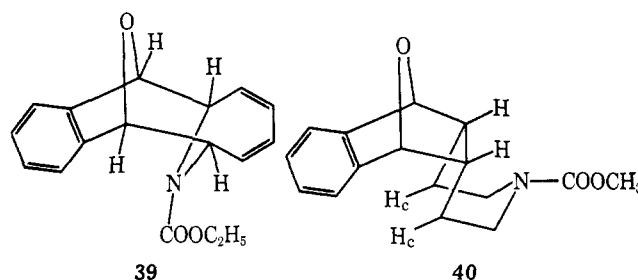
The adducts from N-substituted azepines and isobenzofurans result from $(4 + 2)\pi$ cycloaddition rather than from $(6 + 4)\pi$ cycloaddition. These reactions are presumably, although not necessarily, concerted processes, since the demonstrated high *endo* stereoselectivity is very likely the result of secondary orbital symmetry control in the bond-forming transition state.[27] Because addition to the 4,5 bond of the 1H-azepines occurred exclusively, and since the reasons for this unexpected behavior were not clearly understood, there arose a need for comparison with similar reactions of cyclopentadienones. The results of this study follow.

2,5-Dimethyl-3,4-diphenylcyclopentadienone.—The failure of 1H-azepines to function as 6π donors toward isobenzofurans could conceivably be caused by an adverse electronic effect in the isobenzofurans. Thus, these dienes may be considered as electron-rich 4π donors. Since electronic effects on $(6 + 4)\pi$ cycloadditions have not yet been investigated, it is conceivable that the electron nature of the isobenzofurans is not conducive to ready $(6 + 4)\pi$ cycloaddition with 1H-azepines bearing electronegative substituents on nitrogen. In other words, the possibility exists that $(6 + 4)\pi$ cycloadditions may be subject to subtle electronic demands in much the same fashion as Diels–Alder reactions.[38]

Derivatives of cyclopentadienone are electron-deficient 4π donors and thus were considered to be appropriate examples of the "inverse" electronic situation. Upon heating a solution of N-carbethoxyazepine and **41**

(34) For comparison purposes, see R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1951, Spectra No. 195–228.

(35) For example, compare 2,3-dimethylnaphthalene: W. Brügel, "Nuclear Magnetic Resonance Spectra and Chemical Structure," Vol. I, Academic Press, Inc., New York, N. Y., 1967, p 128.

(36) For a review, see S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

(37) C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

(38) For recent discussions of the inverse electron demand in Diels–Alder reactions, consult (a) J. Sauer, *Angew. Chem. Intern. Ed. Engl.*, **6**, 16 (1967); (b) D. L. Fields, T. H. Regan, and J. C. Dignan, *J. Org. Chem.*, **33**, 390 (1968); (c) C. K. Bradsher and J. A. Stone, *ibid.*, **33**, 519 (1968); (d) R. A. Carboni and R. V. Lindsey, *J. Amer. Chem. Soc.*, **81**, 4342 (1959).

in benzene under nitrogen for 20 hr, there was obtained after careful column chromatography a 41.4% yield of **42** and a 50% yield of **43** or **44**. Initially, the molecular


41

42

43 or **44**
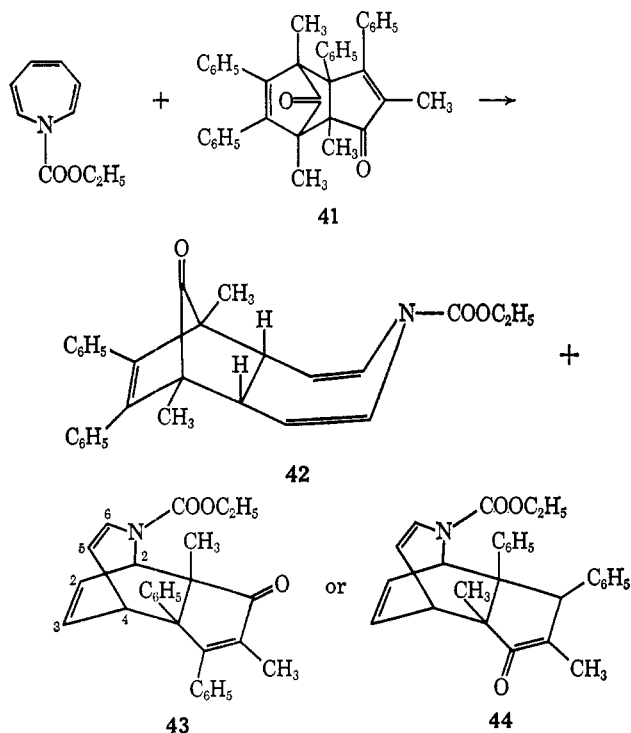
frameworks of **42** and **36** (or **30**) were seen to be closely related. The presence of moiety **33** was apparent from the nmr spectrum, which revealed the presence of two high field protons as a slightly broadened singlet absorption at δ 2.95, two vinyl protons β to nitrogen as a doublet (J = 11 Hz with additional small coupling) at 5.02, and two vinyl protons α to nitrogen (peak overlaps with phenyl absorption at *ca.* 7.05). Again, the symmetry of the molecule was apparent. Further, its infrared spectrum (in Nujol) indicated the presence of a bridged β,γ-unsaturated carbonyl group (1765 cm^{-1}),[39] a urethan carbonyl function (1725 cm^{-1}), and the C=C-N-C=O groupings (1680 cm^{-1}). The presence of the unsaturated urethan linkages in **42** could also be derived from its ultraviolet spectrum, which exhibited absorption in ethanol at 251 mμ (ϵ 11,800) in addition to the *cis*-stilbene band at 281 mμ (ϵ 15,850).[40]

The nmr spectrum of the second 1:1 adduct (CDCl$_3$ solution) clearly shows the magnetic nonequivalence of the methyl substituents adjacent to the carbonyl group, there being two singlets at δ 0.94 and 1.90. The first methyl group is obviously bonded to saturated carbon while the second is attached to sp^2-hybridized carbon. The remaining portion of the spectrum consists of absorptions characteristic of the azepine ring to which 1,4 bonding has occurred (see Figure 1). H$_1$ is seen as a doublet (J = 8.5 Hz) at δ 5.30, whereas H$_2$, H$_3$, H$_4$, and H$_5$ appear as the expected doublet of doublets at δ 6.23, 6.78, 2.64, and 5.08, respectively, and H$_6$ consists of a doublet at 6.86. The ultraviolet spectrum in ethanol has a maximum at 227 mμ (ϵ 27,850) and a shoulder at 270 mμ (ϵ 6700). The infrared spectrum

shows a conjugated cyclopentenone carbonyl band at 1670 cm^{-1} and double-bond stretching modes at 1665 and 1640 cm^{-1}.

Comparison of the nmr spectra of this adduct and **25** revealed that H$_4$ (δ 2.64) has undergone a substantial upfield shift relative to H$_B$ (δ 3.10), whereas the chemical shifts of H$_1$ (δ 5.50) and H$_F$ (δ 5.30) have remained essentially invariant. These observations are in best agreement with structure **43**, since in this formulation, H$_4$ is not *vis-a-vis* a carbonyl group but is proximate to two phenyl groups. On the other hand, the chemical environment about H$_1$ is only little altered from that found in **25**. The reverse structural alternatives are at play in **44**. Further support for **43** was derived from its sizable dipole moment, 3.38 D in benzene.[41]

In similar fashion, the interaction of **41** and N-methanesulfonylazepine led to the formation of a lone adduct (**45**) in 42% yield. The structure **45** was likewise ascertained on the basis of spectral evidence (see Experimental Section).

45
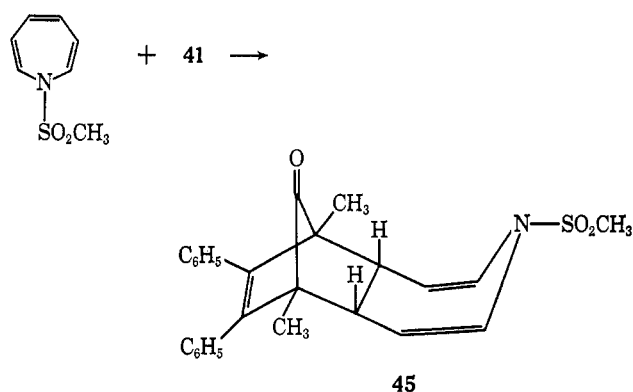
With the establishment of structures **42** and **45**, it was clear that the electronic nature of the 4π donor is not a significant factor in the direction taken by the cycloaddition. Subsequent to the completion of this study, however, a report appeared which described the 1,6 addition of nitrosobenzene and N-carbethoxyazepine to give **46**.[32d] At the present time, these differing

46
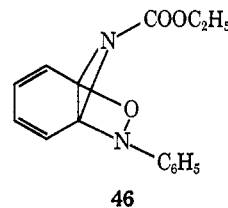
modes of chemical behavior are not readily reconcilable from the theoretical viewpoint It is nevertheless significant to note that the 1H-azepine ring is unique in its capability to function as a 2π, 4π, and 6π donor without recourse to valence tautomerism in thermally induced cycloaddition reactions.[41a]

(39) Compare the bands for the bridged carbonyl groups in **41** (1760 cm^{-1}) and 7-ketonorbornene (1780 cm^{-1}) [P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964)].

(40) For *cis*-stilbene: uv $\lambda_{max}^{C_2H_5OH}$ 224 (ϵ 24,400) and 280 mμ (ϵ 10,500) [R. N. Beale and E. M. F. Rowe, *J. Chem. Soc.*, 2755 (1953)].

(41) We thank Professor Norman L. Allinger for this determination.

(41a) NOTE ADDED IN PROOF.—Since the submission of this paper, a report by J. R. Wiseman and B. P. Chong has appeared [*Tetrahedron Lett.*, 1619 (1969)] which reports the related (4 + 2) cycloaddition of 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene to the 4,5 bond of N-carbethoxyazepine.

Experimental Section[42]

Addition of TCNE to 4-Methyl-N-carbomethoxyazepine (12).—To a solution of 1.20 g (7.3 mmol) of **12** in 10 ml of toluene was added a solution of 960 mg (7.5 mmol) of freshly sublimed TCNE in 90 ml of the same solvent. The reaction mixture was stirred at room temperature for 15 hr and then refluxed for 1 hr. The solvent was evaporated until 15 ml of liquid remained. Cooling of this material caused 1.37 g (64.5%) of **13** to be deposited. Additional recrystallization from toluene gave pure **13** as a fluffy white solid, mp 139–141° (lit.[8a] mp 128–130°). An nmr spectrum of the crude reaction mixture and thin layer chromatography showed no indication that any of isomeric adduct **14** was formed.

Anal. Calcd for $C_{15}H_{11}N_5O_2$: C, 61.43; H, 3.78; N, 23.88. Found: C, 61.46; H, 3.98; N, 24.14.

Addition of TCNE to 2-Methyl-N-carbomethoxyazepine (15).—When 2.40 g (14.5 mmol) of **15** and 1.92 g (15.0 mmol) of TCNE in 100 ml of toluene were reacted as above, there was obtained only a brown oil after concentration of this solution. This oil was chromatographed on Florisil (100 g) to give 121 mg (5%) of 2-methyl-N-carbomethoxyaniline, mp 59.5–60.5°, upon elution with hexane–ether (19:1) and 103 mg (2.5%) of **19** upon elution with hexane–ether (4:1). Again in this instance, nmr and thin layer analyses of the crude reaction mixture provided no indication of the formation of **17**.

Pure **19** was obtained by recrystallization from acetone–hexane as a white solid, mp 149–151° (prior sintering beginning at 130°).

Anal. Calcd for $C_{15}H_{11}N_5O_2$: C, 61.43; H, 3.78; N, 23.88. Found: C, 61.46; H, 4.08; N, 23.90.

Addition of TCNE to 3-Methyl-N-carbomethoxyazepine (18).—Treatment of 730 mg (4.4 mmol) of **18**, 570 mg (4.4 mmol) of TCNE, and 75 ml of toluene in the above manner gave 1.2 g of a viscous brown oil. Rapid chromatography of this oil on Florisil (50 g) with ether–hexane (1:3) elution gave 860 mg (66%) of yellow oil. An nmr analysis of this crude oil indicated the presence of **19** and **20** in a ratio of 55:45 by integration of the two methyl peaks at δ 2.15 and 2.77. Thin layer chromatography [3 developments with hexane–ether (7:3) on activity II alumina] showed the oil to be composed of two substances with nearly identical R_f values. When an acetone–hexane solution of this oil was seeded with a crystal of **13**, 312 mg (24%) of an off-white solid was isolated. Four recrystallizations of this material from the same solvent pair gave pure **19**, mp 146.5–148.5°; ir ν_{max}^{KBr} 1727 cm^{-1}.

Anal. Calcd for $C_{15}H_{11}N_5O_2$: C, 61.43; H, 3.78; N, 23.88. Found: C, 61.55; H, 3.91; N, 23.84.

The combined filtrates, when concentrated, cooled, and seeded, yielded no additional crystalline material.

Ethyl 3,5-Dioxo-4-phenyl-4,8-diazatricyclo[5.3.2.0²,⁶]dodeca-9,11-diene-8-carboxylate (25). A solution of 3.3 g (20 mmol) of N-carbethoxyazepine and 3.46 g (20 mmol) of N-phenylmaleimide in 15 ml of toluene was refluxed for 16 hr. The solvent was removed under reduced pressure and the resulting semisolid mixture was chromatographed on Florisil (100 g) using pentane and gradually increasing amounts of ether. A white solid (1.72 g, 25.4%) was isolated which gave an analytical sample upon recrystallization from methanol, mp 177–179°, ir $\nu_{max}^{CHCl_3}$ 1715 (C=O) and 1650 cm^{-1} (C=N–C=O); uv $\lambda_{max}^{C_2H_5OH}$ 215 (ε 15,700) and 248 mμ (ε 7700).

Anal. Calcd for $C_{19}H_{18}N_2O_4$: C, 67.44; H, 5.36; N, 8.28. Found: C, 67.33; H, 5.44; N, 8.19.

Addition of N-Phenylmaleimide to 10-Carbomethoxy-10-azatricyclo[4.3.1.0¹,⁶]deca-2,4-diene (21).—A solution of 270 mg (1.4 mmol) of **21** and 245 mg (1.4 mmol) of N-phenylmaleimide in 25 ml of benzene was blanketed with nitrogen, stirred at room temperature for 3 hr, and finally heated at reflux for 3 hr. Solvent removal *in vacuo* yielded 510 mg (99%) of a white solid, mp 115–118°. Recrystallization from benzene–hexane afforded 430 mg of **26** as white crystals, mp 218.5–220°; ir $\nu_{max}^{CDCl_3}$ 1715 and 1664 cm^{-1}.

Anal. Calcd for $C_{21}H_{20}N_2O_4$: C, 69.21; H, 5.53; N, 7.69. Found: C, 69.51; H, 5.31; N, 7.58.

Addition of Diphenylisobenzofuran (27) to 1H-Azepines.—A solution of 1.65 g (0.01 mol) of N-carbethoxyazepine and 2.70 g

(42) The microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Infrared spectra were determined with a Perkin-Elmer Model 237 spectrophotometer. Ultraviolet spectra were determined with a Cary 14 spectrometer and the nmr spectra were recorded with a Varian A-60A spectrometer.

(0.01 mol) of **27**[30a] in 30 ml of benzene was refluxed under nitrogen for 72 hr. The resulting orange solution was concentrated under reduced pressure to give a tan solid. Column chromatography on 70 g of Florisil and elution with hexane followed by hexane–ether (9:1) gave 2.26 g (52%) of **30**, mp 120–121° (yellows at 115°: reverse cycloaddition); ir $\nu_{max}^{CCl_4}$ 1720, 1680, and 1660 cm^{-1}.

Anal. Calcd for $C_{29}H_{25}NO_3$: C, 79.97; H, 5.79; N, 3.22. Found: C, 79.92; H, 5.84; N, 3.12.

From 6.93 g (0.026 mol) of **27** and 3.90 g (0.026 mol) of N-N-carbomethoxyazepine in 80 ml of benzene (reflux 100 hr), there was isolated 4.8 g (44%) of **31**, mp 119.5–121° (from ether–hexane); ir $\nu_{max}^{CCl_4}$ 1725 and 1685 cm^{-1}.

Anal. Calcd for $C_{28}H_{23}NO_3$: C, 79.79; H, 5.50; N, 3.32. Found: C, 79.75; H, 5.40; N, 3.34.

From 6.75 g (0.025 mol) of **27** and 4.28 g (0.025 mol) of N-methanesulfonylazepine in 150 ml of benzene (reflux, 56 hr), there was isolated 3.97 g (36%) of **32**, mp 138–139° dec (from methylene chloride–hexane).

Anal. Calcd for $C_{27}H_{23}NO_3S$: C, 73.45; H, 5.25; N, 3.17. Found: C, 73.26; H, 5.19; N, 3.14.

Addition of Isobenzofuran (28) to 1H-Azepines.—To 100 ml of purified diglyme which had been preheated to 140° was added in one portion 13.2 g (25 mmol) of **35**[30b,c] and 3.3 g (20 mmol) of N-carbethoxyazepine. The solution was refluxed for 2 hr and then concentrated under reduced pressure to give a tan solid. This solid was chromatographed on 300 g of Florisil using hexane with graduated amounts of benzene. The first compound eluted was 1,2,3,4-tetraphenylbenzene, 8.8 g (92%), mp 190°. Elution with pure benzene gave 1.21 g (21.8%) of **36a** as a white solid, mp 132.5–133° (from ether); ir $\nu_{max}^{CHCl_3}$ 1725 and 1695 cm^{-1}. No other material was isolated.

Anal. Calcd for $C_{17}H_{17}NO_3$: C, 72.06; H, 6.05; N, 4.94. Found: C, 71.84; H, 6.21; N, 4.91.

From 14.0 g (26.5 mmol) of **35** and 3.78 g (25 mmol) of N-carbomethoxyazepine in 100 ml of diglyme, there was obtained 3.16 g (47%) of **36b**, white crystals from benzene–pentane, mp 132–139° dec, with yellowing; ir $\nu_{max}^{CHCl_3}$ 1725 and 1695 cm^{-1}.

Anal. Calcd for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20. Found: C, 71.66; H, 5.56; N, 5.01.

From 1.74 g (3.3 mmol) of **35** and 446 mg (3.3 mmol) of N-acetylazepine in 25 ml of diglyme, there was obtained 414 mg (49.5%) of **36c**, white crystals from methylene chloride–pentane, mp 186–188.5° dec; ir $\nu_{max}^{CHCl_3}$ 1695 and 1660 cm^{-1}.

Anal. Calcd for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.62; H, 6.01; N, 5.46.

From 1.55 g (2.93 mmol) of **35** and 502 mg (2.93 mmol) of N-methanesulfonylazepine in 50 ml of diglyme, there was obtained 196 mg (23%) of **36d**, long white needles from benzene–pentane, mp 162–164°; ir $\nu_{max}^{CHCl_3}$ 1680, 1350, and 1165 cm^{-1}.

Anal. Calcd for $C_{15}H_{15}NO_3S$: C, 62.26; H, 5.23; N, 4.84. Found: C, 62.36; H, 5.22; N, 4.74.

N-Acetylazepine.—To a stirred solution of 12.2 g (0.128 mol) of 1,2-iminocyclohex-4-ene[10a] and 13.1 g (0.130 mol) of triethylamine in 180 ml of anhydrous ether was added dropwise a solution of 9.65 g (0.128 mol) of acetyl chloride in 60 ml of the same solvent with ice cooling. After the reaction mixture had stirred for 2 hr, amine hydrochloride was filtered and the filtrate was evaporated. Distillation of the residue afforded 13.2 g (76.5%) of the N-acetyl derivative, bp 55–58° (0.5 mm); ir $\nu_{max}^{CHCl_3}$ 1690 cm^{-1}.

Anal. Calcd for $C_8H_{11}NO$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.62; H, 6.01; N, 5.46.

The dibromide was obtained as an oil which was subjected directly to the action of potassium t-butoxide in dry tetrahydrofuran.[10a] Distillation of the residual orange oil gave 1.63 g (14.9%), bp 71° (0.3 mm); ir $\nu_{max}^{CHCl_3}$ 1670 cm^{-1}; nmr $\delta_{TMS}^{CDCl_3}$ 2.08 (s, 3 H) and 5.12–6.30 (m, 6 H).

Anal. Calcd for C_8H_9NO: C, 71.09; H, 6.71. Found: C, 71.19; H, 7.26.

Hydrogenation of 36b.—A 1.0-g sample of **36b** was hydrogenated at atmospheric pressure over Adams catalyst in tetrahydrofuran solution (50 ml). The uptake of hydrogen ceased after the uptake of 2 mol equiv. Recrystallization of the resulting solid from benzene–pentane gave **37** as white crystals, mp 148.5–149°; ir $\nu_{max}^{CCl_4}$ 1695 cm^{-1}; nmr $\delta_{TMS}^{CDCl_3}$ 0.57 (br t, 2 H), 1.87 (br d, 2 H), 2.53–3.12 (m, 4 H), 3.59 (s, 3 H), 3.80–4.25 (m, 4 H), 5.20 (slightly split m, 2 H), and 7.28 (s, 4 H).

Anal. Calcd for $C_{16}H_{19}NO_3$: C, 70.31; H, 7.01; N, 5.13. Found: 70.42; H, 6.97; N, 5.02.

Dehydration of 37.—A mixture of 500 mg (1.83 mmol) of **37** and 15 ml of polyphosphoric acid was heated on a steam bath for 3 hr with occasional stirring. After standing overnight at room temperature, this mixture was added to 80 ml of ice water. The organic product was extracted with four 75-ml portions of chloroform and the combined organic layers were washed with water. The solution was dried and evaporated, and the residue was chromatographed on 10 g of alumina. Elution with ether–hexane (1:1) gave 387 mg (83%) of **38**, mp 138.5–139° (from benzene–hexane); ir $\nu_{max}^{CHCl_3}$ 1690 cm^{-1}; $\lambda_{max}^{C_2H_5OH}$ 261 (ϵ 4500), 269 (ϵ 5600), 279 (ϵ 5600), and 289 mμ (ϵ 3400); nmr $\delta_{TMS}^{CDCl_3}$ 3.00 and 3.62 (centrosymmetric A$_2$B$_2$ pattern, 2 H each), 3.72 (s, 3 H), and 7.46 (characteristic m for 2,3-disubstituted naphthalene).

Anal. Calcd for C$_{16}$H$_{17}$NO$_2$: C, 75.27; H, 6.71; N, 5.49. Found: C, 75.40; H, 6.71; N, 5.45.

Addition of 2,5-Dimethyl-4,5-diphenylcyclopentadienone to 1H-Azepines.—A solution of 3.30 g (20.0 mmol) of 1-carbethoxyazepine and 5.22 g (10.0 mmol) of **41**[43] in 40 ml of benzene was refluxed under nitrogen with magnetic stirring for 20 hr. The solvent was evaporated under reduced pressure and the residue was chromatographed carefully on Florisil. Elution with 2% ether in hexane gave 3.0 g of recovered **41**, mp 186–187° dec. Elution with 5% ether in hexane gave 1.45 g (41.4%) of **42**, mp 140–141° dec (from ether). Elution with 10% ether in hexane and 25% ether in hexane gave 1.75 g (50%) of **43**, mp 146–147° (from ether–hexane).

42 had ν_{max}^{Nujol} 1765, 1725, and 1680 cm^{-1}; uv $\lambda_{max}^{C_2H_5OH}$ 251 (ϵ 11,800) and 281 mμ (ϵ 15,850); for nmr, see text.

(43) F. W. Gray, *J. Chem. Soc.*, **95**, 2131 (1909); C. F. H. Allen and J. A. Van Allan, *J. Amer. Chem. Soc.*, **64**, 1260 (1942).

Anal. Calcd for C$_{28}$H$_{27}$NO$_3$: C, 79.03; H, 6.40; N, 3.29 Found: C, 78.84; H, 6.24; N, 3.04.

43 had ir ν_{max}^{Nujol} 1670, 1665, and 1460 cm^{-1}; uv $\lambda_{max}^{C_2H_5OH}$ 227 (ϵ 27,850) and 270 sh mμ (ϵ 6700); for nmr, see text.

Anal. Calcd for C$_{28}$H$_{27}$NO$_3$: C, 79.03; H, 6.40; N, 3.29. Found: C, 78,75; H, 6.04; N, 3.06.

From 5.2 g (10 mmol) of **41** and 3.42 g (20 mmol) of N-methanesulfonylazepine in 40 ml of benzene (reflux, 20 hr), there was obtained 1.2 g of recovered **41** and 2.74 g (42%) of **45**, fine white needles from methylene chloride–pentane, mp 158° dec; ir $\nu_{max}^{CHCl_3}$ 1760, 1350, and 1155 cm^{-1}; uv $\lambda_{max}^{CH_2Cl_2}$ 222 sh (ϵ 20,700) and 253 sh mμ (ϵ 9200); nmr $\delta_{TMS}^{CDCl_3}$ 1.39 (s, 3 H), 2.90 (s, 3 H), *ca.* 2.90 (m, 2 H), 5.00 (br d, *J* = 10.5 Hz, 2 H), 6.70–7.2 (m, 12 H, aromatic and α-vinyl protons).

Anal. Calcd for C$_{26}$H$_{25}$NO$_3$S: C, 72.37; H, 5.84; N, 3.25. Found: C, 72.35; H, 5.89; N, 3.14.

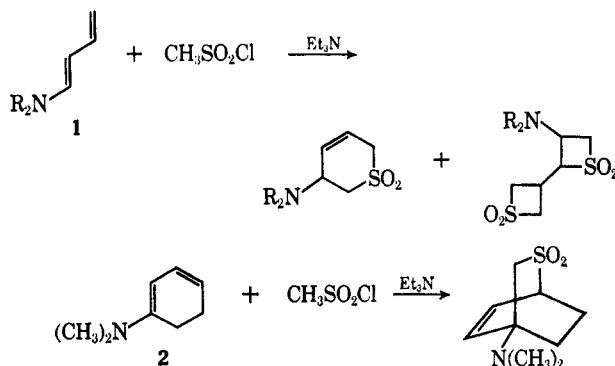# Unsaturated Heterocyclic Systems. LVI.
The Reaction of a Mesocyclic Dienamine with Sulfene[1]

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Reaction of 1-dimethylamino-1,3-cyclooctadiene (**3**) with sulfene, generated *in situ* from methanesulfonyl chloride and triethylamine, in tetrahydrofuran solution was found to yield seven crystalline sulfones after chromatographic work-up. The product composition was seen to be dependent upon temperature, rate of addition of the sulfonyl chloride, rate of elution from the chromatography column, and adsorbent. The structure of each of the adducts has been assigned on the basis of elemental analysis, spectral (particularly nmr) data, and chemical transformations in a number of instances. 3-Aminothietane dioxide **7** was shown to be the precursor of sulfones **8**, **9**, **10**, and **11**; the mechanisms of these transformations are presented. Pathways for the formation of **6** and **12** are also proposed. The particular role played by the medium-sized ring of **3** in these reactions is discussed.

Although a stable free sulfene remains to be isolated,[2] the transient generation of these reactive intermediates in the reaction of numerous alkyl, cycloalkyl, and aralkyl sulfonyl chlorides with tertiary amines has been widely accepted and has attracted much recent attention.[3–5] The chemical reactivity of sulfenes is characterized chiefly by their propensity for (2 + 2) cycloaddition to electron-rich double and triple bonds. With dienamines of type 1 and 2, (4 + 2) cycloaddition is found to compete favorably with the formation of bithietane tetroxides.[5–7] In a significant number of

instances, the sulfene–enamine condensation has been observed to produce open-chain products;[8] also, rearrangement products have been isolated from the reaction of sulfenes with certain 1,3-bis(dimethyl-

(1) For the previous paper in this series, see L. A. Paquette, D. E. Kuhla, J. H. Barrett, and L. M. Leichter, *J. Org. Chem.*, **34**, 2888 (1969).

(2) For a more extensive discussion of this topic, see L. A. Paquette, J. P. Freeman, and R. W. Houser, *ibid.*, **34**, 2901 (1969).

(3) T. J. Wallace, *Quart. Rev.*, **20**, 67 (1966).

(4) G. Optiz, *Angew. Chem. Intern. Ed. Engl.*, **6**, 107 (1967).

(5) L. A. Paquette and M. Rosen, *J. Amer. Chem. Soc.*, **89**, 4102 (1967).

(6) G. Opitz and F. Schweinsberg, *Angew. Chem.*, **77**, 811 (1965); *Angew. Chem. Intern. Ed. Engl.*, **4**, 786 (1965).

(7) G. Opitz and F. Schweinsberg, unpublished results noted in footnote 121 of ref 4.

(8) Consult, for example, (a) G. Opitz, H. Schempp, and H. Adolph, *Ann.*, **684**, 92 (1965); (b) J. J. Looker, *J. Org. Chem.*, **31**, 2973 (1966); A. M. Hamid and S. Trippett, *J. Chem. Soc.*, *C*, 1612 (1968).