Model 11SC-1[17] was positioned within a cylindrical 2-mm Vycor filter about which the table rotated. The filter was totally blackened except for eight, equally spaced, horizontal, 0.5-mm slits located at the level of the lamp. The 2537-A light passed through the slits and struck the vertical Vycor sample tubes positioned 8 cm from the lamp. The rotation of the table compensated for any slight nonuniformities in the lamp, slit size, filter thickness, or distance from the lamp.

The sample tubes were shaken to break up the mercury, wiped clean, and equilibrated in the photolysis apparatus for 9 hr at 40° to saturate the vapor with mercury. After reequilibration at 30° for 20 min, the tubes were rotated and photolyzed at 30° (pressure, 2.65 ± 0.35 mm throughout the reaction).

For the analysis of its contents, a Vycor sample tube was scratched on the neck, wiped clean with tissue, and placed inside the vacuum system. After evacuation to 10^{-4} mm, the tube was broken open near the scratch by turning a stopcock with an eccentric end.[18] The volatile contents were frozen into a 7 × 50 mm Pyrex tube which was sealed off with a hand torch leaving at least 95% of the mercury in the Vycor sample tube. The volatile photolyzate was quantatively analyzed by crushing the small Pyrex tube in the gas stream leading to the injection port of a Perkin-Elmer Model F-11 gas chromatograph using the flash vaporizer depicted in Figure 8. The tube remained about 30 sec in the flash vaporizer at 150–60° before it was crushed and analyzed on a 0.31-cm o.d. by 3-m column containing 10% diisodecyl phthalate on Anakrom (90/100) ABS at 30° for 14 min and then at temperatures increasing 4° per min to 100°. Peak areas were integrated with a polar planimeter. The response of the flame ionization detector was taken to be proportional to the number of carbon atoms present per molecule as suggested by Purnell.[19]

The peaks were identified by adding authentic material to a photolyzed sample and noting the peak enhancement. Carbon monoxide was determined as noncondensable gas. All sample tubes were found to transmit similar intensities of 2537 A light after the photolyses. Plots of the data obtained are presented in Figures 2–5.

Kinetic Study of the Mercury-Sensitized Gas Phase Photolysis of Bicyclo[2.1.1]hexane.—Bicyclo[2.1.1]hexane was obtained by glpc separation of the norcamphor photolyzate as described above. The amount of material in each tube was determined by standard pressure techniques. The data were corrected for the slight variation in initial concentration of hydrocarbon. The photolysis and analytical procedure were identical with those described above for the norcamphor work; the results obtained are given in Figure 6.

Registry No.—**1**, 14075-12-8; **2**, 592-42-7; **3**, 285-86-9; **4**, 4663-23-4; **1** semicarbazone, 2630-42-4; **1** 2,4-dinitrophenylhydrazone, 3281-03-6; (3-cyclopentenyl)-ethanal, 14055-37-9.

Acknowledgments.—We thank Professor R. F. Nystrom for suggestions concerning vacuum techniques and Professor R. J. Crawford for design information helpful in developing the flash vaporizer shown in Figure 8.

(17) The manufacturer's specifications indicate over 90% 2537-A emission, and the remaining 10% would not be absorbed significantly by the norcamphor.

(18) An apparatus similar to the one used here has been described by R. J. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p 67.

(19) H. Purnell, "Gas Chromatography," John Wiley and Sons, Inc., New York, N. Y., 1962, p 302.

Cycloadditions. XVI. On the Relative Selectivity of Carbomethoxycarbene and Carbomethoxynitrene in Cycloadditions with Toluene and *t*-Butylbenzene[1,2]

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Carbomethoxynitrene generated thermally from methyl azidoformate adds to the aromatic nuclei of toluene and *t*-butylbenzene indiscriminately; all three possible isomeric alkyl-N-carbomethoxyazepines are formed in comparable amounts in both cases. The reactions of thermally generated carbomethoxycarbene with toluene and *t*-butylbenzene give rearrangement products from which isomer distributions of the initially formed alkyl-7-carbomethoxycycloheptatrienes could not be deduced.

Four intermolecular reactions common to carbalkoxycarbenes **1** and carbalkoxynitrenes **2** are insertions into carbon–hydrogen bonds, additions to olefinic and aromatic carbon–carbon bonds, and 1,3 cycloadditions. Through quantitative comparisons of the relative reactivity and selectivity of these short-lived chemical intermediates in all four types of processes, more complete understandings of their versatile behaviors may be gained.

1 **2**

The relative reactivity of carbethoxycarbene and carbethoxynitrene in one of these reactions, cycloadditions with aromatics, has recently been established.[5] A log–log plot for the relative rate constants for the reactions of monosubstituted benzenes with carbethoxycarbene and -nitrene gave a linear correlation with a slope of 3.3. This linear free-energy relationship provided a quantitative measure of the greater reactivity and diminished discrimination between different monosubstituted benzenes characteristic of the carbethoxycarbene, relative to the -nitrene.

Carbalkoxynitrenes have been inferred to be more selective than carbalkoxycarbenes in insertions into aliphatic carbon–hydrogen bonds by a factor of about 10.[6-8] The selectivity of the two reactive intermediates in cycloadditions with olefinic double bonds[9-13]

(1) Paper XV in this series: J. E. Baldwin and J. E. Gano, *J. Org. Chem.*, **32**, 3506 (1967).

(2) Supported in part by the National Science Foundation (Grant GP-522) and a Du Pont Grant-in-Aid to the Department of Chemistry and Chemical Engineering of the University of Illinois.

(3) Alfred P. Sloan Research Fellow.

(4) Archer Daniels Midland Co. Fellow, 1964–1965.

(5) J. E. Baldwin and R. A. Smith, *J. Am. Chem. Soc.*, **89**, 1886 (1967).

(6) W. von E. Doering and L. H. Knox, *ibid.*, **83**, 1989 (1961).

(7) W. Lwowski and T. J. Maricich, *ibid.*, **86**, 3164 (1964).

(8) M. F. Sloan, T. J. Prosser, N. R. Newburg, and D. S. Breslow, *Tetrahedron Letters*, 2945 (1964).

(9) I. A. Dyakonov, *Zh. Obshch. Khim.*, **19**, 1734 (1949).

(10) C. von der Heide, *Chem. Ber.*, **37**, 2101 (1904).

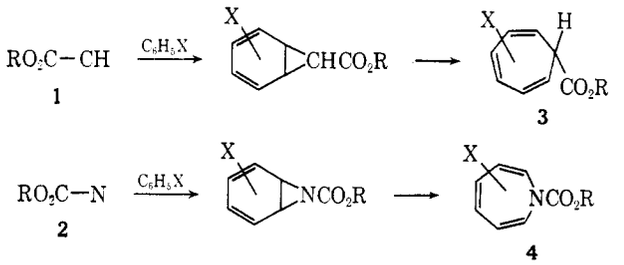
(11) P. S. Skell and R. M. Etter, *Proc. Chem. Soc.* (London), 443 (1961).

(12) I. A. Dyakonov and V. F. Myznikova, *Sbornik Statei Obshchei Khim., Akad. Nauk SSSR*, **1**, 489 (1954); *Chem. Abstr.*, **49**, 883 (1955).

(13) S. H. Harper and H. W. B. Reed, *J. Chem. Soc.*, 779 (1955).

is now being investigated by Hafner and co-workers.[14] In unpublished work,[14] Hafner has carried out the monoaddition of carbethoxynitrene with isoprene and found that the ratio of addition at the methyl-substituted 1,2 bond to addition at the unsubstituted 3,4 bond was about 1:1 for the nitrene. Carboxycarbene–carboxynitrene relative selectivity in 1,3 cycloadditions has not been determined.

The relative selectivity of carbalkoxycarbenes and -nitrenes in cycloadditions with aromatics would be secured through reliable data for the distributions of isomers formed from these reactions with monosubstituted benzenes. From a carbalkoxycarbene and monosubstituted benzene, cycloaddition and electrocyclic ring-opening of the presumed initially formed norcaradienes would give three isomeric 7-carbalkoxycycloheptatrienes, **3**. From a carbalkoxynitrene, three isomeric N-carbalkoxyazepines, **4**, would be produced.



Experimentally, definitive data on the isomer distributions have not been obtained and the relative selectivity of carbalkoxycarbenes and -nitrenes has remained unsettled.

In 1959 Alder and co-workers reported isomer distributions for the cycloheptatrienes produced in the reaction of photolytically generated carbomethoxycarbene with a series of substituted benzenes.[15] Methyl diazoacetate in the aromatic solvent was irradiated for 70 hr with Pyrex-filtered ultraviolet light[16] from a high-pressure mercury lamp. The crude products were distilled under vacuum at maximum bath temperatures ranging from about 70° to 110°, and reacted with dimethyl acetylenedicarboxylate in xylene at 140° for 10 hr. The crude Diels–Alder adducts were vacuum distilled and pyrolyzed for 4 hr at 260–300°. Isolation and identification of the resulting substituted dimethyl phthalates provided data from which an estimate of the isomer distributions in the crude cycloheptatriene mixture was made (Table I).

These data have been adduced as evidence for a dominance of steric over polar effects controlling the selectivity of cycloadditions of carbomethoxycarbene with benzenes. The point has been argued chiefly on the basis of the isomer distributions obtained for the methyl- and *t*-butylcarbomethoxycycloheptatrienes.[17]

The data, however, do not require such a mechanistic inference. The isomer ratios reported may not have corresponded to the kinetically controlled ratios. If the inefficient Diels–Alder reactions or pyrolyses were selective, or if rearrangements of the initially formed 7-carbomethoxycycloheptatrienes were significant, the phthalate isomer distributions reported

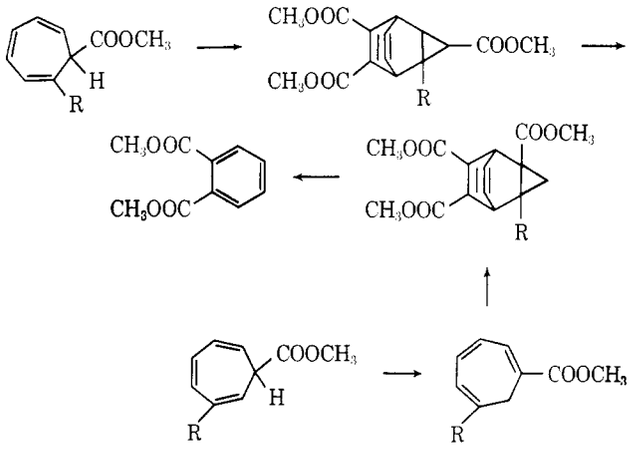
(14) K. Hafner, private communication.
(15) K. Alder, R. Muders, W. Krane, and P. Wirtz, *Ann.*, **627**, 59 (1959).
(16) G. O. Schenck and H. Zigler, *ibid.*, **584**, 221 (1953).
(17) W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, p 102.

TABLE I
ISOMER RATIOS FOR CARBOMETHOXYCARBENE CYCLOADDITIONS WITH MONOSUBSTITUTED BENZENES[a]

Substituent	Yields,[b] % Photolysis[c]	Yields,[b] % Diels–Alder	Isomer distribution[d] 3:2:1
Methyl	43	74	12:7:1
Ethyl	37	66	
t-Butyl	23	39	1
Chloro	27	38	1:1
Bromo	17	35	1:1

[a] Compiled from data in ref 15. [b] The only yield given for the pyrolysis step was for the adduct derived from toluene, 64%. [c] Yield of crude distillate; 7-carbomethoxycycloheptatriene content was not determined. [d] Ratio of phthalates presumed to have come from 3-, 2-, and 1-substituted cycloheptatriene-7-carboxylates.

may well not represent the ratios sought. For example, if hydrogen shifts occurred in some cycloheptatrienes before the addition with acetylene dicarboxylate, two different initially formed isomers could well have given the same phthalate.



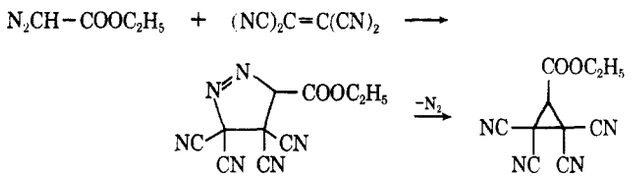
Hafner and colleagues reported isomer ratios for the azepines derived from toluene and chlorobenzene.[18] The ratios for the azepines derived from toluene were about the same as the corresponding cycloheptatriene ratios obtained by Alder (Table I), and the ratios for the azepines stemming from chlorobenzene were said to be about 1:1:1. A reinvestigation, however, has given revised values for the ratios of isomeric azepines arising from toluene, and further work with other monosubstituted benzenes is in progress.[14]

Our earlier work[19] on substituted N-carbomethoxyazepine Diels–Alder cycloadditions with tetracyanoethylene provided some incidental information which might have had a bearing on carbalkoxycarbene or -nitrene selectivity toward aromatics, but further investigation has demonstrated that this is not the case. Conversion of mixtures of isomeric azepines to the corresponding Diels–Alder adducts was found to be far from quantitative and nonselective, either at room temperature or at 130°; and, for the one adduct on which an X-ray crystallographic structure determination was accomplished,[20,21] the crystals, even after five recrystallizations, were found to contain some 15% of an isomeric adduct. These results emphasize the haz-

(18) K. Hafner, D. Zinser, and K.-L. Moritz, *Tetrahedron Letters*, 1733 (1964).
(19) J. E. Baldwin and R. A. Smith, *J. Am. Chem. Soc.*, **87**, 4819 (1965).
(20) I. C. Paul, J. E. Baldwin, and R. A. Smith, *ibid.*, **88**, 3653 (1966).
(21) R. A. Smith, J. E. Baldwin, and I. C. Paul, *J. Chem. Soc., Sect. B*, 112 (1967).

ards of methods based on chemical conversions and separations; they must be quantitative and complete to have analytical value.

That methyl azidoformate and tetracyanoethylene (TCNE) in bromobenzene at 120° gave an azepine–TCNE adduct, while ethyl diazoacetate with the same reagents at 150° gave 1-carbethoxy-2,2,3,3 tetracyanocyclopropane, appeared to indicate a discrimination between an electron-deficient double bond and an aromatic system reversed for the carboxynitrene and carboxycarbene, but in fact the results probably give no comparison of these reactive intermediates: the cyclopropane **6** probably stemmed[22] from the 3 + 2 cycloadduct **5**, mp 114–115° dec, which could be obtained in high yield from TCNE and ethyl diazoacetate at 25°.



5 **6**

In the present study, we have attempted to get data on the isomer distributions of cycloheptatrienes, **3**, and azepines, **4**, derived from the reactions of toluene or *t*-butylbenzene with carbomethoxycarbene or carbomethoxynitrene. The results demonstrate that the carbomethoxynitrene intermediate is indiscriminate and produces comparable ratios of isomers with both toluene and *t*-butylbenzene. The products isolated from the carbomethoxycarbene reactions stemmed from rearrangements of the initially formed cycloheptatrienes, and estimates of isomer distributions were not secured.

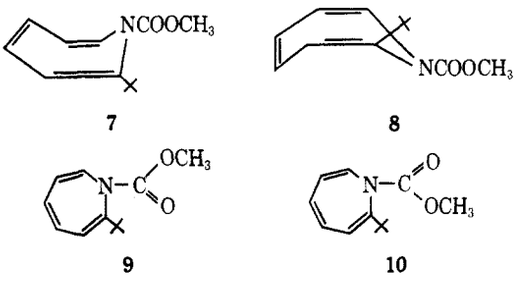
Results and Discussion

A direct method for analyzing mixtures of substituted azepines, nmr spectroscopy, has proven useful in the present work for the analysis of methyl and *t*-butyl-N-carbomethoxyazepines.

The nmr spectrum of the mixture of isomeric methyl-N-carbomethoxyazepines derived from the thermolysis of methyl azidoformate in toluene at 130° showed three doublets, ascribable to the protons of methyl groups situated on the azepine ring, at τ 7.92 (J = 1.2 cps), 8.18 (J = 0.8 cps), and 8.25 (J = 1.5 cps) in area ratios of 1.2:1:1.2.[23] Carbomethoxynitrene therefore displayed no appreciable selectivity in reactions with toluene.

The nmr spectrum of the azepines produced in the thermal reaction of methyl azidoformate with *t*-butylbenzene at 130° showed four singlets at τ 8.82, 8.86, 8.90, and 8.94. As the temperature was raised to 80°, the singlets at τ 8.82 and 8.86 sharpened without converging, and their ratio appeared to change slightly favoring the downfield signal at higher temperatures.

We interpret the four singlet absorptions as signals characteristic of the *t*-butyl protons of the 2-, 3-, and 4-*t*-butyl-N-carbomethoxyazepines. The 2-*t*-butyl-N-carbomethoxyazepine is considered responsible for the two downfield singlets. As the temperature is raised, interconversion of conformational isomers (perhaps **7** and **8**) becomes rapid compared with the nmr time scale, but the equilibration between the *cis,trans* isomers **9** and **10** remains slow; the *t*-butyl peaks thus sharpen as one rate process becomes rapid, but do not coalesce.[24]

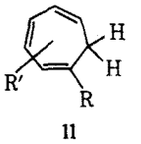


7 **8**

9 **10**

Integration of the spectrum indicates that the three isomers of *t*-butyl-N-carbomethoxyazepine are formed in the ratios 2:3:2. There is little discrimination among the three types of aromatic carbon–carbon bonds in *t*-butylbenzene by the carbomethoxynitrene. The steric differences between toluene and *t*-butylbenzene exert only a slight moderating influence on the indiscriminate cycloadditions of carbomethoxynitrene with their aromatic nuclei.

Thermolysis of methyl diazoacetate in toluene at 130° gave products which, after elution through a bed of basic alumina, exhibited the nmr spectrum reproduced in Figure 1. This spectrum lacks a one-proton triplet in the region τ 7.5–8.0; instead, a two-proton doublet appears at τ 7.68 (J = 7.0 cps). Thus 7-carbomethoxycycloheptatrienes are not significant constituents in the mixture of reaction products; the two-proton doublet and the remainder of the spectrum are consistent with the moiety $=CH-CH_2-CR=$, where R is either $-CH_3$ or $-CO_2CH_3$, and the principle product may be assigned partial structure **11**.



11

R′,R or R, R′ = CH_3, CO_2CH_3

The major disubstituted cycloheptatriene isomer was isolated by column chromatography. It analyzed for $C_{10}H_{12}O_2$ and had λ_{max} 215 mμ (ϵ 1.53 × 10^4) and 284 (6.17 × 10^3). The elucidation of its structure was accomplished by a detailed examination of its nmr spectrum (Figure 2).

There are eight possible structures for a 1-R-, 2,3,4-, or 5-R′-cycloheptatriene, **11**. The C-7 protons in cycloheptatriene give rise to a signal at τ 7.80,[25] whereas those in the disubstituted cycloheptatriene **11** absorb at 7.68. There is good precedent for the expectation that a C-methyl group would shield, rather than de-

(22) *Cf.* R. M. Scribner, G. N. Sausen, and W. W. Prichard, *J. Org. Chem.*, **25**, 1440 (1960).

(23) Professor Hafner's new results[14] show that 2-, 3-, and 4-methyl-N-carbethoxyazepines are formed in ratios of 1:1.2:1.3.

(24) K. Conrow, M. E. H. Howden, and D. Davis [*J. Am. Chem. Soc.*, **85**, 1929 (1963)], demonstrate a lower energy barrier for inversion of 2-*t*-butyl-3,7,7-trimethyltropilidine through its average plane.

(25) "Catalog of NMR Spectra," Vol. 1, Varian Associates, Palo Alto, Calif., 1962, Spectrum No. 158.

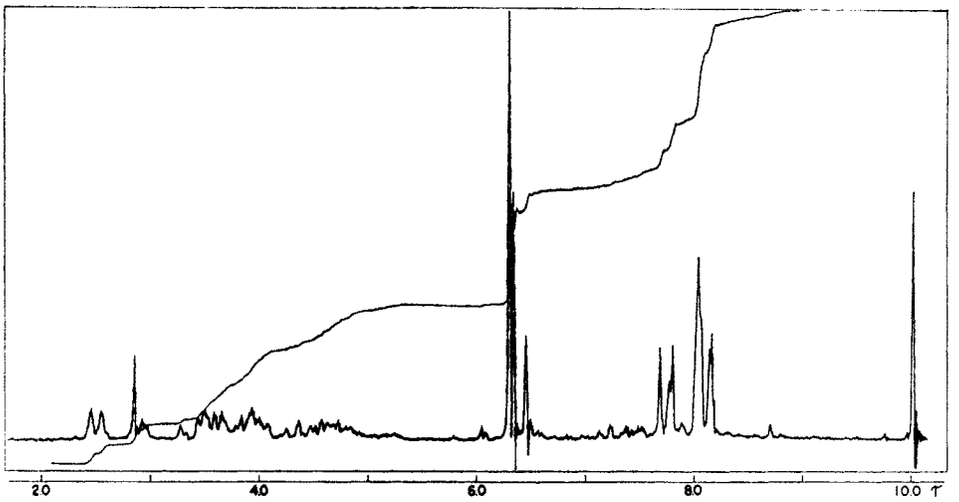


Figure 1.—Nuclear magnetic resonance spectrum of crude methylcarbomethoxycycloheptatrienes.

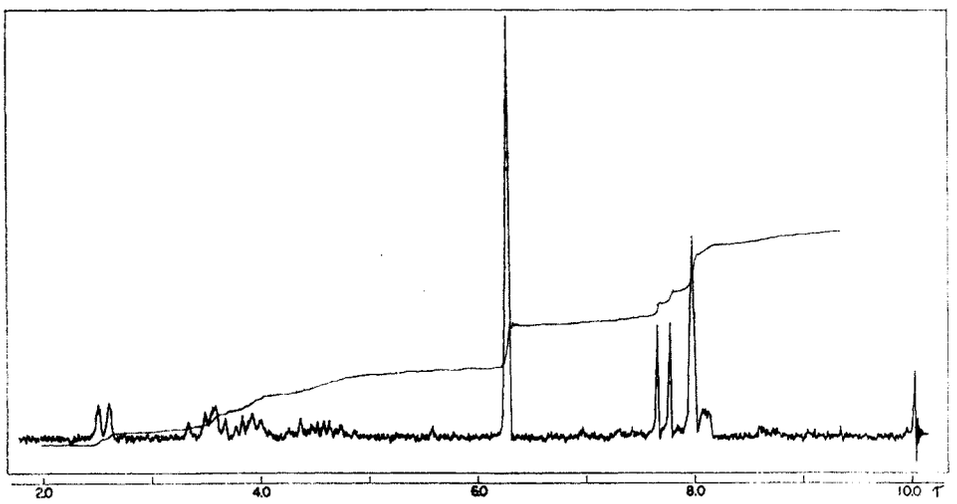
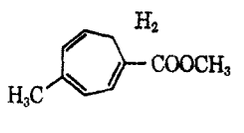


Figure 2.—Nuclear magnetic resonance spectrum of the major methylcarbomethoxycycloheptatriene isomer.

shield the C-7 protons. For example, the C-6 allylic protons of 1-methylcyclohexene absorb at τ 8.14, while those of cyclohexene itself absorb at 8.04.[26] The opposite effect would be expected for a carbalkoxy substituent at C-1.[27] Thus the observed chemical shift of the C-7 protons indicates a 1-carbomethoxy rather than a 1-methyl substituent.

The broad doublet in the nmr at τ 2.52 (J = 6 cps, 1 H) was assigned to a vinyl proton vicinal and *cis* to the carbomethoxy group, and split by one vicinal proton. This assignment reduces the structural possibilities to **12** and **13**.



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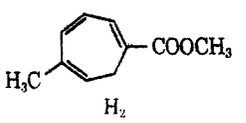

13

Although the structure of the major product of the thermal decomposition of methyl diazoacetate in toluene was not assigned, the formal origin of this product may be traced. Structures **12** and **13** may both be derived from 3-methyl-7-carbomethoxycycloheptatriene through hydrogen migrations.[28]

Thermolysis of methyl diazoacetate in *t*-butylbenzene at 150° gave a mixture of products; isolation of the major isomer by chromatography gave material which exhibited an nmr spectrum indicative of a rearranged structure (Figure 3).

Thermal rearrangements of 7-carboalkoxycycloheptatrienes at rates comparable with the thermal decomposition of alkyl diazoacetates thus preclude determining the desired quantitative information on isomer distributions by a simple direct examination of the reaction products. Indirect methods based on analysis of the products that do appear in the reaction mixture seem difficult in light of the controls which would have to be run; although hydrogen migrations would not destroy the positional relationships between alkyl and carboxy groups, other intramolecular rearrangements[29] or elimination and readdition of a carbenoid species could.

(26) G. V. D. Tiers, "Characteristic NMR 'Shielding Values' for Hydrogen in Organic Structures," Minnesota Mining and Manufacturing Company, St. Paul, Minn., 1958, p 23f.

(27) L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press Ltd., Oxford, 1959, p 53.

(28) Compare W. von E. Doering, G. Laber, R. Vonderwahl, N. F. Chamberlain, and R. B. Williams, *J. Am. Chem. Soc.*, **78**, 5448 (1956).

(29) J. A. Berson and M. R. Willcott, III, *ibid.*, **88**, 2494 (1966).

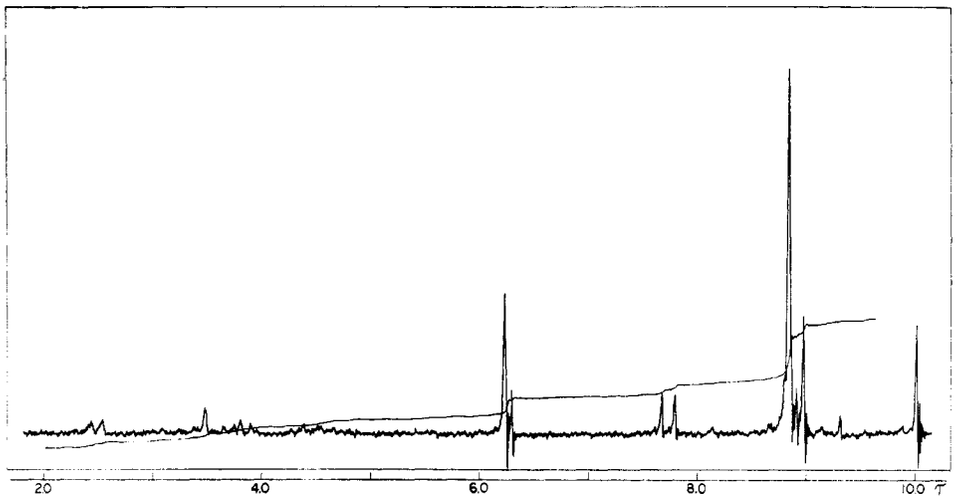

Figure 3.—Nuclear magnetic resonance spectrum of the major *t*-butylcarbomethoxycycloheptatriene isomer.

Experimental Section[30]

1-Carbethoxy-2,2,3,3-tetracyanocyclopropane.—Ethyl diazoacetate[31] (13 ml, 115 mmoles) was added over a 3.5-hr period to a refluxing solution of tetracyanoethylene (10 g, 80 mmoles) in 275 ml of bromobenzene. Distillation of the solvent under reduced pressure gave a solid residue which was washed repeatedly with ether; the dry brown solid weighed 10.0 g, 59%, mp 154–158°. Sublimation of this material gave long white needles of the cyclopropane; mp 157–159°. Recrystallization of the crude material from ethanol–petroleum ether (bp 30–60°) afforded white crystals: mp 157–158°; nmr peaks (acetone-d_6) at τ 5.56 (1 H, singlet), 5.62 (2 H, quartet, J = 7.5 cps), and at 8.67 (3 H, triplet, J = 7.5 cps).

Anal. Calcd for $C_{10}H_6N_4O_2$: C, 56.08; H, 2.82; N, 26.16; mol wt, 214.2. Found: C, 56.07; H, 3.13; N, 26.31; mol wt, 209 (osmometric in acetone).

Tetracyanoethylene–Ethyl Diazoacetate Adduct.—To a stirred solution of tetracyanoethylene (4.0 g, 31 mmoles) in 200 ml of benzene was added during 25 min a solution of ethyl diazoacetate (6.0 g, 53 mmoles) in 50 ml of benzene. The mixture was stirred at room temperature for 15 hr. Filtration of the mixture gave an off-white solid which was washed three times with benzene and dried under vacuum at 25°: 6.4 g, 86%, mp 115° dec. This compound decomposed in the presence of light or heat; in benzene, decomposition was rapid at reflux; in acidic solvents, decomposition was observed at 20°. Recrystallization was effected on a small scale from isopropyl ether–petroleum ether or benzene–ethanol to give material having mp 114–115° with decomposition and gas evolution. The nmr spectrum of this compound in acetone-d_6 showed only two groups of absorptions, τ 5.50 (2 H, quartet, J = 7.2 cps, CH_2—CH_3) and 8.61 (3 H, triplet, J = 7.2 cps, CH_2—CH_3). The infrared spectrum (KBr) had major bands at 1750, 1735 (sh), and 1605 cm^{-1}.

Anal. Calcd for $C_{10}H_6N_6O_2$: C, 49.59; H, 2.50; N, 34.70. Found: C, 49.18; H, 2.41; N, 34.27.

Methyl-N-Carbomethoxyazepines.—Methyl azidoformate[32] (5.0 ml) and 37 ml of toluene were sealed at −80° in thick-walled Pyrex tubes, heated at 130 ± 5° for 30 min, cooled, and cautiously opened. The reaction mixture was treated with a few grains of anhydrous potassium carbonate and concentrated by vacuum distillation. The viscous residue was taken up in about 100 ml of ether; the ethereal solution was filtered, washed six times with a total of 100 ml of 5% aqueous sodium hydroxide and three times with a total of 60 ml of water, shaken for 5 min with 2 g of anhydrous sodium sulfate, filtered, and dried over sodium sulfate containing a few grains of potassium carbonate. The orange liquid (3.45 g) left after filtration and evaporation of the ether was examined by nmr spectroscopy in deuteriochloroform; the methyl region showed a toluene CH_3 absorption (τ 7.68) and three methyl doublets at 8.25, 8.18, and 7.92, in the relative intensities 1.2:1.0:1.2. Chromatography of this crude material on a 2 × 25 cm column of Woelm basic alumina (Alupharm Chemicals) eluting with methylene chloride produced a yellow fraction which was treated with a few grains of anhydrous potassium carbonate and concentrated on a rotary evaporator at a maximum bath temperature of 40° to a bright yellow mixture of azepines, stable in the dark at −20° in a sealed glass ampoule containing anhydrous potassium carbonate. The methyl-N-carbomethoxyazepine was obtained in 38% yield: n^{25}D 1.5306; λ_{max}^{hexane} 240 mμ (ϵ 3.1 × 10^3), 210 (2.3 × 10^4). The nmr spectrum had peaks at τ 3.63–4.80 (5 H, multiplet, olefinic protons), 6.24 (3 H, singlet, CO_2CH_3), 7.92 (1 H, doublet, J = 1.2 cps, CH_3), 8.18 (1 H, broad doublet, J = 0.8 cps, CH_3), and at 8.25 (1 H, doublet, J = 1.5 cps, CH_3).

Anal. Calcd for $C_9H_{11}NO_2$: C, 65.44; H, 6.71; N, 8.48. Found: C, 64.98; H, 6.61; N, 8.30.

The azepine (106 mg, analytical sample) was heated at 130 ± 3° for 14 hr in a dry, base-washed, sealed tube. Chromatography on Woelm basic alumina (6 × 25 mm) with methylene chloride (20 ml, fraction 1) and chloroform (20 ml, fraction 2) eluted about 80 mg of material. The nmr spectrum of the material in fraction 1 was identical with a spectrum obtained from authentic N-(2-methylphenyl)methylurethan. The spectrum of the material in fraction 2 was identified as N-(4-methylphenyl)methylurethan by a comparison with the spectrum of authentic material. The urethans were made independently by the reaction of 2 and 4-methylaniline with methyl chloroformate: mp 54–55° and mp 96–98° for the 2- and 4-methylphenylurethans, respectively.

***t*-Butyl-N-Carbomethoxyazepines.**—Methyl azidoformate (5.0 g) was injected into 30 ml of *t*-butylbenzene at 130° and heated for 30 min. The solution was worked-up as described above. The mixture of azepines obtained showed nmr peaks at τ 3.2–4.9 (5 H, multiplet, olefinic protons), 6.32 (2.7 H, singlet, CO_2CH_3), 6.48 (0.3 H, singlet, CO_2CH_3), 8.82 (broad singlet), 8.86 (broad singlet), 8.90 (singlet), and at 8.94 (singlet). The last four signals were assigned to protons in *t*-butyl groups; the total area of these signals was approximately 9 H; the relative area of the signals was 1:1:3:2, in the same order as listed. The temperature dependence of the methyl peaks was discussed above.

Carbomethoxymethylcycloheptatrienes.—Methyl diazoacetate (2.0 ml) and 18 ml of toluene were heated at 130° for 14.5 hr (about three half-lives) in a 25 × 250 mm thick-walled Pyrex tube. Distillation of the solvent at reduced pressure gave 1.7 g of a clear pale yellow liquid residue. Chromatography of 1.5 g of this liquid on a 25 × 300 mm column of Merck silica gel gave, upon elution with cyclohexane, benzene, and methylene chloride, a series of fractions, each of which after evaporation of the solvents was taken up in carbon tetrachloride and examined by nmr. Fractions 1–3 displayed nmr signals ascribable to aromatic, olefinic, methoxy, and methyl protons. Fractions 4 and 5 appeared to consist of a relatively pure compound with absorptions at τ 2.52 (1 H, broad doublet, J = 6 cps), 3.26–4.88

(30) Analyses by J. Nemeth and associates, Urbana, Ill. Melting points are uncorrected. Nuclear magnetic resonance spectra were obtained with Varian A-60 or A56/60 instruments. Ultraviolet spectra were recorded with a Perkin-Elmer Model 202 spectrophotometer, purchased with funds from the Research Board of the University of Illinois.

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(3 H, multiplet, olefinic protons), 6.23 (3 H, singlet, CO_2CH_3), 7.68 (2 H, doublet, J = 7.0 cps), and at 7.95 (3 H, broad singlet, CH_3) (Figure 2). The spectrum of fraction 6 differed from that of fraction 5 only in the presence of additional minor peaks. Fraction 7 appeared to be devoid of olefinic protons.

The nmr solution containing the material from fraction 5 was filtered through charcoal, concentrated, passed through a 7 × 50 mm column of Woelm basic alumina with methylene chloride, and concentrated to give 109 mg of a clear straw-colored liquid: $n^{25}D$ 1.5344; ultraviolet absorption (MeOH) at 284 mμ (ϵ 6.17 × 10^3) and 215 (1.53 × 10^4).

Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 73.40; H, 7.35.

The cycloheptatriene from fraction 4 above (190 mg), dimethyl acetylenedicarboxylate (200 mg; Eastman), and 10 ml of *p*-xylene were heated at 140° for 11 hr. Removal of the xylene at reduced pressure (bp 80–82° at 94 mm) left a liquid which was distilled at 0.6 mm with the bath temperature raised slowly to a maximum of 200°. Analysis of the distillate by nmr spectroscopy revealed nearly complete recovery of unchanged reactants. The residue after distillation amounted to about 30 mg.

Reaction of methyl diazoacetate (2.5 ml) and toluene (25 ml) as before produced 2.5 g of the cycloheptatriene mixture upon distillation of the solvent at a maximum bath temperature of 110°. The crude material (1.0 g) was placed on a 1 × 25 cm column of Woelm basic alumina packed in carbon tetrachloride. Elution with 125 ml of carbon tetrachloride followed by 125 ml of methylene chloride gave 0.8 g of a straw-colored liquid. From the nmr spectrum (Figure 1) it was apparent that the major constituent of this mixture was identical with that isolated in fraction 5 above; additional signals appeared in the aromatic, methoxy, and aliphatic regions.

Carbomethoxy-*t*-butylcycloheptatrienes.—Methyl diazoacetate (4 ml) and *t*-butylbenzene (40 ml) were heated at 150° for 1 hr. The solvent was vacuum distilled at 108° (100 mm) and the residue was flash distilled at 90–95° (1 mm). Redistillation gave 2 g of material having bp 88–89° (1 mm). A 0.6-g sample of the crude mixture was chromatographed on a 1 × 15 mm column of Woelm basic alumina packed in hexane. After elution with 30 ml of hexane to remove residual *t*-butylbenzene, five hexane fractions were cut (a total of 165 ml), followed by one fraction (250 ml) eluted by benzene, chloroform, and methanol in succession. Fractions 1–5 appeared (nmr) to be mixtures of two cycloheptatrienes. The major isomer (Figure 3) had peaks at τ 2.48 (1 H, broad doublet, J = 6 cps), 3.3–4.7 (3 H, multiplet, olefinic protons), 6.23 (3 H, singlet, CO_2CH_3), 7.72 (2 H, doublet, J = 7.2 cps), and at 8.83 (9 H, singlet, $C(CH_3)_3$).

Registry No.—**1** (R = Me), 7264-18-8; **2** (R = Me), 14194-58-2; **4** (X = 2-Me), 14194-59-3; **4** (X = 3-Me), 14194-60-6; **4** (X = 4-Me), 14194-61-7; **4** (X = 3-Bu-*t*), 14194-62-8; **4** (X = 4-Bu-*t*), 14320-33-3; **5**, 14194-63-9; **6**, 14194-64-0; **9**, 14194-65-1; **10**, 14194-66-2; **12**, 14194-67-3; **13**, 14194-68-4; toluene, 108-88-3; *t*-butylbenzene, 98-06-6.

Behavior of Ketene toward α-Methoxy Hemiacetal Halides Related to Tetrahydropyran and to Carbohydrates

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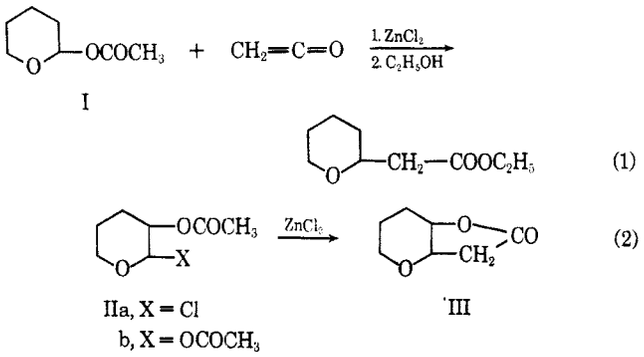
A 3-methoxyl substituent in tetrahydropyran-2-yl chloride inhibits reactivity of the halogen toward ketene and zinc chloride more than does a 3-acetoxyl group. Both give rise to a γ-lactone. A trace of γ-lactone results also from interaction of ketene ($ZnCl_2$) with tetra-*O*-methyl-D-glucopyranosyl bromide. Related structures in the tetrahydropyran series which showed negative response with ketene are discussed and alternate syntheses of many of them are included.

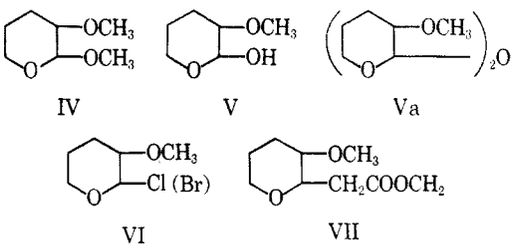
Tetrahydropyran-2-yl acetate, tetrahydropyran-2,3-diol diacetate, and 3-acetoxytetrahydropyran-2-yl chloride have been shown to react at the acylal function or the chloride position with ketene[2] in the presence of zinc chloride. The yield of ester from I was 70% (eq 1), that of lactone III from IIa was 43%, and



from IIb only a trace (eq 2). Thus, the 3-acetoxyl group lessens the reactivity at position 2. This lessening effect was magnified by having several acetoxyl groups in the molecule, for 2,3,4-tri-*O*-acetyl-α-D-xylosyl chloride yielded no lactone when treated with ketene and zinc chloride.

The present paper takes up the related question of the effect of a methoxyl group at position 3 on the reactivity of substituents at position 2. Several compounds related to 3-methoxytetrahydropyran were synthesized, and methyl ethers of carbohydrate analogs were included.

The hemiacetal hydroxyl of tetrahydropyran-2,3-diol[3] was methylated by refluxing with methanol (HCl) after which the alcoholic hydroxyl, as the anion, was converted to ether IV by reaction with methyl



iodide. Then the 2-methoxyl was removed by acid hydrolysis, yielding V. Compound V was obtained

(1) Sugar Research Foundation Fellow, 1961–1963.

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