cis–trans isomerization[5] of 1,3-dienes that decay from *s-cis* triplets should favor the *trans,trans*-diene isomer.

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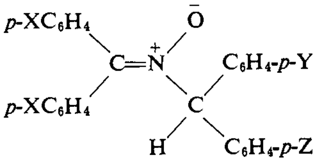
A Homolytic Mechanism for the Thermal Isomerization and Decomposition of N-Benzhydryl-α,α-diaryl Nitrones

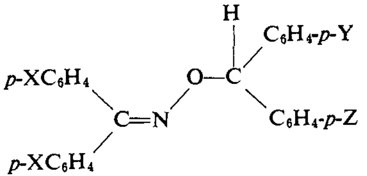
Sir:

In 1950 Cope and Haven[1] reported that α,α-diphenyl-N-benzhydryl nitrone (Ia) undergoes a nearly quantitative rearrangement to benzophenone O-benzhydryloxime (IIa) when heated above its melting point. The disappearance of Ia in dilute solutions of diethyl Carbitol exhibited good first-order kinetics. The rate data reported[1] in the temperature range of 160–176° lead to an Arrhenius activation energy of about 37 kcal/mole and an entropy of activation of approximately 6 eu. On the basis of these kinetic data and seemingly apparent similarities of this reaction with other amine oxide rearrangements,[2] these authors postulated a concerted intramolecular mechanism involving a quasi-three-membered-ring transition state. An alternate route which they dismissed as unlikely, namely an initial ionization to form an oxime anion and a benzhydryl cation, could not, however, be ruled out on the basis of the experimental evidence.

Recently we reported the preparation of several nitrones (Ia–d) and the corresponding isomeric oxime O-ethers (IIa–d).[3] Our original intent was a more detailed kinetic probe of this reaction which might serve to distinguish between these two mechanisms.



Ia, $X = Y = Z = H$
b, $X = Y = H; Z = CH_3$
c, $X = CH_3; Y = Z = H$
d, $X = Cl; Y = Z = H$



IIa, $X = Y = Z = H$
b, $X = Y = H; Z = CH_3$
c, $X = CH_3; Y = Z = H$
d, $X = Cl; X = Z = H$

In the course of our kinetic experiments we observed that the ultraviolet spectra of our "infinity" solutions differed somewhat from that of the expected oxime O-ether. Furthermore, the product isolation from a rearrangement under kinetic conditions (dilute solution in diethyl Carbitol) reported previously[1] accounts for less than 79% of starting nitrone. Because of these uncertainties we decided to repeat the product analysis. A thoroughly degassed solution of 100 mg of Ia in 75 ml of diethyl Carbitol was sealed in a Pyrex bulb and heated at 144° for 46 hr. The resulting solution was concentrated to remove solvent and the residue was carefully chromatographed through a column packed with acid-washed alumina. A clean separation led to the isolation and characterization of *three compounds: sym*-tetraphenylethane (16 mg), benzophenone O-benzhydryloxime (IIa) (44 mg), and benzophenone oxime (12 mg).[4]

The first and third products isolated are most easily accounted for by assuming the intermediacy of benzhydryl and diphenyliminoxy[5] free radicals. This suggests that the first step in this reaction sequence may be a *homolytic dissociation at the carbon–nitrogen single bond.*

The rate constants for the disappearance of Ia–d in diethyl Carbitol at 144° all differ from each other by less than a factor of 2. Our kinetic data for the decomposition of Ia in the same solvent over the temperature range 130 to 160° yield an activation energy of 38.8 ± 0.3 kcal/mole and an entropy of activation of 11 eu, in fair agreement with the data of Cope and Haven. The activation parameters for Id are nearly identical ($E_a = 37.9 \pm 0.2$ kcal/mole, $\Delta S^{\ddagger} = 9$ eu). The insensitivity of decomposition rates to substituent changes is consistent with an initial homolytic cleavage of the carbon–nitrogen single bond. It also appears that the large positive entropy of activation is more easily accommodated by a homolytic dissociation in the transition state than it was assuming a concerted rearrangement.

Recently we have obtained additional evidence for the intermediacy of radicals during the decomposition of Ia by using epr methods. Radicals were observed in degassed solutions (*ca.* 0.1 *M*) of Ia in diethyl Carbitol at temperatures between 100 and 180°. We also observed radicals in melts of pure Ia above 160°.[6] The failure to observe a signal when benzophenone O-benzhydryloxime (IIa) was examined under comparable conditions precludes this rearrangement product as a source of the radicals. The stability of IIa under conditions in which the nitrone readily decomposes was confirmed by the nearly quantitative (99%) recovery of a sample of IIa which had been heated in diethyl Carbitol for 48 hr at 144°.

On the basis of these observations we propose Scheme I for the decomposition of Ia in diethyl Carbitol.

The reasons for the relatively high yields[7] of oxime

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(1) A. C. Cope and A. C. Haven, Jr., *J. Am. Chem. Soc.*, **72**, 4896 (1950).

(2) (a) J. Meisenheimer, *Ber.*, **52**, 1667 (1919); (b) J. Meisenheimer, H. Greeske, and A. Willmersdorf, *ibid.*, **55**, 513 (1922); (c) R. F. Kleinschmidt and A. C. Cope, *J. Am. Chem. Soc.*, **66**, 1929 (1944).

(3) E. J. Grubbs, J. D. McCullough, Jr., B. H. Weber, and J. R. Maley, *J. Org. Chem.*, **31**, 1098 (1966).

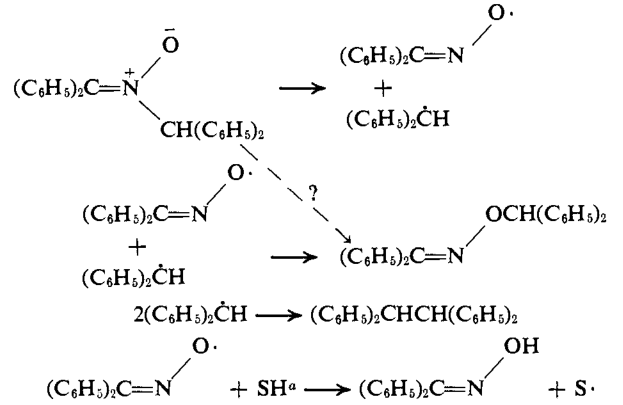
(4) This represents a total product balance of 72%. Small amounts of several other components which were eluted later have not been characterized yet.

(5) Iminoxy radicals have been recently generated by the oxidation of oximes with ceric ammonium nitrate or lead tetraacetate. See, for example: (a) J. R. Thomas, *J. Am. Chem. Soc.*, **86**, 1446 (1964); (b) M. Bethoux, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. France*, 1985 (1964); (c) B. C. Gilbert, R. O. C. Norman, and D. C. Price, *Proc. Chem. Soc.*, 234 (1964); (d) B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc., B*, 3119 (1966); (e) J. W. Lown, *ibid., B*, 441 (1966); and (f) *ibid., B*, 644 (1966).

(6) The nature of the observed radicals will constitute a portion of a forthcoming publication.

(7) Cope[1] reported a 96% conversion of Ia to IIa when this nitrone was heated at 200° for 0.5 hr. Our highest yield in a thermal rearrange-

Scheme I



[a] SH represents the solvent, bis(β-ethoxyethyl) ether (diethyl Carbitol). The products derived from the solvent following hydrogen atom abstraction have not yet been characterized.

O-ethers obtained by thermal rearrangement of the pure nitrones (in the absence of solvent) is not entirely clear. It may indicate an increase in product formation *via* radical-cage recombination in a viscous medium.[8] Experiments in progress will determine the effects of solvent (of varying polarity, viscosity, and hydrogen atom donating ability) on rates and product distribution.

Finally, the possibility that some of the nitrone (Ia) is converted to the oxime O-ether (IIa) in diethyl Carbitol directly by a concerted intramolecular nucleophilic displacement cannot be excluded. A study of the geometric stereochemical course of this isomerization currently in progress may provide an answer to this question.

In connection with our observations, it is of interest to note that Schöllkopf, *et al.*,[9] have recently detected radical intermediates by epr in the rearrangement of benzylmethylaniline oxide to O-benzyl-N-methyl-N-phenylhydroxylamine. Furthermore, these workers have found that the rearrangement of N,N-dimethylbenzylamine oxide to N,N-dimethyl-O-benzylhydroxylamine proceeds with net retention of configuration at the benzyl carbon atom, but accompanied by extensive racemization.[10] The kinetic data of Shulman, *et al.*,[11] for this rearrangement tend to support the conclusion[10] that a radical dissociation–recombination mechanism[12] is operative.

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ment was obtained in the thermal rearrangement of Ib to IIb and amounted to 82%.[3]

[8] Of interest in this regard is the recent study by R. Hiatt and T. G. Traylor [*J. Am. Chem. Soc.*, **87**, 3766 (1965)] which reveals the dependence of *t*-butoxy radical cage recombination on solvent viscosity.

[9] U. Schöllkopf, M. Patsch, and H. Schäfer, *Tetrahedron Letters*, 2515 (1964).

[10] U. Schöllkopf and H. Schäfer, *Ann.*, **683**, 42 (1965).

[11] G. P. Shulman, P. Ellgen, and M. Connor, *Can. J. Chem.*, **43**, 3459 (1965).

[12] Evidence in support of a similar radical dissociation–recombination mechanism for the thermal rearrangement of benzyl *p*-toluenesulfenate to benzyl *p*-tolyl sulfoxide has been offered by E. G. Miller, D. R. Rayner, and K. Mislow, *J. Am. Chem. Soc.*, **88**, 3139 (1966).

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Five-Coordinate Nickel(II) Complexes with Nitrogen–Phosphorus and Nitrogen–Arsenic Tetradentate Ligands

Sir:

A considerable number of five-coordinate complexes of nickel(II) have already been synthesized and characterized. They have been found to be either of the low-spin[1] or high-spin[2] type. The polyfunctional ligands which induce a low-spin ground state have been found to always contain the atoms P and/or As and never O or N as donor atoms. The reverse is true for complexes of high spin.

We have prepared two new ligands which contain donor atoms of both low and high crystal field splitting strength. They are tris(2-diphenylphosphinoethyl)amine, $N(CH_2–CH_2–PPh_2)_3$ (TPN, set NP_3) and tris(2-diphenylarsinoethyl)amine, $N(CH_2–CH_2–AsPh_2)_3$ (TAN, set NAs_3). With nickel(II) salts these tetradentate ligands form compounds of the types $Ni(TPN)X_2$ and $Ni(TPN)XBPh_4$ (X = Cl, Br, I) and $Ni(TAN)XBPh_4$, where X = Br, I. These crystalline compounds are stable and are intensely colored (dark blue, dark green, violet). The analyses for C, H, P, Ni, and halogen are in good agreement with calculated theoretical values.

These complexes are all diamagnetic. The spectra of the complexes in the solid state and in solution in dichloroethane and nitroethane are identical. In these solvents they behave as 1:1 electrolytes. Their spectra in the range 5000–22,000 cm^{-1} exhibit two bands in the range at 13,200–13,900 cm^{-1} (ϵ 2800–3100) and 18,200–20,000 cm^{-1} (ϵ 800–1450) for the TPN complexes and 12,650–13,150 cm^{-1} (ϵ 1000–2620) and 17,100–18,100 cm^{-1} (ϵ 600–1400) for the two TAN derivatives (Figure 1). These spectra are very similar to those of the diamagnetic trigonal bipyramidal nickel(II) complexes.[1c,d] Thus these complexes can be assigned a five-coordinate structure with formulas [Ni(TPN)X]X, $[Ni(TPN)X]BPh_4$, and $[Ni(TAN)X]BPh_4$. The frequencies of the bands are in agreement with the respective positions of the halogen, phosphorus, and arsenic atoms in the spectrochemical series. The two bands can be assigned[3] to the transitions from the $^1A_1$ state to the two ^1E states, arising from the ^1D state of the free ion, in symmetry field C_{3v}. This symmetry is the highest possible consistent with the geometry of the two tetradentate ligands TPN and TAN. Also the relative intensity of the two bands is consistent with this symmetry.[3b]

All of the five-coordinate complexes of nickel(II) described to date containing tetradentate ligands with

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[1] (a) C. M. Harris, R. S. Nyholm, and D. J. Phillips, *J. Chem. Soc.*, 4379 (1960); G. A. Barclay, R. S. Nyholm, and R. V. Parish, *ibid.*, 4433 (1961); (b) R. G. Heyter, *Inorg. Chem.*, **2**, 932 (1963); (c) L. Venanzi, *Angew. Chem. Intern. Ed. Engl.*, **3**, 453 (1964); G. Dyer, J. C. Hartley, and L. M. Venanzi, *J. Chem. Soc.*, 1293 (1965); G. Dyer and L. M. Venanzi, *ibid.*, 2771 (1965); (d) G. S. Benner, W. E. Hatfield, and D. W. Meek, *Inorg. Chem.*, **3**, 1544 (1964); G. Dyer and D. W. Meek, *ibid.*, **4**, 1398 (1965); **6**, 149 (1967), and references therein; (e) K. N. Raymond and F. Basolo, *ibid.*, **5**, 949 (1966).

[2] (a) L. Sacconi, P. Nannelli, N. Nardi, and U. Campigli, *ibid.*, **4**, 943 (1965); L. Sacconi, P. L. Orioli, and M. DiVaira, *J. Am. Chem. Soc.*, **87**, 2059 (1965); L. Sacconi, M. Ciampolini, and G. P. Speroni, *ibid.*, **87**, 3102 (1965); L. Sacconi and I. Bertini, *ibid.*, **88**, 5182 (1966); (b) M. Ciampolini and N. Nardi, *Inorg. Chem.*, **5**, 41 (1966); M. Ciampolini and G. P. Speroni *ibid.*, **5**, 45 (1966); M. Ciampolini and N. Nardi, *ibid.*, **6**, 445 (1967).

[3] (a) M. Ciampolini, *ibid.*, **5**, 35 (1966); (b) M. J. Norgett, J. H. M. Thornley, and L. M. Venanzi, *J. Chem. Soc.*, in press.