Photolysis of Diazocyclopentadiene. Reactivity of Cyclopentadienylidene

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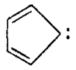
Photolysis of diazocyclopentadiene in saturated hydrocarbons led to carbon–hydrogen insertion of (presumed) intermediate cyclopentadienylidene. For 2,3-dimethylbutane, the tertiary/primary insertion ratio was 7.32. With olefins, both insertion and addition reactions were observed. For tetramethylethylene, addition/insertion was 20.9. Relative addition rates were determined for several olefins, and indicated neither electrophilic nor radical, rather only steric selectivity for the intermediate.

Diazocyclopentadiene (DCPD) was first prepared by Doering and DePuy in 1953.[1] Several years later, its photolysis in the saturated hydrocarbons, cyclopentane and cyclohexane, was shown to yield carbon–hydrogen insertion products; these were attributed to the intermediacy of cyclopentadienylidene, I.[2] Subsequently, DCPD was photolyzed in various matrices at low temperature. Save for evidence of the formation of fulvalene, electronic spectra obtained were ambiguous.[3] Subsequent low-temperature photolyses, coupled with epr observation, demonstrated that I could be obtained from DCPD, and, moreover, that it was a triplet in its ground state.[4] Unfortunately, these elegant experiments permit no conclusions as to the identity, chemical properties, or multiplicity of the initial intermediate(s) stemming from photoexcitation of DCPD.

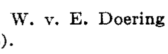


I

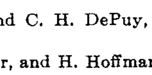
I is a divinylcarbene in which the ordinary vinylcarbene–cyclopropene rearrangement[5] is not expected. It is, moreover, conceivable that I could exhibit profound interaction between the carbenic center and the adjacent π system, detectable as a dramatic alteration in reactivity, relative to suitable models. Some spur to such hopes was found in the report that photolysis of DCPD in diethyl ether produced an intermediate which inserted 23 times more often in the α-C–H bonds than in the β-C–H bonds of the substrate.[6]

Results

Repetition of the reported DCPD–cyclopentane photolysis afforded a liquid of literature boiling point, better than 97% homogeneous to vpc. Its nmr spectrum, however, was clearly not that expected for II, but more in keeping with a mixture of III and IV. Thus, integral areas of vinyl, allyl, and alkyl protons were in the ratio 1:1:2.9. That only three vinyl protons were present was demonstrated by determining these protons relative to an internal chloroform standard.



II



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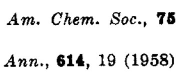
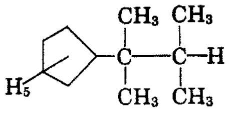


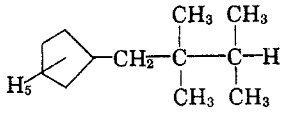
IV

Actually, these results were to be expected, it having been demonstrated that 5-alkylcyclopentadienes very rapidly undergo isomerization to a mixture of the 1 and 2 isomers.[7] Using data of McLean and Haynes,[7] it was clear that after only a short time at room temperature, let alone under conditions necessary to distil, II would have been reduced to less than 5% of the product mixture. Mironov,[7] in fact, had already suggested that the original report[2] was most likely in error.[8]

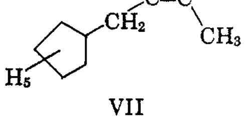
Photolysis of DCPD in 2,3-dimethylbutane afforded the expected skeletal isomers, V and VI, each of which was isolated (vpc) as a mixture of double-bond isomers analogous to III and IV. Structural assignment was based on elemental analysis and infrared and nmr spectroscopy. Reduction of the mixture gave the two saturated analogs, similarly identified. In addition, the reduction product of VI was identical with the reduction product of VII, obtained from photolysis of DCPD in tetramethylethylene (see below).



V



VI



VII

The ratio V/VI was identical with that determined from the reduced analogs, and was invariant whether determined by vpc on a packed column (thermal conductivity detector), or on a capillary column (flame ionization detector). The latter analysis was calibrated with a prepared mixture of V and VI. (No correction for relative detector response was necessary.) Results for six irradiations (Pyrex test tubes) at *ca.* 30°, gave V/VI = 1.22 ± 0.03. Corrected for statis-

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[1] W. v. E. Doering and C. H. DePuy, *J. Am. Chem. Soc.*, **75**, 5955 (1953).

[2] W. Kirmse, L. Horner, and H. Hoffmann, *Ann.*, **614**, 19 (1958).

[3] W. B. DeMore, H. O. Pritchard, and N. Davidson, *J. Am. Chem. Soc.*, **81**, 5874 (1959).

[4] E. Wasserman, L. Barash, A. M. Trozzolo, R. W. Murray, and W. A. Yager, *ibid.*, **86**, 2304 (1964).

[5] See G. L. Closs, L. E. Closs, and W. A. Böll, *ibid.*, **85**, 3796 (1963); and earlier papers.

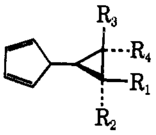
[6] J. E. Basinski, Ph.D. Thesis, Yale University, 1961.

[7] J. W. De Haan and H. Kloosterziel, *Rec. Trav. Chim.*, **84**, 1594 (1965); W. R. Roth, *Tetrahedron Letters*, 1009 (1964); S. McLean and P. Haynes, *ibid.*, 2385 (1964); V. A. Mironov, E. V. Sobolev, and A. N. Elizarova, *Tetrahedron*, **19**, 1939 (1963).

[8] In his later text, Kirmse indicated that the location of the double bonds in his product[2] "has not been ascertained" [W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, p 68].

tical factors, insertion occurred 7.32 times more often tertiary than at primary carbon–hydrogen bonds of 2,3-dimethylbutane. This value was essentially independent of DCPD concentration over the range 0.0032–0.096 *M*. It was unaltered when the radiant source was changed from a Hanovia high pressure mercury lamp to a G.E. sunlamp. Finally, no significant deviation was observed when irradiation was conducted under nitrogen, rather than laboratory atmosphere.

Irradiation of DCPD in olefinic solution led to cyclopropanation and insertion reactions. Olefins used were tetramethylethylene, trimethylethylene, cyclohexene, *t*-butylethylene, hexene-1, and styrene. Irradiation of DCPD in tetramethylethylene afforded a mixture of two products (vpc). One was identified as 1,1,2,2-tetramethylspiro[2.4]heptadiene (VIIIa), a white solid, mp 57–58°, easily purified by sublimation. It gave evidence of alkenyl hydrogens and carbon–carbon unsaturation in the infrared, and, in the nmr, featured a low-field multiplet (6.38–6.07 ppm downfield from internal TMS) and a high-field singlet (1.38 ppm), in the ratio 1/3.[9] In the ultraviolet, VIIIa had a maximum at 237 mμ (ϵ 9500) with a shoulder at 273 mμ (ϵ 1800). The spectrum of the parent spiro[2.4]heptadiene, prepared from sodium cyclopentadienide and ethylene bromide,[10] has been discussed by Wilcox[11] and by Chiurdoglu,[12] who report maxima at 223 and 257 mμ. All compounds VIII examined in the present study (except VIIIf, see the Experimental Section) showed similar ultraviolet spectra. It is of interest that, relative to the parent compound, bathochromic shifts of both maxima attend successive alkylation of the cyclopropyl ring.



VIIIa, $R_1 = R_2 = R_3 = R_4 = CH_3$
b, $R_1 = H$; $R_2 = R_3 = R_4 = CH_3$
c, $R_1 = R_3 = H$; R_2–$R_4 = (CH_2)_4$
d, $R_1 = R_2 = R_3 = H$; $R_4 = t\text{-}C_4H_9$
e, $R_1 = R_2 = R_3 = H$; $R_4 = n\text{-}C_4H_9$
f, $R_1 = R_2 = R_3 = H$; $R_4 = C_6H_5$

The second product isolated from photolysis of DCPD in tetramethylethylene was VII, a liquid whose structure was established by nmr and by the fact that, upon hydrogenation, it afforded the reduction product of VI. Vpc analysis of four DCPD–tetramethylethylene irradiations gave VIIIa/VII as 1.74 ± 0.10. Corrected for the presence of 12 equivalent C–H bonds, addition/insertion was 20.9.

DCPD photolysis in the other olefins gave substantial yields of expected addition products. These were purified by vpc, and characterized by elemental analysis and spectroscopy. An interesting feature of the nmr spectra was the deshielding of cyclopropyl relative to alkyl protons. For example, in VIIId, cyclopropyl protons appeared as a multiplet, 2.17–1.50 ppm (downfield from internal TMS), whereas the *t*-butyl protons appeared as a sharp singlet at 0.95 ppm. This effect is presumably a consequence of carbon–carbon double-bond anisotropy. Similar effects have been previously observed in spiro[2.4]heptadienes.[13]

Insertion products were not characterized for olefins other than tetramethylethylene. However, the beautiful cleanliness of the reactions with cyclopentane, 2,3-dimethylbutane, and tetramethylethylene suggests that nonaddition products observed (vpc) in these other photolyses were insertion products. In each olefin irradiation, the addition product was dominant, and was sufficiently well resolved to permit vpc analysis.

Competition experiments were carried out for the several olefins; relative rates thus obtained are gathered in Table I.

Table I

Relative Rates of Spiro[2.4]heptadiene Formation from Photolysis of DCPD in Olefins (*ca.* 30°)

Olefin	Relative rate[a]	(Av dev)$_n$[b]
Tetramethylethylene	0.74	0.04_4
Trimethylethylene	0.75	0.04_2
Cyclohexene	1.00	. . .
1-Hexene	0.94	0.04_2
Styrene	0.94[c]	0.04_2
t-Butylethylene	0.70	0.05_3

[a] Different olefin compositions were used in each experiment. [b] Average deviation; the subscript indicates the number of experiments. [c] Measured in competition with hexene-1. All other olefins were measured in competition with cyclohexene.

In all cases, 0.05–0.06 *M* solutions of DCPD in 10 ml of mixed olefins were irradiated for 1 hr, in Pyrex test tubes, with a G.E. sunlamp. Analyses were carried out by vpc on a 20 ft × 0.375 in. SF-96 column. The thermal conductivity detector was calibrated for relative detector response with prepared mixtures of purified adducts. The cyclohexene adduct VIIIc underwent slight cracking during analysis. For example, it was necessary to multiply the observed peak area ratio VIIIc/VIIIe of a known mixture by 1.29 in order to obtain the true mole ratio. For a mixture of VIIIc and VIIId, the observed correction factor was 1.23, whereas no correction was needed for mixtures of VIIId and VIIIe. Controls established that (product ratios of) prepared mixtures were invariant to photolytically decomposing DCPD, and that dark reactions did not contribute to significant product formation. Competition ratios were not significantly different when obtained under nitrogen, rather than laboratory atmosphere. Finally, excess olefin could be recovered unchanged after photolyses, and, in the styrene–hexene-1 competition, it was shown that olefin composition was identical before and after photolysis.

Discussion

There are alternatives to considering the above chemistry in terms of I, two of which should be mentioned: first, that no carbene is involved, excited DCPD being the sole intermediate; second, that cyclopropanation occurs *via* prior pyrazoline formation.

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[9] The synthesis of several spiro[2,4]heptadienes has already been communicated: R. A. Moss, *Chem. Commun.*, 622 (1965).

[10] R. Ya. Levina, N. N. Mezentsova, and O. V. Lebedev, *Zh. Obshch. Khim.*, **25**, 1097 (1955).

[11] C. F. Wilcox, Jr., and R. R. Craig, *J. Am. Chem. Soc.*, **83**, 4258 (1961).

[12] G. Chiurdoglu and B. Tursch, *Bull. Soc. Chim. Belges*, **66**, 600 (1957).

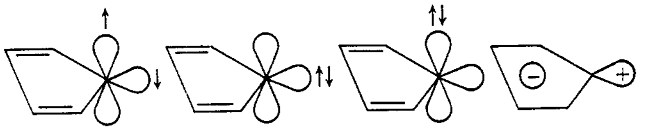
[13] K. Bangert and V. Boekelheide, *Tetrahedron Letters*, 1119 (1963).

Neither of these alternatives have been excluded.[14] In the absence of any evidence in favor of them and in accord with what appears to be common practice, results will be discussed in terms of a carbene intermediate.

Ground state I seems best described as a triplet in which a single electron is localized on the carbenic center and the second electron is delocalized in the π system.[4] We do not believe that a triplet is responsible for the presently observed chemistry. Extensive insertion into C–H bonds is *not* a property expected of triplet carbenes.[15] Furthermore, the nondescript competitive behavior of styrene seems inconsistent with a triplet intermediate.[16]

The most popular test for detecting a triplet carbene is the nonstereospecificity of its addition reactions.[17] Photolysis of DCPD in *cis*-butene did lead to about 8% nonstereospecific addition.[18] Recently, McBee reported that photolysis of tetrachloro-DCPD led to additions of tetrachloro-I which were also somewhat nonstereospecific.[19] We do not believe that the present observation of a *small* nonstereospecificity demands intervention of *substantial* triplet I. It is quite possible that a small triplet component to the reaction coincides with a larger singlet contribution, though the insensitivity of intermediate reactivity to the presence of oxygen seems to rule against a large triplet contribution, as do the styrene data. On the other hand, it has been argued that observation of nonstereospecific addition is not inconsistent with a singlet carbene intermediate.[15,20–22]

If, then, a singlet I is responsible for the observed chemistry, does that chemistry suggest any particular kind of singlet I? There are, *a priori*, several singlet electronic configurations which should be considered. For a cyclopentadienylidene with a carbenic center approximating sp^3 hybridization, one electron could reside in the in-plane σ orbital, and the second in the p orbital, Ia; alternatively, both electrons could reside in the σ orbital, Ib; and, finally, both electrons could be placed in the p orbital, Ic.

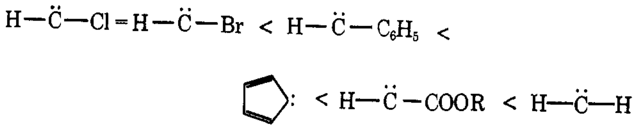


Ia Ib Ic Id

Configuration Ic is of particular interest, for here the carbenic pair ought to be delocalized over the π system; that is, the localized structure Ic is only a single canonic form among several contributing resonance structures, all of which might perhaps be better represented as Id, a "σ cation of cyclopentadienyl anion."[23] Experimentally, one might hope that such a species would be characteristically electrophilic, dramatically selecting in favor of highly alkylated olefins at the expense of less substituted substrates.[24]

Present results do not, unfortunately, reveal any striking selectivity for I. Its tertiary/primary C–H insertion selectivity (7.32) shows it to be somewhat more discriminating than carbomethoxycarbene, 2.9, but less discriminating than biscarbomethoxycarbene, 12.5.[25,26] Relative rates determined for the addition reaction show no electrophilic sequence. The data do, however, suggest a steric discrimination on the part of the intermediate. Thus, increasing alkylation of the substrate is attended by decreasing reactivity, the tetraalkylated olefin being no better than the hindered monosubstituted olefin, *t*-butylethylene. The sequence is remeniscent of that observed for addition reactions of 2,2-diphenylcyclopropylidene.[28,29]

The addition/insertion ratio (20.9), observed for photolysis of DCPD in tetramethylethylene, may be a minimal value, because addition is sterically hindered, while insertion occurs at allylic C–H bonds,[30] but the contrast is striking when this behavior is compared with the observed lack of competitive C–H insertion during addition of photolytically produced halocarbenes to olefins[31] and with the formation of only trace amounts of insertion products during phenylcarbene additions.[22,32] On the basis of insertion, addition/insertion, and addition discrimination, the series of increasingly reactive carbenes suggested by Closs[31] can be expanded as shown.



Experimental Section

Apparatus and Materials.—Infrared spectra were determined on a Beckman infrared 5A instrument. Nmr spectra were measured on a Varian A-60 instrument, at room temperature, as dilute solutions in (5% TMS) CCl$_4$. Ultraviolet spectra were measured on a Cary-14 instrument, as pentane solutions. Vpc was carried out on an Aerograph A-90 instrument, with glass-lined injector port and a 20 ft × 0.375 in. preparative SF-96 column (20% on 40–60 Chromosorb W). Injector temperature

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[14] Limits can be set to the pyrazoline hypothesis. Pyrazolines would have to be formed from excited DCPD, since olefinic DCPD solutions are stable for several hours in the dark. Furthermore, since insertion products are formed competitively with cyclopropanes, pyrazoline formation could not be the only reaction of excited DCPD in olefins.

[15] See the discussion in Chapter 12 of ref 8.

[16] Phenylethylenes and 1,3-dienes are generally efficient scavengers of triplet carbenes: M. Jones, Jr., and K. R. Rettig, *J. Am. Chem. Soc.*, **87**, 4015 (1965), and references cited therein.

[17] P. S. Skell and R. C. Woodworth, *ibid.*, **78**, 4496 (1956).

[18] Private communication from Dr. M. Jones, Jr., Princeton University.

[19] E. T. McBee, J. A. Bosoms, and C. J. Morton, *J. Org. Chem.*, **31**, 768 (1966).

[20] W. B. DeMore and S. W. Benson, *Advan. Photochem.*, **2**, 219 (1964).

[21] R. Hoffmann, Abstracts of Papers, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, p 109 K.

[22] Similar arguments and conclusions have been presented for phenylcarbene additions, which are also somewhat nonstereospecific: G. L. Closs and R. A. Moss, *J. Am. Chem. Soc.*, **86**, 4042 (1964).

[23] Preliminary calculations indicate that Id should be the lowest singlet cyclopentadienylidene: private communication from Professor Roald Hoffmann, Cornell University.

[24] P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.*, **78**, 5430 (1956).

[25] W. v. E. Doering and L. H. Knox, *ibid.*, **83**, 1989 (1961).

[26] The discriminations are in inverse order to the equilibrium acidities of the related hydrocarbons, acetic ester, cyclopentadiene, and malonic ester.[27] Increasing carbene selectivity thus parallels increasing stability of the related carbanion, a trend consistant with Doering's description of the C–H insertion reaction.[25]

[27] D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, Chapter 1.

[28] W. M. Jones, M. H. Grasley, and W. S. Brey, Jr., *J. Am. Chem. Soc.*, **85**, 2754 (1963).

[29] Other examples of steric hinderance in carbenic cyclopropanation reactions are cited in R. A. Moss, *J. Org. Chem.*, **30**, 3261 (1965).

[30] Preliminary experiments with cyclohexene, however, suggest a very similar addition–insertion. The tetramethylethylene value, then, is probably not unrepresentative.

[31] G. L. Closs and J. J. Coyle, *J. Am. Chem. Soc.*, **87**, 4270 (1965).

[32] McBee's observation, that only addition products form upon irradiation of tetrachloro-DCPD in cyclohexene,[19] suggests that tetrachloro-I is less reactive than I.

was maintained at 193° for analyses and calibrations, helium at 30 psig. Column temperature varied from 110° for VIIIb to 150° for VIIIc, and was manually programmed between these limits for mixtures. Analyses and calibrations involving VIIIf were carried out with injector at 245° and column at 180°. Analyses of 2,3-dimethylbutane reactions were performed on a Barber-Colman unit, fitted with a 100-ft Apiezon-L Golay column, operated at 123°, and 16 psig of nitrogen.

Melting points and boiling points are uncorrected. Hydrocarbons were obtained commercially, were all CP grade or better, and were distilled prior to use.

Diazocyclopentadiene was prepared by the method of Weil.[33] It was not distilled but concentrated on a rotary evaporator at room temperature. Its infrared properties were in agreement with those reported by Doering,[1] and its nmr spectrum was in agreement with that reported by Ledwith.[34] As used in the present work, DCPD was usually not concentrated more than 1:1 in pentane. (Purity was determined by nmr.) The amount of pentane introduced into both preparative and competitive runs was insufficient to allow detection of products formed from action of I on pentane. DCPD was stored over Dry Ice. Aged DCPD and fresh DCPD showed no differences in competition experiments.

Reaction of DCPD with Cyclopentane.[2]—DCPD (2.2 g) was dissolved in 200 ml of cyclopentane and irradiated for 5 hr with a 450-w Hanovia Type L lamp in a quartz immersion apparatus (Pyrex filter). Excess cyclopentane was stripped, and the residue was distilled at 62–64° (13 mm), yielding 1.28 g of off-white liquid.[35] The product was 97% homogeneous on SF-96 vpc. It was identified as a mixture of III and IV: infrared, λ^{CCl_4} 6.25 μ (w); nmr, 6.43–5.83 (*3.0*, m, vinyl), 2.98–2.50 (3.0, m, allyl), 2.11–1.16 (8.7, m, alkyl).[36] A mixture of 99 mg of chloroform and 76 mg of product gave an integral ratio of 0.50 ± 0.025 for chloroform singlet to product vinyl protons. The calculated ratio for such a mixture of chloroform and pure III + IV is 0.49.

Reaction of DCPD with 2,3-Dimethylbutane.—DCPD (4.58 g) was dissolved in 200 ml of 2,3-dimethylbutane. Irradiation and workup, as above, gave 3.22 g of off-white liquid, bp 58–61° (15 mm). Vpc on SF-96 revealed only two components, ratio 1.49 (1.51, capillary), the shorter retention time product in excess. The products were separated by preparative vpc and were identified as compounds V (shorter retention time) and VI.

Compound V showed infrared λ^{CCl_4} 6.27 μ (w); nmr 6.51–5.80 (*3.0*, m, vinyl), 2.92–2.75 (2.0, m, allyl), 2.0–1.50 (1.2, m, isopropyl carbinyl), 1.07 (6.1, *gem*-methyl), 0.78 (6.1 d, J = 7 cps, isopropyl methyl). *Anal.* Calcd for $C_{11}H_{18}$ (150.26): C, 87.92; H, 12.08. Found: C, 87.67; H, 12.18.

Compound VI showed infrared λ^{CCl_4} 6.24 μ (w); nmr 6.40–5.76 (*3.0*, m, vinyl), 2.95–2.68 (2.0, m, ring allyl), 2.44–2.04 and 2.04–1.20 (4.3, m, side-chain allyl and carbinyl protons), 1.1–0.70 (9.0, m, methyl). *Anal.* Calcd for $C_{11}H_{18}$ (150.26): C, 87.92; H, 12.08. Found: C, 87.64; h, 12.08.

A mixture of 38.0 mg of chloroform and 29.8 mg of V gave an integral ratio of 0.57 chloroform singlet to vinyl protons (calcd, 0.54).

The product mixture (1.0 g) was dissolved in 80 ml of ether and shaken with 20 mg of Adams catalyst under 42 psig of hydrogen for 19 hr. Work-up afforded 1.0 g of liquid which, on vpc, showed only two components, of new retention times. The order of retention times had reversed; the ratio of the *longer* retention time component to the *shorter* was 1.57. Purification was by preparative vpc.

Nmr (shorter retention time component, reduction product of VI) showed 1.98–1.00 (broad m ring, secondary and tertiary alkyl), 0.96–0.68 (m, four lines, methyl). Ratio of low-field to high-field absorption was 1.40 (theory predicts 1.40). Nmr (reduction product of V) showed 1.78–1.31 (m, ring and carbinyl), 0.82 (d, J = 6.6 cps, isopropylmethyl), 0.72 (s, *gem*-methyl). Ratio of low-field to high-field absorption was 0.83 (theory predicts 0.83). *Anal.* (both components). Calcd for $C_{11}H_{22}$ (154.29): C, 85.62; H, 14.37. Found: C, 85.68; H, 14.33.

Quantitative determination of the insertion selectivity of I in 2,3-dimethylbutane was carried out by photolyzing 0.05–0.06 *M* solutions of DCPD in 10 ml of hydrocarbon with a G.E. sunlamp for 1 hr. Solutions were contained in Pyrex test tubes, and maintained at *ca.* 30° by a water bath. After irradiation, hydrocarbon was stripped, and residue was immediately analyzed by capillary vpc. A summary of results and control experiments appears above.

Reaction of DCPD with Tetramethylethylene.—Irradiation (6 hr) of 2.75 g of DCPD in 150 ml of olefin with the Hanovia lamp, followed by removal of excess olefin and distillation of the residue, gave 1.56 g (35%) of white needles (VIIIa). The product was further purified by sublimation, and had mp 57–58.°

Nmr showed 6.38–6.07 (*4.0*, m, vinyl), 1.38 11.8, and (s, methyl). Ultraviolet showed λ_{max} 237 mμ (ϵ 9500) and 273 mμ (sh) (ϵ 1800). *Anal.* Calcd for $C_{11}H_{16}$ (148.25): C, 89.11; H, 10.89. Found: C, 89.06; H, 11.02.

Repetition of the above experiment afforded a distillate which, by vpc on SF-96, consisted of two components. The earliest eluted was VIIIa. The second component was isolated and identified as VII. Nmr showed 6.53–5.75 (*3.0*, m, vinyl), 3.18–2.58 (4.0, m, allyl), 1.78–1.50 (8.6, m, methyl).

Hydrogenation of VII over Adams catalyst afforded material which was identical in retention time and nmr spectrum with the reduction product of VI (see above).

Preparation of Other Spiro[2.4]heptadienes (VIII).—These were prepared as described for VIIIa. All purification was effected by vpc. Yields represent that portion of the distilled product mixture which was VIII, as determined by vpc and related to starting DCPD.

VIIIb.—Yield of liquid, bp 56–59° (15 mm), was 33%. Nmr showed 6.45–5.95 (*4.0*, m, vinyl), 2.00 (0.96 q, J = 7 cps, cyclopropyl), 1.33 and 1.37 (9.3, s and d, J = 7 cps, one line falls under the 1.33 singlet, methyl). Ultraviolet showed λ_{max} 234 mμ (ϵ 14,000) (sh), and 262 mμ (ϵ 3900). *Anal.* Calcd for $C_{10}H_{14}$ (134.22): C, 89.49; H, 10.51. Found: C, 89.44; H, 10.55.

VIIIc.—Yield of liquid, bp 90–105° (16 mm), was 23%. Nmr showed 6.50–6.10 (2.9, m, vinyl), 5.93–5.72 (*1.0*, m, vinyl), 2.30–1.22 (10.0, m, cycloalkyl). The infrared spectrum was similar to but not identical with that published by Chiurdoglu.[12] The present material, obtained by vpc, is presumably purer. Ultraviolet showed λ_{max} 238 mμ (ϵ 4600), 247 mμ (sh), and 260 mμ (sh) (ϵ 2900). *Anal.* Calcd for $C_{11}H_{14}$ (146.22): C, 90.35; H, 9.65. Found: C, 9.15; H, 9.90.

VIIId.—Yield of liquid, bp 65–66° (18 mm), was 46%. Nmr showed 6.48–6.21 (2.9, m, vinyl), 5.94–5.76 (*1.0*, m, vinyl), 2.17–1.50 (3.3, m, cyclopropyl), 0.95 (9.5, s, *t*-butyl). Ultraviolet showed λ_{max} 228 mμ (ϵ 9400) and 258 mμ (sh) (ϵ 3100). *Anal.* Calcd for $C_{11}H_{16}$ (148.25): C, 89.11; H, 10.89. Found: C, 89.10; H, 10.81.

VIIIe.—Yield of liquid, bp 71–76° (14 mm), was 30%. Nmr showed 6.51–5.77 (*4.0*, m, vinyl), 2.17–0.69 (12.0, m, cyclopropyl and alkyl). Ultraviolet showed λ_{max} 228 mμ (ϵ 5600) and 257 mμ (sh) (2500). *Anal.* Calcd for $C_{11}H_{16}$ (148.25): C, 89.11; H, 10.89. Found: C, 89.44; H, 10.88.

VIIIf.—Yield of liquid, bp 63–78° (0.14 mm), was 20%. Nmr showed 7.12 (*5.0*, s, phenyl), 6.46–5.65 (4.0, m, vinyl), 3.22 (1.2, "t", central line showed overlapping of two components, benzylic), 2.33–1.81 (2.2, m, cyclopropyl). *Anal.* Calcd for $C_{13}H_{12}$ (168.24): C, 92.81; H, 7.19. Found: C, 92.11; H, 7.37.[37]

Competition Experiments.—Olefin 1 (4 ml) was weighed and mixed with olefin 2 (6 ml). Enough DCPD was added to make the resulting solution 0.05–0.06 *M*. The solution, in a Pyrex test tube, was immersed in a water bath (maintained at *ca.* 30°) and irradiated for 1 hr with a G.E. sunlamp. Olefins were stripped and the residue was submitted to vpc.

Relative rates were derived from the standard expression k_2/k_1 = $([P_2]/[P_1])$ $([O_1]/[O_2])$ where $[P_2]/[P_1]$ is the cyclopropane product ratio (corrected for relative detector response) and $[O_1]/[O_2]$ represents the mole ratio of starting olefins. Results

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(33) T. Weil and M. Cais, *J. Org. Chem.*, **28**, 2472 (1963).

(34) A. Ledwith and E. C. Friedrich, *J. Chem. Soc.*, 504 (1964).

(35) Lit.[2] bp, 69–70° (15 mm).

(36) Nmr spectra are reported in ppm downfield from internal TMS as chemical shift, integral area (italic integral is assumed to represent a whole number of protons, consistant with structure), signal appearance (s = singlet, d = doublet, m = multiplet, etc.), assignment.

(37) Freshly isolated samples yellowed very rapidly. Although nmr data are in good accord with the structure, it is probable that some trace impurity oxidizes, accounting for the poor analysis. We were also unable to obtain a distinct ultraviolet spectrum. Instead, we found a broad absorption, the extinction of which increased during 1 hr of observation. That VIIIf itself is not very unstable was apparent, since trapped samples could be mixed with VIIIe and rechromatographed, yielding very reasonable calibration data and no evidence of extra peaks.

appear in Table I. In all cases, only expected components appeared in vpc traces. Olefin composition was varied in duplicate experiments.

Control Experiments.—The thermal conductivity detector was calibrated with purified adduct mixtures. With exception of VIIIc (see above) the observed correction factors were quite similar to expectations.[38]

The stability of products to reaction conditions was demonstrated for every competitive pair reported in the table. An example follows. Crude product mixture (VIIIc, 39.0 mg) and crude product mixture (VIIIe, 36.0 mg) were dissolved in 0.5 ml of *t*-butylethylene. Vpc gave VIIIc/VIIIe as 0.84. Another 9.5 ml of *t*-butylethylene was added, followed by DCPD to *ca.* 0.034 *M*. Irradiation and work-up afforded a residue which was submitted to vpc. The trace showed that VIIId had formed in yield comparable with the adducts originally present. VIIIc/VIIIe was 0.86. Results of other control experiments appear above.

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[38] N. Brenner, J. E. Callen, M. D. Weiss, Ed., "Gas Chromatography," Academic Press Inc., New York, N. Y., 1962, pp 231–327.

Dodecahydro-1,4,7,9b-tetraazaphenalene, a Condensate of Acrolein and Ammonia

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Dodecahydro-1,4,7,9b-tetraazaphenalene (I), a new substance, has been obtained in high yield by the condensation of acrolein and ammonia at 150°. Its structure was established by spectral studies and by the nature of the products obtained from several of its chemical reactions. Oxidation of I with mercuric acetate introduced a carbon–nitrogen double bond in a position allylic to the central nitrogen. Heating I to 250° with a palladium catalyst gave 4-amino-2-ethylpyrimidine as a degradation product. Oxidation with potassium permanganate afforded 1,5,9-triazacyclododecane-4,8,12-trione. A number of other reactions of I have been investigated. Condensations of methacrolein and crotonaldehyde with ammonia yielded substances which appear to be homologs of the acrolein–ammonia condensate.

The reactions of acrolein with ammonia have been well explored.[1] Spectroscopic studies have indicated that mixtures of the two compounds do not react at temperatures below −130°. In the range −130 to about −60° the carbonyl function disappeared and it was evident from spectral data and elemental analyses of precipitated products that the simple carbonyl-addition compounds, $CH_2{=}CHCH(OH)NH_2$ and $CH_2{=}CHCH(OH)NHCH(OH)CH{=}CH_2$, were formed. These products on being warmed to 0° evolved acrolein and ammonia and formed condensates containing formyl, amino, and imino groups.

At temperatures above 0°, acrolein and ammonia combine by additions both to the carbonyl and the vinyl group, and the products characteristically have been polymeric condensates and mixtures of simple nitrogen base compounds. Reactions in methanol at 50° have given solid nitrogen-rich polymers, and condensations in the presence of hydrogen and a nickel catalyst, in aqueous methanol at 125°, have yielded 1,3-diaminopropane, *n*-propylamine, di-*n*-propylamine, and higher molecular weight condensates. Vapor phase reactions at 350° over acidic catalysts, with steam as diluent, have given mixtures of pyridine, β-picoline, and higher boiling nitrogen bases.

It has now been found[2] that under certain conditions 3 moles of acrolein and 4 of ammonia condense in the liquid phase to form a new substance, $C_9H_{18}N_4$, identified as dodecahydro-1,4,7,9b-tetraazaphenalene (I). The reaction proceeds readily in methanol at temperatures of 140–150°, and the yield is at least 85% under optimum conditions. The isolated product is a white, hydroscopic crystalline solid, melting at 118–120°.

Methacrolein and crotonaldehyde combine with ammonia under similar conditions, affording condensates of composition $C_{12}H_{24}N_4$ in 49 and 94% distilled yields, respectively. The structures of these two substances have not been established by chemical means, but on the basis of composition, molecular weight, and spectral data they are believed to be homologs of the acrolein–ammonia condensate. Accordingly, the methacrolein derivative is tentatively assigned structure II, 3,6,9-trimethyldodecahydro-1,4,7,9b-tetraazaphenalene, and the crotonaldehyde derivative, structure III, 2,5,8-trimethyldodecahydro-1,4,7,9b-tetraazaphenalene.

Structure III is also the structure that Delépine,[3] on the basis of skilled and imaginative studies, proposed for the "tricrotonylenamine" (tricrotonylidene tetramine), $C_{12}H_{24}N_4$, that Wurtz[4] obtained in 1879 on heating either aldol or crotonaldehyde with ammonia in sealed containers. The source and composition of the Wurtz product suggest that it was, indeed, the same substance as our crotonaldehyde–ammonia condensate, but this has not been demonstrated in any manner. Further, similarities in chemical properties and results of oxidative degradation indicate that the Wurtz compound, as described by Delépine,[3] and our acrolein–ammonia condensate, I, are homologous substances.

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[1] See H. D. Finch, "Acrolein," C. W. Smith, Ed., John Wiley and Sons, Inc., New York, N. Y., 1962, Chapter 6, pp 96–109, for a review of the reactions of acrolein with ammonia and other nitrogen bases.

[2] J. L. Van Winkle, U. S. Patent 3,112,315 (Nov 26, 1963).

[3] (a) M. Delépine, *Compt. Rend.*, **144**, 853 (1907); (b) *ibid.*, **216**, 649; (c) *ibid.*, **216**, 785 (1943). Delépine observed[3b] that Wurtz' "tricrotonylenamine" was the same as one of two conformational isomers (designated α and β) of composition $C_{12}H_{24}N_4$ that could be isolated, as hydrates, from the product of reaction of crotonaldehyde and aqueous ammonia at 0° to room temperature for 1–2 days, followed by heating on a water bath. Oxidation of the α isomer (the isomer isolated by Wurtz) with potassium permanganate, afforded an "anhydride" of β-aminobutyric acid in 7–8% yield.[3b] However, since neither the molecular weight of the "anhydride" nor the amount of β-aminobutyric acid released on hydrolysis was determined, the cyclic, trimeric structure of the anhydride was not unequivocably established.

[4] A. Wurtz, *Compt. Rend.*, **88**, 940, 1154 (1879).