Since the observed life should be the reciprocal of the sum of all first order rate constants it is at present impossible to tell what rate constant to use for the self-quenching of benzene vapor fluorescence. The effective cross section will be either about 0.04 or 0.15×10^{-16} cm.^{2} depending on the assumption made.

If a mixture of benzene and biacetyl vapors is irradiated at 2537 Å. there is dissociation of the biacetyl sensitized by the benzene with a quantum yield of about 0.06, corresponding roughly to that in pure biacetyl at 3130 Å.[8] Thus, as would be expected, not all of the electronic energy of the benzene is used to activate the biacetyl. There is also strong emission from the biacetyl and the ratio of phosphorescence to fluorescence is very high and may be infinity. This strongly suggests the presence of triplet state benzene molecules which transfer energy to normal biacetyl to produce excited triplet state molecules.

In a mixture of 20 mm. of benzene and 0.1 mm. of biacetyl the efficiency of the phosphorescent emission of the biacetyl is about 0.12. The benzene fluorescence efficiency under these conditions is about 0.22, *i.e.*, 78% of the absorbing benzene molecules do not fluoresce. If now one assumes that every benzene molecule which does not fluoresce goes to the triplet state by an intersystem cross-over and then is deactivated by biacetyl to produce triplet state biacetyl molecules the fraction of these which should phosphoresce is 0.15.[5] Thus the expected phosphorescence efficiency from the biacetyl would be $0.78 \times 0.15 = 0.12$, in far better agreement with the found value than the data warrant.

The rate of the process benzene (triplet) + biacetyl = biacetyl (triplet) + benzene may not be estimated in the absence of knowledge of the mean life of the triplet state of benzene. Unless it is much less than a second the effective cross section for this reaction would be extremely small. If it is about the same as for other aromatic hydrocarbons[11] the effective cross section is reasonable.

The data strongly suggest, therefore, that in the gas phase every benzene molecule which absorbs at 2537 Å. either fluoresces or crosses over to a triplet state. The fates of the triplet state molecules are at present unknown in detail. They may do one of several things: (a) cross over to the ground state with ultimate loss of vibration energy by collision; (b) be destroyed on the walls; (c) undergo reaction to an intermediate which reverts ultimately to normal benzene. More work on this subject is needed.

(11) G. Porter and F. J. Wright, *Trans. Faraday Soc.*, **51**, 1205 (1955).

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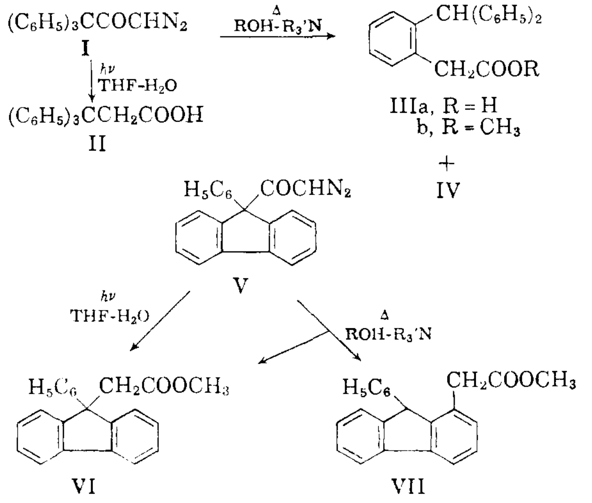
RECEIVED MARCH 7, 1962

ABNORMAL ACIDS FROM THE ARNDT-EISTERT SYNTHESIS

Sir:

Because of brevity, convenience and structural reliability of the product, the Arndt–Eistert synthesis has become the standard method for converting an acid into its higher homolog. Wolff rearrangement of the intermediate diazoketone derived from diazomethane or higher diazohydrocarbons can be made to go satisfactorily in nearly all cases by one of the improved rearrangement procedures,[1,2,3] often in excellent yield. We are now reporting an example in which this rearrangement not only failed to go normally, but gave abnormal acid derivatives isomeric with the expected product.

Triphenylacetyldiazomethane (I, m.p. 162.5–164.5° dec.; $C_{21}H_{16}N_2O$, found: C, 80.3; H, 5.12; diazo N, 96% of calcd.), prepared in excellent yield from the acid chloride, failed[4] to undergo normal rearrangement by the silver oxide–methanol, silver benzoate–triethylamine–methanol,[2] or even the tertiary amine–high boiling alcohol (at 180°) procedure,[1] which in our hands has never failed otherwise. In all cases in which nitrogen was evolved the product was not the normal rearranged ester, and failed to give the acid II on hydrolysis. With pyridine and benzyl alcohol at 110° and then hydrolysis, I gave 40% of the isomeric acid IIIa (m.p. 207.5–208.5°; $C_{21}H_{18}O_2$, found: C, 83.65; H, 5.76). The structure of IIIa was established by Arndt–Eistert synthesis from triphenylmethane-*o*-carboxylic acid and preparation from I by a second sequence. Heating I with boron trifluoride in ether gave 90–100% of 1,1-diphenyl-2-indanone (m.p. 129–130.5°, 120.5–121.5°; λ_{max}^{EtOH} 262, 267, 276 and 303 mμ, ϵ 1720, 1850, 1630 and 545; $\lambda_{max}^{CHCl_3}$ 5.77 μ; $C_{21}H_{16}O$, found: C, 88.4; H, 5.91), which was cleaved to IIIa by potassium hydroxide at 190°.



Heating triphenylacetyldiazomethane (I) with 1-hexanol and N-ethylmorpholine, followed by alkaline hydrolysis and esterification, gave 35% of the abnormal methyl ester IIIb (m.p. 79.5–80.5°; $C_{22}H_{20}O_2$, found: C, 83.4; H, 6.27) and 18% of a second abnormal ester IV (m.p. 178.5–179°;

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(1) A. L. Wilds and A. L. Meader, Jr., *J. Org. Chem.*, **13**, 763 (1948).

(2) M. S. Newman and P. F. Beal, *J. Am. Chem. Soc.*, **72**, 5163 (1950).

(3) L. Horner, E. Spietschka and A. Gross, *Ann.*, **573**, 17 (1951).

(4) John Van Den Berghe, Ph.D. Thesis, University of Wisconsin, 1952.

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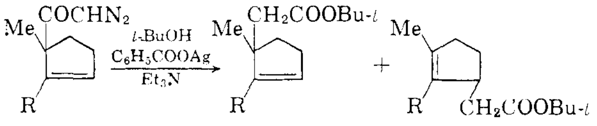
(5) *Cf.* the synthesis of II by L. Hellerman, *J. Am. Chem. Soc.*, **49**, 1737 (1927).

(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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RECEIVED FEBRUARY 14, 1962

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