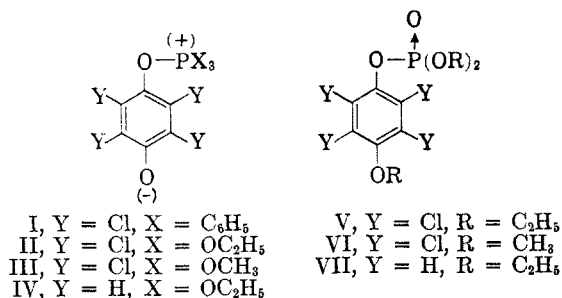trialkyl phosphate and the unalkylated hydro-quinone, in high yields. This is essentially the coupling of the two half-equations[4]: $X_3P + H_2O \rightleftarrows X_3PO + 2H^{(+)} + 2e$ and quinone $+ 2H^{(+)} + 2e \rightleftarrows$ hydroquinone, where X_3P is a tricovalent organophosphorous compound with phosphorous in the $+3$ oxidation state. In other words, trialkyl phosphites can be used, in the presence of water, to reduce quinones. Intermediates such as II, III, and IV (cf. isolation[2a] of I) would explain these processes. Evidently, the possibility of an irreversible group translocation (to V, VI, and VII) in the phosphorus compound, as well as the structural features of the quinone itself (oxidation potential, steric effects) can determine the over-all course of the reactions.[2]

The ether-phosphates, V,[2b] VI, and VII, exhibited the typical nonbonded phosphate P → O band at 7.85 μ and the expected ultraviolet spectra. VI had m.p. 94–95° (cyclohexane); found: C, 29.4; H, 2.7. VII had b.p. 139–140° (0.25 mm.), $n_D^{25°}$ 1.4829; found: C, 52.2; H, 6.0. The quinol-monoalkylethers (IX, m.p. 84–85°; X, m.p. 114–115°; XI, m.p. 66–67°) were characterized as such and as the corresponding well-known dialkyl ethers.[3,5]
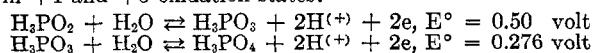

I, Y = Cl, X = C_6H_5
II, Y = Cl, X = OC_2H_5
III, Y = Cl, X = OCH_3
IV, Y = H, X = OC_2H_5

V, Y = Cl, R = C_2H_5
VI, Y = Cl, R = CH_3
VII, Y = H, R = C_2H_5

VIII; X = C_6H_5

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(4) Standard potentials are known for half-equations involving certain phosphorus compounds with phosphorus in $+1$ and $+3$ oxidation states:

$H_3PO_2 + H_2O \rightleftarrows H_3PO_3 + 2H^{(+)} + 2e$, E° = 0.50 volt
$H_3PO_3 + H_2O \rightleftarrows H_3PO_4 + 2H^{(+)} + 2e$, E° = 0.276 volt

The expressions given for the hypophosphorus and phosphorus acids involve four atoms around the phosphorus. For a recent summary see: H. H. Sisler in M. C. Sneed and R. C. Brasted, Comprehensive Inorganic Chemistry, D. van Nostrand Co., Inc., N. Y., 1956; Vol. V, pp. 118, 126.

(5) (a) Cf. Beilstein's Handbuch der organishen Chemie, 4th Ed., 6, 843 (I 416), (II 840), J. Springer, Berlin 1918; (b) A. Binz and C. Rath, Ber., 58, 309 (1925); (c) C. Graebe, Ann., 146, 20 (1868); (d) E. Banberger and J. Frei, Ber., 40, 1932 (1907), p. 1944.

Radiolysis of 1-Hexene[1]

Sir:

In order to investigate the mechanism of radiation-induced polymerization of simple olefins, we have irradiated 1-hexene with high energy electrons and gamma rays[2] at room temperature with exclusion of oxygen. Total doses varied from 12 to 40 $\times$ 10^{20} ev/g at rates between 6×10^{19} (gamma) and 6×10^{22} (electron) ev/g per hour. Gaseous products were analyzed mass spectrometrically and found to consist of hydrogen (G_{H_2} 0.8 ± 0.1) plus light hydrocarbons ($G_{L.H.}$ 0.12 ± 0.03). The recovered 1-hexene, analyzed by gas chromatography, was found to contain n-hexane ($G_{n-C_6H_{14}}$ 0.11 ± 0.02) and smaller amounts of other hexenes. The heavier materials consisted entirely of polymeric compounds, with G<0.01 for the total of compounds with carbon numbers not multiples of six. Yields determined by fractional distillation, with molecular weight confirmation by mass spectrometry, were G_{dimer} 0.98 ± 0.05, G_{trimer} 0.76 ± 0.05, $G_{tetramer}$ 0.22 ± 0.1 and $G_{pentamer}$ 0.35 ± 0.1 with overall $-G_{1-hexene}$ 10.5 ± 0.5. Unsaturation appeared to increase with molecular weight; the pentamer had as much diolefin as monoolefin.

The dimeric fraction by mass spectrometric analysis appeared to be approximately 90% monoolefin, with some saturated hydrocarbon and some diolefin. This is in contrast with the diolefinic dimer obtained from 1-octene by Kharasch, Schwartz, and Nudenberg,[3] who used free radicals from isopropyl bromide photolysis, and demonstrates that, in the present case, dimerization does not occur predominantly by combination of allyl-type radicals. The infrared spectrum of the dimer showed 27% terminal, 57% trans non-terminal and 3% vinylidene-type double bonds. Information on the location of the non-terminal double bonds was obtained by gas chromatographic analysis of methyl esters of the carboxylic acids obtained by oxidation of ozonolysis products. Methyl acetate, propionate, n-butyrate, n-valerate, hexanoate, 2-methylhexanoate, heptanoate, octanoate, nonanoate, and decanoate, plus the methyl esters of a branched C_{10} acid and a branched C_8 acid (not 2-methylheptanoate) were the only monocarboxylic esters found. Traces of dicarboxylic acids (from diolefins) and ketones (from vinylidene double bonds) were also products of ozonolysis. Identification of these compounds is in progress.

(2) The source of electrons was the 3 Mev. Van de Graaff accelerator at the Shell Development Company, Emeryville, Calif. The source of gamma rays was the High Level Gamma Irradiation Facility of the Argonne National Laboratory, Lemont, Ill.

(3) M. S. Kharasch, D. Schwartz, and W. Nudenberg, J. Org. Chem., 18, 337 (1953).

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 sort[5]

$$C_nH_{2n}^+ + C_nH_{2n} \longrightarrow C_nH_{2n+1}^+ + \cdot C_nH_{2n-1}$$
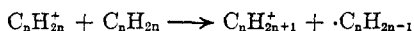
as an important initiating event.

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(4) V. Mark and H. Pines, J. Am. Chem. Soc., 78, 5946 (1956).
(5) D. O. Schissler and D. P. Stevenson, J. Chem. Phys., 24, 926 (1956).
(6) Deceased.

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 solutes[2]

(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°, λ_{max}^{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] λ_{max}^{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°), λ_{max}^{KBr} 1670, 1600, 1575, 1470, 1365, 1270, 1250, 935, 838, 808, 778, 752, 733, 697, 685. Anal. Calcd. for $C_{10}H_{13}O_2N$: 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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(3) R. Cuisa and A. Buogo, Atti. accad. naz. Lincei, Rend. Classe sci. fis. mat. e nat., (5) 23, II, 265.