Calcd. for $C_{22}H_{17}IS$; I, 28.84; S, 7.29. Found: I, 28.31, 28.49; S, 7.66. When II is heated in cyclohexane at the boiling temperature until all has dissolved, or when II and III are exposed in CCl_4 to sunlight or ultraviolet light for 48 hours, with stirring, at room temperature and under nitrogen, decomposition occurs to iodo compounds and free radicals which react with each other and with the solvent. From II and cyclohexane has been isolated and identified, 2-iodobiphenyl (72%), 2,2′-dinaphthyl disulfide (IV, 9%) and 2-naphthylcyclohexyl sulfide (V, 57%), m.p. 47°. *Anal.* Calcd. for $C_{16}H_{18}S$: C, 79.28; H, 7.49; S, 13.23. Found: C, 79.46; H, 7.61; S, 13.38. Oxidation of V yields the sulfone, m.p. 98°. *Anal.* Calcd. for $C_{16}H_{18}O_2S$: C, 70.04; H, 6.61; S, 11.69. Found: C, 70.28; H, 6.70; S, 11.59. II and CCl_4 has afforded 2-chloro-2′-iodobiphenyl (52%), diphenyleneiodonium chloride (12%), and IV (12%). III and cyclohexane exposed to ultraviolet light has given benzene (30%, determined by quantitative vapor phase chromatography), phenyl iodide (99%, v.p.c.), IV (17%), V identified as sulfone and 2-naphthylphenyl sulfide characterized as sulfone, m.p. 115°. *Anal.* Calcd. for $C_{16}H_{12}O_2S$: C, 71.64; H, 4.51; S, 11.95. Found: C, 71.34; H, 4.70; S, 11.95. III and CCl_4 has afforded phenyl chloride (28% v.p.c.), phenyl iodide (94%, v.p.c.), IV, and diphenyliodonium chloride (5%).

A possible mechanism for the decomposition in cyclohexane is[6]

$$R_2ISR' \longrightarrow RI + R\cdot + R'S\cdot$$
$$2R'S\cdot \longrightarrow R'\text{-}S\text{-}S\text{-}R'$$
$$R\cdot + C_6H_{12} \longrightarrow RH + C_6H_{11}\cdot$$
$$R'S\cdot + C_6H_{11}\cdot \longrightarrow R'SC_6H_{11}$$
$$R'S\cdot + R\cdot \longrightarrow R'SR$$

The addition of the anion of dimedone in water to I in water affords the *colorless dihydrate* of the iodonium dimedone derivative (V·2H_2O). *Anal.* Calcd. for $C_{20}H_{19}O_2I\cdot 2H_2O$: H_2O, 7.93. Found: H_2O, 7.50. Heating at 50° or drying at room temperature in vacuum yields the *yellow, anhydrous* V. *Anal.* Calcd. for $C_{20}H_{19}O_2I$: I, 30.34. Found: I, 30.38, 30.20. The reversible reaction shown is demonstrated readily and may indicate the facile change of a covalent bond to a bond which is less covalent.[7] Diphenyleneiodonium hydroxide has

$$\underset{\text{colorless}}{V\cdot 2H_5O} \underset{25^\circ \text{ in air}}{\overset{50^\circ \text{ in air}}{\rightleftarrows}} \underset{\text{yellow}}{V + 2H_5O}$$

been obtained as a colorless monohydrate. *Anal.* Calcd. for $C_{12}H_9OI\cdot H_2O$: H_2O, 5.73. Found: H_2O, 5.75. It changes at 75° to the *pale yellow* and *brown* anhydrous hydroxide. *Anal.* Calcd. for $C_{12}H_9OI$: I, 42.86. Found: I, 42.80, 43.14. This is interesting in view of the fact that Caserio, Glusker and Roberts[8] have obtained very convincing evidence for homolytic fission in the hydrolysis of iodonium salts. They suggest the formation of an unstable *covalent iodonium hydroxide.* Diphenyleneiodonium sulfate and the anion of barbituric acid has afforded a *colorless* monohydrate and a *yellow anhydrous* derivative. Similarly the anion from 2-phenyldimedone has yielded a *bright yellow* derivative.

This work is being continued and a complete description will be published later.

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decomposes slowly at room temperature, is stable at 10° in the dark, and has been known to *decompose with some violence*, when attempts have been made to pulverize it. Getting III on the skin should be avoided. In the original preparation, II and III are collected rapidly, washed with water and air dried.

[6] Diphenyl and diphenyleneiodonium tosylate (anion a "weak" nucleophile) undergo no detectable decomposition in CCl_4 when exposed to ultraviolet light for 4 days.

[7] Although there is no conclusive evidence for the covalence of V, the proposal may have significance in view of the work of Beringer, *et al.* (F. M. Beringer, P. S. Forgione and M. D. Yudis, *Tetrahedron*, **8**, 49 (1960); F. M. Beringer, A. Brierley, M. Drexler, E. M. Gindler and C. C. Lumpkin, *J. Am. Chem. Soc.*, **75**, 2708 (1953)) who have found that reactions of iodonium salts with the anion of dimedone in methanol and ethanol gave mainly products arising from *dehydrogenation* of the solvent. In contrast to this, with no dimedone, reactions of iodonium salts with sodium methoxide in methanol gave anisole and its derivatives.

[8] M. C. Caserio, D. L. Glusker and J. D. Roberts, *ibid.*, **81**, 336 (1959).

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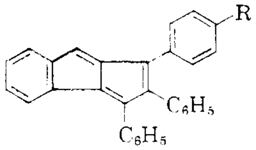
PSEUDOAROMATICS: SYNTHESIS OF 1,2,3-TRIPHENYLBENZOPENTALENE AND 1-(*p*-METHOXYPHENYL)-2,3-DIPHENYLBENZOPENTALENE

Sir:

Because its coplanar conjugated tricyclic system contains only 4n π-electron, the pseudoaromatic,[1] benzopentalene (cyclopent[*a*]indene), is of interest to both the theoretical and organic chemist. While calculations predict some interesting properties for benzopentalene,[2] all efforts to synthesize this pseudoaromatic[3] as well as several of its mono and di-substituted derivatives[4] have thus far been unsuccessful[5].

In contrast the 1,2,3-triarylbenzopentalenes, Ia and Ib, are readily prepared and isolated.



Ia, R = H
b, R = OCH_3

Excess lithium aluminum hydride in tetrahydrofuran reduced 2,3,3a,8a-tetrahydro-3,3a-dihydroxy-1,2,3-triphenylcyclopent[*a*]inden-8-[1*H*]-one[6] [m.p.

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[1] For pertinent discussion of pseudoaromaticity see: (a) D. P. Craig, *J. Chem. Soc.* 3175 (1951); (b) W. von E. Doering and D. W. Wiley, *Tetrahedron*, **11**, 183 (1960).

[2] (a) B. Pullman, *et al.*, *J. Chim. Soc.*, **49**, 24 (1952); (b) D. Peters, *J. Chem. Soc.*, 1028 (1958).

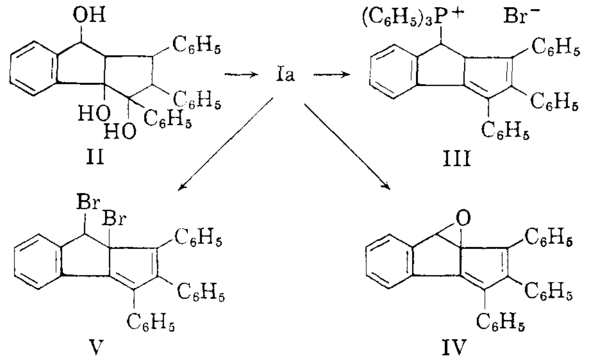
[3] W. Baker and P. G. Jones, *ibid.*, 787 (1951).

[4] (a) L. H. Groves and G. A. Swan, *ibid.*, 867 (1951); (b) W. Baker, V. F. W. McOmie and T. L. V. Ulbricht, *ibid.*, 4022 (1957); (c) H. Dahn, *Helv. Chim. Acta*, **34**, 1087 (1951).

[5] As yet, no simple pentalenes are known [see reviews in "Nonbenzenoid Aromatic Compounds" (D. Ginsburg, editor), Interscience Publishers, New York, N. Y., 1959 and M. E. Vol'pin, *Uspekhi Khim.*, **29**, 298 (1960)] however, several fused ring derivatives have been reported: (a) 5,10-disubstituted indeno[2,1-*a*]indenes, K. Brand, *Ber.*, **45**, 3071 (1912); (b) indeno[2,1-*a*]indenes, C. T. Blood and R. P. Linstead, *J. Chem. Soc.*, 2263 (1952); (c) 3,5-dimethylcyclohepta-[c,d]pentalene, K. Hafner and J. Schneider, *Ann.*, **624**, 37 (1959).

[6] M. V. Ionescu and O. G. Popescu, *Bull. soc. chim. France*, **51**, 1231 (1932).

110–120°. Calcd. for $C_{30}H_{24}O_3$: C, 83.31; H, 5.59; found: C, 83.31; H, 5.84. Infrared (chloroform): 2.82, 3.33, 5.85, 6.25μ] to the triol II [m.p. 241–242°. Calcd. for $C_{30}H_{26}O_3$: C, 82.92; H, 6.03; found: C, 82.92; H, 6.04. Infrared (chloroform): 2.80, 2.92, 6.24μ]. Dehydration of triol II with phosphorus oxychloride in excess pyridine for 1 hr. at 80–90° afforded in 70% yield a green crystalline hydrocarbon, Ia [m.p. 186–187°. Calcd. for $C_{30}H_{20}$: C, 94.70; H, 5.30; mol. wt., 380.5; found: C, 94.70, 94.50; H, 5.47, 5.47; mol. wt. 390 (Signer–Clark). $\lambda\lambda_{max}$ mμ (log ε): 272 (4.47), 293 (4.48), 409 (3.89), 425sh (3.85), 585 (2.39); $\lambda\lambda_{min}$ 240 (4.13), 278 (4.47), 351 (3.66), 500 (2.28), 791 (1.83) (cyclohexane). Infrared (chloroform): 3.24, 6.24, 6.34, 6.67, 6.73, 6.90 μ. N.m.r.($DCCl_3$): complex benzenoid multiplet centered at $\tau = 3.1$ and a singlet at $\tau = 3.75$ (=CH—) in the ratio of 19:1. While Ia is stable to air, heat, and moderately strong acid (it is not extracted from a cyclohexane solution with either 85% phosphoric or 50% sulfuric acids, but is slowly destroyed over several days), nucleophiles rapidly react with it. Strongly nucleophilic substances (pyrrolidine, hydroxide and methoxide ions) quickly destroy Ia while weaker nucleophiles rapidly form isolatable addition product: triphenylphosphine hydrobromide (in CH_3CN)[7] forms in 39% yield a yellow crystalline adduct, III [m.p. 189–190.5°. Calcd. for $C_{48}H_{36}BrP$: C, 79.66; H, 5.01; Br, 11.04; P, 4.28; found: C, 79.65; H, 5.24; Br, 11.00; P, 4.29. $\lambda\lambda_{max}$ mμ (log ε): 248 (4.51), 269 (4.43), 356 (4.03) (CH_3CN). N.m.r. ($DCCl_3$): doublet at $\tau = 1.27$, complex benzenoid multiplet centered at $\tau = 2.6$, and a doublet at $\tau = 4.17$ in the approximate ratio of 1:34:1]. Alkaline hydrogen peroxide converts Ia in 71% yield to a light and air sensitive yellow compound [m.p. 166–167° (dec.). Calcd. for $C_{30}H_{20}O$: C, 90.88; H, 5.09; found: C, 90.11; H, 5.13. Infrared (chloroform): 3.34, 6.27, 6.37, 6.43μ. $\lambda\lambda_{max}$ mμ (log ε): 257 (3.35), 281 (4.35), 400 (3.68) (cyclohexane). N.m.r. ($DCCl_3$): complex benzenoid centered at $\tau = 2.8$ and a singlet at $\tau = 5.15$] tentatively assigned structure IV. Bromine in carbon tetrachloride instantly adds to Ia to form in 75% yield an orange dibromo adduct, V [m.p. 167–168°. Calcd. for $C_{30}H_{20}Br_2$: C, 66.67; H, 3.73; found: C, 66.77; H, 3.98. $\lambda\lambda_{max}$ mμ (log ε): 253 (4.45), 293 (4.38), 393 (3.59) (cyclohexane). N.m.r. ($DCCl_3$): complex benzenoid multiplet centered at $\tau = 2.8$ and a singlet at $\tau = 3.53$]. Alkaline permanganate oxidation of Ia affords benzil and benzoic acid.



To establish unambiguously the trisubstituted benzopentalene structure for Ia the methoxy labeled derivative, Ib [m.p. 176–177°. Calcd. for $C_{31}H_{22}O$: C, 90.70; H, 5.40; found: C, 90.53; H, 5.62. $\lambda\lambda_{max}$ mμ (log ε): 225sh (4.42), 268 (4.54), 303 (4.54), 391sh (3.88), 408 (3.91), 605 (2.59). N.m.r. ($DCCl_3$): complex benzenoid multiplet centered at $\tau = 3.1$, a singlet at $\tau = 3.72$ (=CH—), and methoxy singlet at $\tau = 6.28$] was prepared in a manner analogous to Ia and oxidized with alkaline permanganate. The identification of benzil and *p*-methoxybenzoic acid among the oxidation products coupled with the observed physical and chemical properties are only compatible with a triarylated benzopentalene.

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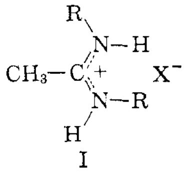
RECEIVED FEBRUARY 9, 1962

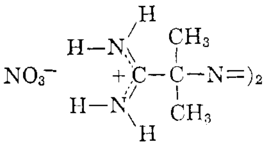
THE NATURE OF AMIDINIUM GROUPS

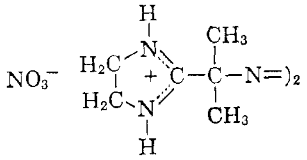
Sir:

Structures of amidinium salts of types I and II have been investigated by n.m.r. techniques.


I

Ia. R = H, $X^- = Cl^-$
Ib. R = H, $X^- = NO_3^-$
Ic, R = CH_3, $X^- = Cl^-$


IIa


IIb

These conclusions have been reached: (1) rotation about C$\overset{\cdots}{-}$N bonds is restricted; (2) compound Ic exists in the configuration indicated with magnetically nonequivalent pairs of H's and R's and *nitrogens which differ in chemical reactivity;* (3) proton exchange in dilute aqueous acid involves hydroxide ion and (4) exchange in strongly acidic media involves formation of second conjugate acids.

The spectra of Ia–c and IIa in anhydrous dimethylsulfoxide (Table I) show two resonance signals of equal intensity for nitrogen protons.

TABLE I

CHEMICAL SHIFTS OF GROUPS ATTACHED TO NITROGEN IN AMIDINIUM SALTS

Compound	Solvent	N-H(c.p.s.)[a]	N-CH_3(c.p.s.)[a]
Ia	DMSO[b]	530, 560	....
Ib	DMSO	530, 560	....
Ic	DMSO	554, 609	171.5, 176.5[c]
Ic	H_2O	.....	177.5, 187.0
Ic	15% H_2SO_4-H_2O	~425, ~455	179.0, 188.5[c]
IIa	DMSO	534, 547	....
IIb	DMSO	608	....

[a] Referred to tetramethylsilane (external), downfield, 60 M., room temperature. [b] Dimethylsulfoxide. [c] Positions of doublet centers ($J = 5.0$ c.p.s. for each doublet).

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[7] H. Hoffman, *Ber.*, **94**, 1331 (1961).