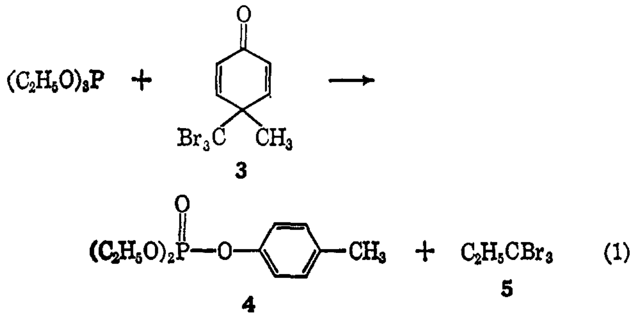
refluxing toluene for 42 hr gave (in addition to 20% of recovered **3**) a 60% yield of diethyl *p*-tolyl phosphate (**4**)[8] and a 43% yield of 1,1,1-tribromopropane (**5**).[9]



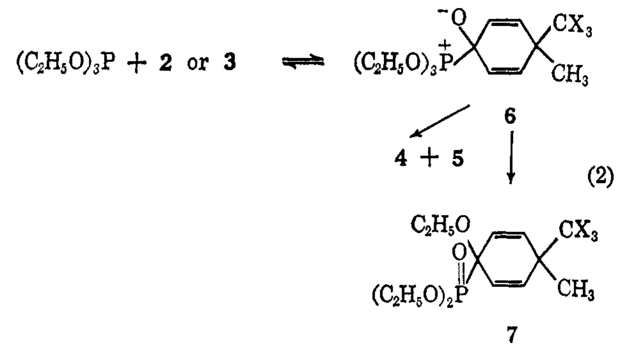
3

4

5

(1)

Formation of **4** and **5** would be quite difficult to explain by any reasonable mechanisms involving free-radical paths or nucleophilic attack at halogen. Attempts to rationalize the relative reactivities of **2a** and **3** by postulating initial addition of triethyl phosphite to the carbonyl carbon and a subsequent rearrangement to oxygen would also run into difficulties. If the addition step were rate determining and the subsequent rearrangement step were fast, **2a** should be more reactive than **3**, since addition to the carbonyl should be aided by the inductive effect of the trichloromethyl group. If addition to the carbonyl group were fast and reversible and the rearrangement step were rate determining (eq 2), the intermediate zwitterion **6** would be expected to undergo transfer of an alkyl group to oxygen to give **7** in an Arbuzov rearrangement[10,11] since dealkylation of tetraalkoxyphosphonium salts occurs very rapidly at temperatures far below that of refluxing toluene.[2a,4] The absence of **7** or any related product, particularly from the prolonged reaction with **2**, suggests that no addition to the carbonyl group of **2** or **3** occurs.

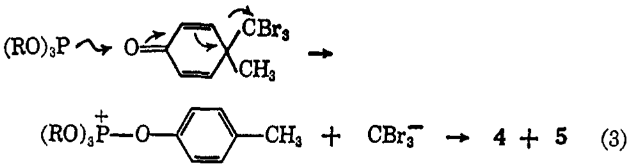


6

7

(2)

The most probable mechanism for reaction 1 is a nucleophilic attack of the phosphite upon the carbonyl oxygen with simultaneous elimination of the tribromomethyl anion (eq 3).[12] The relative ease of formation of the tribromomethyl anion compared to the trichloromethyl anion is consistent with previous demonstrations that the tribromomethyl anion is far more rapidly formed in reactions of haloforms with alkali[13] and in decarboxylation of trihaloacetic acid salts.[14] It is possible that displacement of a tribromomethyl anion from **3** is further favored by steric repulsions between the tribromomethyl group and the adjacent quaternary carbon.



(3)

Nucleophilic displacement of a tribromomethyl anion from a saturated carbon and alkylation of that anion appear to be novel reactions.

---

[8] G. W. Kenner and N. R. Williams, *J. Chem. Soc.*, 522 (1955).

[9] J. C. Conly, *J. Am. Chem. Soc.*, **75**, 1148 (1953).

[10] V. S. Abramov and N. A. Il'ina, *Dokl. Akad. Nauk SSSR*, **125**, 1027 (1959); *Chem. Abstr.*, **53**, 21747 (1959).

[11] B. A. Arbusow, *Pure Appl. Chem.*, **9**, 307 (1964).

[12] A referee has suggested that a pentacovalent intermediate may be formed by addition of phosphorus to both carbon and oxygen. The effects of the leaving group, however, make it clear that formation of such an intermediate cannot be rate determining. The alternative possibility that formation of a complex is rapid and reversible, and that occasionally the carbon-phosphorus bond in the complex breaks, seems, even conceptually, almost indistinguishable from complete dissociation followed by attack at the carbonyl oxygen.

[13] J. Hine, N. W. Burske, M. Hine, and P. B. Langford, *J. Am. Chem. Soc.*, **79**, 1406 (1957).

[14] R. A. Fairclough, *J. Chem. Soc.*, 1187 (1938).

Bernard Miller
Chemical Research and Development, Agricultural Division
American Cyanamid Company, Princeton, New Jersey

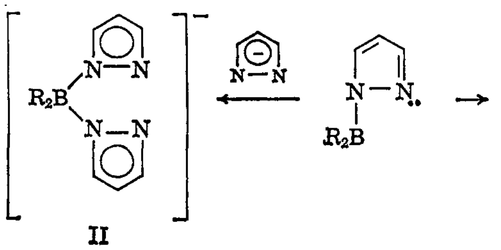
Received December 4, 1965

Boron–Pyrazole Chemistry

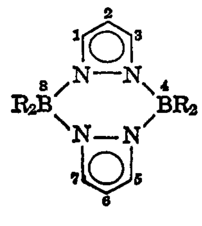
Sir:

Boron–pyrazole chemistry, which deals with compounds containing boron bonded to nitrogen of a pyrazole nucleus,[1] is a new and fertile field of remarkable scope. It has yielded novel classes of boron heterocycles, chelating ligands, and transition metal compounds.

Such versatility stems from the singular combination of electronic and geometric features of the 1-borylpyrazole fragment that leads to its facile stabilization either through dimerization or through coordination with a pyrazolide ion.[2] In this manner structures I and II, respectively, are produced; they are representa-



II



I

---

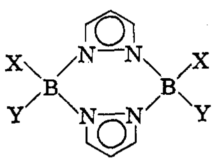
[1] The only reported boron-pyrazole compound is 4,5(3)-diphenylpyrazole-3(5)-boronic acid: D. S. Matteson, *J. Org. Chem.*, **27**, 4293 (1962).

[2] Coordination with a neutral pyrazole molecule gives rise to the free acid derived from II.

tive of the two main subareas of boron–pyrazole chemistry: pyrazaboles[3] and poly(1-pyrazolyl)borates.

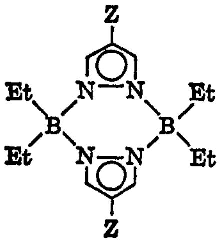
The parent pyrazabole (I, R = H) has been prepared by refluxing equimolar amounts of trimethylamine borane and pyrazole in toluene. It is a sublimable white solid of camphoraceous odor which melts at 80–81°, dissolves readily in organic solvents, is insoluble in and unaffected by water, and has been stored for 2 years in air without deterioration. The nmr spectrum of pyrazabole has only two C–H peaks at τ 2.49 (doublet) and 3.83 (triplet), with $J = 2.0$ cps and relative intensities 2:1, indicating equivalence of the 1, 3, 5, and 7 positions. These positions are also equivalent by nmr in all symmetrically substituted derivatives. The B^{11} nmr has a triplet ($J = 108$ cps) at +27.1 ppm from trimethyl borate.

Substitution chemistry of pyrazabole is confined largely to the boron atoms and is exemplified by the formation of derivatives IIIa, mp 222–223°, IIIb, mp 259–260°, and IIIc, mp 232–233°, upon treatment of pyrazabole with chlorine, pyrazole, and pyrocatechol, respectively.



IIIa, X = Y = Cl
b, X = Y = 1-pyrazolyl
c, XY = *o*-phenylenedioxy
d, X = Y = phenyl

Pyrazaboles with substituents on carbon or boron have been prepared by the reaction of appropriately substituted pyrazole and boron components. In this manner were synthesized, for instance, compounds IIId, mp 273–274°, IVa, mp 264–265°, and IVb, mp 127–128°. The viability of the pyrazabole nucleus during diverse chemical operations performed on functional groups is attested by the alkaline hydrolysis of IVa to IVc[4] and by conversions IVb → IVd → IVe, mp 124–125°; IVd → IVc; and IVf, mp 186–180° dec → IVg, mp 125–126°.

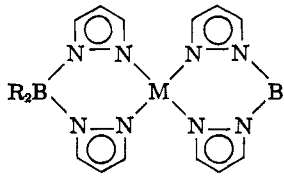


IVa, Z = CN
b, Z = Br
c, Z = COOH
d, Z = Li
e, Z = CHO
f, Z = NO_2
g, Z = NH_2

Parent poly(1-pyrazolyl)borates representing the second subarea of boron–pyrazole chemistry are prepared most conveniently by heating an alkali metal borohydride with pyrazole. By maintaining temperature around 110, 180, and >210°, respectively, di-, tri- and tetra(1-pyrazolyl)borates are obtained. They are water-soluble compounds stable to storage and yield the isolable, free acids on acidification.

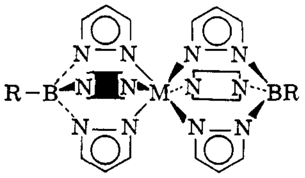
In dipyrazolylborates of structure II, both pyrazole rings are spectroscopically equivalent. Thus, the dihydro- (as well as dialkyl- and diaryl-) di(1-pyrazolyl)borates resemble enolizable β-dicarbonyl compounds in being uninegative bidentates and possessing similar geometries. First-row transition elements in the +2 oxidation state react readily with di(1-pyrazolyl)borate ions, even in acid solution, forming sublimable chelates such as Va, mp 180–182°, Vb, mp 200–201°, and Vc, mp 296–298°.

While di(1-pyrazolyl)borates resemble β-diketonates, tri(1-pyrazolyl)borates are symmetrical uninegative tridentates and as such have no precedent. They react with transition metals in the +2 oxidation state forming sublimable octahedral coordination compounds, a simple representative of which is VIa, mp 283–284°.



V

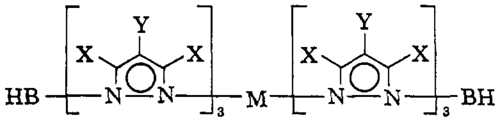
Va, R = H; M = Ni
b, R = Et; M = Cu
c, R = C_6H_5; M = Co



VI

VIa, R = H; M = Mn
b, R = 1-pyrazolyl; M = Co
c, R = C_6H_5; M = Fe
d, R = Bu; M = Co

Structure VI is supported by H^1 nmr which shows the three coordinating pyrazole rings to be identical. This is seen particularly well in octahedral Co(II) compounds which display large contact shifts.[5] For instance, in VIb, mp 364–365°, three identical and one different pyrazole rings can be discerned. Additional octahedral complexes containing boron substituents are exemplified by VIc, mp 368–370° dec, and the thermochromic VId, mp 274–275°; those with carbon substituents by VIIa,[6] dec > 430°, and VIIb, mp 238–240°.[7]



VIIa, X = H, Y = Cl,
M = Mn
b, X = CH_3, Y = Bu,
M = Zn

---

[3] Considerable difficulty was encountered in trying to name structure I in systematic fashion. Consequently, the trivial name "pyrazabole" has been adopted with numbering as shown.

[4] This diacid slowly turns yellow from 300°, but is still solid at 400°.

(5) A detailed study of this is to be published.

(6) This structure has the same stereochemistry as VI.

(7) Structures of all the representative compounds mentioned in this communication have been established by elemental analyses, molecular weight determinations, and infrared, ultraviolet, and nmr spectroscopy. Synthetic and structural details will be published in a series of papers being presently prepared. Mechanistic studies pertaining to boron–pyrazole chemistry are in progress.

Most transition metal polypyrazolylborates are stable to air, water, dilute acids, and bases.

Analogs of pyrazaboles and poly(1-pyrazolyl)borates were also obtained from 1,2,4-triazole.

S. Trofimenko
Contribution No. 1196
Central Research Department, Experimental Station
E. I. du Pont de Nemours and Company
Wilmington, Delaware 19898

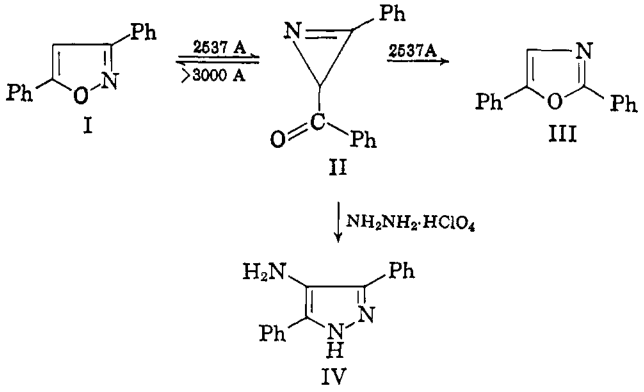
Received February 2, 1966

Photochemical Transposition of Ring Atoms in Five-Membered Heterocycles. The Photorearrangement of 3,5-Diphenylisoxazole

Sir:

Recently there have been described several examples of light-induced rearrangements of five-membered-ring heterocyclic compounds. In each case, the product could be formally derived by the transposition of two ring atoms together with their substituents. Thus, indazoles were found to rearrange to benzimidazoles,[1] pyrazoles to imidazoles,[1] and 2-substituted thiophenes to 3-substituted thiophenes.[2] An interesting suggestion has been made that these reactions may proceed by way of bridged valence tautomers[2] akin to those found as intermediates in the superficially similar phototransposition reactions of benzene derivatives.[3] We report here another example of the five-membered heterocyclic phototransposition reaction together with evidence concerning its mechanism.

Irradiation of 3,5-diphenylisoxazole[4] (I) ($\lambda\lambda_{\max}^{\text{ether}}$ 245 mμ (ϵ 22,000); 265 mμ (ϵ 24,000)) in ether solution with 2537-A light[5] led to the formation of 2,5-diphenyloxazole[6] (III) ($\lambda\lambda_{\max}^{\text{ether}}$ 302 mμ (ϵ 30,000); 315 mμ (ϵ 27,600)) in 50% yield. The reaction could conveniently be followed by ultraviolet spectroscopy and was found to proceed in yields of up to 84% under the spectroscopic conditions. However, spectra taken during the course of the reaction did not display isosbestic points as expected of a simple two-component system. Interruption of the reaction before completion led to isolation (silica chromatography) of a third substance, II ($\lambda_{\max}^{\text{ether}}$ 247 mμ (ϵ 24,300)) in 12% yield.[7] This compound was an oil which on further irradiation in ether with 2537-A light was converted to the oxazole III. When the reaction was followed spectroscopically the envelope of curves crossed at nearly one point, 267 mμ, and conversions of up to 82% were obtained. Additional prolonged irradiation of the oxazole III with >3000-A light[8] led to the gradual precipitation of a highly insoluble crystalline solid which reverted back to III on standing or heating in a solvent.



The analytical and mass spectral data for the oily compound II require that it be isomeric with the starting material. Its infared spectrum showed distinctive maxima at 5.63 and 5.99 μ which were in accord with the band positions expected for azirine C=N[9] and aromatic ketone stretching frequencies. The ultraviolet maximum of II at 247 mμ is close to the maxima of both phenyl cyclopropyl ketone[10] and N-phenylketimines,[9b,c] and the long wavelength tail of the band shows a shoulder at 350 mμ (ϵ 150) (partially obscured by traces of III) suggestive of an $n \rightarrow \pi^*$ band of an aromatic ketone. Since longer wavelength absorption would be expected if the ketimine and ketone groupings were conjugated, only the azirine structure II is compatible with these facts. This structure is further supported by (a) the appearance in the nmr of a single uncoupled proton signal at τ 6.25 (=NCHCO) together with signals at τ 1.8–2.6 (10 H, aromatic), (b) conversion of II to 4-amino-3,5-diphenylpyrazole[11] (IV) on warming with aqueous or alcoholic hydrazine perchlorate, (c) the thermal (200°) conversion of II in nonhydroxylic solvents to the isoxazole I, and (d) the near-quantitative conversion of II to the oxazole III in boiling methanol.[12]

Investigation of the effect of different wavelengths of light on the azirine II revealed a striking dependence of its photochemistry with wavelength. Irradiation of ether solutions of II with >3000-A light[8] led to near-quantitative conversion to the isoxazole I (nearly perfect isosbestic point at 258 mμ). This contrasts sharply with the observed 82% conversion of the azirine II to the oxazole III with 2537-A light. Two interpretations of these observations must be considered. Either (1) different wavelengths of light produce different reactions of the azirine II, or (2) the conversion of the azirine II to the oxazole III actually proceeds by way of the isoxazole I, but with >3000-A light the

---

(1) H. Tiefenthaler, W. Dörscheln, H. Göth, and H. Schmid, *Tetrahedron Letters*, 2999 (1964).

(2) H. Wynberg and H. van Driel, *J. Am. Chem. Soc.*, **87**, 3998 (1965).

(3) K. E. Wilzbach and L. Kaplan, *ibid.*, **86**, 2307 (1964); **87**, 4004 (1965); A. W. Burgstahler and P. L. Chien, *ibid.*, **86**, 2940, 5281 (1964); E. M. Arnett and J. M. Bollinger, *Tetrahedron Letters*, 3803 (1964); L. Kaplan, K. E. Wilzbach, W. G. Brown, and S. S. Yang, *J. Am. Chem. Soc.*, **87**, 675 (1965).

(4) C. Goldschmidt, *Ber.*, **28**, 2540 (1895).

(5) An Hanovia 100-w medium-pressure U-shaped mercury vapor arc was used together with Kasha's filter combination E; M. Kasha, *J. Opt. Soc. Am.*, **38**, 929 (1948).

(6) R. Robinson, *J. Chem. Soc.*, **95**, 2167 (1909).

(7) Up to 38% yields of II could be obtained by irradiation of ether solutions of I in Pyrex glass flasks with a GE B-H6 lamp with no filter (<1.0% of light transmitted to solution below 2800 A).

(8) A 6-mm thick Pyrex glass filter was used together with a GE B-H6 lamp (<1.0% of light transmitted below 3000 A).

(9) (a) D. J. Cram and M. J. Hatch, *J. Am. Chem. Soc.*, **75**, 33 (1953); (b) G. Smolinsky, *ibid.*, **83**, 4483 (1961); (c) R. F. Parcell, *Chem. Ind.* (London), 1396 (1963).

(10) R. P. Mariella and R. R. Raube, *J. Am. Chem. Soc.*, **74**, 518, 525 (1952).

(11) M. Ruccia, *Ann. Chim.* (Rome) **49**, 720 (1959); *Chem. Abstr.*, **53**, 21892*i* (1959).

(12) This reaction also occurred at 25° in weakly alkaline methanol.