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-dihydroxy-isocoumarin (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).
(11) Roche Foundation Fellow, 1963-1965.

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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 $\times$ 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 $\times$ 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.
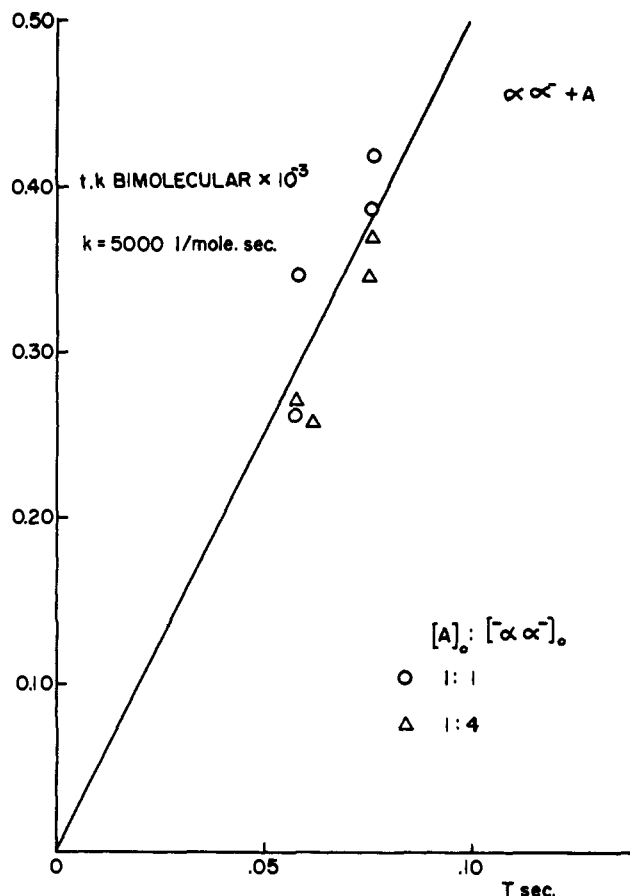
graphically in Figure 1 as a plot

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

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)

$2[^-\alpha\alpha^-]_0$, $M \times 10^3$	$[A]_0$, $M \times 10^3$	$[A]_t$, $M \times 10^3$	$0.1ff \cdot (x)dx^a$	Time, sec.	
2.72	0.66	0.23	41.92	0.076	
2.71	0.66	0.28	34.72	0.058	$\dfrac{2[^-\alpha\alpha^-]_0}{[A]_0} = 4$
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	
2.67	2.56	1.32	34.20	0.075	
2.54	2.69	1.60	27.11	0.058	$\dfrac{2[^-\alpha\alpha^-]_0}{[A]_0} = 1$
2.64	2.58	1.51	25.67	0.061	
2.64	2.59	1.42	30.71	0.075^b	

^{a} $\int f(x)dx = (2[^-\alpha\alpha^-]_0 - [A]_0)^{-1} \ln \left\{ \dfrac{(2[^-\alpha\alpha^-]_0 - x)[A]_0}{([A]_0 - x)2[^-\alpha\alpha^-]_0} \right\}$

The factor 2 arises from the presence of 2 living ends in the dimer. ^{b} Killed in the presence of air.

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

$$\int F(x)dx = (2[A]_0 - [LIV. ENDS]_0)^{-1}$$

$$\ln\left\{ [LIV. ENDS]_0([A]_0 - x)/[A]_0(2[LIV. ENDS]_0 - x) \right\}$$
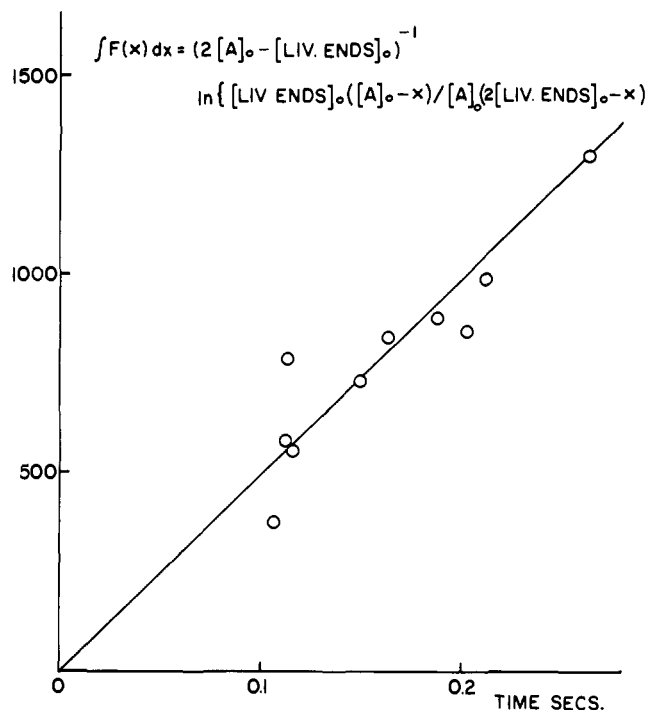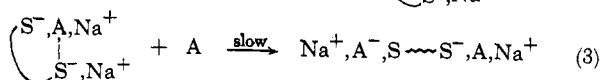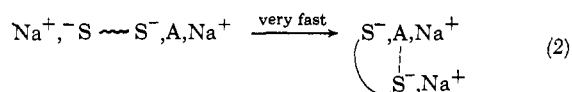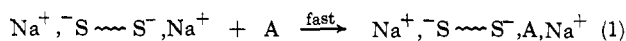
Figure 2.

Studies of the kinetics of anthracene addition to living polystyrene in THF revealed a most interesting phenomenon. Two types of polymers were examined: (1) polymers initiated by an electron-transfer process[5,6] possessing two living ends per chain, $Na^+,^-S\sim S^-,Na^+$, and (2) polymers initiated by monofunctional anions, e.g. $PhCH_2^-,Na^+$ or cumylpotassium, having only one living end per chain, $X\sim S^-,Na^+$. Anthracene reacts rapidly and virtually quantitatively with the latter

$$X\sim S^-,Na^+ + A \longrightarrow X\sim S^-,A,Na^+$$

However, only one-half of the living ends of a low molecular weight two-ended living polystyrene (degree of polymerization, D.P. $\sim$ 20–30) reacts rapidly (in less than a second) with anthracene; the addition to the other half requires 15–30 min. This behavior is clearly demonstrated by the data given in Table II and presented graphically in Figure 2. The reaction is again bimolecular, but *two* living ends are consumed for each anthracene, *i.e.*, the conversion is given by the equation

$$-d[A]/dt = k\{[\text{living ends}]_0 - 2x\}\{[A]_0 - x\}$$

The two stages of the reaction imply the following mechanism of the addition

$$Na^+,^-S\sim S^-,Na^+ + A \xrightarrow{\text{fast}} Na^+,^-S\sim S^-,A,Na^+ \quad (1)$$

$$Na^+,^-S\sim S^-,A,Na^+ \xrightarrow{\text{very fast}} \overset{S^-,A,Na^+}{\underset{S^-,Na^+}{\bigcirc}} \quad (2)$$

$$\overset{S^-,A,Na^+}{\underset{S^-,Na^+}{\bigcirc}} + A \xrightarrow{\text{slow}} Na^+,A^-,S\sim S^-,A,Na^+ \quad (3)$$
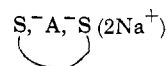
The scheme assumes that the other end of a two-ended living polystyrene reacts *intra*-molecularly with the one

(5) M. Szwarc, M. Levy, and R. Milkovich, *J. Am. Chem. Soc.*, **78**, 2656 (1956).
(6) M. Szwarc, *Nature*, **178**, 1168 (1956).

which has been complexed to anthracene, the intramolecular association into a

$$\underset{\underbrace{\qquad\qquad}}{S,^-A,^-S}\,(2Na^+)$$

complex being much faster than the bimolecular reaction with anthracene because the "local" concentration of those ends is so high, *viz.*, equivalent to $\sim$0.1 *M*.
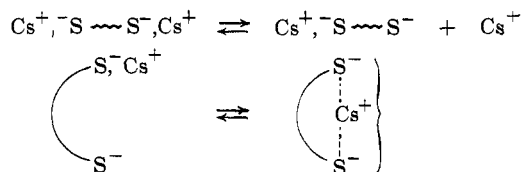
Table II. Addition of Anthracene to $Na^+,S^-\sim S^-,Na^+$ in THF at 25°[a]

[living ends]$_0$, $M \times 10^3$	[A]$_0$, $M \times 10^3$	[$\sim$S$^-$,A, Na$^+$]$_t$, $M \times 10^3$ (denoted by x)	$\int f(x)dx^{a,b}$	Time, sec.	[living ends]/[living ends]$_0$ after 25 sec.
2.17	0.77	0.53	792	0.11	...
4.08	2.64	1.85	990	0.21	...
4.00	2.51	1.76	895	0.19	0.52
3.92	2.97	1.68	556	0.12	0.44
3.95	2.78	1.66	582	0.11	0.50
3.92*	5.80*	1.85*	375	0.12	0.51[c]
1.90	2.30	0.89	838	0.16	...
1.57	1.97	0.69	726	0.15	...
1.67	1.82	0.80	1300	0.26	...

[a] Flow technique, conversion measured by the increase in the optical density at 440 mμ (absorption maximum of $\sim$S$^-$,A,Na$^+$ complex. [b] $\int f(x)dx = (2[A]_0 - [\text{living ends}]_0)^{-1} \ln \{[\text{living ends}]_0 \cdot [(A]_0 - x)/[A]_0([\text{living ends}]_0 - 2x)\}$. [c] Notice that 47% of $\sim$S$^-$, Na$^+$ reacted after 0.12 sec. and still 51% was left after 25 sec., although anthracene was in excess. In no case did reaction progress much over $\sim$50% of the living ends.

The association of $\sim$S$^-$,A,Na$^+$ with $\sim$S$^-$,Na$^+$ may be also demonstrated by the following experiment. On mixing the solution of one-ended living polystyrene with an equivalent amount of anthracene one obtains quantitatively the complex $\sim$S$^-$,A,Na$^+$. To this solution we added slightly less than an equivalent amount of $\sim$S$^-$,Na$^+$. The spectrum of the resulting mixture was given by the superposition of the spectra of the components. Nevertheless, the addition of anthracene solution to this mixture led only to the slow reaction; virtually no anthracene is consumed in one second. We deal here with a physical association which does not affect appreciably the spectra of the components but strongly influences their reactivity. In this respect the situation resembles that found in $\sim$S$^-$,Li$^+$ solution in benzene.[7]

A similar phenomenon has been described recently.[8] A two-ended living polystyrene having Cs$^+$ counterions gives in THF cyclic triple ions, the course of the reaction being

$$Cs^+,^-S\sim S^-,Cs^+ \rightleftarrows Cs^+,^-S\sim S^- + Cs^+$$

$$\overset{S,^-Cs^+}{\underset{S^-}{\bigcirc}} \rightleftarrows \overset{S^-}{\underset{S^-}{\left(\bigcirc\, Cs^+\right)}}$$

(7) D. J. Worsfold and S. Bywater, *Can. J. Chem.*, **38**, 1891 (1960).
(8) D. N. Bhattacharyya, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, **86**, 5024 (1964).

The equilibrium constant for cyclization depends on the molecular weight, e.g., at 25° it is found to be about 5 for D.P. ~ 25, and less for higher D.P. values.

Steric reasons make it obvious that the cyclization caused by the anthracene addition cannot take place with the living α-methylstyrene dimer, and consequently this two-living-ended oligomer reacts quantitatively with anthracene, adding 2A per $^-\alpha\alpha^-$ in the course of the very fast reaction.

In the reaction of one-ended living polystyrene the dilution makes the association of $\sim$S,$^-$A,Na$^+$ with $\sim$S$^-$,Na$^+$ relatively slow, and consequently anthracene competes favorably for $\sim$S$^-$,Na$^+$. Thus virtually 100% of conversion is achieved in fast reaction, although more accurate experiments show that in this step the conversion is always slightly lower than 100%.

The described phenomenon should be kept in mind when studying the reactions of two-living-ended low molecular weight polymers. For example, the carboxylation may give cyclic ketones instead of dicarboxylic acids, since after the addition of the first molecule of CO_2 to one end the other may react with the formed carboxylate and eventually give the ketone derivative. Such processes may account for synthetic difficulties experienced by some workers in this field.

The detailed kinetic studies of the fast and slow stages of the anthracene addition are now in progress and the results will be reported later.

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Nuclear Magnetic Resonance Study of Weak Acids in Liquid Ammonia

Sir:

Because liquid ammonia is a basic solvent with a very low self-ionization constant (2×10^{-28} at 25°),[1] it can serve as a solvent for comparing the acidities of weak acids over an enormous span of pK values. We have found that n.m.r. spectroscopy in ammonia is a useful tool for determining relative acidities and for measuring rates of proton exchange between acids and ammonia.

Acids can be roughly divided into three categories based on their behavior in liquid ammonia. (1) Relatively strong acids (aqueous pK less than ~15) exchange their acidic protons rapidly with ammonia. Malononitrile (aqueous pK = 11.14)[2] is an example of this type; ammonia solutions of this acid show only one proton resonance, which is a time-averaged signal of the solvent and acid protons. (2) Acids of intermediate strength (aqueous pK ~ 15–42) exchange their acidic protons slowly with ammonia and yield appreciable amounts of their corresponding anions only upon the addition of amide ion. We have studied several examples of this type; the results are discussed below.

(1) L. V. Coulter, J. R. Sinclair, A. G. Cole, and G. C. Roper, *J. Am. Chem. Soc.*, 81, 2986 (1959).
(2) K. Bowden and R. Stewart, *Tetrahedron*, 21, 261 (1965).

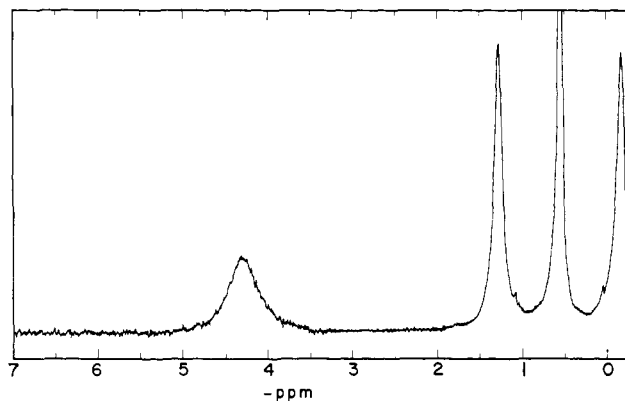

Figure 1. Proton n.m.r. spectrum of a solution of 0.86 M water in liquid ammonia saturated with sodium hydroxide.

(3) Very weak acids (aqueous pK greater than ~42) exchange their protons slowly and do not react appreciably with the amide ion. Toluene (aqueous pK ~ 59)[3] is an example of this type.

A solution of an acid of the second category together with its anion generally shows distinct n.m.r. signals for both the acid and the anion. The spectrum of the solvent ammonia is observed as a sharp multiplet ($J_{N^{14}-H}$ = 43.5 c.p.s.; $J_{N^{15}-H}$ = 61 c.p.s.) or in various states of collapse, depending on the acid and the acid-to-anion ratio. Thus acetophenone (aqueous pK ~ 19)[3] and indene (aqueous pK ~ 21),[3] in the presence of their anions, give spectra in which the ammonia triplet is sharp and in which the N^{15} satellite peaks are easily seen. This indicates that proton exchange is negligible in these solutions. However, in solutions of cyclopentadiene (aqueous pK ~ 15)[3] and sodium cyclopentadienide, the triplet can be made to collapse by increasing the acid-to-anion ratio. This result suggests that the collapse of the triplet is due to the exchange reaction

$$NH_4^+ + NH_3 \rightleftharpoons NH_3 + NH_4^+$$
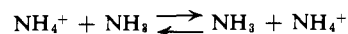
The ammonium ion concentration, and hence the rate of the exchange reaction, would be expected to increase with decreasing pK of the acid and increasing acid-to-anion ratio. We have usually found collapse of the acidic proton signal and the ammonia signal to a single sharp line in plain solutions of acids stronger than cyclopentadiene (o-nitroacetanilide, malononitrile, and diethyl malonate). Nitromethane (aqueous pK ~ 10)[3] is an exception; separate sharp lines are observed for the nitromethane and the ammonia. This result is consistent with the slowness of the reactions of nitromethane in aqueous systems.[4]

We have also examined the behavior of some acids of the type ROH, where R = hydrogen, methyl, isopropyl. The n.m.r. spectra of solutions of these acids, in the presence of their anions, show the ammonia triplet, the shape of which depends upon the acid and the acid-to-anion ratio. Separate peaks characteristic of the acid and anion are not observed but only an averaged spectrum: the acidic proton exchanging between the acid and anion sites. The

(3) D. J. Cram, *Chem. Eng. News*, 93, 92 (Aug. 19, 1963).
(4) R. G. Pearson and R. L. Dillon, *J. Am. Chem. Soc.*, 75, 2439 (1953).