Nitrene Insertion Reactions. I. Dimethyl-*N*-carbethoxyazepines and Their Cycloaddition Reaction Products. (1)

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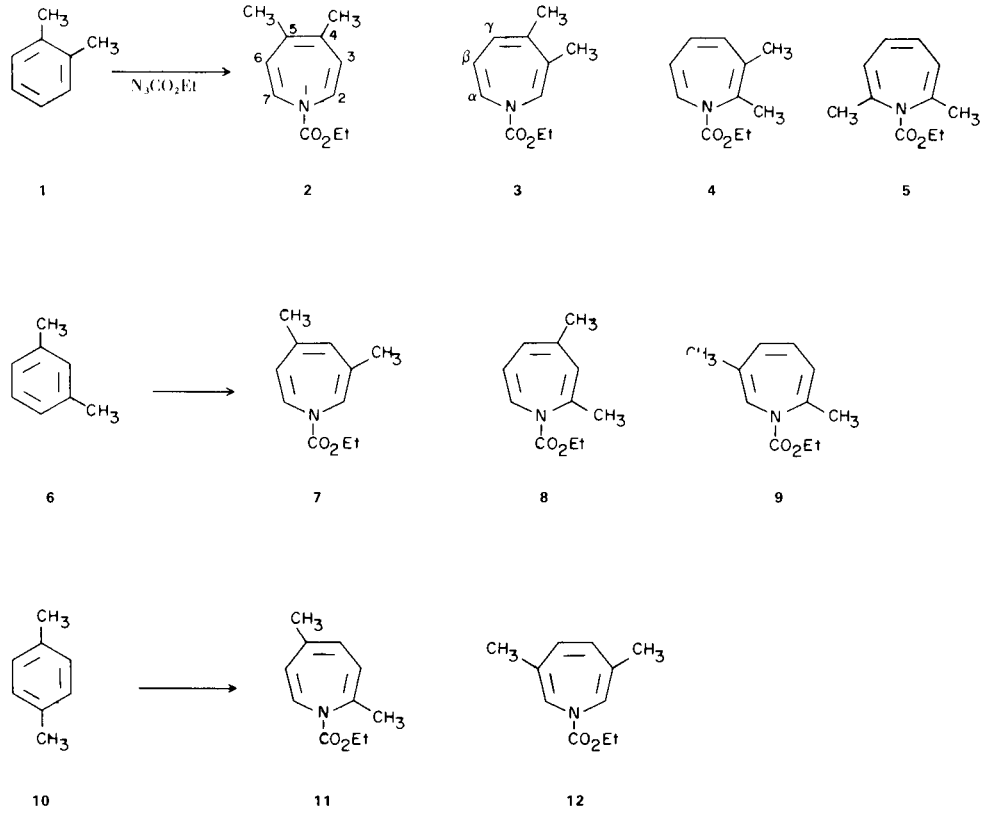
Dimethyl-*N*-carbethoxyazepines, isolated from the reaction between ethyl azidoformate and *o*-, *m*- and *p*-xylenes, react with tetracyanoethylene to give [4 + 2] Diels-Alder adducts. Nitrosobenzene is inert toward 2-methylazepines, but reacts with 3,6-dimethyl-*N*-carbethoxyazepine to give a [6 + 2] cycloadduct. The effect of two methyl substituents on the course of the cycloaddition reactions is discussed.

The thermal reaction of ethyl azidoformate with the three xylenes to give isomeric mixtures of dimethyl-*N*-carbethoxyazepines has been studied by Hafner (3). He reported that gas chromatographic analysis showed isomer distributions similar to those obtained from carbenes (4). Hafner has given no details of the reactions or isolation procedures and it is recognized that isomeric mixtures of azepines derived from nitrenes cannot be resolved by means of preparative vpc (5). In view of these uncertainties, we undertook a study to first synthesize the azepine mixtures from the xylenes and then to perfect techniques for the isolation of each isomer. Several, but not all, of the azepines from each xylene were separable. Although a method designed to afford only one specific isomeric azepine has been disclosed by Paquette (5,6), nitrene reactions provide a direct route to azepines from readily available starting materials (3,7).

With the isolation of several dimethylazepines it became possible to study the effect of two substituents on the course of the cycloaddition reactions with tetracyano-

SCHEME I



ethylene (TCNE) and nitrosobenzene. Much attention has been given recently to the cycloaddition reactions of the azepine nucleus. The reaction between unsubstituted *N*-carbalkoxyazepines and TCNE was shown by Baldwin and Smith and others (8) to be of the [4 + 2] Diels-Alder type rather than [6 + 2] as previously suggested (9). The addition of TCNE to monosubstituted azepines has been studied by Paquette (10) and Baldwin and Smith (8a) who reported the formation of analogous [4 + 2] adducts. Nitrosobenzene was reported to yield a [6 + 2] cycloadduct (11) with *N*-carbethoxyazepine, while 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene (12), isobenzofurans (10) and 3,4-diphenylcyclopentadienone (10) were reported to give [4 + 2] cycloaddition products.

Dimethyl-*N*-carbethoxyazepines.

Ethyl azidoformate was allowed to decompose in the appropriate xylene at reflux temperature and the excess xylene was removed under vacuum. The crude mixture of azepines thus obtained was purified by column chromatography on alumina and the azepines were collected initially as one fraction. The nmr spectra of the mixtures obtained in this way displayed between three and five methyl signals in the region δ 1.72-2.04 and extremely complex multiplets ascribable to the vinylic protons between δ 5.00-6.20. Attempts were then made to obtain pure samples of each azepine.

The reaction with *o*-xylene, **1**, could yield four azepines, **2-5** (Scheme I). The nmr spectrum of the mixture as obtained from alumina showed five distinguishable methyl signals of varying intensities. However, when this mixture was then passed through a silica gel column, some of the azepines were removed and only three signals remained. This mixture was separable by column chromatography into two compounds, identified as **2** and **3** by their nmr spectrum. The spectrum of **2** was simple (see Figure 1a) and showed only two doublets in the vinylic region and a single methyl peak (see Table I) (13). The spectrum of **3** showed two methyl peaks (Table I). The vinylic region (Figure 1b) still appeared somewhat complex although a singlet and high field triplet corresponding to H-2 and H-6 (14), respectively, were apparent. Structure **5**, which should also give rise to only one methyl peak, was eliminated since the nmr spectrum of the vinylic region of the corresponding carbomethoxy derivative has been published (5) and is not similar to that of **2**. Structure **4** was also eliminated since it would not be expected to display a singlet vinylic absorption. The yield of the mixture of **2** and **3** was 34%, but that of the separated isomers was very low.

TABLE I

Proton nmr data (60 MHz, carbon tetrachloride) for dimethyl-*N*-carbethoxyazepines

δ CH_3 predicted (5,6)

α 2.04
β 1.73
γ 1.78

Compound	CH_3 (α)	CH_3 (β)	CH_3 (γ)
2	----	----	1.76
3	----	1.80	1.90
7	----	1.72	1.82
8	2.04	----	1.76
11	2.04	----	1.88

Three possible azepines, **7-9**, could be obtained from *m*-xylene, **6** (Scheme I). The nmr spectrum of the mixture (from alumina) displayed four methyl signals and the vinylic region is illustrated in Figure 2a. A small amount of one isomer was separated by column chromatography on silica gel. The structure was readily established as **7** by its nmr spectrum (Figure 2b) which clearly showed two doublets and two singlets in the vinylic region. Another isomer was isolated from the chromatographed mixture in 20% yield *via* the selective removal of **7** with tetracyanoethylene which converted **7** to a crystalline adduct (to be discussed). The second isomer showed two methyl signals (Table I) and had the vinylic absorption pattern shown in Figure 2c. This pattern is believed to fit structure **8** rather than **9**. The spectrum shows two two-proton multiplets. If the structure were **9**, then the lone β-proton might be expected to be significantly different from the others (as H-6 in **7** and **3**). The small coupling constant (3.0 Hz), as seen in the lower field multiplet (α and γ-hydrogens) is easily buried in the broadened high field multiplet. Since the sum of the spectrum of **7** and **8** completely accounts for the signals seen in the mixture, as illustrated in Figure 2, there is little evidence for the existance of the third isomer in the chromatographed mixture. Azepines **7** and **8** were present in amounts of approximately 40% and 60%, respectively (35% total yield) as determined from the integration of the methyl signals in the nmr spectrum of the mixture.

The reaction of ethyl azidoformate with *p*-xylene, **10**, yielded the two possible azepines, **11** and **12**, which could not be separated by chromatography. It was possible, however, to selectively destroy **12** with alcoholic potassium hydroxide (15) to obtain a pure sample of **11** in 26% yield. The nmr spectrum of the purified azepine mixture revealed three methyl signals of equal intensity. After reaction with potassium hydroxide, the highest field methyl signal disappeared (see Table I) and the vinylic

region became somewhat clearer (Figure 3). The asymmetry of the molecule as shown by the nmr spectrum could only agree with structure **11**. The β-hydrogens are assigned to the high field multiplet and the α and γ hydrogens to the low field multiplet. Each multiplet is skewed toward the other and can be visualized as a combination of two doublets. The azepine mixture from *p*-xylene was obtained in 41% yield, composed of approximately 66% **11** and 34% **12**.

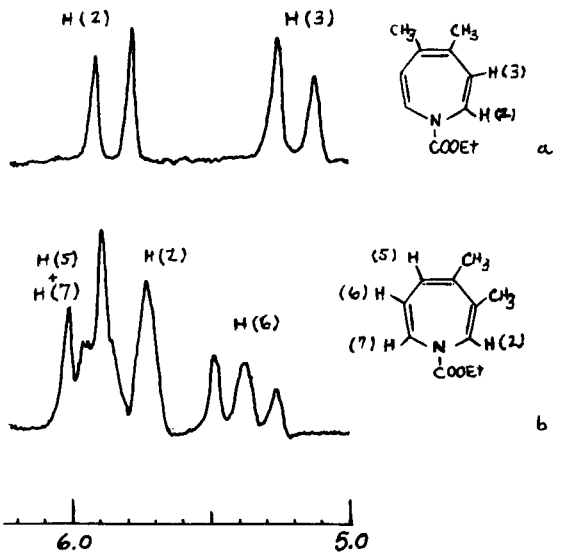


Figure 1. Sixty MHz nmr spectra of the vinylic regions of a) azepine **2** and b) azepine **3**, both derived from *o*-xylene.

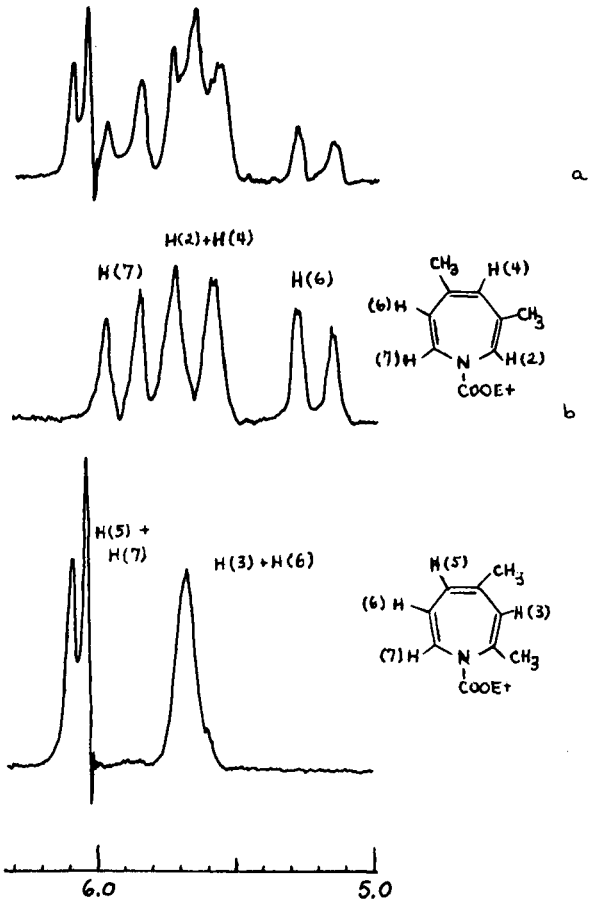
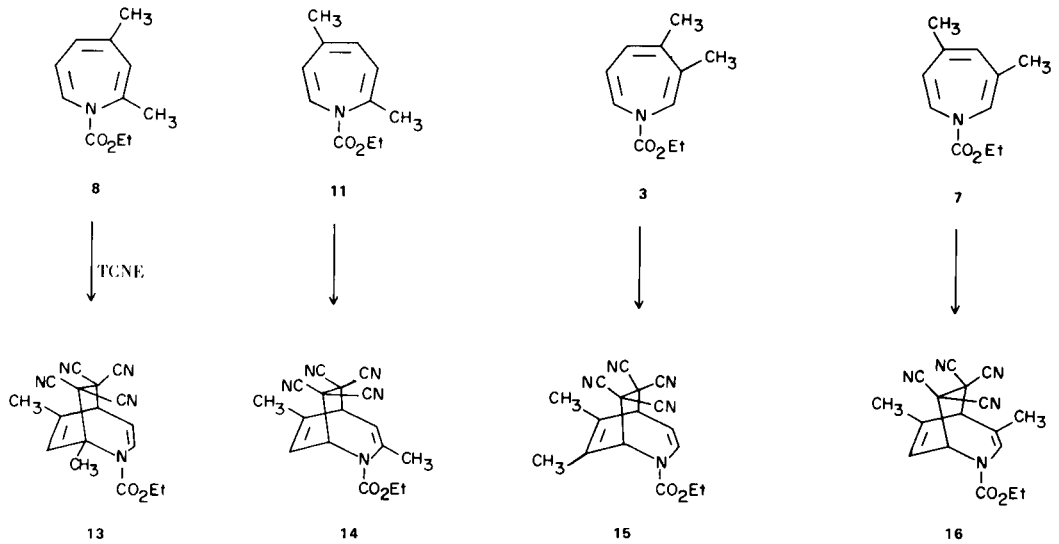


Figure 2. Sixty MHz nmr spectra of the vinylic regions of a) the mixture of azepines from *m*-xylene, b) azepine **7** and c) azepine **8**.

SCHEME II



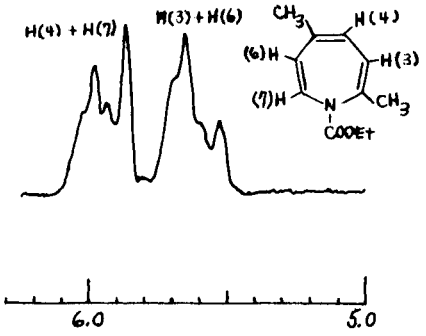


Figure 3. Sixty MHz nmr spectrum of the vinylic region of azepine **11**, derived from *p*-xylene.

Cycloaddition Products.

Dimethyl-*N*-carbethoxyazepines, **8** and **11**, were found to react at room temperature with TCNE in benzene to give the Diels-Alder adducts **13** and **14** (Scheme II) and their 100 MHz nmr spectra are illustrated in Figures 4 and 5. Adducts **15** and **16** were isolated after TCNE was allowed to react in a similar way with the mixtures of azepines containing **2** and **3** and **7** and **8**, respectively. Although each azepine, **3**, **7**, **8** and **11**, is unsymmetrically substituted and therefore presents two different sites for the dienophile to attack, only one adduct was isolated from each reaction. In the cases of azepines **3**, **7** and **11**, the adduct produced resulted from attack at the least hindered positions of the ring, *i.e.*, those positions not substituted by methyl groups. Paquette and Kuhla (10) have noted similar positional selectivity with monomethyl-*N*-carbomethoxyazepines.

Addition occurred preferentially to those azepines having free 2 and 5 positions since only adducts **15** and **16** were isolated when a limited amount of TCNE reacted with mixtures of **2** and **3** and of **7** and **8**, respectively. In this way TCNE exhibits isomer selectivity as well as positional selectivity. It is the former behavior that allowed the isolation of **8**.

When pure 2,4-dimethyl-*N*-carbethoxyazepine, **8**, was reacted with TCNE, however, addition was forced to occur at a position occupied by a methyl group, since neither pair of 2,5-positions was open. Only adduct **13** was

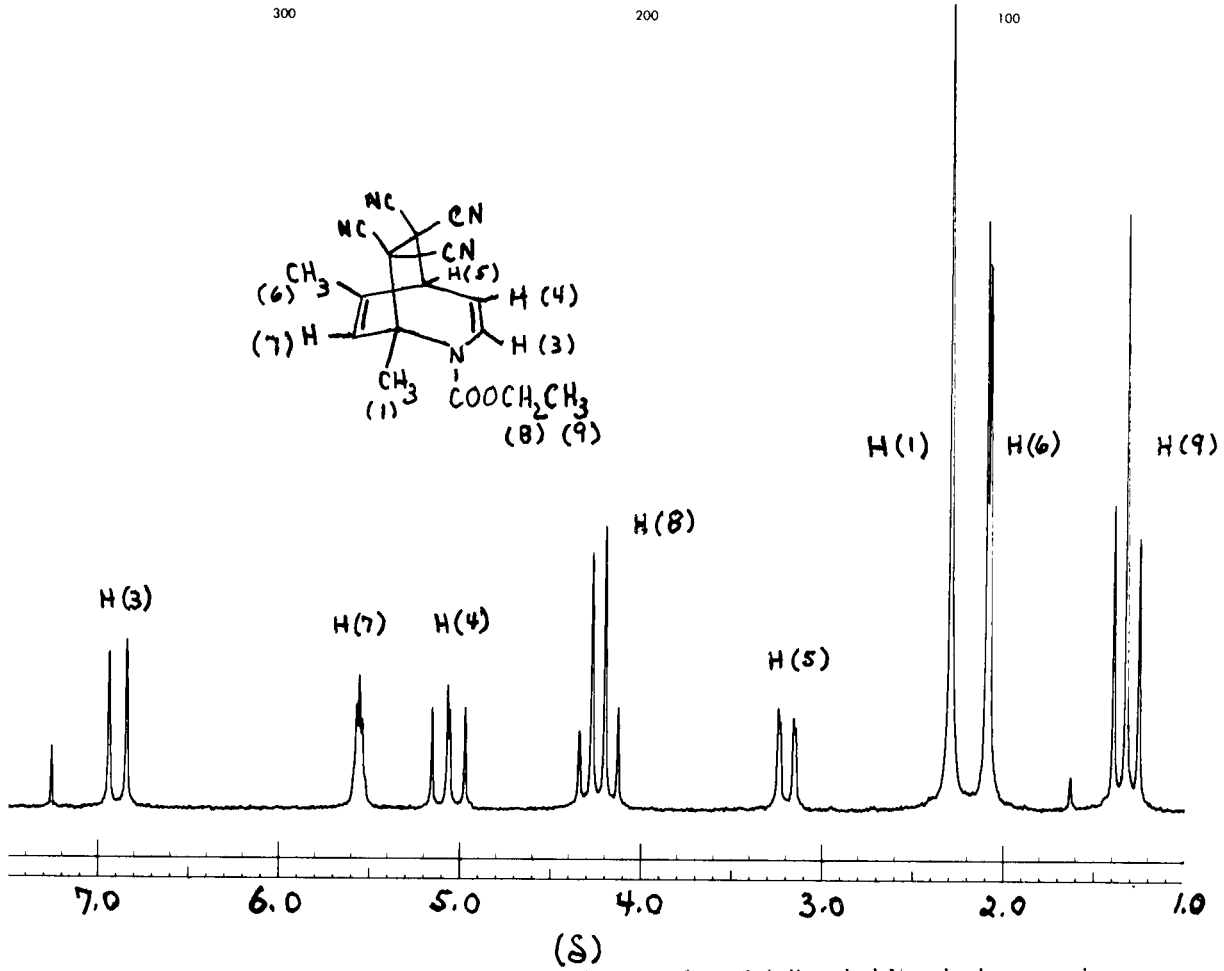


Fig. 4. 100 MHz nmr spectrum of the TCNE adduct, **13**, from 2,4-dimethyl-*N*-carbethoxyazepine.

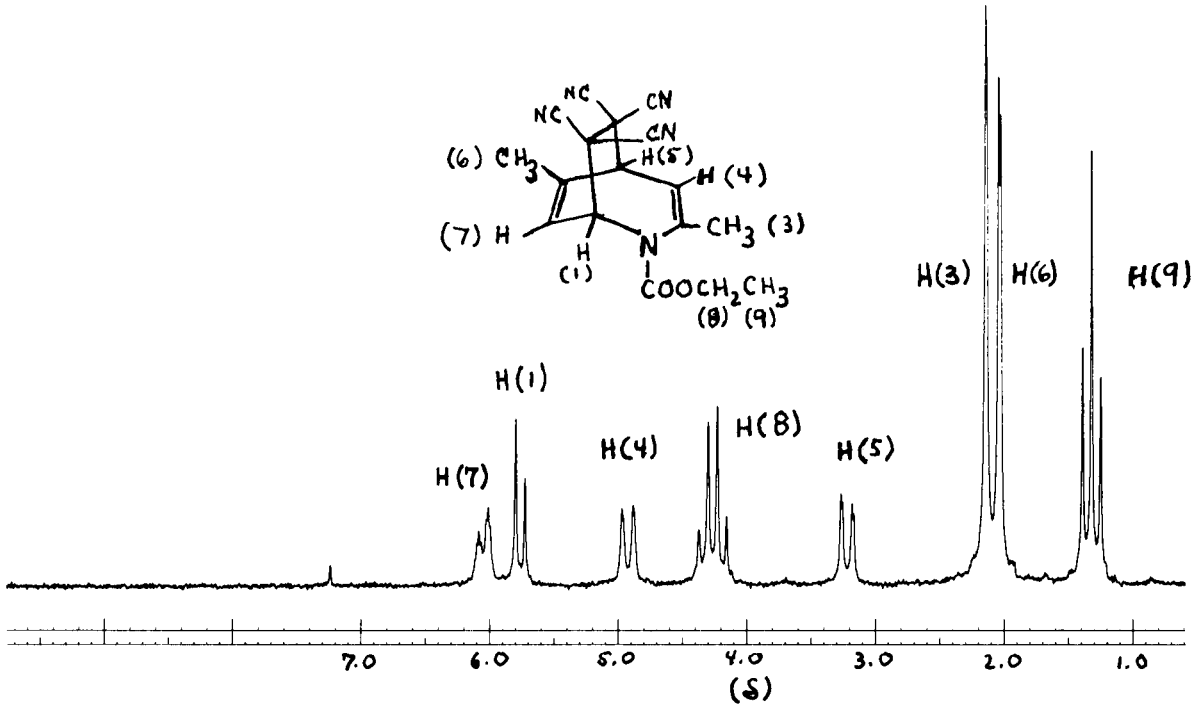


Fig. 5. 100 MHz nmr spectrum of the TCNE adduct, **14**, from 2,5-dimethyl-*N*-carbethoxyazepine.

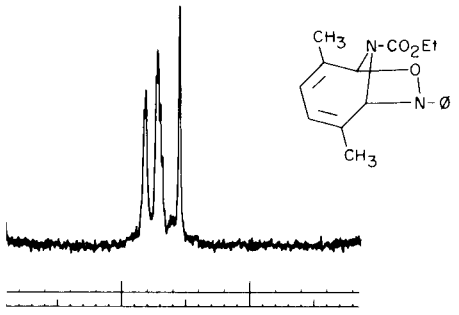
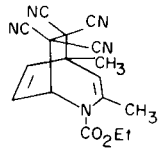


Fig. 6. 100 MHz nmr spectrum in the region δ 5-6 of the nitrosobenzene adduct, **18**, from 3,6-dimethyl-*N*-carbethoxyazepine.

isolated in which the bridgehead C-1 is substituted by a methyl group. There was no evidence in the nmr spectrum (Figure 5) for the presence of the other possibility, **17**. Thus it appears that a methyl group in the 4-position of the azepine ring exerts a stronger blocking tendency than a methyl at the 2-position.

The structure of each adduct was established by its nmr spectrum. Each displayed a characteristic high field signal corresponding to the bridgehead proton, H-5, and a lower field signal (absent in **13**) between δ 5.60 and 5.82 for the other bridgehead proton, H-1. The lowest field signal present in the spectrum of **13**, **15** and **16** (δ 6.60-6.90) was indicative of H-3 (see Table II). The alternative structure, **17**, in place of **13** was easily eliminated since the nmr spectrum of this compound would not show a high field doublet (H-5) nor a low field doublet (H-3, (Figure 4).

Nitrosobenzene reacted with the mixture of 2,5- and 3,6-dimethyl-*N*-carbethoxyazepines (**11** and **12**) in benzene under nitrogen to give only the [6 + 2] adduct, **18**, derived from the 3,6-isomer. The 100 MHz nmr spectrum in the region δ 5-6 is illustrated in Figure 6. When pure **11** was treated with nitrosobenzene, it was recovered unchanged (95%) and no pure adducts could be isolated from reaction with the dimethylazepines from *o*- or *m*-xylene (**2** and **3**, **7** and **8**).



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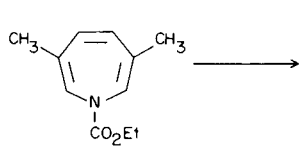

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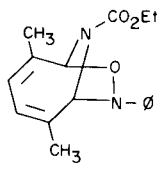

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TABLE II

Proton nmr Data for Dimethylazepine-TCNE Adducts (100 MHz, Deuteriochloroform)

	Coupling constants, Hz						Chemical shifts, δ					
Compound	$J_{3,4}$	$J_{4,5}$	$J_{3,5}$	$J_{5,7}$	$J_{1,7}$	$J_{CH_3\text{-}6,7}$	H-1	H-3	H-4	H-5	CH_3-6	H-7
13	9.9	8.0	0	1.2	---	2.1	(a)	6.89	5.06	3.20	2.09	5.57
14	(b)	8.5	---	1.5	7.3	1.6	5.79	(c)	4.96	3.23	2.07	6.08
15	8.9	8.9	0	---	---	---	5.60 (d,e)	6.84 (d,e)	5.03	3.19	2.04 (f)	(f)
16	---	---	1.0	1.2	7.5	1.9	5.82 (d,e)	6.60 (d,e)	(g)	3.07	2.09	5.98

(a) δ_{CH_3} (singlet) = 2.29; (b) $J_{CH_3\text{-}3,4}$ = 1.2 Hz; (c) δ_{CH_3} = 2.18; (d) broadened signals; (e) At 60° the signals for H-1 and H-3 sharpened and a coupling of 1.4 Hz between them was observed (16); (f) In deuteriochloroform solution the methyl signals for CH_3-6 and CH_3-7 coincided at δ 2.04. In 50:50 deuteriochloroform-deuteriobenzene solution the two methyl signals separated (δ 1.60 and 1.68) and showed small coupling (J = 1.0 Hz) to each other; (g) $\delta_{CH_3\text{-}4}$ = 1.93 (17), $J_{CH_3\text{-}4,3}$ = 1.8 Hz.

The relative simplicity of the vinylic region of the nmr spectrum (Figure 6) could only agree with the somewhat symmetrical structure, **18**. At room temperature very broad signals were observed for the carbethoxy group, but at 78° they sharpened to the quartet (CH_2) and triplet (CH_3) expected of an ethyl ester. In addition, the lower field multiplet sharpened to three singlets (δ 5.53, 1H; 5.71, 2H; 5.80, 1H), two of which showed small long range coupling (0.5-1.0 Hz). See Figure 6.

EXPERIMENTAL (18)

Ethyl azidoformate was made by the method given by Cotter and Beach (7d) and used directly. The general procedure employed for the synthesis of the dimethyl-*N*-carbethoxyazepines was as follows: 20 g. (0.174 mole) of ethyl azidoformate was added to 500 ml. of the appropriate xylene and the solution was refluxed for one hour with constant mechanical stirring. Evaporation under aspirator pressure at 80° gave an orange, oily mixture of crude azepines.

4,5- and 3,4-Dimethyl-*N*-carbethoxyazepines (**2** and **3**).

Five g. of the crude mixture (30.0 g.) from *o*-xylene was chromatographed on 100 g. of silica gel with benzene and eluted rapidly with more benzene to give 1.9 g. (34%) of a purified mixture of **2** and **3** as a yellow-orange oil. This mixture was rechromatographed on 200 g. of silica gel that had been thoroughly mixed with 2 ml. of concentrated, aqueous ammonia in benzene. Slow elution with benzene gave pure **2** and urethane (19) in the first fractions, pure **3** and urethane (19) in the last fractions. Rechromatographing with carbon tetrachloride on 50 g. of silica gel mixed with 5 ml. of concentrated, aqueous ammonia separated the pure azepines as yellow oils from the dimethyl-*N*-phenylurethanes. There was obtained 175 mg. (9.2%) of isomer **2** and 125 mg. (6.6%) of isomer **3**; ir ν max 1720 (**2**), 1710 (**3**) cm^{-1} (C=O).

Anal. Calcd. for **2** and **3**: $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found for **2**: C, 68.86; H, 7.62; N, 7.52. Found for **3**: C, 68.46; H, 7.59; N, 7.24.

3,5-Dimethyl-*N*-carbethoxyazepine (**7**).

Five g. of crude azepines (29.0 g.) from *m*-xylene was chromatographed with benzene on 100 g. of alumina to give 2.0 g. (35%) of a purified mixture of **7** and **8**. Rechromatographing on 150 g. of silica gel and eluting rapidly with benzene gave 190 mg. (9.5%) of **7** as a yellow oil in the first fractions; ir ν max 1720 cm^{-1} (C=O).

Anal. Calcd. for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.09; H, 7.74; N, 6.99.

2,4-Dimethyl-*N*-carbethoxyazepine (**8**).

Tetracyanoethylene (4.5 g., 35 mmoles) was added to 10.0 g. (52 mmoles) of the chromatographed mixture of azepines from *m*-xylene in 200 ml. of benzene. The dark colored solution was allowed to stand at room temperature for 24 hours and evaporated to give a black, viscous oil which was washed three times with 100 ml. of hexane. The hexane washings were combined and allowed to stand at 0° until the solution became clear. Separation of the solution from a small amount of insoluble oil and evaporation yielded an orange oil. This residue was chromatographed on 100 g. alumina. Benzene eluted 1.2 g. of **8** (20%) as a pale yellow oil; ir ν max 1715 cm^{-1} (C=O).

Anal. Calcd. for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.07; H, 8.07; N, 7.33.

2,5-Dimethyl-*N*-carbethoxyazepine (**11**).

Five g. of the crude mixture (29.9 g.) from *p*-xylene was chromatographed on alumina as before to give 2.3 g. (41%) of a mixture of **11** and **12**. Twenty five g. of the crude mixture in 30 ml. of 95% ethanol was added to a stirred solution of 20 g. of potassium hydroxide in 250 ml. of 95% ethanol. The resulting dark, olive green solution was refluxed for 5 hours, filtered, poured into 850 ml. of cold water and extracted with three 350 ml. portions of ether. Evaporation of the dried ether extracts gave a dark brown oil which was chromatographed on 200 g. of alumina. Elution with benzene gave 6.5 g. (26%) of **11** as a red-orange oil; ir ν max 1720 cm^{-1} (C=O).

Anal. Calcd. for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.25; H, 7.70; N, 6.94.

1,6-Dimethyl-8,8,9,9-tetracyano-2-carbethoxy-2-azabicyclo[3.2.2]-nona-3,6-diene (**13**).

To 3.0 g. (15.5 mmoles) of **8** in 100 ml. of benzene was added 1.0 g. (87 mmoles) TCNE. After allowing the solution to stand for 24 hours it was evaporated and the dark red residual oil was

washed three times with 30 ml. portions of hexane. The portion of the oil that remained insoluble was taken up in hexane-ethyl acetate mixture and was crystallized in the cold by seeding with a minute crystal of **16**, yield 1.05 g. (42%) of light tan crystals, dec., 91-93°; ir ν max 2950, 1730, 1650, 1470, 1260, 910 and 720 cm^{-1}.

Anal. Calcd. for $C_{17}H_{15}N_5O_2$: C, 63.54; H, 4.70; N, 21.80. Found: C, 63.60; H, 4.71; N, 22.08.

3,6-Dimethyl-8,8,9,9-tetracyano-2-carbethoxy-2-azabicyclo[3.2.2]-nona-3,6-diene (**14**).

To 1.0 g. (52 mmoles) of **11** in 20 ml. benzene was added 0.67 g. (52 mmoles) tetracyanoethylene. After 24 hours, evaporation of the solution gave a dark orange oil which crystallized from hexane-ethyl acetate as light tan crystals, yield, 1.01 g. of **14**, m.p. 98-100°; ir ν max 2900, 1730, 1640, 1450, 1270, 840 and 750 cm^{-1}.

Anal. Calcd. for $C_{17}H_{15}N_5O_2$: C, 63.54; H, 4.70; N, 21.80. Found: C, 63.58; H, 4.78; N, 21.95.

6,7-Dimethyl-8,8,9,9-tetracyano-2-carbethoxy-2-azabicyclo[3.2.2]-nona-3,6-diene (**15**).

Three g. (15.5 mmoles) of the chromatographed mixture of azepines from *o*-xylene was reacted similarly with TCNE (1.0 g., 78 mmoles) in benzene. The dark colored oil obtained after evaporation was treated exactly as described for **13**. This yielded 1.1 g. (44%) of **15** as nearly white crystals, m.p. 158-159°; ir ν max 2900, 1720, 1650, 1450, 1270, 850 and 770 cm^{-1}.

Anal. Calcd. for $C_{17}H_{15}N_5O_2$: C, 63.54; H, 4.70; N, 21.80. Found: C, 63.51; H, 4.55; N, 21.96.

4,6-Dimethyl-8,8,9,9-tetracyano-2-carbethoxy-2-azabicyclo[3.2.2]-nona-3,6-diene (**16**).

Three g. of the chromatographed mixture of azepines from *m*-xylene was reacted similarly with TCNE (0.67 g., 52 mmoles). Workup as for **13** gave a dark colored oil which crystallized from hexane-ethyl acetate to give 0.48 g. of **16** (29%) as small, white crystals, m.p. 193-194°; ir ν max 2900, 1710, 1670, 1420, 1250, 860 and 760 cm^{-1}.

Anal. Calcd. for $C_{17}H_{15}N_5O_2$: C, 63.54; H, 4.70; N, 21.80. Found: C, 63.43; H, 4.90; N, 21.85.

Nitrosobenzene Adduct of 3,6-Dimethyl-*N*-carbethoxyazepine. (**18**).

Nitrosobenzene (0.91 g., 8.5 mmoles) was added to the chromatographed mixture of azepines from *p*-xylene (5.0 g., 26 mmoles) in 30 ml. benzene under nitrogen. After 20 hours the color of the solution had changed from green to orange. Evaporation at 40° gave a dark red oil which was dissolved in 40 ml. of hexane. The solution was filtered and allowed to stand in the cold for several days to give 0.65 g. (26%) of **18**, recrystallized from hexane as small, light yellow needles, m.p. 99-100.5°; ir ν max 2950, 1710, 1600, 1290, 1030, 760 and 695 cm^{-1}; uv λ max (hexane) 233 (ϵ, 10,800) and 266 mμ (ϵ, 8,370); nmr δ (deuteriochloroform-TMS) 2.08 and 2.17 (s, 6H, $-CH_3$), 6.90-7.40 (m, 5H, $-C_6H_5$).

Anal. Calcd. for $C_{17}H_{20}N_2O_3$: C, 67.98; H, 6.71; N, 9.33. Found: C, 67.73; H, 6.58; N, 9.26.

Acknowledgment.

The author expresses his gratitude to Professor J. M. Bobbitt and Mr. L. Knack for their guidance and encouragement during the early phase of this work, and to Mrs. M. Neglia and Dr. J. E. Lancaster for recording the 100 MHz nmr spectra and Mr. N. Colthup and his group for recording the infrared spectra. Their helpful interpretations were appreciated.

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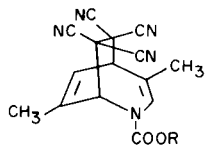
(13) Paquette (5) has synthesized the corresponding *N*-carbomethoxyazepine and the nmr spectrum is quite similar to that of **2**.

(14) The β-hydrogens have been shown by Paquette (5) to be at highest field.

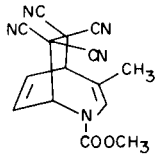
(15) It is known (9) that *N*-carbethoxyazepine, itself, reacts with potassium hydroxide. It is quite possible that the methyl group at C-2 in **11** offers just enough resistance to the base reaction to allow the isolation of **11**.

(16) Baldwin and Smith (8a) observed a coupling of 1.3-1.5 Hz between H-1 and H-3 in a series of 7-substituted adducts.

(17) It has been reported (8a,10) that CH_3-4 occurred at δ 2.70 (**ia**, deuteriochloroform) and δ 2.77 (**ii**, DMSO). Compound **16** in d_6-DMSO showed two methyl signals at δ 2.00 and 1.84. When a mixture of the two azepines from *p*-xylene was allowed to react with TCNE, a mixture of **14** and **ib** was isolated. The nmr spectrum of this mixture (deuteriochloroform) showed no signal as low as δ 2.70-2.77.



ia; R = CH_3
ib, R = C_2H_5



ii

(18) The analytical samples for the dimethylazepines were prepared by bulb to bulb distillation under vacuum (0.1 mm) at 125°. Sixty MHz nmr spectra in carbon tetrachloride were recorded on a Varian A-60 instrument and the 100 MHz spectra in deuteriochloroform were recorded on a Varian HA-100 instrument and are relative to tetramethylsilane. Silica gel from Gebruder Herman (Köln, Germany) and Alcoa, F-20, alumina were used for chromatography. Melting points were taken on a Thomas Hoover Melting Point apparatus and are uncorrected. Yields for the separated azepines are based upon the quantity of the purified mixture used.

(19) *N*-Carbalkoxyazepines are subject to rearrangement to phenylurethanes (20). Silica gel evidently contains acidic sites that cause the transformation to occur even in the presence of ammonia.

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Received July 13, 1970

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