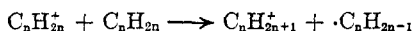


Examination by mass spectrometry of the dimeric material that resisted ozonolysis disclosed a ratio of ion intensity at $m/q = 170$ to that at $m/q = 168$ of 0.60. This ratio is very much lower than the corresponding ratio for any of the octanes and indicates a substantial yield of cyclane relative to paraffin (mass spectra of all octanes, but no similar set of isomeric hydrocarbons of higher molecular weight, are available for comparison). Cyclization has not been reported heretofore in radiolysis of simple olefins or paraffins, but has been reported in thermal reactions of olefins.⁴

The very low yield of compounds other than polymers indicates that radical production by carbon-carbon scission of 1-hexene is not important in chain initiation. Moreover, the extent of unsaturation in the dimer, the location of its double bond, and the nature of its skeleton suggest that the initiating radical is formed by hydrogen atom transfer to the double bond. We suggest an ion-molecule reaction of the sort⁵



as an important initiating event.

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Specificity of Phenyllithium Addition Reactions

Sir:

It is generally well known that the addition of lithium aryls to aromatic heterocyclic compounds containing an azomethine linkage proceeds to give substitution adjacent to the nitrogen atom in this group.¹ In connection with our work on the synthesis and characterization of pyridine analogs of ter- and quaterphenyl for use as scintillation solutes²

(1) E. A. Braude, in *Progress in Organic Chemistry*, Vol. 3, Academic Press, New York, 1955.

(2) This research was performed under contract No. AT-(40-1)-2162 between the Atomic Energy Commission and the University of Louisville. We gratefully acknowledge this support.

we have observed an unexpected and previously unrecognized specificity of addition in this reaction. We wish to report upon a portion of our activities in this area and in particular upon the reaction of 3-phenylpyridine with phenyllithium, the singular nature of the product isolated and the unequivocal proof of its identity as 2,5-diphenylpyridine. The selectivity of this addition is of additional interest because it makes pyridine analogs of terphenyl available for the first time by a direct route.

The addition of phenyllithium to 3-phenylpyridine was run in sodium-dried ether under oxygen-free nitrogen and allowed to proceed for 24 hours at room temperature. The crude product isolated from the water-washed ether solution was put into benzene, eluted through a column of acidic alumina and found to contain only one component, m.p. 174–175°, $\lambda_{\max}^{\text{KBr}}$ 1580, 1470, 1460, 1370, 1072, 1017, 1003, 905, 835, 752, 735, 687 cm^{-1} . *Anal.* Calcd. for $C_{17}H_{13}N$: C, 88.28; H, 5.67; N, 6.06. Found: C, 88.18; H, 5.79; N, 6.10.

On the basis of the above analytical and spectral data, in particular the C-H out of plane deformation frequencies, the product was tentatively assigned the 2,5-diphenylpyridine structure rather than that of the alternate and slightly less probable 2,3-diphenylpyridine. The validity of this assignment was confirmed by independent synthesis of the diphenylpyridine *via* alkaline permanganate oxidation of 3-phenylbenzo[*f*]quinoline to 2-phenyl-5-(*o*-carboxyphenyl)-6-carboxypyridine, m.p. 196°, reported 198°,³ $\lambda_{\max}^{\text{KBr}}$ 1765, 1670, 1600, 1475, 1450, 1330, 1300, 1258, 930, 852, 848, 775, 758, 725, 705, 687 cm^{-1} . This dicarboxylic derivative of 2,5-diphenylpyridine lost carbon dioxide upon melting to form 2-phenyl-5-(*o*-carboxyphenyl) pyridine, m.p. 195° (mixed m.p. 151°), $\lambda_{\max}^{\text{KBr}}$ 1670, 1600, 1575, 1470, 1365, 1270, 1250, 935, 838, 808, 778, 752, 733, 697, 685. *Anal.* Calcd. for $C_{16}H_{13}O_2N$: C, 78.53, H, 4.76. Found: C, 78.40; H, 4.81. The decarboxylation of this monocarboxylic acid was accomplished by pyrolysis of the compound with electrolytic copper in an atmosphere of oxygen-free nitrogen. The product 2,5-diphenylpyridine, m.p. 174°, was obtained by benzene extraction of the reaction mass. A mixed melting point of this substance with that obtained from the addition of phenyl lithium to 3-phenylpyridine was 174°.

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