found, C, 83.6; H, 6.17). The absorption spectrum of the latter (λ_{max}^{EtOH} 281 mμ, ε 13,400) shows that one aromatic ring of the three has been modified, while in the n.m.r. spectrum (split aryl hydrogens at 2.83τ, vinyl hydrogens 3.73–4.68τ, unsplit CH_2 6.32τ, CH_3O 6.57τ, allylic hydrogens 6.80–8.18τ) the complexity of splitting for the resulting vinyl H's points to a dimeric structure.

The conclusion that the failure of the triphenylmethyl group to migrate is in part due to steric factors, suggested by the normal rearrangement of diphenylacetyldiazomethane,[4] was strengthened by the results with 9-phenylfluorene-9-carbonyldiazomethane (V, m.p. 159–160° dec.; diazo N, 99% of calcd.). With hot 1-hexanol and N-ethylmorpholine, or with triethanolamine, then hydrolysis and esterification, both the normal (VI, m.p. 91.5–92.5°; $C_{22}H_{18}O_2$, found: C, 84.0; H, 5.74) and abnormal (VII, m.p. 100.6–101.4°; found: C, 84.0; H, 5.86) esters were isolated in a ratio of *ca.* 2:1. The structure of VI-acid was confirmed by synthesis from 9-phenyl-9-fluorenol and malonic acid.[5] VII-acid was decarboxylated to 1-methyl-9-phenylfluorene, identified by comparison with an authentic sample (m.p. 153–153.5°; $C_{20}H_{16}$, found: C, 93.8; H, 6.38) synthesized from 1-methyl-9-fluorenone.

The obvious possibility that these abnormal products arise by cyclization to an indanone, with subsequent cleavage, either during rearrangement or the later hydrolysis, appears not to be the case. Crude triphenylacetyldiazoethane, on heating in γ-collidine with or without benzyl alcohol, did give 1,1-diphenyl-3-methyl-2-indanone[4] (m.p. 154.5–156°; $\lambda_{max}^{CHCl_3}$ 5.78μ; $C_{22}H_{18}O$, found: C, 88.3; H, 6.07). But the diazoketone I *did not* give 1,1-diphenyl-2-indanone under similar conditions, and the latter failed to give IIIa, either on direct alkaline hydrolysis or subsequent to longer heating with 1-hexanol and N-ethylmorpholine than for the rearrangement of I; thus the indanone seems to be ruled out as an intermediate. The elegant cyclization of 5-hexenoyldiazomethane to [0,1,4]-bicycloheptanone-2 reported recently,[6] therefore, is not mechanistically similar to the present abnormal rearrangements, but probably is to the formation of 1,1-diphenyl-3-methyl-2-indanone.

In contrast to the complete failure of the triphenylmethyl group of diazoketone I to migrate under thermal Wolff rearrangement conditions, triphenylacetyl azide underwent normal Curtius rearrangement to the isocyanate (m.p. 92.5–93°, λ_{max}^{KBr} 4.43μ; $C_{20}H_{15}NO$, found: C, 84.4; H, 5.02) so easily that the azide (m.p. 94.5–98° dec.; λ_{max}^{KBr} 4.69s, 5.87s and weak peak at 4.43μ) contained some isocyanate even when prepared and dried at 0°.

Evidently abnormal isomers such as IIIa and VII can result in substantial yields instead of or accompanying the normal product of an Arndt–Eistert synthesis. Although the present examples are derived from triaryl substituted acetic acids, it is to be expected that others may result from sterically hindered acids having a π-electron system suitably disposed for reaction in the diazoketone and with a cleavable bond to the carbonyl group.[7]

Ultraviolet initiated rearrangement of diazoketone I in tetrahydrofuran–water, gave the *normal* acid II and V gave VI-acid with none of VII-acid isolable. The significance of these and related results for the mechanisms of the Wolff rearrangement, and the lack of any real evidence for a ketocarbene–ketene mechanism for the thermal procedure, will be discussed elsewhere.

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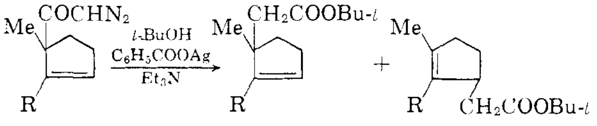
[5] *Cf.* the synthesis of II by L. Hellerman, *J. Am. Chem. Soc.*, **49**, 1737 (1927).

[6] G. Stork and J. Ficini, *ibid.*, **83**, 4678 (1961).

[7] ADDENDUM: Products from the Arndt–Eistert synthesis with β,γ-unsaturated acids should be examined critically, particularly when steric hindrance is involved. Professor M. S. Newman has pointed out a case of such an abnormal rearrangement in their work; see G. Eglinton, J. C. Nevenzel, M. S. Newman and A. I. Scott, *Chemistry and Industry*, 686 (1953); *J. Am. Chem. Soc.*, **78**, 2331 (1956). Structure A is postulated for the abnormal product (personal communication from Drs. Eglinton, Newman and Scott).



R = 6-methoxy-2-naphthyl- A

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STABLE COMPOUNDS FROM IODONIUM SALTS AND "STRONG" NUCLEOPHILES

Sir:

The addition of an iodonium halide to a "strong" nucleophile such as an organometallic compound or the sulfide ion, gives rise to a transient *yellow* color or an unstable *yellow* to *orange* precipitate.[1,2,3]

We wish to report the preparation of *stable, yellow* compounds from iodonium salts and the anion from 2-naphthalenethiol and the anions from some diketones. Rapid addition of less than the stoichiometric amount of 2-naphthalenethiol in dilute aqueous NaOH to diphenyleneiodonium chloride (I) in H_2O, affords a *yellow stable* compound, and we propose that this compound is a covalent 2 naphthyl sulfide II, m.p. 94°, dec. *Anal.* Calcd. for $C_{22}H_{15}IS$: I, 28.95; S, 7.32.[4] Found: I, 28.54, 29.20; S, 7.32. Similarly diphenyliodonium chloride and the anion of 2-naphthalenethiol affords III,[5] *yellow,* m.p. 74–78°, dec. *Anal.*

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[1] F. M. Beringer, J. W. Dehn, Jr., and M. Winicov, *J. Am. Chem. Soc.*, **82**, 2948 (1960). Beringer, *et al.*, propose the formation of trisubstituted iodides which decompose into free radicals which react with each other and the solvent.

[2] (a) C. Hartmann and V. Meyer, *Ber.*, **27**, 502 (1894); (b) R. B. Sandin, F. T. McClure and F. Irwin, *J. Am. Chem. Soc.*, **61**, 2944 (1939); (c) R. B. Sandin, R. G. Christiansen, R. K. Brown and S. Kirkwood, *ibid.*, **69**, 1550 (1947).

[3] Only two trisubstituted iodine compounds have been isolated. Both are *yellow* and readily decompose; see (a) G. Wittig and K. Clauss, *Ann.*, 578, 136 (1952); (b) K. Clauss, *Chem. Ber.*, **88**, 258 (1955).

[4] The ultraviolet spectrum of II in ethanol is different from that of the iodonium chloride (I) or the tosylate in ethanol, which show the characteristic peak, 263 mμ (log ε 4.05) of the diphenyleneiodonium cation; see H. Irving, G. P. A. Turner and R. W. Reid, *J. Chem. Soc.*, 2082 (1960). In this region II shows continuous absorption from 214 mμ to 290 mμ. Moreover the spectrum of II in ethanol is not due to decomposition products which show a different spectrum. In dimethyl sulfoxide II shows λ_{max} 364 mμ (log ε ~ 4.00) which is not shown by the tosylate *in dimethyl sulfoxide*. The spectrum of II in ethanol gives no indication of the anion of 2-naphthalenethiol which shows peaks at 263, 297 and 306 mμ, all of high intensity; see R. B. Hannan, Jr., J. H. Lieblich and A. G. Renfrew, *J. Am. Chem. Soc.*, **71**, 3733 (1949).

[5] Although II has been kept at room temperature for several months without any evident decomposition, III in the dry condition

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]

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

The addition of the anion of dimedone in water to I in water affords the *colorless dihydrate* of the iodonium dimedone derivative ($V\cdot 2H_2O$). *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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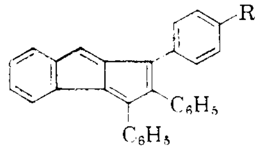
PSEUDOAROMATICS: SYNTHESIS OF 1,2,3-TRIPHENYLBENZOPENTALENE AND 1-(*p*-METHOXYPHENYL)-2,3-DIPHENYLBENZOPENTALENE

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).