

tion with iodine and following injection of phthalic anhydride yielded essentially the same rate of loss of the absorbing species. Measurements at 302 $m\mu$ yielded excellent linear semilogarithmic plots against time with a half-life of 69 sec in both instances. This is in good agreement with the hydrolytic rate of phthalic anhydride previously observed in this laboratory.⁴

Although both spontaneous⁵ and catalyzed formation⁶ of acid anhydrides in aqueous solution have been demonstrated, the equilibrium concentrations of these unstable species are usually quite low. In the present instance the deficit in free energy has been provided through coupled oxidation of a sulfur-containing compound.

Since it has already been shown that the anhydride character of cyclic dicarboxylic anhydrides can be rapidly and readily interconverted to other forms of high-energy species including acylimidazole⁷ and acyl phosphate in aqueous solution,⁴ it is evident that mechanisms of this type can play a significant role in biochemical energy transfer.

(4) G. L. Flynn, Ph.D. Dissertation, University of Wisconsin, 1965.

(5) T. Higuchi, T. Miki, A. C. Shah, and A. Herd, *J. Am. Chem. Soc.*, **85**, 3655, 1963.

(6) T. Higuchi, A. C. Shah, J. McRae, and H. Uno, *ibid.*, in press.

(7) A. Shah, Ph.D. Dissertation, University of Wisconsin, 1965.

Takeru Higuchi, Karl-Heinz Gensch

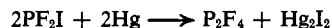
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Received June 9, 1966

Diphosphorus Tetrafluoride and Diphosphorus Oxytetrafluoride¹

Sir:

Although diphosphorus tetrachloride and diphosphorus tetraiodide have been prepared, the corresponding fluoride is unknown. A report concerning its possible existence has appeared,² but little evidence was given. We have now obtained diphosphorus tetrafluoride, P_2F_4 , in yields up to 85% by the reaction of phosphorus(III) iododifluoride³ with mercury at ambient temperature.



Purification of the product was accomplished by fractionation through -95 , -135 , and -196° cold traps. The product was retained in the trap set at -135° .

Characterization of P_2F_4 was accomplished by elementary analysis (*Anal.* Calcd for P_2F_4 : P, 44.9; F, 55.1. Found: P, 44.1; F, 53.8), vapor density molecular weight [138.7 g/mole (calcd for P_2F_4 , 138.0)], melting point ($-86.5 \pm 0.5^\circ$), boiling point ($-6.2 \pm 0.4^\circ$), Trouton constant (22.11 eu), and heat of vaporization (5.90 kcal/mole). The vapor pressure data follow the equation $\log p = (-1290/T) + 7.716$. In addition the mass cracking pattern is also consistent with its formulation as P_2F_4 and contained the following major peaks given as mass number (species) and relative abundance: 31 (P^+), 7.7; 50 (PF^+), 15.9; 69 (PF_2^+), 100.0; 119 ($P_2F_3^+$), 6.9; and 138 ($P_2F_4^+$), 27.0. The peak due to the parent molecule ion is considerably stronger in

(1) For additional information, see R. W. Rudolph, R. C. Taylor, and R. W. Parry, *J. Am. Chem. Soc.*, **88**, 3729 (1966).

(2) D. S. Payne, *Quart. Rev.* (London), **15**, 189 (1961).

(3) R. G. Cavell, *J. Chem. Soc.*, 1992 (1964).

the pattern of P_2F_4 than it is in that of N_2F_4 . In fact, under the experimental conditions used, the spectrum of N_2F_4 has no parent peak. This has been attributed to the facile dissociation of N_2F_4 into NF_2 radicals.⁴ The contrasting behavior of P_2F_4 is perhaps indicative of its greater P-P bond strength than the N-N bond energy found in N_2F_4 . The infrared spectrum of P_2F_4 contains absorptions at 842 (s), 830 (vs) and 820 (s) (P-F str), 408 (vw), and 356 cm^{-1} (w). The ^{19}F nmr spectrum taken at room temperature in CCl_3F solvent is complex and symmetric and is centered at ϕ 115.2. The spectrum is currently being analyzed as an $A_2A_2'XX'$ system.

A side product formed in small yield in the preparation of P_2F_4 has tentatively been identified as diphosphorus oxytetrafluoride, PF_2OPF_2 , by its vapor density molecular weight [153.0 (calcd for P_2F_4O , 154.0)], infrared spectrum [bands at 1081 (w), 971 (vs) (P-O-P asym str), 850 (vs, broad) (P-F str), 678 (m) (P-O-P sym str), 518 (m), 459 (w), and 353 cm^{-1} (w)], and mass spectrum [major absorptions at 31 (P^+), 2.7; 47 (PO^+), 28.3; 50 (PF^+), 13.1; 66 (POF^+), 2.8; 69 (PF_2^+), 100.0; 85 (POF_2^+), 2.6; 88 (PF_3^+), 2.9; 135 (PF_2OPF^+), 1.1; 154 ($PF_2OPF_2^+$), 16.7]. The same compound can be also prepared directly in a 67% yield by reaction between P_2F_4 and oxygen.

Acknowledgment. This work was carried out under Army Ordnance Contract No. DA-01-021 AMC-11536 (Z).

(4) C. B. Colburn and F. A. Johnson, *J. Chem. Phys.*, **33**, 1869 (1960).

Max Lustig, John K. Ruff, Charles B. Colburn

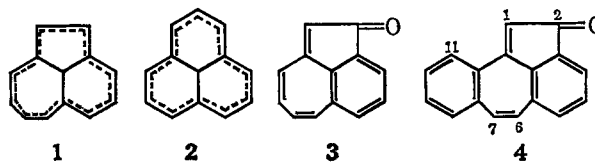
Rohm and Haas Company, Redstone Research Laboratories
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Received May 2, 1966

2H-Dibenz[*c,d,h*]azulen-2-one

Sir:

Preparative pathways have been recently opened¹ to benz[*c,d*]azulenyl (1), a theoretically interesting² non-alternant analog of the phenalenyl system 2. Yet unknown is 2H-benz[*c,d*]azulen-2-one (3), analogous to phenalenone, the unusually basic and polarized ketone with a key role in phenalene chemistry.³



Now we find 2H-dibenz[*c,d,h*]azulen-2-one (4) to be accessible by facile Friedel-Crafts cyclization. 5 (mp 103°), prepared from 5H-dibenzo[*a,d*]cyclohepten-5-one by the Reformatsky sequence, is added at -10° to 2 moles of $AlCl_3$ in CS_2 and the violet complex decomposed (0° , 2 *N* HCl, light excluded) to yield, almost

(1) (a) V. Boekelheide and C. D. Smith, 146th National Meeting of American Chemical Society, Chicago, Ill., Sept 1964, Abstracts of Papers, p 34C; *J. Am. Chem. Soc.*, in press. We thank V. Boekelheide for a manuscript. (b) K. Hafner and H. Schaum, *Angew. Chem. Intern. Ed. Engl.*, **2**, 95 (1963); **3**, 165 (1964).

(2) R. Zahradnik, *ibid.*, **4**, 1039 (1965).

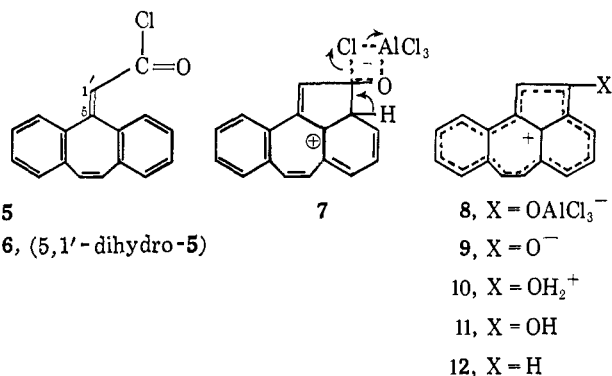
(3) D. H. Reid, *Quart. Rev.* (London), **19**, 274 (1965).

Table I. Ultraviolet Absorption Spectra^a

4 in		H ₂ SO ₄ , 96% (≡ 10) ^{b,c}	12 in H ₂ SO ₄ , 96% ^c	14 in C ₂ H ₅ OH	15 ^{1b} (no solvent reported)
CH ₂ Cl ₂	C ₂ H ₅ OH				
508 (3.39)	523 (3.37)	545 (3.62)	553 (3.361)		
495 (3.28)	504 (3.41)	511 (3.60)	524 sh (3.50)		
		486 (3.32)			
		450 sh (2.36)			
		402 (3.97)	407 sh (3.13)		
	390 (3.38)		399 (3.73)		
	384 sh (3.48)	384 (3.94)	384 (3.80)		406 (3.20)
372 (3.50)	370 (3.52)			365 (3.57)	
359 (3.94)				348 (3.60)	340 (3.59)
330 (3.82)	328 (3.78)			321 (4.19)	325 (3.69)
315 (3.89)		314 (4.82)	310 (4.72)	308 (4.07)	312 (3.71)
303 (3.98)	303 (3.95)	306 sh (4.73)		295 (3.83)	291 (3.80)
268 (4.65)	266 (4.63)		275 sh (4.07)	278 (4.05)	
		245 sh (4.21)	240 (4.20)	267 (4.31)	
		235 (4.28)		255 sh (4.51)	
				238 (4.58)	235 (4.55)
	225 (4.32)			231 (4.59)	231 (4.55)

^a Obtained on a Cary Model 14 recording spectrophotometer in the specified solvents. Wavelengths of maxima and shoulders (sh) are in $m\mu$; $\log \epsilon$ values in parentheses. ^b This spectrum is essentially unchanged on gradual dilution of the sulfuric acid with water until the acid concentration reaches 68.5%. On further dilution, the original spectrum rapidly loses intensity and no other spectrum develops. This is explained by the formation of the highly insoluble species 13. ^c Spectra of 10 and 12 show a certain resemblance to the reported (G. Berti, *J. Org. Chem.*, **22**, 230 (1957)) spectrum of the dibenzo [*a,d*]tropylium cation.

quantitatively, maroon crystals of 4, ^{4,5} mp 171–173°, *p*-nitrophenylhydrazone mp 283–285°.



The smoothness of this reaction, contrasting with the complete failure of 6 to undergo cyclization,⁶ is undoubtedly due to the favorable rigid geometry of 5 and to the stability of the developing (7 → 8) dibenz[*c,d,h*]azulenium cation. 4 is also formed when a H₂SO₄ solution of the 6,7-dihydro-4 (mp 66–67°)⁷ is kept at 80°.

As indicated by its infrared spectrum ($\nu_{C=O}$ 1685 cm^{-1}) and R_f values, 4 is highly polarized; a probable reason is the ground-state contribution of the dipolar form 9. In concentrated sulfuric or trifluoroacetic acid, 4 dissolves as the violet diprotonated⁸ species 10; by quenching such solutions with ice, 4 can be quantitatively recovered. Estimation of the basicity of 4 by the usual method⁹ or preparation of salt-like derivatives is prevented by its conversion, in moderately acid media¹⁰—presumably *via* 11—into a colorless, highly

(4) Satisfactory elemental analyses and mass spectra were obtained. Catalytic hydrogenation to the known^{6,7} 1,6,7,11b-tetrahydro derivative was carried out.

(5) Nmr (CDCl₃): singlets at (δ) 6.11, 6.45, and 6.47 (1 H each); multiplets centered at 7.28 and 7.83 (5 + 2 H).

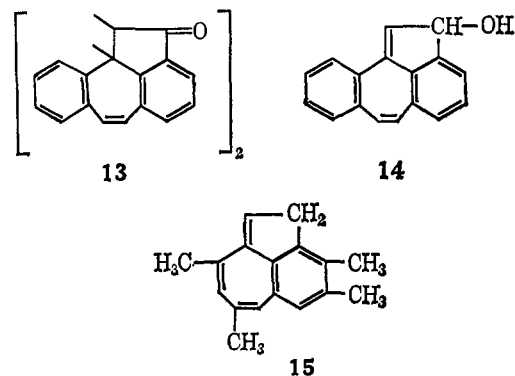
(6) C. Van der Stelt, A. Haasje, H. H. Terstege, and W. Th. Nauta, *Rec. Trav. Chim.*, **84**, 1466 (1965).

(7) A. J. Frey and E. Galantay, pending U. S. Patent application.

(8) Cryoscopic (100% H₂SO₄) i values were in the vicinity of 3.

(9) L. A. Flexer, L. P. Hammett, and A. Dingwall, *J. Am. Chem. Soc.*, **57**, 2103 (1935).

insoluble product (mp 240° dec, λ_{max}^{KBr} 1706 cm^{-1} ; $\lambda_{max}^{CH_2Cl_2}$ 277 $m\mu$ ($\log \epsilon$ 4.21)) thought to be one of the truxone-type¹¹ dimers 13. An apparent isomer, mp 305° dec, is obtained on irradiation (360 $m\mu$, Pyrex vessel) of 4 in CH₂Cl₂ solution. Both dimers regenerate 4 under sublimation conditions (160° (0.1 μ)) or on dissolution in H₂SO₄ followed by quenching with ice.



Reduction of 4 by an excess of NaBH₄ yields the yellow covalent alcohol 14,^{4,12} apparently the first stable compound incorporating a 2-unsubstituted 1-indenol moiety. Its ultraviolet spectrum (see Table I), with a pronounced fine structure, reveals relation to the tetramethylbenzazulene 15^{1b} rather than to 2,3,6,7-dibenzoheptafulvene.¹³ 14 is converted, by strong acids, to the violet dibenz[*c,d,h*]azulenium cation 12, solid derivatives of which (perchlorate¹⁴ mp 200° dec; tetrafluoroborate¹⁴ mp 177° dec) are, in the

(10) 11 *N* HCl; HClO₄-ether; (C₂H₅)₃O⁺BF₄⁻-CH₂Cl₂; see also footnote b in Table I.

(11) R. de Fazi, *Gazz. Chim. Ital.*, **253** (1919).

(12) Nmr (DMSO-*d*₆): multiplets centered at (δ) 7.85 (1 H), 7.28 (6 H), 5.32 (1 H), and 5.03 (1 H); doublet at 6.68 (1 H, J = 2.6 cps); singlet at 6.22 (2 H); with D₂O added, 5.32 resonance disappears, 5.03 collapses into doublet, J = 2.6 cps.

(13) E. D. Bergmann, E. Fischer, D. Ginsberg, Y. Hirschberg, D. Lavie, M. Mayot, A. Pullman, and B. Pullman, *Bull. Soc. Chim. France*, **18**, 684 (1951).

(14) Precipitated from dilute ethereal solutions of 14 and analyzed (C, H) without further purification. The nmr spectra of 10 and 12 showed line broadening. For a similar observation with phenalenium perchlorate, see ref 3.

absence of moisture, relatively stable. From their complicated reaction with water, no **14** or other pseudo-basic carbinol, but some **4**, can be recovered.

Interesting is the base-catalyzed air oxidation of **14** to **4**. Whereas, *e.g.*, an oxygen-free DMF solution of **14** and $\text{KOC}(\text{CH}_3)_3$, 0.5 *M* in each, is stable at room temperature, upon admission of air **4** is rapidly and exclusively formed.

Acknowledgment. We thank Professor James B. Hendrickson for his challenging discussions and Messrs. U. Stoeckli and H. Sylvester of our Analytical Department for nmr and ultraviolet spectra.

Eugene Galantay, Harry Agahigian, Nicholas Paoella
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Received May 16, 1966

7,12-Dihydropleiadenes. III. Conformational Preferences in 7-Alkyl-7,12-dihydropleiadenes

Sir:

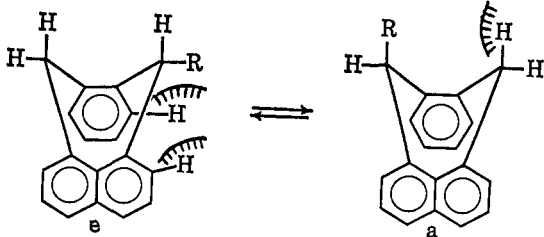
The effective steric bulks of methyl, ethyl, and isopropyl groups are generally considered^{1,2} to be of comparable magnitude and substantially less than the

to report on the conformational preferences of 7-methyl-, 7-ethyl-, and 7-isopropyl-7,12-dihydropleiadenes,⁵ noting that there are great differences in their conformational equilibria, contrary to the usually encountered similarities.

The two conformers of each 7-alkyl-7,12-dihydropleiadene were clearly evident in the low-temperature (*ca.* -20 to -40°) nmr spectra⁶ and were characterized by the appropriate C_7 -methine proton signal. We have previously shown that equatorial C_7 and C_{12} protons in 7,12-dihydropleiadenes (DHP) resonate at higher field than the axial protons.⁷ Comparison of $\delta_{\text{C}_7\text{-H}}$ with the chemical shifts of axial and equatorial C_{12} protons in the 7-alkyl-DHP's thus allows one to deduce the position of the methine proton, and consequently the alkyl group as well. Pertinent nmr data are presented in Table I.

The following conclusions emerge from the chemical shift data and integrated peak areas. (1) The major C_7 -methine quartet in 7-methyl-DHP appears at low field relative to the minor quartet. The former signal corresponds to the *axial* C_{12} -methylene proton and the latter with the *equatorial* C_{12} proton, these assignments having been established previously. Thus the main conformer has the C_7 -methyl group equatorial,⁸ with ΔF°_{253}

Table I. Low-Temperature Nmr Spectra of Conformational Isomers of 7-Alkyl-7,12-dihydropleiadenes^a



Compd	$\delta_{\text{C}_7\text{-H}}$	$\text{C}_7\text{-R}$	[a]/[e]	ΔF°_{253} , kcal/mole
7-Methyl-7,12-DHP-12,12- <i>d</i> ₂	e 303 (<i>J</i> ~ 7)	0.13 ^b	+1.0
	a 259 (<i>J</i> ~ 7)		
7-(Ethyl- α,α - <i>d</i> ₂)-7,12-DHP	e 293	e 64	1.05 ^c	0.0
	a 240	a 54		
7-(Ethyl- α,α - <i>d</i> ₂)-7,12-DHP-12,12- <i>d</i> ₂	e 294	e 66	$\geq 20^d$	-1.5 ^d
	a 242	a 55		
7-Isopropyl-7,12-DHP	a 209 (<i>J</i> [10])		

^a Measurements were made at $T = -20 \pm 2^\circ$ on an A-60 spectrometer equipped with A-6040 variable temperature controller; chemical shifts (probable accuracy ± 1 cps) are reported in cycles per second downfield from internal TMS in CDCl_3 solvent. The axial C_{12} -proton doublet appears at 306 ± 6 cps in all compounds not C_{12} deuterated, whereas the equatorial C_{12} protons showed up at 229 ± 7 cps (all geminal coupling constants *ca.* 15 cps). All ΔF° values reported are estimated to be accurate to ± 0.1 kcal/mole. ^b Integrated area of C_7 -proton signals. ^c Integrated area ratio of methyl signals (in $\text{C}_7\text{-CD}_2\text{CH}_3$). ^d No detectable signal for conformer e (therefore, $\ll 5\%$ present, if any).

corresponding bulk of the spherically symmetrical *t*-butyl group, due to the ability of the unsymmetrical ethyl and isopropyl substituents to rotate in such a way that their β -methyl groups are removed from compression with proximal atoms.^{1,2} The resulting small decrease in entropy produces only minor changes in the conformational energies of these alkyl groups on cyclohexanes^{1,2} and their effect on acid-base equilibria^{3,4} and nucleophilicity of 2-alkylpyridines.^{3,4} We wish

- (1) (a) E. L. Eliel, *Angew. Chem. Intern. Ed. Engl.*, **4**, 761 (1965); (b) E. L. Eliel and T. J. Brett, *J. Am. Chem. Soc.*, **87**, 5039 (1965).
(2) (a) N. L. Allinger and L. A. Freiberg, *J. Org. Chem.*, **31**, 894 (1966); (b) N. L. Allinger and S. E. Hu, *ibid.*, **27**, 3417 (1962).
(3) V. Gold, *Progr. Stereochem.*, **3**, 172, 191 (1962).
(4) H. C. Brown, *J. Chem. Educ.*, **36**, 424 (1959).

(5) All compounds gave satisfactory elemental analyses and had spectral properties consistent with their structures.

(6) A variety of dihydropleiadenes show free energy barriers for ring inversion of *ca.* 13.5–15 kcal/mole (P. T. Lansbury, J. F. Bieron, and M. Klein, *J. Am. Chem. Soc.*, **88**, 1477 (1966)). Thus, whereas isolation and study of diastereomeric conformers of 7-alkyl-DHP's are virtually impossible, it is nevertheless quite simple to "freeze out" ring inversion, on the nmr time scale, at temperatures of *ca.* -10° and below.

(7) P. T. Lansbury, J. F. Bieron, and A. J. Lacher, *ibid.*, **88**, 1482 (1966).

(8) Additional evidence for the equatorial preference of methyl comes from base-catalyzed equilibration studies of *cis*- and *trans*-7,12-dimethyl-7,12-dihydropleiadenes, where it was shown that the former isomer (diequatorial) predominates at equilibrium. By contrast, *trans*-7,12-dimethoxy-7,12-DHP predominated over the *cis* isomer after acid-catalyzed equilibration in methanol, as predicted from the previously observed *axial* preferences of the methoxyl group. These studies will be discussed further in the full paper.