

sidered analogous to this group of compounds, did not show photochromic behavior under the conditions of these experiments.

Details of the scope and mechanism of this photochromic reaction are being further investigated in these laboratories.

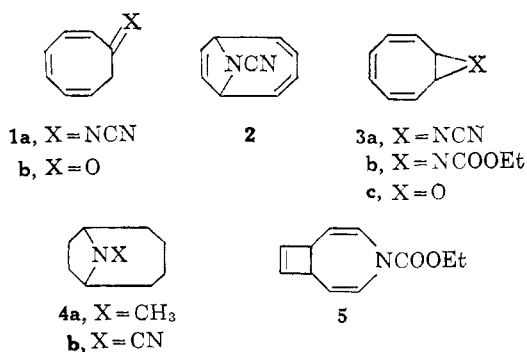
Acknowledgment. The authors wish to acknowledge helpful discussions with Dr. E. T. Strom and Mr. F. H. Bissett. We also wish to thank Mr. J. A. Sousa for some of the preliminary flash photolysis measurements and Mr. R. Petkun for preparation of compounds IV and IX.

Aaron L. Bluhm, Julius Weinstein
Pioneering Research Division
U. S. Army Natick Laboratories
Natick, Massachusetts
Received September 22, 1965

Reaction of Cyanonitrene with Cyclooctatetraene. 1,4 and 1,2 Adducts

Sir:

We wish to report a case of 1,4 addition of a nitrene to a polyene.¹ Treatment of a dilute solution of cyclooctatetraene (COT) in ethyl acetate (*ca.* 12%) with cyanogen azide (N₃CN) at 78° results in evolution of 1 mole equiv. of nitrogen and the formation of two products in 31% yield. The predominant component² (68% of the mixture) is an orange, viscous liquid purified by high vacuum distillation and identified as **1a**: $\lambda_{\text{max}}^{\text{CH}_3\text{ON}}$ 243 m μ (ϵ 16,000) and 331 (6900), $\nu_{\text{max}}^{\text{nat}}$ 2180 (C \equiv N) and 1540 cm.⁻¹ (C=N) and n.m.r. (neat) multiplets centered at τ 3.5 (5 H), 4.5 (1 H), and 7.2 (2 H). Chemical proof for structure **1a** derives from its hydrolysis with moist alumina to the known³ ketone **1b** in 75% yield. The less abundant component² (32% of the mixture) is a white, sublimable solid (m.p. 102–103°) identified as the 1,4 adduct **2**: $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$ 255 m μ (ϵ 4500), $\nu_{\text{max}}^{\text{KBr}}$ 2220 cm.⁻¹ (C \equiv N), and n.m.r. (CDCl₃), narrow multiplets at τ 3.7 (4 H), 4.6 (2 H), and a broader peak at τ 5.3 (2 H; width at half-height = 5 c.p.s.). On catalytic hydrogenation over rhodium at room temperature and atmospheric pressure, **2** took up 3 mole equiv. of hydrogen to yield N-cyano-9-azabicyclo[4.2.1]nonane (**4b**) ($\nu_{\text{max}}^{\text{KBr}}$ 2210 cm.⁻¹, n.m.r. (CDCl₃) multiplets at τ 5.9 (2 H) and



(1) For equivocal reports of 1,4 addition see: R. Appel and O. Buchner, *Angew. Chem.*, **74**, 430 (1962); K. Hafner and W. Kaiser, *Tetrahedron Letters*, No. 32, 2185 (1964). The ambiguity in these reports arises from failure to observe 1,2 addition products, which could conceivably be the progenitors of the 1,4 adducts.

(2) Satisfactory elemental analysis was obtained for this material.

(3) A. C. Cope and B. D. Tiffany, *J. Am. Chem. Soc.*, **73**, 4158 (1951).

7.5–8.4 (12 H)), identical (n.m.r., infrared) with an authentic sample (m.p. 114–116°) prepared from homotropene⁴ (**4a**) and cyanogen bromide.

At room temperature a mixture of cyanogen azide and COT slowly evolves 1 mole equiv. of nitrogen and gives exclusively **1a**⁵ in 73% yield.

The absence of **2** when the reaction was carried out at room temperature coupled with the temperature (*ca.* 40°) at which cyanogen azide is known to fragment to nitrogen and cyanonitrene⁶ (NCN) indicates⁷ that **2** is the product not of cyanogen azide but of NCN.

When the reaction of N₃CN with COT at 78° in the presence of a large excess of ethyl acetate was interrupted prior to completion, aziridine **3a** was observed in addition to **1a** and **2**. The relative amounts⁸ of **1a**, **2**, and **3a** were found to be essentially constant (38:14:48) from 10% reaction (4 min.) to 75% reaction (40 min.), whereas in the later stages of the reaction the amount of **3a** in the mixture decreases and when the reaction is 91% complete (130 min.) **1a**, **2**, and **3a** are present in ratios of 56:33:11, respectively. Compound **3a** could not be obtained in the pure state on account of its low thermal stability, and the structural assignment derives from its n.m.r. spectrum (in the mixture), which is virtually identical with those of **3b**⁹ and **3c**³; n.m.r. (CDCl₃), unsymmetrical doublet centered at τ 3.9 (6 H) and a sharp singlet at τ 6.6 (2 H; width at half-height = 1.5 c.p.s.).

More information concerning the origin of the products was obtained from the results of a control experiment in which a known mixture of **1a**, **2**, **3a** and a standard¹⁰ (2.0:0.9:1.7:1.0) in ethyl acetate was maintained at 78° for 30 min. Under these conditions **1a** and **3a** decreased by 10 and 24%, respectively,¹¹ whereas the amount of **2** remained unaltered.¹⁰

The constant ratio in which the three products are formed in the first 75% of the reaction coupled with the failure of either **1a** or **3a** to isomerize to **2** when maintained at the reaction temperature for 0.5 hr. and the presence of **2** in the first 4 min. of the reaction indicates that the 1,4 adduct **2** is primarily a direct product of NCN and COT and does not arise to any appreciable extent from isomerization of **1a** or **3a**.¹²

Although the detailed mechanism for the formation of the 1,4 adduct is now known, it appears likely that it is formed in a nonconcerted fashion from triplet NCN.^{13,14} On the basis of the data presented here, the following

(4) A. C. Cope, H. R. Nace, and L. L. Estes, Jr., *ibid.*, **72**, 1134 (1950).

(5) The reaction of cyanogen azide with olefins leads to N-cyanoaziridines and/or alkylidene cyanamides: F. D. Marsh and M. E. Hermes, *ibid.*, **86**, 4506 (1964).

(6) A. G. Anastassiou, H. E. Simmons, and F. D. Marsh, *ibid.*, **87**, 2296 (1965).

(7) Compound **1a** does not isomerize to **2** at 80° in ethyl acetate.

(8) These were determined from the n.m.r. spectra of the crude mixtures using the signals due to the allylic hydrogens.

(9) S. Masamune and N. T. Castellucci, *Angew. Chem.*, **76**, 569 (1964).

(10) Dimethyl phthalate was used as the standard. The composition was determined by n.m.r. using the allylic hydrogens of the three products and the aromatic as well as aliphatic hydrogens of the standard.

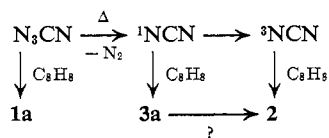
(11) The predominant product of the thermal decomposition is an insoluble, high-melting (>300°) amorphous solid.

(12) The structurally related aziridine **3b** is known⁹ to isomerize to **5** at 80°.

(13) The ground state of NCN is ³ Σ_g^- : G. Herzberg and D. N. Travis, *Can. J. Phys.*, **42**, 1658 (1964); G. J. Pontrelli and A. G. Anastassiou, *J. Chem. Phys.*, **42**, 3755 (1965); E. Wasserman, L. Barash, and W. A. Yager, *J. Am. Chem. Soc.*, **87**, 2075 (1965).

(14) The addition of α -cyanoisopropyl radicals to COT occurs in a 1,4 fashion: J. L. Kice and T. S. Cantrell, *J. Am. Chem. Soc.*, **85**, 2298 (1963).

mechanism, depicting the major sources of products, is advanced.



A. G. Anastassiou

Contribution No. 1109

Central Research Department, Experimental Station

E. I. du Pont de Nemours and Company

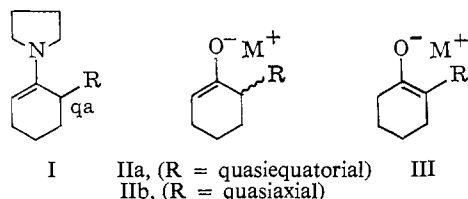
Wilmington, Delaware 19898

Received August 11, 1965

The Stereochemistry of the Anions of 2-Alkylcyclohexanones

Sir:

In previous papers^{1,2} we have demonstrated that the pyrrolidine enamines of 2-substituted cyclohexanones, represented by I, have the substituent R in the quasi-axial position. The preference for this conformation is almost certainly a result of the fact that in the alterna-

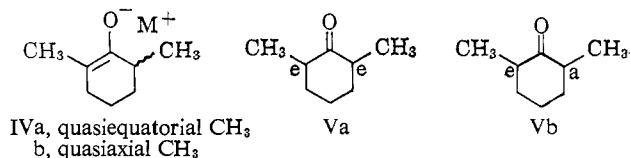


tive quasiequatorial position R would have a nonbonded steric interaction with one of the CH₂ groups on nitrogen.³ We have now extended our studies to investigate whether the solvent has any role in modifying the stereochemistry of the alkyl group in the less substituted enolate anions (II) derived from 2-alkylcyclohexanones.

Aprotic solvents are capable of cation solvation either by a π -orbital or a lone-pair mechanism.⁴ Consequently the solvent shell, which is partly interspersed between the anionic oxygen atom and the cation and partly surrounding them, might interact with the alkyl group when it is in the quasiequatorial orientation (IIa). This nonbonded interaction which would depend on the size of both the solvent shell and the alkyl group should disappear if the alkyl group becomes quasixial (IIb); the latter would of course have a 1,3-diaxial interaction between the methyl group and the hydrogen atom at C-4. If the magnitude of the 1,3-diaxial interaction in IIb and the relative concentrations of IIa and IIb are known for a particular solvent, then the energy associated with the

interaction of the solvent shell and the alkyl group in IIa can be readily calculated.

Since in 2-alkyl substituted ketones the generation of the less substituted enolate anion II is complicated by the concurrent formation of the more substituted anion III,⁵ we selected 2,6-dimethylcyclohexanone as a substrate for our studies. This ketone on treatment with base affords only one enolate anion, IV, which is of course a mixture of conformers IVa and IVb.



The respective concentrations of IVa and IVb in a particular solvent were easily determined by carrying out their protonation with dilute acetic acid, under nonequilibrating conditions, which led to Va and Vb, respectively.⁶ The experimental detail is outlined below.

A solution of V (Va:Vb \sim 92:8 under equilibrating conditions)⁷ in a given aprotic solvent was treated with 2 equiv. of anhydrous potassium *t*-butoxide at room temperature, and the mixture was stirred for 2 hr. under nitrogen. The resulting solution was added dropwise to 50% aqueous acetic acid maintained at 0° and contained in a Morten flask equipped with a high speed stirrer. The amounts of Va and Vb obtained were quantitatively determined by g.l.p.c. The extent of enolate anion formation was determined by quenching an aliquot of the reaction solution with acetic anhydride and determining the amounts of enol acetate (directly representative of enolate anion formed^{8,9}) and starting ketone again by g.l.p.c., and also by treating it with 50% deuterioacetic acid⁵-deuterium oxide (inverse addition) which led to almost exclusively monodeuterated species. Estimates of the concentrations of enolate anion obtained by these two procedures were in good agreement. The results obtained are summarized in Table I.

The results of the table demonstrate conclusively that the solvent shell around the ion pair interacts quite strongly with the adjacent methyl group when the latter is equatorially oriented. To a first approximation it probably can be assumed that a similar effect occurs with the less substituted anions of the simpler 2-alkylcyclohexanones. This has important implications for the alkylation of such systems since the presence of a considerable proportion of IIb in II will undoubtedly slow down axial alkylation⁹ of II by virtue of a steric interaction between the 2-axial alkyl group and the incoming reagent (1,3-diaxial interaction) as in the analogous case of enamines of II.^{1,2} This would of course

(1) F. Johnson and A. Whitehead, *Tetrahedron Letters*, 3825 (1964).

(2) S. K. Malhotra and F. Johnson, *ibid.*, 87, 4027 (1965).

(3) It is important to note (a) that in this system the pair of electrons on nitrogen conjugates with the double bond maintaining planarity and thus ensuring this steric interaction and (b) that the dihedral angle between R and the nitrogen atom is quite small, as can be seen from models.

(4) H. E. Zaugg, B. W. Horrom, and S. Borgwardt, *J. Am. Chem. Soc.*, 82, 2895 (1960); H. E. Zaugg, *ibid.*, 82, 2903 (1960); H. E. Zaugg, D. A. Dunnigan, R. J. Michaels, L. R. Swett, T. S. Wang, A. H. Sommers, and R. W. Denet, *J. Org. Chem.*, 26, 644 (1961); H. E. Zaugg and A. D. Schaefer, *J. Am. Chem. Soc.*, 87, 1857 (1965); H. D. Zook and T. J. Russo, *ibid.*, 82, 1386 (1960); A. J. Parker, *Quart. Rev. (London)*, 16, 163 (1962).

(5) H. O. House and V. Kramar, *J. Org. Chem.*, 28, 3362 (1963); D. Caine, *ibid.*, 29, 1868 (1964).

(6) This protonation was shown to be subject to stereoelectronic control by quenching the enolate anion derived from 2,6-dimethyl-4-*t*-butylcyclohexanone with 50% deuterioacetic acid-deuterium oxide under irreversible conditions. The infrared spectrum of the product showed principal absorption in the C-D stretching region at 2140 cm.⁻¹ (axial C-D).

(7) B. Rickhorn, *J. Am. Chem. Soc.*, 84, 2414 (1962); W. D. Cotterill and M. J. T. Robinson, *Tetrahedron*, 20, 765, 777 (1964).

(8) H. J. Ringold and S. K. Malhotra, *J. Am. Chem. Soc.*, 84, 3402 (1962).

(9) Cf. E. J. Corey and R. A. Sreen, *ibid.*, 78, 6269 (1956).