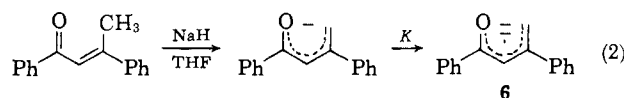


vacant MO at -0.73β . A close facsimile, the 2,4-dimethyl-1,5-dioxapentadienyl system fails to react with potassium in THF. However, another example, dimedon enolate, does react to form a stable lavender dianion radical (5). We attribute this difference in reactivity to the fact that the more stable conformer of the dianion radical, *i.e.*, the *trans,trans* conformer, in which the negatively charged oxygens are maximally separated, can be formed directly in the cyclic case but not in the acyclic one, where the chelated enolate prefers the *cis,cis* formation, the worst for dianion radical formation.

The 2,4-diphenyl-1-oxapentadienyl dianion radical (6) has also been prepared, by sequence 2. The HMO energy level is -0.63β . Reaction stops at the



deep blue dianion radical stage (titration), at which point dypnone can be regenerated by nickel chloride treatment.

Finally, 2,4-diphenylpentadienyl anion (purple) has been prepared and treated with potassium. Here, even the dianion radical fails to form. The HMO energy level (-0.72β) is about the same as for the unsubstituted 1,5-dioxapentadienyl system, the acyclic analog of which also did not react.

Acknowledgment.—We wish to acknowledge support from the University Research Institute and the National Science Foundation.

DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF TEXAS
AUSTIN 12, TEXAS

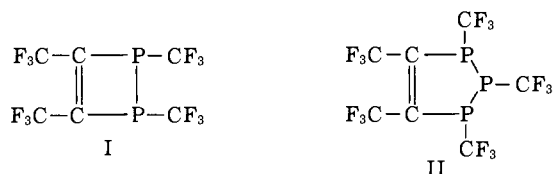
NATHAN L. BAULD

RECEIVED FEBRUARY 21, 1964

Polyphosphine Heterocycles

Sir:

One of the more elegant synthetic applications of biphosphine chemistry is the pseudo-halogen addition to multiple bonds.^{1,2} We have extended this principle to cyclopolyposphines and thereby attained the C_2P_2 and C_2P_3 ring systems in the compounds 1,2,3,4-tetrakis(trifluoromethyl)-3,4-diphosphacyclobutene (I) and 1,2,3,4,5-pentakis(trifluoromethyl)-3,4,5-triphosphacyclopentene (II).



$(CF_3P)_4$ and $(CF_3P)_5$ in the presence of excess $CF_3C\equiv CCF_3$ at 170° for 70 hr. gave 55% of I and 31% of II.

(1) J. Chatt, F. A. Hart, and H. C. Fielding, U. S. Patent 2,922,819 (1960).

(2) A. B. Burg, *J. Am. Chem. Soc.*, **83**, 2226 (1961).

Anal. Calcd. for $C_6F_{12}P_2$ (I): C, 19.89; F, 62.99; P, 17.12; mol. wt., 362. Found: C, 19.82; F, 63.70; P, 17.48; mol. wt., 366 (gas density), 362 (mass spectrometer).

Anal. Calcd. for $C_7F_{15}P_3$ (II): C, 18.18; F, 61.71; P, 20.11; mol. wt., 462. Found: C, 18.25; F, 62.26; P, 20.28; mol. wt., 462 (mass spectrometer).

The vapor pressure of I is 6 mm. at 0° and 26 mm. at 25° , from which the boiling point is estimated as 110° . The vapor pressure of II is 1.5 mm. at 25° , implying a boiling point near 160° . Both I and II are colorless liquids that do not freeze at -120° . They are spontaneously flammable in air, but in isolation they are stable at 200° . The double-bond absorption for I occurs at 1625 cm.^{-1} and that for II at 1560 cm.^{-1} .

F^{19} n.m.r. of I shows two kinds of fluorine in equal amounts. The CF_3 groups attached to P have the X pattern of an $X_3AA'X_3'$ system^{3,4} in which eight lines can be resolved. From the F^{19} spectrum the coupling constants (including J_{P-P}) were derived (Table I); these values give a calculated spectrum in good

TABLE I
NUCLEAR MAGNETIC RESONANCE PARAMETERS

	$J_{P-P'}$ c.p.s.	J_{P-F} c.p.s.	$J_{P'-F}$ c.p.s.	δF , p.p.m. CF_3COOH = 0	δP , p.p.m. H_3PO_4 = 0
Compound I					
$F_3C-P-P'-CF_3'$	55	59	18	-25	+40
$F_3C-C=C-CF_3$	$J_{P-F} + J_{P'-F} = 10$			-13	
Compound II					
$(P')_2-P-CF_3$	220	60	20	-30	+41
$(CF_3-P)_2-P'$	220	65	23	-28	-55
$CF_3-C=C-CF_3$				-24	

agreement with the line positions and intensities observed. The sign of the coupling constant of F with the near P is the same as that with the far P. At high resolution there is further splitting (1.5 c.p.s.) from the other set of CF_3 groups. This F-F coupling is again seen in the F^{19} spectrum of the CF_3 groups on carbon and can be removed by double resonance. This reduces the spectrum of the carbon CF_3 groups to a triplet which is the theoretical X pattern of an $X_3AA'X_3'$ system when AA' coupling is large relative to AX couplings.⁵

The n.m.r. spectra of II are fully consistent with its structure. The resonances of the CF_3 groups attached to phosphorus appear as two triplets and two doublets in accord with expectations for first-order F-P spin-spin interactions. There are two kinds of P^{31} nuclei, in the ratio 1:2, and they appear as a triplet and doublet, as expected.

At 170° , iodine converts II to equimolar amounts of CF_3PI_2 and the diphosphacyclobutene I; the latter is resistant to further action of iodine. The P-P bonds of the heterocycles are in marked contrast to those of the homocyclic polyphosphines which are quantitatively cleaved by iodine at room temperature.⁶

(3) A. A. Bothner-By and C. Naar-Colin, *ibid.*, **84**, 743 (1962).

(4) F. A. L. Anet, *ibid.*, **84**, 747 (1962).

(5) A similar situation exists in $(CH_3)_2PP(CH_3)_2$, where the proton spectrum is an almost perfect 1:2:1 triplet; the ringing of the middle line is less pronounced than that of the outer two and indicates unresolvable structure.

(6) W. Mahler and A. B. Burg, *J. Am. Chem. Soc.*, **80**, 6161 (1958).

TABLE II

GAS PHASE ULTRAVIOLET ABSORPTION MAXIMA, Å. (ε)			
C ₂ P ₂ (CF ₃) ₄ (I)	C ₂ P ₃ (CF ₃) ₅ (II)	H ₂ (CF ₃ P) ₂ ⁵	H ₂ (CF ₃ P) ₃ ⁶
2480 (2300)	2750 (3600)	2040 (7400)	2240 (5500)
2150 (4500)	2120 (9200)		2075 (7600)
2000 (8400)			

We had earlier argued that the (formally) nonbonding electron pair on each phosphorus atom in polyphosphines was delocalized in π -type orbitals.⁶ This concept receives further support from the observation that the heterocyclic polyphosphines absorb ultraviolet light at longer wave length than the corresponding open-chain di- and triphosphine (Table II). This clearly suggests that the orbitals of the polyphosphine portion of the ring overlap with the carbon-carbon π -orbitals.

CONTRIBUTION NO. 961
CENTRAL RESEARCH DEPARTMENT
EXPERIMENTAL STATION
E. I. DU PONT DE NEMOURS AND COMPANY
WILMINGTON 98, DELAWARE

WALTER MAHLER

RECEIVED APRIL 20, 1964

Photoisomerization of Dialkylbenzenes¹

Sir:

In previous investigations^{2,3} of the products of photolysis of alkylbenzenes attention has been confined to the gaseous and polymerized products. We wish to report that hydrocarbons of intermediate volatility are also formed in significant amounts and particularly that photoisomerization is an important process in the case of dialkylbenzenes.

Some of the products found upon irradiating the vapors of *o*-xylene, *m*-xylene, and toluene with mercury arcs are shown in Table I. Volatile products were

TABLE I
VAPOR-PHASE PHOTOLYSIS OF SOME METHYLBENZENES

Conditions ^{a,b} Time, min.	<i>o</i> -Xylene		<i>m</i> -Xylene	Toluene
	<i>a</i>	<i>b</i>	<i>b</i>	<i>b</i>
Product	Yield, mole %			
H ₂	1.52	1.02	0.56	0.28
CH ₄	0.31	0.18	0.11	0.08
C ₂ H ₆	0.17	0.10	0.01	0.01
C ₃ H ₈	0.05	0.04	0.004	0.28
C ₆ H ₅ CH ₃	1.24	1.08	0.31	(94.0)
C ₆ H ₅ C ₂ H ₅	0.04	0.016	0.004	0.19
C ₆ H ₄ (CH ₃) ₂				
<i>o</i> -	(74.0)	(81.3)	1.09	0.005
<i>m</i> -	5.44	3.66	(85.5)	0.007
<i>p</i> -	0.49	0.20	4.1	0.003
C ₆ H ₄ (CH ₃)C ₂ H ₅				
<i>o</i> -	0.58	0.48	0.016	
<i>m</i> -	0.11	0.09	0.14	
<i>p</i> -	0.01	0.01	0.07	
"Polymer"	18.0 ^c	13.1 ^c	8.8 ^c	5.3 ^c

^a Irradiated at 35° with a mercury resonance lamp, Nestor and Faust NFUV-300, at a pressure of 6 mm. in an annular quartz vessel of 800 cc. volume. ^b Irradiated at 35° with a high pressure mercury lamp, Hanovia 673-A, at pressures of 5-7 mm. in a 630-cc. Vycor vessel. ^c Weight per cent of products not volatile at room temperature and 10⁻⁴ mm. pressure.

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) R. R. Hentz and M. Burton, *J. Am. Chem. Soc.*, **73**, 532 (1951).

(3) A. H. Schon and B. de B. Darwent, *J. Chem. Phys.*, **23**, 822 (1955).

identified and measured by vapor phase chromatography; "polymer" was determined as the difference in weight between the initial sample and recovered material volatile at room temperature and 10⁻⁴ mm. pressure. In each case the major product is polymer; other important products include hydrogen, methane, and molecules in which a hydrogen atom replaces or is replaced by a methyl group. In the case of the xylenes, the yield of isomeric products is exceeded only by that of polymer. This contrasts sharply with γ -radiolysis⁴ where isomeric products are relatively minor products.

The distribution of isomeric xylenes indicates that photoisomerization is a highly selective process. Since only a small proportion of *p*-xylene is found in the photolyses of *o*-xylene, and this is completely eliminated at lower conversions, the process cannot involve a 1,3 shift of the methyl group. A 1,2 shift is at least the predominant path in photoisomerization of *m*-xylene since the yield of *o*-xylene, which can be formed by either a 1,2 or 1,4 shift, is much less than that of *p*-xylene.

Quantum yields for isomerization and polymerization in photolysis of *o*-xylene with the resonance lamp were determined by uranyl oxalate actinometry to be 0.012 and 0.032, respectively. The value for isomerization is in excellent agreement with one of 0.014 \pm 0.002 obtained at one-thirtieth the conversion and one-thousandth the intensity using light from a high pressure mercury arc, passed through a monochromator set at 2500 Å., and measured with a calibrated thermopile.

Direct determination of quantum yields for the experiments of Table I with the high pressure arc was not feasible, but they are essentially proportional to the yields of product per unit time, since conditions of illumination were identical and the absorption spectra of the three hydrocarbons are very similar. The quantum yield for isomerization of *m*-xylene is thus somewhat more than twice that of *o*-xylene. Based on a value of 0.012 for isomerization of *o*-xylene, the calculated quantum yields for "gas" and "polymer" from toluene are 0.0010 and 0.015, respectively, about fifteen times those estimated by Hentz and Burton.²

The isomerization of *m*-xylene has also been observed in the liquid phase. The ratio of *ortho* to *para* isomers is essentially the same in the pure liquid, in isohexane solution, and in the vapor; the quantum yield in solution is 0.006, about one-fifth that in the vapor.

The migration of ethyl groups has also been demonstrated. The quantum yield for isomerization of *o*-diethylbenzene vapor is about twice that for *o*-xylene.

In order to obtain additional information about the process of photoisomerization, *m*-xylene has been photolyzed in the presence of foreign gases. The results are summarized in Table II. The ratio of *o*- to *p*-xylene produced is relatively constant, suggesting that both isomers are formed from a common precursor. Although radicals are known⁵ to be formed by photolysis of xylenes, our results indicate that the isomers are not formed by radical recombination. The fact that ethylene has no effect on the yield excludes participation of hydrogen atoms⁶; the relatively small

(4) K. E. Wilzbach and L. Kaplan, unpublished results.

(5) G. Porter and E. J. Wright, *Trans. Faraday Soc.*, **51**, 1469 (1955).

(6) K. Yang, *J. Am. Chem. Soc.*, **84**, 719 (1962).