Cycloadditions V. Tetracyanoethylene Adducts of 1-Carbomethoxyazepines[1]

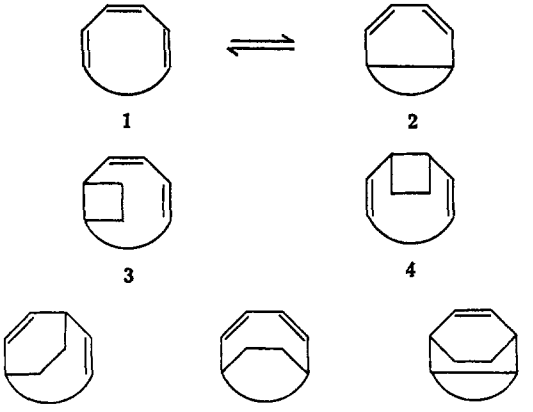
John E. Baldwin and Roger A. Smith[2]

Contribution from the Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61803. *Received June 22, 1965*

The adducts from tetracyanoethylene and 1-carbomethoxyazepines arise from 2 + 4 Diels–Alder cycloaddition reactions, rather than from 2 + 6 cycloadditions as previously suggested. Spin–spin couplings across the H–C–N–C–H system of the adducts **23** *of 1.3–1.5 c.p.s. have been found. Carbalkoxynitrenes and carbalkoxycarbenes apparently have quite dissimilar reactivities toward aromatic nuclei.*

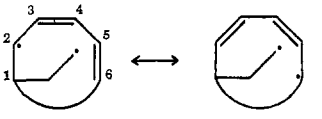
Introduction

Cycloadditions between a suitable olefin and a cyclic conjugated triene (**1**) might take a variety of courses. The olefin and triene **1** might give 2 + 2, 2 + 4, or 2 + 6 cycloaddition products (**3**, **4**, **5**, or **6**), and adducts of type **7**, from a Diels–Alder reaction of the valence tautomer **2** of the triene system or from a 2 + 2 + 2 cycloaddition[3] of olefin and triene **1**. For substituted trienes, further structural or stereochemical alternatives for the cycloaddition reaction obtain.



1 **2** **3** **4** **5** **6** **7**

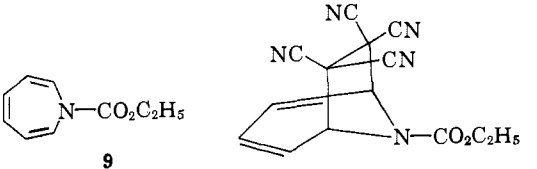
Theoretical generalizations based on symmetry arguments and molecular correlation diagrams predict that the thermal 2 + 4 cycloadditions of **1** or **2** and the thermal 2 + 2 + 2 cycloaddition of **1** with olefins may be concerted.[3,4] Examples of such reactions are well known. The thermally nonconcerted[3,4] processes, involving 2 + 2 or 2 + 6 cycloadditions, may not be summarily dismissed as inconsequential alternatives for such reactions. Thermal 2 + 2 cycloadditions have merited thorough review[5] and the bifunctional intermediate[6] (**8**) involved in such a cycloaddition from **1** to give **3** might also have some opportunity for reaction at C-6.



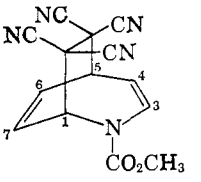
8

A number of cycloaddition reactions between cyclic conjugated trienes and olefins have been reported. Cycloheptatriene,[7] 1,3,5-cyclooctatriene,[8] cyclooctatetraene,[9] and oxepine[10] all give Diels–Alder adducts of type **7**. Tropones and tropolones give 2 + 4 cycloadditions directly to afford products of type **5**.[11]

In sharp contrast to these many examples of cycloadditions between olefins and cyclic conjugated trienes which may be concerted is the indication that 1-carbethoxyazepine (**9**) and tetracyanoethylene give a 2 + 6 cycloaddition product (**10**).[12]



9 **10**



11

We have synthesized a series of adducts from substituted 1-carbomethoxyazepines and tetracyanoethylene. The n.m.r. spectra of the adducts reveal that they are 8,8,9,9-tetracyano-2-carbomethoxy-2-azabicyclo[3.2.2]nona-3,6-dienes (**11**). The spectra also afford new data on "long-range" spin–spin couplings. Some information on the selectivity of the postulated carboxynitrene intermediate in reactions with aromatic compounds was obtained. These three topics, structural assignments for the azepine–tetracyanoethylene

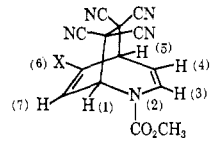
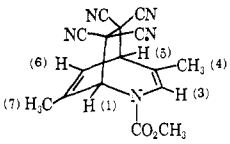
(1) Paper IV: J. E. Baldwin and R. H. Greeley, *J. Am. Chem. Soc.*, 87, 4514 (1965).
(2) Archer Daniels Midland Co. Fellow, 1964–1965.
(3) R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, 87, 2046 (1965).
(4) H. C. Longuet-Higgens and E. W. Abrahamson, *ibid.*, 87, 2045 (1965).
(5) J. D. Roberts and C. M. Sharts, *Org. Reactions*, 12, 1 (1962).
(6) *Cf.* P. D. Bartlett, L. K. Montgomery, and B. Seidel, *J. Am. Chem. Soc.*, 86, 616 (1964); L. K. Montgomery, K. Schueller, and P. D. Bartlett, *ibid.*, 86, 622 (1964); P. D. Bartlett and L. K. Montgomery, *ibi d.* 86, 628 (1964).
(7) K. Alder and G. Jacobs, *Chem. Ber.*, 86, 1528 (1953); however, see G. Kresze and G. Schulz, *Tetrahedron*, 12, 7 (1961).
(8) A. C. Cope, A. C. Haven, Jr., F. L. Ramp, and E. R. Trumbull, *J. Am. Chem. Soc.*, 74, 4867 (1952).
(9) R. Huisgen and F. Mietzsch, *Angew. Chem.*, 76, 36 (1964); *Angew. Chem. Intern. Ed. Engl.*, 3, 83 (1964); E. Vogel, H. Kiefer, and W. R. Roth, *Angew. Chem.*, 76, 432 (1964).
(10) E. Vogel, W. A. Böll, and H. Günther, *Tetrahedron Letters*, No. 10, 609 (1965).
(11) *Cf.* P. L. Pauson, *Chem. Rev.*, 55, 9 (1955).
(12) K. Hafner, *Angew. Chem.*, 75, 1041 (1963); *Angew. Chem. Intern. Ed. Engl.*, 3, 165 (1964).

Table I. Tetracyanoethylene–Azepine Adducts[a]

Azepine precurser	Yield of adduct,[b] %	Structure	M.p.,[c] °C.	Formula	Anal., % C Calcd.	C Found	H Calcd.	H Found	N Calcd.	N Found
Bromobenzene	36 (2X)[d]	**23a**	167–169	$C_{14}H_8N_5O_2Br$[e]	46.95	46.94	2.25	2.05	19.55	19.34
Chlorobenzene	30	**23b**	152.5–154.5	$C_{14}H_8N_5O_2Cl$[f]	53.60	53.65	2.57	2.60	22.32	22.55
Fluorobenzene	28 (3X)	**23c**	168–170	$C_{14}H_8N_5O_2F$	56.57	56.56	2.71	2.69	23.56	23.32
Benzene	38 (3X)	**23d**	165–167	$C_{14}H_9N_5O_2$	60.21	60.22	3.25	3.24	25.08	24.76
Toluene	15	**23e**	128–130	$C_{15}H_{11}N_5O_2$	61.43	61.62	3.78	3.86	23.88	23.81
Anisole	34	**23f**	156–158	$C_{15}H_{11}N_5O_3$	58.25	58.25	3.58	3.49	22.64	22.77
p-Xylene	27	**18**	172–173.5	$C_{16}H_{13}N_5O_2$	62.53	62.36	4.20	4.37	22.79	22.06 22.20 21.71

[a] Prepared from an aromatic precurser, methyl azidoformate, and tetracyanoethylene. [b] No attempt has been made to improve yields by altering reaction conditions or initial concentrations. [c] From toluene; uncorrected. [d] 2X signifies after two recrystallizations. [e] Calcd.: mol. wt., 358; Br, 22.31; Found: mol. wt., 376 (osmometric in acetone); Br, 21.93. [f] Calcd.: Cl, 11.30; Found: Cl, 11.13.

Table II. Coupling Constants and Chemical Shifts in Tetracyanoethylene–Azepine Adducts

Formula		Compd.	Coupling constants,[a] c.p.s. J_{45}	J_{34}	J_{17}	J_{57}[c]	J_{13}[d]	Chemical shifts,[b,g] τ H-1	H-3	H-4	H-5	H-7
	X = Br	**23a**	9.0	8.9	7.7	1.8	1.5	3.96	2.93	4.68	5.70	3.07
	X = Cl	**23b**	9.1	9.2	8.0	1.9	1.5	3.87	2.93	4.65	5.75	3.26
	X = F	**23c**	9.2	9.2		1.6		3.80[i]	2.92	4.66	5.70	3.80[i]
	X = H	**23d**[e]	8.8	8.8	7.5	1.3	1.4	4.05	2.9 ± 0.15	4.78	6.08	3.0 ± 0.15
	X = CH_3	**23e**[f]	9.0	9.2	7.5	1.4	1.5	4.11	3.07	4.78	6.20	3.72
	X = OCH_3	**23f**[g]	9.2	9.3	8.4	2.0	1.3	3.91	3.01	4.75	6.07	4.55
		**18**[h]	J_{56} 7.7	J_{67} 1.6	J_{34} 1.6	J_{35} 1.1		4.38	3.37	*h*	6.84	*h*

[a] All coupling constants range from ±0.1 to 0.3 c.p.s. in estimated error, except where noted. [b] Spectra of all adducts were obtained from 30% d_5-acetone solutions except that of **18** which was determined as a 30% solution in deuteriochloroform; chemical shifts are relative to a tetramethylsilane internal standard, and are estimated accurate to ±0.03 p.p.m. [c] $J_{35} = 0$ was demonstrated by spin decoupling H-3 and H-5 of adduct **23b**. [d] $J_{13} = 1.5$ was demonstrated by spin decoupling H-1 and H-3 of adduct **23b**. [e] $J_{67} = 8.1 \pm 0.6$, $J_{56} = 8.1 \pm 0.6$, $J_{16} = 1.2$ c.p.s.; H-6 τ 3.45. [f] Methyl at C-6; τ 7.86, $J_{67} = 1.6$ c.p.s. [g] OCH_3 τ 6.19. [h] H-6 τ 3.67; CH_3(4), CH_3(7) τ 7.30 and 8.10. [i] Carbomethoxy τ 6.12 ± 0.01 for all adducts. [j] Center of a complex multiplet.

adducts, "long-range" n.m.r. spin–spin coupling constants in the 2-azabicyclo[3.2.2]nona-3,6-diene system, and carbomethoxynitrene reactivity toward aromatic substrates, are now considered in turn.

Structures of Adducts

Thermal[13] or photochemical[14–16] decomposition of an azidoformate in the presence of an aromatic substrate leads, probably through electrophilic attack of a carboxynitrene on the benzenoid system, to 1-carboxyazepines. When methyl azidoformate was decomposed at 120° in bromobenzene, 1-carbomethoxybromoazepine was obtained. Although this product showed but a single OCH_3 absorption in the n.m.r. (at τ 6.20) it may still have been a mixture of two or three isomers. Treatment of the 1-carbomethoxybromoazepine(s) with tetracyanoethylene gave a 1:1 adduct of m.p. 167–169°.

The same adduct was obtained more conveniently by decomposing methyl azidoformate at 120° in the presence of bromobenzene and tetracyanoethylene.[17] Other azepine adducts were obtained in the same manner. All gave excellent analyses for 1:1 adducts (Table I).

Structural assignments for these adducts were made through consideration of their spectral characteristics. Even casual examination of the n.m.r., ultraviolet, and infrared spectra of the seven adducts (Tables II, III, and IV) indicates that they must have basic structural similarities. Since the n.m.r. spectrum of the adduct derived from 1-carbomethoxyazepine

Table III. Ultraviolet Spectra of Tetracyanoethylene–Azepine Adducts[a]

Azepine precursor	Structure	λ,[b] mμ	ε[b]	λ_{max}, mμ	ε
Bromobenzene	**23a**	219	9100	255	4300
Chlorobenzene	**23b**	218	7500	252	4200
Fluorobenzene	**23c**	218	4700	244	6400
Benzene	**23d**	219	4400	252	4700
Toluene	**23e**	218	5300	247	6000
Anisole	**23f**	220	7900	236	7900
p-Xylene	**18**	218	8000	254	5300

[a] Acetonitrile solutions, 1×10^{-4} *M*. [b] Close to solvent cutoff.

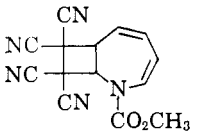
(13) R. J. Cotter and W. F. Beach, *J. Org. Chem.*, **29**, 751 (1964).
(14) K. Hafner and C. König, *Angew. Chem.*, **75**, 89 (1963); *Angew. Chem. Intern. Ed. Engl.*, 2, 96 (1963).
(15) W. Lwowski, T. J. Maricich, and T. W. Mattingly, Jr., *J. Am. Chem. Soc.*, **85**, 1200 (1963).
(16) K. Hafner, D. Zinser, and K-L. Moritz, *Tetrahedron Letters*, **No. 26**, 1733 (1964).
(17) Under analogous reaction conditions, ethyl diazoacetate and tetracyanoethylene in bromobenzene at 150° give 1-carbethoxy-2,2,3,3-tetracyanocyclopropane, m.p. 157–159° dec.; the discrimination between an electron-deficient double bond and an aromatic system appears to be reversed for carboxynitrenes and carboxycarbenes.

Table IV. Infrared Spectra of Tetracyanoethylene–Azepine Adducts[a]

Azepine precursor	Structure	Principal absorptions, cm.$^{-1}$[b,c]									
Bromobenzene	**23a**	1280	1735	1343	1452	1367	1660	905	735	1072	768
Chlorobenzene	**23b**	1272	1735	1340	1447	1362	1655	900	1072	764	1417
Fluorobenzene	**23c**	1270	1735	1336	1360	1444	1644	898	1191	768	1165
Benzene	**23d**	1273	1730	1340	1448	900	1653	1373	732	763	1418
Toluene	**23e**	1734	1272	1445	1340	1314	1363	1647	900	768	1417
Anisole	**23f**	1272	1735	1662	1337	1445	1364	1238	900	1025	770
p-Xylene	**18**	1300	1720	1250	1440	1340	1670	1400	764	912	990

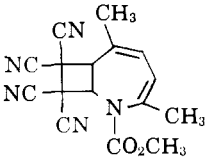
[a] Taken as potassium bromide disks. [b] Listed in order of decreasing intensity, excluding the C–H region near 3000 cm.$^{-1}$. [c] No absorptions in the 2500–2000-cm.$^{-1}$ range were detected.

shows six nonequivalent protons, all structures with planes of symmetry (such as those of type **4**, **6**, and **7**) must be excluded. Only structures of type **3** or **5** are compatible with the dissymmetry of the cycloaddition product indicated by the n.m.r. spectrum, and the unsubstituted adduct must be **11** or **12**.

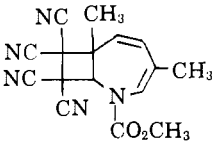


12

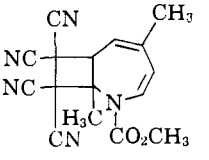
Six possible structures based on systems **11** and **12** may be drawn for the adduct from *p*-xylene (**13** through **18**).



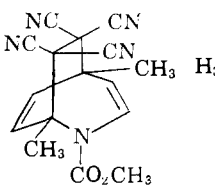
13



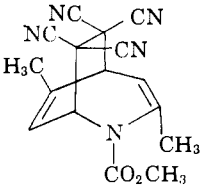
14



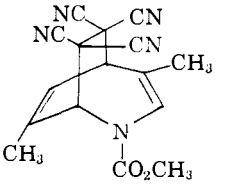
15



16



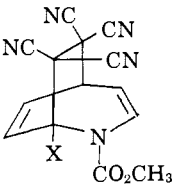
17



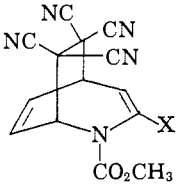
18

Alternatives **13**, **14**, **15**, and **16** may be excluded; they all have vinylic protons in vicinal relationship one to another which would be spin–spin coupled by about 9 c.p.s. No splitting between a pair of vinyl protons of this magnitude is observed in the n.m.r. of the adduct (see Table II). One may conclude at this point that the adduct derived from benzene is **11**,[17a] and that from *p*-xylene is **17** or **18**.

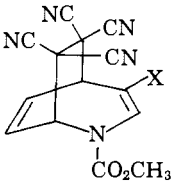
The monosubstituted azepines give adducts which, based on **11**, must be of structure **19**, **20**, **21**, **22**, **23**, or **24**.



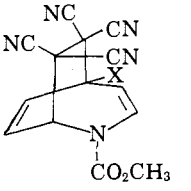
19



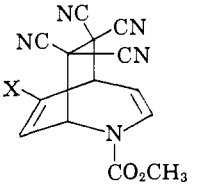
20



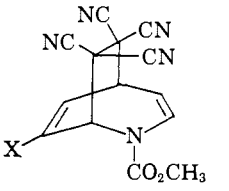
21



22



23



24

a, X = Br
b, X = Cl
c, X = F
d, X = H
e, X = CH_3
f, X = OCH_3

The spectra all show one upfield proton at τ 5.7–6.2 which is split by two couplings of about 9 and 1–2 c.p.s. The upfield proton must be at C-5, and can have only one proton vicinal to it. (In the moderately rigid bicyclic skeleton, dihedral angles between H-4 and H-5, and between H-5 and H-6, are both approximately 0°).[18] Structures **19**, **20**, **22**, and **24** cannot accommodate this requirement; **21** and **23** remain as possible representations for the adducts.

The most deshielded proton in the adducts, at τ near 3, must be vinylic and adjacent to nitrogen, *i.e.*, H-3. It experiences a spin–spin coupling of about 9 c.p.s. and therefore must be vicinal to another proton. Thus structure **21** is excluded, and **23** is assigned to the six adducts from monosubstituted azepines.

The spectrum of the adduct from *p*-xylene (**17** or **18**) shows a signal at τ 3.37 which must be H-3 (*cf.* Table II). The cycloaddition product in this case, then, is **18** rather than **17**.

These structural assignments for the seven adducts are further supported by close perusal of the n.m.r. data, a decoupling analysis of the spectrum of **23b**, and by examination of the fluorine n.m.r. spectrum of **23c**.

N.m.r. Spectra. Two of the five protons in the adducts **23**, H-3 and H-5, were assigned during the analysis leading to the structural assignments. The other three protons may be assigned as follows. The

(17a) Note Added in Proof. The X-ray structure analysis of a methoxybromide derivative of the adduct from N-ethoxycarbonylazepine and tetracyanoethylene just reported by J. H. van den Hende and A. S. Kende, *Chem. Commun.*, 1, 384 (1965), provides unequivocal evidence for the cycloaddition product having structure 11 (with CH_3-CH_2 in place of CH_3). See also A. S. Kende, P. T. Izzo, and J. E. Lancaster, *J. Am. Chem. Soc.*, 87, in press.

(18) *Cf.* N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, p. 49 ff.

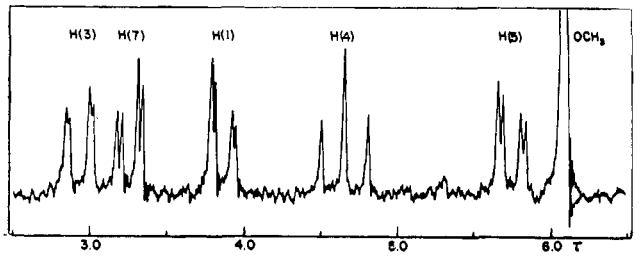


Figure 1. The n.m.r. spectrum of adduct **23b**.

vinyl proton H-4 comes at τ 4.65–4.78 and is split by vicinal hydrogens on either side approximately equally to give a doublet of doublets which appears as a triplet (see Figure 1). The remaining two protons, H-1 and H-7, split one another (J = 7.5 to 8.4 c.p.s.) and are each split by an additional coupling with H-3 or H-5. The two "long-range" couplings in the adducts of 1–2 c.p.s. must then be assigned to J_{15} and J_{37} or J_{13} and J_{57}. Clearly the latter alternative is the more plausible, for it does not postulate the couplings through five bonds.[19] With this identification of the coupling constants, the proton at τ 3.8–4.1 must be H-1 and that ranging from 3.07 to 4.55 is H-7. The great sensitivity in chemical shift of the absorption ascribed to H-7 to the substituent at C-6 reinforces this assignment.

These assignments for the spin–spin coupling interactions were tested through double-resonance[20] experiments on the adduct from chlorobenzene. The results are summarized in Table V. The triplet at 4.65 due to H-4 (*cf.* Figure 1) was proved to be a doublet of doublets and the "long-range" spin–spin interactions J_{13} and J_{57} were confirmed; thus the assignments in Table I were fully verified.

Table V. Double-Resonance Spin Decoupling of Adduct **23b**

Proton observed[a]	Proton irradiated H-1	H-3	H-4	H-5
H-1		Doublet, J = 8.1		
H-3	Doublet, J = 9.5		Doublet, J = 1.5	No interaction
H-4		Doublet, J = 9.2		Doublet, J = 9.1
H-5			Broad singlet	
H-7	Broad singlet			Doublet, J = 8.0

[a] Spin–spin interaction (J) in c.p.s.

The F^{19} n.m.r. spectrum of **23c** showed six distinguishable lines consistent in spacing and relative intensities with couplings between fluorine and three hydrogens of 15, 5, and 5 c.p.s. The proton n.m r. indicated that the J_{HF} of 15 c.p.s. was from coupling of fluorine with H-5, while the two smaller couplings of 5 c.p.s. were with H-1 and H-7. These results are wholly consistent with the assigned structure and with available precedents.[21]

(19) Couplings through five bonds are known: see S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

(20) J. D. Baldeschwieler and E. W. Randall, *Chem. Rev.*, 63, 81 (1963).

The long-range spin–spin couplings for the azepine adducts **23** listed in Table II show an interaction of 1.3–1.5 c.p.s. across the system H–C–N–C–H. The geometry of this moiety of the molecules corresponds to that found favorable for couplings across four single bonds in H–C–C–C–H systems: a W or M coplanar arrangement. Observation of these couplings provides another instance[19] in which long-range spin–spin interactions through heteroatoms follow the patterns first discerned in cyclic and acyclic hydrocarbon derivatives, and augments the single instance of a similar coupling reported recently.[22]

Of the two allylic long-range coupling possibilities in **23**, J_{35} and J_{57}, only the latter is observed (1.3–2.0 c.p.s.). In both allylic systems the angle between the C-5–H-5 bond and the plane of the carbon–carbon double bond is approximately 0°, and the anticipated allylic coupling would be small or zero. That the two couplings are quite different (J_{35} = *ca.* 0 and J_{57} = 1.3–2.0 c.p.s.) in spite of the apparent stereochemical congruence of the two allylic systems stresses the need for assessment of nongeometrical variables in analyses of long-range couplings.[23]

Selectivity of Carbalkoxynitrenes. That yields of adducts from 4-substituted 1-carbomethoxyazepines (Table I) are found to be as high as 30–40% is unexpected.[13,16,24] In fact, these data suggest a fundamental difference in the selectivity of the presumed carbomethoxynitrene and carbomethoxycarbene with respect to aromatic nuclei.

Carbomethoxycarbene has been reported to react with chlorobenzene to afford a 1:1 mixture of 3- and 4-chloro-1-carbomethoxycycloheptatriene in 27% yield.[24] In contrast, a 30% yield of the adduct from 4-chloro-1-carbomethoxyazepine was obtained in the present work. This figure (30%) merely sets a lower limit on the actual yield of the 4-chloroazepine since its subsequent reaction with tetracyanoethylene is probably not quantitative.[25] This contrast would lead to the tentative conclusion that a carbalkoxynitrene may be much more selective than its carbene counterpart toward an aromatic nucleus. While this interpretation would be consistent with the relative selectivity of the two reactive species in C–H insertions,[26] it is inconsistent with the staetment that carbalkoxynitrene and carbalkoxycarbene display about the same selectivity toward substituted benzenes.[16]

It is also of interest that the postulated steric control exerted by the benzene substituent over both the yield[24] and the isomer distribution[27] of 7-carbomethoxycycloheptatrienes may not be extended to 1-carbomethoxy-

(21) *Cf.* N. Muller and D. T. Carr, *J. Phys. Chem.*, 67, 112 (1963).

(22) J. E. Baldwin, G. V. Kaiser, and J. A. Romersberger, *J. Am. Chem. Soc.*, **87**, 4114 (1965).

(23) Compare C. W. Jefford, B. Waegell, and K. Ramey, *ibid.*, **87**, 2191 (1965).

(24) K. Alder, R. Muders, W. Krahne, and P. Wirtz, *Ann.*, 627, 59 (1959), and references therein.

(25) The azepine fraction isolated from thermal decomposition of methyl azidoformate in bromobenzene (shown to be >90% azepine by n.m.r.) afforded 21% of adduct 23a when treated at 120° with tetracyanoethylene in bromobenzene, and 40–45% of 23a when treated at 30° with tetracyanoethylene in toluene. Until pure 4-substituted azepine is in hand neither its extent of decomposition nor the yield of the Diels–Alder reaction can be precisely evaluated.

(26) Carbethoxynitrene is reported to be *ca.* ten times as selective as the corresponding carbene in C–H insertion reactions; *cf.* W. Lwowski and T. Maricich, *J. Am. Chem. Soc.*, **86**, 3164 (1964).

(27) W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, p. 102.

azepine formation. There seems to be no correlation between the nature of the benzene substituent and the yield of 4-substituted azepine. A further indication of profound disparity in the behavior of carbalkoxynitrenes and carbalkoxycarbenes with respect to attack on an aromatic ring has been noted above.[17]

Thus, there is good reason to believe that carbalkoxynitrenes differ substantially from carboalkoxycarbenes in selectivity toward aromatic nuclei. This postulate is being investigated quantitatively in our laboratory. The need for critical comparisons is not only intrinsically great, but becomes essential in view of the conflicting observations discussed in this section.

Conclusions

The adducts from 1-carboxyazepines and tetracyanoethylene result from 2 + 4 concerted[3] cycloadditions, rather than from 2 + 6 nonconcerted[3] cycloadditions as previously suggested[12]; they are derivatives of structure **11**. Long-range n.m.r spin–spin couplings of 1.3–1.5 c.p.s. across the H–C–N–C–H system of 2-azabicyclo[3.2.2]nona-3,6-dienes have been found, and nongeometrical influences on allylic couplings over four bonds inferred. Carbalkoxynitrenes and carbalkoxycarbenes seem to exhibit important dissimilarities in their reactions with aromatic substrates; this divergent behavior is being investigated further.

Experimental Section[28]

Tetracyanoethylene–Azepine Adducts. General Procedure A. Tetracyanoethylene (2.0 g., 15.6 mmoles) and 25 ml. of a substituted benzene were heated to 120° in a 100-ml., round-bottomed flask fitted with a reflux condenser with calcium sulfate drying tube. Methyl azidoformate[29] (n^{20}D 1.4155, 3.0 ml., *ca.* 30 mmoles) was injected into the reaction mixture which was then maintained at 120 ± 2° for 3.5 hr. Concentration of the reaction mixture by distillation at reduced pressure (to 130° and 5 mm.) gave a black viscous residue. This residue and approximately 30 ml. of toluene were boiled for 10 min., treated with charcoal, and filtered. As the dark red filtrate cooled slowly, an adduct crystallized. The material was collected, washed with toluene, and dried thoroughly. Adducts from tetracyanoethylene and bromobenzene, chlorobenzene, and anisole were prepared by this method.

A modification in this procedure was employed to isolate the *p*-xylene adduct. The viscous residue containing the crude adduct was dissolved in methylene chloride; treatment with charcoal, filtration, concentration to 15 ml., and elution through a 16 × 450 mm. column of Merck silica gel with methylene chloride gave an orange eluate. The residue left after evaporation of methylene chloride from the eluate was dissolved in about 20 ml. of hot toluene and allowed to crystallize in the cold.

General Procedure B. Tetracyanoethylene (1.3 g., 10 mmoles), methyl azidoformate (2.0 ml., *ca.* 20 mmoles), and an aromatic compound (10 ml.) were mixed in a 20-ml. glass bomb liner. Reaction in a closed steel bomb at 123 ± 5° for 1.5 hr. and isolation of the product as described above gave adducts from tetracyanoethylene and benzene, toluene, and fluorobenzene.

The crude adducts obtained by procedures A and B were light tan to colorless, melting over a 5–15° range. The adducts were purified for analysis by two to four recrystallizations with charcoal decoloration from toluene. Melting points, yields, and analyses are summarized in Table I.

The infrared spectra for the crude anisole and toluene adducts were indistinguishable from spectra obtained with analytically pure samples.

1-Carbomethoxybromoazepine. Methyl azidoformate (5.0 ml.) was added to 50 ml. of bromobenzene at 120°. After 3 hr. at 120 ± 2° the reaction mixture was concentrated by vacuum distillation (to 120° and 10 mm.). The residue and 25 ml. of cyclohexane were mixed and filtered; the filtrate was eluted from a 16 × 450 mm. column of Merck silica gel with cyclohexane (to remove the remaining bromobenzene). When the bright yellow band corresponding to the azepine had separated from the dark impurities held at the top of the column it was isolated by extrusion, extraction with ether, and concentration of the extract below 40°. The yellow residue (n^{20}D 1.5536, 1.45 g.) was identified as a 1-carbomethoxybromoazepine by its n.m.r. spectrum which showed a singlet at τ 6.20 (3 H) and a complex multiplet at 3.4–4.8 (5 H).[30]

Thin layer chromatography (Eastman Chromagram) with cyclohexane as developer revealed azepine decomposition products at R_f 0.0 and a single, well-defined yellow spot at R_f 0.3. Some impurities of R_f <0.3 were detected in an iodine chamber.

Reactions of 1-Carbomethoxy-4-bromoazepine with Tetracyanoethylene. I. The crude carbomethoxybromoazepine (1.3 g., 5.2 mmoles), tetracyanoethylene (0.75 g., 5.8 mmoles), and bromobenzene (10 ml.) were heated at 120 ± 2° for 1 hr. The reaction mixture was processed as described in procedure A above to give 0.35 g. (21% based on azepine) of an adduct, m.p. 156–162°. Three recrystallizations from toluene afforded a colorless, crystalline compound, m.p. 167–169°, shown by mixture melting point (167–169°) and identical infrared and n.m.r. spectra to be the same adduct obtained from bromobenzene, methyl azidoformate, and tetracyanoethylene.

II. The crude carbomethoxybromoazepine (1.4 g., 6.1 mmoles), tetracyanoethylene (780 mg., 6.1 mmoles), and toluene (60 ml.) were stirred at room temperature for 12 hr. Concentration of the toluene solution and work-up as before produced 900 mg. (43% based on azepine) of an adduct, m.p. 159–166°. Two recrystallizations from toluene gave colorless crystals, m.p.

(28) Analyses are by J. Nemeth and associates, Urbana, Ill. Melting points are uncorrected. Infrared spectra were determined by D. Johnson and associates with a Perkin-Elmer Model 521 spectrometer. Nuclear magnetic resonance spectra were obtained with Varian A-60 or Varian V-4300B instruments. Ultraviolet spectra were recorded with a Perkin-Elmer Model 202 spectrophotometer, purchased with funds from the Research Board of the University of Illinois.

(29) Prepared from methyl chloroformate and sodium azide; *cf.* M. O. Forster and H. E. Fierz, *J. Chem. Soc.*, **93**, 72 (1908).

(30) Compare these data with the n.m.r. spectrum of 1-carbethoxyazepine which shows six ring protons at τ 3.7–4.7 (ref. 14; see also ref. 13 and 15).

167–169°, demonstrated to be adduct **23a** by mixture melting point (167–169°) and identical infrared spectra.

Thermal Stability of the Adducts **23**. The adduct from 1-carbomethoxyazepine and tetracyanoethylene (**23d**, 200 mg., m.p. 165–167°) was refluxed in chlorobenzene (20 ml., b.p. 132°) for 3 hr. The adduct **23d**, m.p. 163–166°, was quantitatively recovered by complete distillation of the solvent. Its identity was confirmed by matched infrared spectra.

Liquid-Phase Oxidations of Cyclic Alkenes[1]

Dale E. Van Sickle, Frank R. Mayo, and Richard M. Arluck

Contribution from Stanford Research Institute, Menlo Park, California 94025.
Received May 22, 1965

This work was undertaken to relate the initial products of liquid-phase oxidations of unsaturated hydrocarbons under mild conditions (and thus their mechanisms of oxidation) to the structures of the hydrocarbons. Results with cyclopentene, cyclohexene, cycloheptene, cyclooctene, cyclododecene, methylenecyclohexane, and vinylcyclohexane at 50–70° are discussed in terms of the addition and hydrogen-abstraction mechanisms. Indicated rates of addition of alkylperoxy radicals to the corresponding cyclic alkenes are very similar. Indicated rates of abstraction (per hydrogen atom) differ by a factor of 22 and depend partly on the degree of reorganization required to give a planar allyl radical. In over-all rate of oxidation, cyclopentene is most reactive and cyclooctene is least reactive. While the other alkenes give mostly allylic hydroperoxides, 70% of the cyclooctene reacts by the addition mechanism, producing epoxide, suberic aldehyde, and polymer. These results are compared with the work of others. The "dimeric" peroxides from cyclopentene and cyclohexene are shown to be 2-(3-cycloalkenylperoxy)cycloalkanyl hydroperoxides.

Introduction

The objective of this work was to relate the initial products of oxidation of unsaturated hydrocarbons under mild conditions (and thus their mechanisms of oxidation) to the structures of the hydrocarbons. Previous workers have established the hydroperoxide or abstraction mechanism for the autoxidation of many olefins.[2,3] In 1956 and 1958, characteristics of the addition mechanism were reported. Two summarizing papers[4] showed that many olefins react partly or entirely through addition of peroxy radicals to double bonds rather than by hydrogen abstraction (or "transfer"). In 1961, quantitative studies were begun on the competition between the abstraction and addition mechanisms of oxidation of alkenes as a function of their structure. This report summarizes our studies on cyclic olefins. Similar research on acyclic olefins is still in progress.

Experimental Section

1. Materials. Cyclopentene was either Phillips research grade or carefully fractionated samples from Columbia Chemical Co.; cyclohexene (reagent grade) was from Matheson Coleman and Bell; cycloheptene was from Columbia (reagent grade) and from the Aldrich Chemical Co. (technical grade). The latter material was fractionated on a Hastelloy helices column of about 90 theoretical plates; the resulting distillate, b.p. 114° (760 mm.), showed two small peaks in the g.l.p.c. (Carbowax 20 M, 18-ft. column) just preceding the main hydrocarbon peak. The combined area of the impurities was 1.6% of the total. G.l.p.c. analysis of the Columbia material indicated a like amount of (presumably) the same impurities. The cyclooctene was obtained from Aldrich and was acid and base washed prior to distillation. The g.l.p.c. trace showed a peak trailing the main hydrocarbon and the impurity is estimated at 1%. The cyclododecene was a complimentary sample from Columbian Carbon Co. The *cis* and *trans* isomers could not be effectively separated by distillation and the experiments were performed on material that was approximately 90% *trans*, 10% *cis*. Methylenecyclohexane and vinylcyclohexane were obtained from Columbia Chemical Co.

All hydrocarbons were routinely distilled and then passed over activated alumina immediately prior to use. Except as noted, the materials appeared homogeneous in g.l.p.c. In a test case, no isomerization of methylenecyclohexane to methylcyclohexene could be detected as a result of the alumina treatment. ABN, azobis(2-methylpropionitrile), was Eastman White Label and was recrystallized from acetone. Triphenylphosphine (Matheson Coleman and Bell) was recrystallized from 95% ethanol and then sublimed.

Hydroperoxide samples, where used as initiators, were prepared by high-vacuum (0.05 mm.) distillation of the products from the oxidation of the corresponding olefin. The purity of the samples, as well as the determination of hydroperoxides for other analyses, was established by the Wibaut[5] titration procedure.

(1) Support by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Contract No. AF 49 (638)-1102 is gratefully acknowledged. This work was presented to the Division of Organic Chemistry at the 145th National Meeting of the American Chemical Society, Sept. 10, 1963; Abstracts of Papers, p. 26Q.

(2) L. Bateman, *Quart. Rev.* (London), **8**, 147 (1954).

(3) D. Barnard, L. Bateman, J. I. Cunneen, and J. T. Smith, "The Chemistry and Physics of Rubber-Like Substances," L. Bateman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1963, Chapter 17.

(4) F. R. Mayo, *J. Am. Chem. Soc.*, **80**, 2497 (1958); F. R. Mayo, A. A. Miller, and G. A. Russell, *ibid.*, **80**, 2500 (1958).

(5) J. P. Wibaut, A. B. van Leeuwen, and B. van der Wal, *Rec. Trav. Chim.*, **23**, 1033 (1954).