these data, are $\Delta H_1^* = 10.9 \pm 0.5$ kcal./mole and $\Delta S_1^* = -17 \pm 2$ e.u. and are, within experimental error, the same for the hydrido and deuterido compounds.

The large *trans* effect of hydride cannot be associated with π-bonding effects such as have been invoked to explain the large *trans*-labilizing influence of other ligands, *e.g.*, CO and CN^-, and has been attributed[1] instead to the high polarizability and inductive influence of the hydride ion. It is unlikely that either of these are sufficiently different for deuteride and hydride to account for the large observed kinetic isotope effect. Instead it seems likely that this isotope effect reflects weakening of the Pt–H (Pt–D) binding in the transition state, relative to the initial reactant state, owing to electron donation to the platinum by the incoming pyridine ligand. This is consistent with, and may be considered as providing some supporting evidence for, the widely accepted interpretation of the substitution reactions of square-planar platinum(II) complexes in terms of an SN2 mechanism involving a five-coordinate (possibly trigonal bipyramid) transition state.

It would be of interest in the light of these observations to determine the corresponding labilizing influence and secondary isotope effect for a *cis*-hydride ligand, *e.g.*, in the substitution of pyridine for chloride in the complex *cis*-$PtHCl(PEt_3)_2$. Unfortunately, attempts to prepare this compound do not appear thus far to have been successful.

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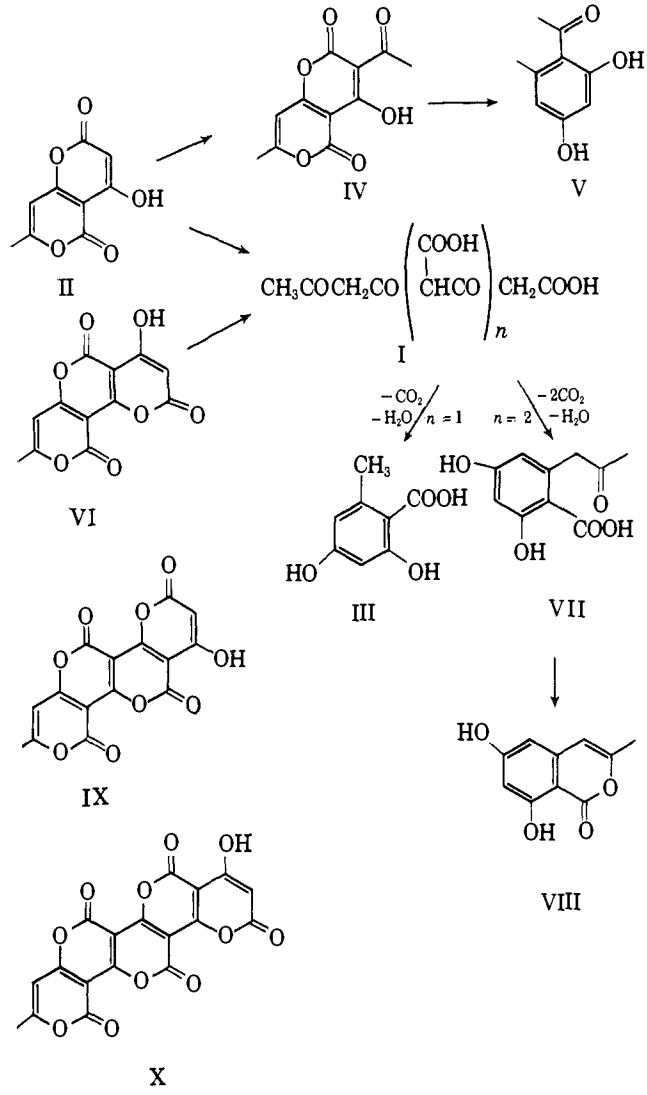
Chemistry of Polypyrones. A Model for Acetogenin Biosynthesis

Sir:

In marked contrast to our intimate knowledge of the (reductive) condensation of acetate and malonate units in fatty acid biosynthesis,[1] the details of metabolism intermediary between acetate–malonate primers and their "polyketide"-derived natural products can at present only be inferred by structural analogy. Thus, satisfactory *rationalization* of the biogenesis of many plant and fungal products can be made by assuming intervention of an acetate–malonate chain (*e.g.*, I),[2] followed by appropriate aldol condensation and decarboxylation.[3-5]



The chemistry of polypyrones (as II) offers not only facile construction of any desired number of acetate–malonate units condensed in a stable, highly crystalline progenitor of the proper head-to-tail sequence but also the opportunity to study for the first time the reactions of poly-β-ketones containing five or more acetate residues.[6]

Thus, treatment of II[7] [λ_{max}^{EtOH} 270 and 330 mμ (log ϵ 3.81 and 3.76)] (prepared from malonyl dichloride and triacetic acid lactone) with methanolic potassium hydroxide solution affords orsellinic acid (III), the prototype of numerous fungal constituents,[4] presumably *via* the anion of I ($n = 1$). Similarly, the acetylpyronopyrone (IV) [λ_{max}^{EtOH} 230, 240, 260, and 347 mμ (log ϵ 3.84, 3.81, 3.72, and 3.93)] (from II and acetyl chloride) is transformed into 2,4-dihydroxy-6-methylacetophenone (V).[8]

This simulation of polyacetate aromatic biosynthesis is further maintained in the trispyrone (VI) [from II and malonyl chloride; λ_{max}^{EtOH} 253, 280, and 373 mμ (log ϵ 3.83, 3.94, and 4.04)] which undergoes decarboxylative

(1) See, *e.g.*, F. Lynen and M. Tada, *Angew. Chem.*, **73**, 513 (1961); R. Bressler and S. J. Wakil, *J. Biol. Chem.*, **237**, 1441 (1963), and references cited.
(2) An arbitrary choice employing acetoacetate as primer.
(3) A. J. Birch, *Proc. Chem. Soc.*, 3 (1962).
(4) J. H. Richards and J. B. Hendrickson, "The Biosynthesis of Steroids, Terpenes, and Acetogenins," W. A. Benjamin, Inc., New York, N. Y., 1964.
(5) R. Robinson, "Structural Relations of Natural Products," Clarendon Press, Oxford, England, 1955.
(6) *Cf.* A. J. Birch, P. Fitton, D. C. C. Smith, D. E. Steere, and A. R. Stelfox, *J. Chem. Soc.*, 2209 (1963).
(7) The identities of III, V, VII, and VIII were established by mixture melting point and spectroscopic comparison with authentic samples. Satisfactory analytical data and mass, n.m.r., and infrared spectra were obtained for the new compounds described.
(8) K. Hoesch, *Chem. Ber.*, **48**, 1122 (1915); D. J. Cram and F. W. Cranz, *J. Am. Chem. Soc.*, **72**, 595 (1950).

condensation in base (*via* I; $n = 2$) to a separable mixture of crystalline products, the most abundant of which are the mould metabolite C-acetylorsellinic acid (VII) and its close relative 3-methyl-6,8-dihydroxyisocoumarin (VIII).[9,10]

The nature of the minor constituents of the above condensation and the conversion of the next appropriate members of the series (IX) and X (prepared by successive condensations of VI with malonyl chloride and respectively equivalent to six and seven "acetate" units) to naturally occurring phenols, antibiotics, and macrolides are under investigation, as is the possible role of polypyrones in aromatic biosynthesis.

(9) A. E. Oxford and H. Raistrick, *Biochem. J.*, 27, 634, 1473 (1933).
(10) R. F. Curtis, P. C. Harries, and C. H. Hassall, *J. Chem. Soc.*, 5382 (1964).
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The Intramolecular Cyclization of Two-Living-Ended Polystyrene Caused by Anthracene Addition. The Implications for Synthetic Problems

Sir:

In the course of studies of electron-transfer processes carried out in this laboratory, it was found[1] that living polystyrene, $\sim S^-,Na^+$, associates with anthracene, A, into a 1:1 complex, denoted further as $\sim S^-,A,Na^+$. The absorption band of living polystyrene, λ_{max} 340 mμ (ϵ 1.2 × 10^4), disappears in the reaction and a new band, distinct from that of sodium anthracene, A^-,Na^+, appears at λ_{max} 441 mμ (ϵ 2.7 × 10^4). The conversion is virtually quantitative if anthracene is in a slight excess; *all* the $\sim S^-,Na^+$ are combined into $\sim S^-,A,Na^+$. Similar observations were reported by Medvedev and his associates.[2]

Anthracene reacts also with α-methylstyrene dimer,[3] $K^+,^-\alpha\alpha^-,K^+$ ($K^+,^-C(CH_3)(Ph)CH_2CH_2C^-(CH_3)(Ph),K^+$); the dianion is again quantitatively converted into a dianthracenated complex, $K^+,A,^-\alpha\alpha^-A,K^+$, if anthracene is in excess. The reaction is extremely rapid, the conversion being completed in less than a second.

The kinetics of the addition has been now investigated by a capillary flow technique.[4] The dimer in THF was mixed with a solution of anthracene, the mixture flowed through a capillary, and the reaction quenched at its outlet by wet THF. The initial concentrations of the dimer and anthracene were determined spectrophotometrically and the final concentration of anthracene was determined by v.p.c. The results are summarized in Table I and presented

(1) S. N. Khanna, M. Levy, and M. Szwarc, *Trans. Faraday Soc.*, 58, 747 (1962).
(2) A. A. Arest-Yakubovitch, A. R. Gantmakher, and S. S. Medvedev, *Dokl. Akad. Nauk SSSR*, 139, 1351 (1961).
(3) J. Jagur-Grodzinski and M. Szwarc, *Trans. Faraday Soc.*, 59, 2305 (1963).
(4) C. Geacintov, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, 84, 2508 (1962).

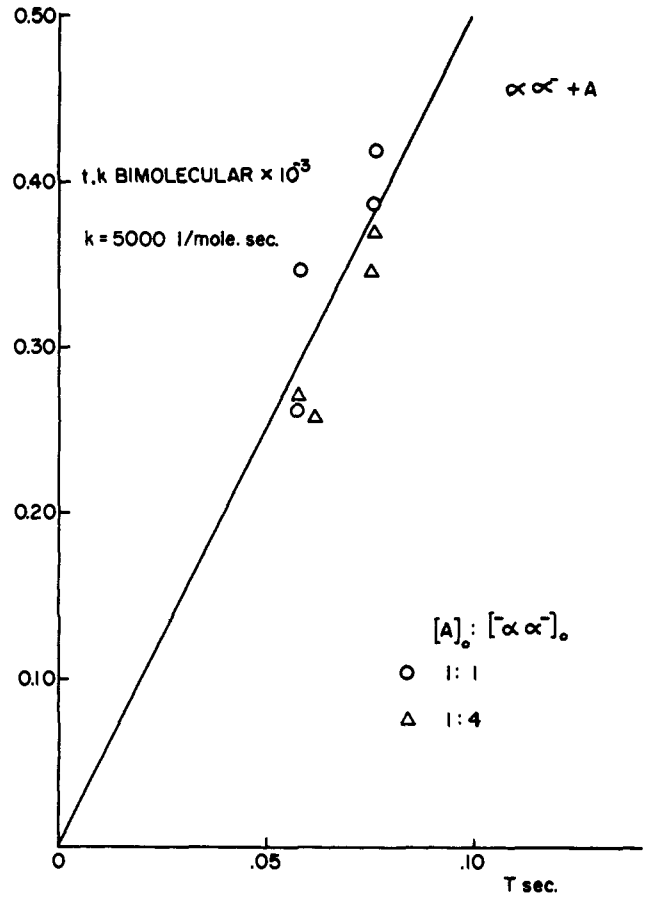

Figure 1.

graphically in Figure 1 as a plot

$$(2[^-\alpha\alpha^-]_0 - [A]_0)^{-1} \ln \{(2[^-\alpha\alpha^-]_0 - x) \times [A]_0/([A]_0 - x)2[^-\alpha\alpha^-]_0\}$$

the factor 2 arising from the presence of 2 living ends in the dimer. It is obvious that the reaction is bimolecular, its stoichiometry being one A per one living end,

Table I. α-Methylstyrene Dimer–Anthracene in THF at 25° (Capillary Flow)

$2[^-\alpha\alpha^-]_0$, $M \times 10^3$	$[A]_0$, $M \times 10^3$	$[A]_t$, $M \times 10^3$	$0.1\int f \cdot (x)dx$[a]	Time, sec.	
2.72	0.66	0.23	41.92	0.076	$\frac{2[^-\alpha\alpha^-]_0}{[A]_0} = 4$
2.71	0.66	0.28	34.72	0.058	
2.76	0.65	0.32	26.70	0.058	
2.68	0.67	0.23	38.67	0.075	
2.58	2.65	1.37	37.03	0.076	$\frac{2[^-\alpha\alpha^-]_0}{[A]_0} = 1$
2.67	2.56	1.32	34.20	0.075	
2.54	2.69	1.60	27.11	0.058	
2.64	2.58	1.51	25.67	0.061	
2.64	2.59	1.42	30.71	0.075[b]	

[a] $\int f(x)dx = (2[^-\alpha\alpha^-]_0 - [A]_0)^{-1} \ln \left\{\frac{(2[^-\alpha\alpha^-]_0 - x)[A]_0}{([A]_0 - x)2[^-\alpha\alpha^-]_0}\right\}$
The factor 2 arises from the presence of 2 living ends in the dimer. [b] Killed in the presence of air.

i.e., $-d[A]/dt = k_\alpha$[living ends][A], where [living ends] = [living ends]$_0 - x$ and [A] = $[A]_0 - x$ (x = the amount of reacted anthracene). The bimolecular rate constant is ~5000 l./mole sec. at 25°.