

mechanisms is not yet possible. We are in the process of examining the solvolysis of the 5-methyl-5,9-decadienyl *p*-nitrobenzenesulfonates in order to determine if this system behaves like the present case or whether the relative stability of the potential tertiary cation IV (CH₃ in place of H) will result in a changeover to a common carbonium ion process. This study may have a bearing on the mechanism of cyclizations in the biosynthesis of polycycloisoprenoids.

Acknowledgment.—We wish to thank the U. S. Public Health Service and the National Science Foundation for assisting this study.

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY
STANFORD, CALIFORNIA

WILLIAM S. JOHNSON
JACK K. CRANDALL

RECEIVED MARCH 23, 1964

Novel Ring Expansion and Carbon Insertion Reactions of Isatogens

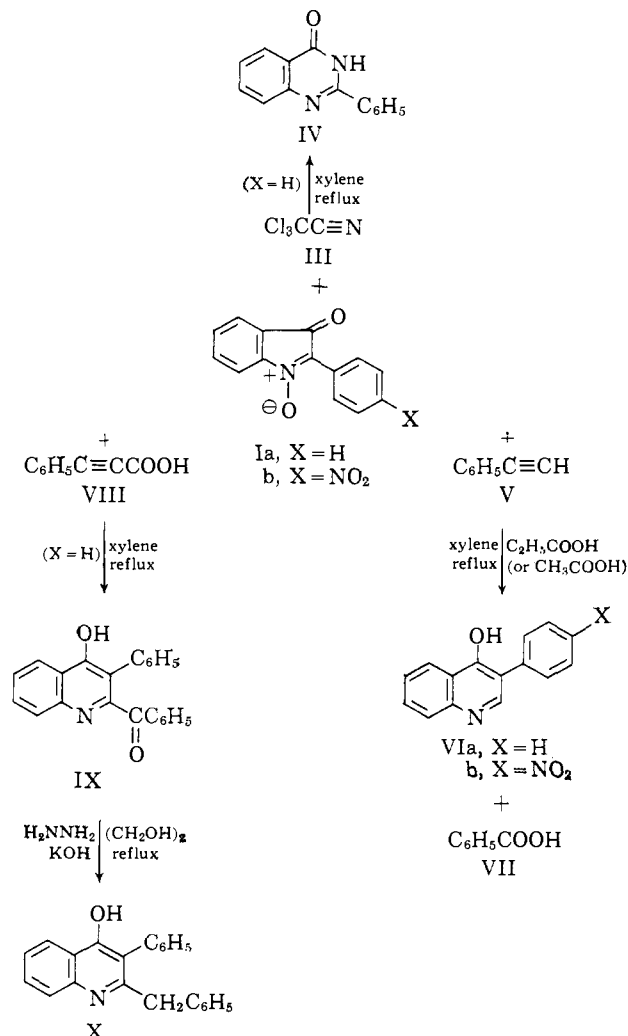
Sir:

Recently, 2-phenylisatogen¹ (Ia) was reported to undergo two types of ring expansion reactions involving nitrogen insertion, resulting in a 4-cinnolinol 1-oxide derivative from ammonia and a 3,4-dihydro-4-quinazolinone derivative from tetracyanoethylene (II).² It has now been found that the reaction of the latter type, of Ia with II, goes even better with another negatively substituted nitrile, trichloroacetonitrile (III). Thus, reaction of Ia (0.0143 mole) with III (0.070 mole) in refluxing xylene (40 ml.) for 5 hr. gave 2-phenyl-3,4-dihydro-4-quinazolinone (IV) in 88% yield (in contrast to 30–39% yields with II²), m.p. 240.5–241°, identical, as shown by mixture melting point, 239–240°, and infrared comparison in Nujol, with a sample prepared² from II.

We report now two types of ring expansion reactions of Ia with acetylenes, which involve carbon insertion. Refluxing a solution of Ia (0.0224 mole) with phenylacetylene (V, 0.091 mole) and propionic acid (0.107 mole) in xylene (100 ml.) for 13 hr. gave a crystalline precipitate, which increased in amount upon cooling. Filtration removed pale straw-colored crystals (VIa, 42%), m.p. 254–256°. Concentration of the filtrate gave an oil, which was taken up in ether and extracted with sodium bicarbonate. Acidification of the bicarbonate extract and extraction with ether gave benzoic acid (VII, 44%, m.p. 113°; recrystallization from water gave a sample, m.p. 119–123°, identified by mixture melting point, 119–123°, with an authentic sample). Concentration of the ether which had been extracted with bicarbonate gave additional VIa (5%; total 47%). Recrystallization of the combined VIa from ethanol gave a sample, m.p. 261.5–262°,³ identical with the known⁴ 3-phenyl-4-quinolinol as shown by mixture melting point, ultraviolet, and infrared comparison in Nujol with a sample of m.p. 259.5–260.5°³ prepared⁴ by the Conrad-Limpach method⁵ from aniline and ethyl phenylmalonaldehyde; λ_{max} mμ (log ε) in 95% ethanol:

- (1) (a) F. Kröhnke and M. Meyer-Delius, *Chem. Ber.*, **84**, 932 (1951)
(b) F. Kröhnke and I. Vogt, *ibid.*, **85**, 376 (1952).
(2) W. E. Noland and D. A. Jones, *J. Org. Chem.*, **27**, 341 (1962).
(3) These melting points were determined in capillary tubes; all others were determined on calibrated Fisher-Johns hot stages.
(4) (a) W. J. Adams and D. H. Hey, *J. Chem. Soc.*, 3254 (1950); (b) R. C. Elderfield and J. B. Wright, *J. Am. Chem. Soc.*, **68**, 1276 (1946).
(5) (a) M. Conrad and L. Limpach, *Chem. Ber.*, **20**, 944 (1887); (b) *ibid.*, **21**, 521 (1888); (c) L. Limpach, *ibid.*, **64B**, 969, 970 (1931).

ethanol: 263 (4.42), 309 (3.99), 329 (4.01), and 334 (infl, 4.00). The mixture melting point with a sample of the isomeric 2-phenyl-4-quinolinol⁶ (m.p. 258.5–261.5°³) was depressed, 213.5–254.5°,³ and the infrared spectra in Nujol and halocarbon oil were different. Replacement of propionic acid with acetic acid in the reaction of Ia with V also gave VIa (40%).



Addition of Ia to V is assumed to proceed through normal orientation of addition⁷ by the cyclic nitron system, followed by a hydrolytic rearrangement and ring expansion to VIa. That the phenyl substituent retained in VIa is derived from Ia (and not from V) is shown by the analogous reaction of 2-(4-nitrophenyl)-isatogen^{1a} (Ib, 0.0073 mole) with V (0.072 mole) and propionic acid (0.080 mole) in refluxing xylene (60 ml.) for 3 hr. The products were VII (45%, m.p. 120–122°) and 3-(4-nitrophenyl)-4-quinolinol (VIb, 95%), yellow solid, m.p. 368–369° dec.³ (from ethanol); λ_{max} mμ (log ε) in 95% ethanol: 238 (4.41), 290 (3.85), 328 (infl, 4.26), 336 (4.28), and 353 (infl, 4.15); ν_{NO₂} cm.⁻¹ in KBr: 1516 (vs), 1343 (vs).

Anal. Calcd. for C₁₅H₁₀N₂O₃ (mol. wt. 266.25): C, 67.66; H, 3.79; N, 10.52. Found: C, 67.50; H, 3.95; N, 10.27.

Location of the 4-nitrophenyl substituent in the hydroxyl-conjugated 3-position (analogous to VIa) is

- (6) C. E. Kaslow and W. R. Lawton, *J. Am. Chem. Soc.*, **72**, 1723 (1950).
(7) (a) W. E. Noland and D. A. Jones, *Chem. Ind. (London)*, 363 (1962); (b) G. R. Delpierre and M. Lamchen, *J. Chem. Soc.*, 4693 (1963); (c) R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, **2**, 588 (1963).

indicated by the marked (nitrophenolate anion) bathochromic shift which the spectrum of VIb ($1.47 \times 10^{-5} M$) undergoes in alkaline (0.022 *N* in NaOH) 95% ethanol solution, $m\mu$ ($\log \epsilon$): 243 (infl, 4.28), 285 (4.03), 315 (4.07), and 415 (b, 4.08).

Refluxing a solution of Ia (0.0090 mole) with phenylpropionic acid (VIII, 0.0137 mole) in xylene (40 ml.) for 3.25 hr. gave a crystalline precipitate, which increased in amount upon cooling. Filtration removed white crystals (IX, 38%), m.p. 319–321°. Concentration of the filtrate gave additional IX (10%; total 48%; average yield 45%). Three recrystallizations of the combined IX from ethanol and two from chloroform-1-butanol, with slow cooling, gave 2-benzoyl-3-phenyl-4-quinolinol (IX) as small white needles, m.p. 326–327°; $\lambda_{\max} m\mu$ ($\log \epsilon$) in 95% ethanol: 255 (4.50), 288 (d infl, 3.98), 328 (infl, 3.89), and 335 (3.90); $\nu_{C=O} \text{ cm.}^{-1}$ in Nujol: 1678 (s).

Anal. Calcd. for $C_{22}H_{15}NO_2$ (mol. wt. 325.35): C, 81.21; H, 4.65; N, 4.31. Found: C, 80.85; H, 4.91; N, 4.12.

The structure of IX was proved by Wolff-Kishner reduction in refluxing ethylene glycol to the known⁸ 2-benzyl-3-phenyl-4-quinolinol (X, 87%), small white needles (from ethanol), m.p. 320–322° (turn yellow), identical, as shown by mixture melting point, ultraviolet, and infrared comparison in Nujol and halo-carbon oil, with samples of m.p. 320–323° prepared by the Conrad-Limpach method⁵ in 12% yield from aniline and ethyl 2,4-diphenylacetoacetate, and also by heating of anthranilic acid with dibenzyl ketone^{8a} (34%); $\lambda_{\max} m\mu$ ($\log \epsilon$) in 95% ethanol: 249 (4.44), 298 (infl, 3.6), 323 (4.02), and 335 (4.04).

That IX is not an intermediate in the formation of VIa from Ia and V is shown by recovery of unchanged IX in 92% yield from refluxing xylene containing propionic acid, conditions under which VIa was formed.

The generality of the ring expansion reactions of isotogens with acetylenes is currently under investigation.

(8) (a) H. P. W. Huggill and S. G. P. Plant, *J. Chem. Soc.*, 784 (1939); (b) J. von Braun and A. Heymons, *Chem. Ber.*, **63B**, 3191 (1930).

(9) National Science Foundation Graduate Fellow, June 16, 1962, to the present.

SCHOOL OF CHEMISTRY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINNESOTA 55455

WAYLAND E. NOLAND
ROBERT F. MODLER⁹

RECEIVED FEBRUARY 17, 1964

trans-2-Cyclooctenone

Sir:

The ethylenic portion of the triplet state of an α,β -unsaturated ketone can be treated, in useful simplification, rather like the triplet state of an unconjugated olefin. The antagonistic interactions of unpaired electronic spins should induce a torsional distortion about the α,β -bond.¹ A 90° twist places the unpaired electrons in noninteracting orthogonal orbitals. In flexible acyclic systems such an orthogonal triplet can return either to a *cis* or *trans* ground state configuration.² The geometric constraint imposed on the α,β -bond in small, cyclic, α,β -unsaturated ketones pre-

vents full relief of electronic repulsions in the triplet states of these less flexible systems.³ A Drieding model of triplet 2-cyclopentenone permits under maximum stress a twist of only about 20° in the α,β -dihedral angle; a similar model of 2-cyclohexenone allows a 60° twist. These are maximal figures and are most certainly reduced by the strain concomitantly imposed on the ring and by the loss in overlap energy with the carbonyl group. 2-Cyclooctenone is the lowest homolog of the cyclic α,β -unsaturated ketones in which twisting about the α,β -bond is nearly unrestricted in the triplet. Thus, ultraviolet excitation of *cis*-2-cyclooctenone might induce isomerization to the *trans* isomer. We have in this way succeeded in the preparation of *trans*-2-cyclooctenone, an α,β -unsaturated ketone of exceptional properties.

Irradiation of a cyclohexane solution of *cis*-2-cyclooctenone with light of wave lengths above 300 $m\mu$ ⁴ leads to a rapid decrease in the concentration of the *cis* ketone. The reaction is best followed spectroscopically. In the ultraviolet spectrum the strong $\pi-\pi^*$ absorption of *cis*-2-cyclooctenone (λ_{\max} 223 $m\mu$, ϵ 7600) is lost; the $n-\pi^*$ maximum of the conjugated ketone (λ_{\max} 321 $m\mu$, $\epsilon \sim 70$) gives way to an absorption at lower wave length appropriate to an unconjugated ketone (λ_{\max} 283 $m\mu$, $\epsilon \sim 60$). Equivalent changes occur in the infrared spectrum. The strong absorption of the conjugated carbonyl group of the starting material (5.97 μ) is replaced by a band at lower wave length (5.79 μ) more common to unconjugated ketones. Distinct new absorptions appear at 6.12, 8.61, and 10.12 μ ; significantly, similar bands are present in the infrared spectrum of *trans*-cyclooctene but not in the spectrum of the *cis* isomer.⁵

Under the irradiation conditions described only about 80% conversion of *cis*-2-cyclooctenone can be obtained; apparently the reaction product and the starting material are in photoequilibrium. The tail of the $n-\pi^*$ absorption of the photoproduct extends above 300 $m\mu$ and allows the light-induced back reaction. In the dark the back reaction is negligible. The smallest trace of mineral acid, however, triggers the nearly instantaneous regeneration of *cis*-2-cyclooctenone.

The reactivity of the photoproduct (*vide infra*) prevents the isolation of a pure sample. The nuclear magnetic resonance spectrum of the reaction product admixed with the photoequilibrium amount of starting material is still useful. Although the vinyl proton absorptions of product and *cis*-2-cyclooctenone overlap confusingly, it is possible to achieve a partial analysis of this area of the spectrum. It appears that the irradiation product contains two coupled vinyl protons with $J = 18$ c.p.s., a value appropriate to the coupling of *trans* vinyl hydrogens in an octene ring.⁶ One of the vinyl protons (center at *ca.* τ 3.5 p.p.m.) is not coupled significantly with the nonolefinic protons. On the other hand, the second vinyl proton (center at *ca.* τ 4.3

(3) The full significance of these differences in angular deformation and the corresponding differences in triplet state energies will be developed in a later paper considering the photocondensation reactions of unsaturated ketones.

(4) The light source is a 450-w. Hanovia mercury arc lamp surrounded by water-cooled Pyrex filters.

(5) A. C. Cope, R. A. Pike, and C. F. Spencer, *J. Am. Chem. Soc.*, **75**, 3212 (1953).

(6) O. L. Chapman, *ibid.*, **85**, 2014 (1963), and L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, New York, N. Y., 1959, p. 85.

(1) Mulliken has pointed out that the energies of the parallel and orthogonal states of triplet ethylene differ substantially. The orthogonal state is the more stable by about 20 kcal./mole [R. S. Mulliken and C. C. J. Roethaan, *Chem. Rev.*, **41**, 219 (1947)].

(2) G. S. Hammond and J. Saltiel, *J. Am. Chem. Soc.*, **84**, 4983 (1962).