identified compounds. No route yet reported[4,7,12] has given tropenium chloride of high quality in good yield with consistency. The hygroscopic nature of the compound renders recrystallization difficult, and since the chloride is thermally unstable sublimation results in extensive decomposition.

These difficulties are obviated by use of tropenium hydrogen dichloride as starting material. A sublimer is charged with the hydrogen dichloride in the glove box, wrapped in foil, and sublimation carried out at 70° and 0.1 mm. for three to five hours to yield 100% tropenium chloride as colorless, hard, free-flowing prisms, ultraviolet spectrum (96% sulfuric acid)[7] λ_{max} 268 (sh), 274 (4340), 280 mμ. *Anal.* Calcd. for C_7H_7Cl: $C_7H_7^+$, 71.99. Found: $C_7H_7^+$, 71.9. The chloride is handled at all times in the glove box where it is stable to the atmosphere for about 24 hours; complete liquidation occurs in 30 seconds on removal to the room. All operations are carried out in a darkened room under red-orange light. Trituration of the hydrogen dichloride with ether gave slightly darkened, less stable tropenium chloride (71.2% tropenium ion) which melted at 101–102° (reported,[4] 101°); however, the sublimed prisms do not show any change under 115° and slowly decompose over 125°.

Studies on carbonium ion hydrogen diiodides are in progress.

[12] D. Bryce-Smith and N. A. Perkins, *J. Chem. Soc.*, 1339 (1962).

[13] National Science Foundation and Petroleum Research Fund Scholar, 1962.

DEPARTMENT OF CHEMISTRY
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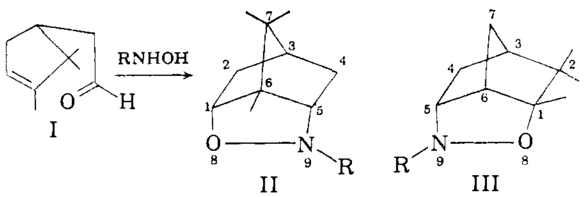
RECEIVED AUGUST 24, 1962

RING CLOSURE TO BRIDGED BICYCLIC SYSTEMS BY THE INTRAMOLECULAR NITRONE-OLEFIN CONDENSATION

Sir:

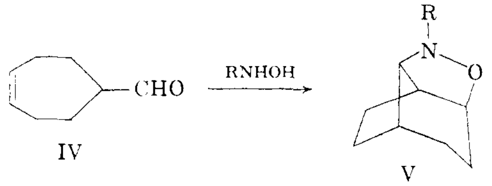
In the course of our investigations of the scope and utility of the intramolecular addition of nitrones to olefins,[1,2] we have observed recently an apparent qualitative relationship between the formation of cyclic products obtained in the condensations of N-alkylhydroxylamines with a 3-cyclopentenylacetaldehyde or 4-cycloheptenylcarboxaldehyde and the reported anchimerically assisted solvolysis of five and seven-membered cycloalkenyl esters to give bridged bicyclic products.[3,4,5] Although these reactions seem to be of widely different nature, we feel that this relationship has some bearing on the mechanism of the intramolecular nitrone–olefin and, perhaps, other 1,3-dipolar additions.

Acetolysis of esters of β-(Δ^3-cyclopentenyl)-ethanol gave high yields of *exo*-norbornyl acetate.[4,5] The condensation of campholenic aldehyde (I) with N-methyl or N-isopropylhydroxylamines afforded, after distillation, a mixture of the tricyclic isoxazolidines II and III (70–80% yield), in the ratio (determined by gas chromatography) of approximately 2:3, respectively. These isomers were separated by careful fractionation. The bornane derivative II (R = CH_3)[6] had b.p. 97° (10 mm.), $n^{25}D$ 1.4858, *picrate* m.p. 198–199° dec., *methiodide* m.p. 149–150° dec. The structure of II was supported by the n.m.r. spectrum which showed (60 mc., CCl_4, TMS) bands at δ = 0.87 and 0.93 (*gem*-diMe), 1.14 (C_6-Me), 2.64 (N-Me), 2.95 broad doublet, J = 8 c.p.s. C_5–H) and 3.95 p.p.m. (broad doublet, J = 7.4 c.p.s., C_1–H). Hydrogenolysis of the isoxazolidine gave an amino alcohol, m.p. 58–59°. The lower boiling camphene compound III (R = CH_3) had b.p. 96° (10 mm.), $n^{25}D$ 1.4830, *picrate* m.p. 216–218° dec., *methiodide* m.p. 169–170° dec. Hydrogenolysis of the isoxazolidine gave an amino alcohol melting at 78.5–79°. The n.m.r. spectrum of III was very similar to that of II, except that the methyl peaks were slightly shifted and no low field hydrogen resonance (**H**–C–O) was observed.



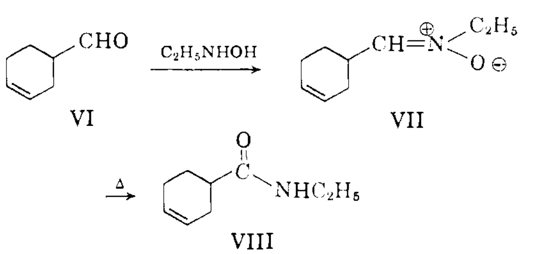
I II III

When 4-cycloheptenecarboxaldehyde (IV) was condensed with N-methylhydroxylamine, a single product V was obtained in 60% yield. The tricyclic isoxazolidine structure V (b.p. 118–120° at 25 mm., $n^{25}D$ 1.5002, *methiodide* m.p. 190.0–190.5° dec.) was consistent with infrared and n.m.r. spectral data, and hydrogenolysis could be effected.



IV V

Several groups have reported the lack of double-bond participation and the failure to isolate bicyclic products from the solvolyses of 3-cyclohexenylcarbinyl esters.[3,7,8] When 3-cyclohexene carboxaldehyde (VI) reacted with N-ethylhydroxylamine, only the corresponding nitrone (VII) was



VI VII VIII

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[1] N. A. LeBel and J. J. Whang, *J. Am. Chem. Soc.*, **81**, 6334 (1959).

[2] N. A. LeBel and J. J. Whang, to be submitted.

[3] G. LeNy, *Compt. rend.*, **251**, 1526 (1960).

[4] R. Lawton, *J. Am. Chem. Soc.*, **83**, 2399 (1961).

[5] P. D. Bartlett and S. Bank, *ibid.*, **83**, 2591 (1961).

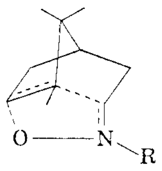
[6] Satisfactory analyses have been obtained for all new compounds described herein.

[7] R. S. Bly, Jr., and H. L. Dryden, Jr., *Chem. and Ind.*, 1287 (1959).

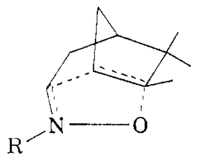
[8] C. F. Wilcox, Jr., and S. S. Chibber, *J. Org. Chem.*, **27**, 2332 (1962).

isolated, b.p. 99–102° (0.9 mm.), $\lambda_{\max}^{\mathrm{EtOH}}$ 238 mμ (ϵ = 9760). Heating VII in refluxing xylene did not afford a cyclized product, but rather a rearrangement to the amide VIII occurred.[9]

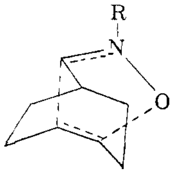
The unique cyclizations reported here are further examples of 1,3-dipolar additions of nitrones to olefins. In these situations, the ring closure reactions are thought to be initiated by electrophilic attack of the nitrone on the olefin, the nitrone carbon atom thus resembling a carbonium ion center. We picture the transition states for the formation of the products as IX, X and XI which collapse to give the isoxazolidines. No distinction is made between a one-step process or a two-stage mechanism involving a *rapid* second step. The transition states thus resemble the proposed bridged-ion intermediates of the solvolysis reactions; however, with the nitrone addition, the charge distribution in the activated complex involves five atoms and the nucleophile is built into the molecule. In addition to the obvious utility for the synthesis of *difunctional* derivatives of bicyclic hydrocarbons, we hope that this reaction can be extended to parallel other situations in which π-routes to non-classical cations have been demonstrated. On the other hand, anchimeric assistance by double bonds in solvolysis reactions may also be expected with substrates analogous to those which have been observed to undergo facile intramolecular nitrone–olefin addition.[2] Such investigations are in progress. One final point is worthy of note: namely, that the product(s) from solvolysis of esters of the alcohol derived from campholenic aldehyde should prove interesting in view of the formation of two products, II and III, from the nitrone reaction.



IX



X



XI

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(9) *Cf.* W. D. Emmons, *J. Am. Chem. Soc.*, **79**, 5739 (1957).

(10) Alfred P. Sloan Fellow, 1961–1963.

(11) National Institutes of Health Predoctoral Fellow, 1961–1962.

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RECEIVED SEPTEMBER 7, 1962

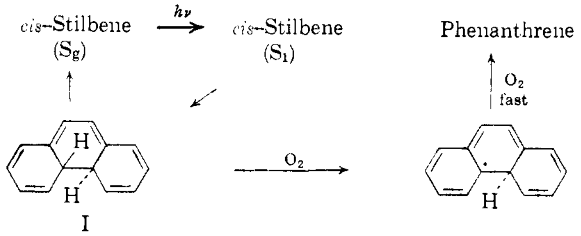
PHOTOCHEMISTRY OF STILBENES. I.[1,2]

Sir:

The photochemical conversion of stilbenes to phenanthrenes has been discovered independently by a number of workers and some limited studies have been reported.[3] This type of reaction has also been found in more complicated molecules such as the bianthrones[4] and mechanistically related ring closures have been observed in the simpler 1,3,5-hexatriene system.[5]

We have shown that the formation of phenanthrene by irradiation of stilbene in cyclohexane solution requires a suitable oxidant such as dissolved molecular oxygen; on irradiation under a nitrogen atmosphere with careful exclusion of oxygen the only net reaction is *cis–trans* isomerism[6] with no detectable conversion to phenanthrene. It seems probable, therefore, that oxidants such as oxygen or peroxides were inadvertently present in the two cases reported recently[3f,3h] of photochemical formation of phenanthrene systems under nitrogen atmospheres.

The reaction is formulated as proceeding by way of the unorthodox dihydrophenanthrene (I) shown below. The molecular oxygen or other oxidant is believed to function by abstracting the tertiary allylic hydrogens from this intermediate. Since I has not been isolated as a product of irradiation in the absence of an oxidant it must also undergo ring opening to give back *cis*-stilbene; this process is estimated from appropriate bond and resonance energy values to be exothermic by about 35 kcal./mole and is therefore expected to occur thermally at a reasonably rapid rate at room temperature. With the light source used in this work[7] it is probable that the steady-state concentration of I is too low for the photochemical ring opening of this intermediate to be of much importance relative to the thermal process.



The *trans* stereochemistry of the tertiary hydrogens in I is tentatively suggested by three lines of argument. First, from consideration of models it appears that the approach of an *ortho* and an *ortho'* carbon of *cis*-stilbene to within bond-forming distance of one another would involve much more severe hydrogen–hydrogen interaction in the transition state leading to the *cis*-dihydrophenanthrene (II) than in the transition state leading to the *trans*-dihydrophenanthrene (I). Second, the analogous photochemical ring closure of 2,4,6-octatriene has been shown[5c] to give *trans*-1,2-dimethyl-3,5-cyclohexadiene; this *trans* stereochemistry

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[1] Presented at the Ninth Conference on Reaction Mechanisms, Brookhaven National Laboratory, Sept. 7, 1962.

[2] Supported by grants from the Research Corporation.

[3] (a) C. O. Parker and P. E. Spoerri, *Nature*, **166**, 603 (1950); (b) R. E. Buckles, *J. Am. Chem. Soc.*, **77**, 1040 (1955); (c) D. G. Coe, E. W. Garnish, M. M. Gale and C. J. Timmons, *Chemistry and Industry*, 665 (1957); (d) F. B. Mallory, Ph.D. Thesis, California Institute of Technology, 1958; (e) E. A. Rick, Ph.D. Thesis, Yale University, 1959; (f) P. Hugelshofer, J. Kalvoda and K. Schaffner, *Helv. Chim. Acta*, **43**, 1322 (1960); (g) H. Stegemeyer, *Z. Naturforsch.*, **17b**, 153 (1962); (h) G. J. Fonken, *Chemistry and Industry*, 1327 (1962); (i) E. J. Moriconi, private communication; (j) G. W. Griffin, private communication; (k) D. H. R. Barton, private communication.

[4] H. Brockmann and R. Mühlmann, *Ber.*, **82**, 348 (1949). See also A. Schönberg, "Präparative Organische Photochemie," Springer-Verlag, Berlin, 1958, pp. 47–70.

[5] (a) E. Havinga and J. L. M. A. Schlatmann, *Tetrahedron*, **16**, 146 (1961); (b) R. Srinivasan, *J. Am. Chem. Soc.*, **83**, 2806 (1961); (c) G. J. Fonken, *Tetrahedron Letters*, 549 (1962).

[6] Photodimerization to tetraphenylcyclobutane is negligible if the stilbene concentration is 10^{-2} *M* or less.

[7] A jacketless 100-watt General Electric H100-A4 mercury arc.