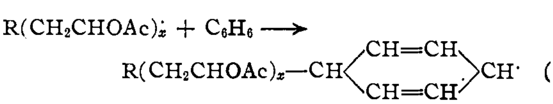
reaction with respect to initiator at its observed value, which is[1,4] scarcely greater than 0.5.

Using great care in purification of materials, we have again measured rates of vinyl acetate polymerization in benzene at 60° and the molecular weights of the polymers produced, with the same anomalous results. To fit the observed rates, we require the transfer constant to benzene to have a value $C = 2.5\ (\pm 0.5) \times 10^{-3}$, while the molecular weights lead to $C = 1.2 \times 10^{-4}$. It would of course still be formally possible to attribute the effect to an unusual type of impurity, but this would merely shift rather than relieve the burden of explanation.

These results require the existence of a reaction which can retard the polymerization without decreasing the molecular weight, namely, the *addition* of a radical to the aromatic nucleus



$$R(CH_2CHOAc)_x^{\cdot} + C_6H_6 \longrightarrow R(CH_2CHOAc)_x{-}CH\langle {}^{CH=CH}_{CH=CH} \rangle CH^{\cdot} \quad (3)$$

This reaction accounts for the retardation as well as does reaction (2), and if the resulting radical can add to monomer

$$R(CH_2CHOAc)_xC_6H_6^{\cdot} + CH_2{=}CHOAc \longrightarrow R(CH_2CHOAc)_xC_6H_6CH_2CHOAc^{\cdot} \quad (4)$$

a self-consistent explanation of all our results can be achieved.

We have shown that reaction (3) actually takes place with about the required frequency, by preparing a sample of low-conversion polyvinyl acetate at 60° in the presence of C^{14}-labelled benzene,[6] using a mole ratio 10.9 of benzene to vinyl acetate. This polymer contained radioactive carbon which could not be removed by repeated precipitations, nor by dilutions with ordinary benzene followed by evaporation; the mole ratio of benzene to vinyl acetate in the polymer remained at 0.029 ± 0.005. This figure gives a ratio of $2.7\ (\pm 0.5) \times 10^{-3}$ for the specific rate of reaction (3) to that of normal propagation, in remarkable agreement with the kinetic value. The polymerization degree $\bar{P}_n$ of the radioactive polymer sample (estimated viscometrically) was about 700, so that there were about 20 benzene residues per average molecule. The reactions above postulated would require these residues first to enter the chains as disubstituted ortho- or para-cyclohexadiene units, but we have been unable to detect any significant unsaturation in our benzene-containing samples. Presumably the cyclohexadiene units are rapidly oxidized to aromatic form, possibly by atmospheric oxygen during dissolution and precipitation of the polymer.

Addition of a free radical to an aromatic nucleus is scarcely a novel reaction.[5] Within the field of polymerization mechanism, it has been postulated as a possible step in retardation by aromatic nitrocompounds,[7] in the polymerization of styrene in aromatic solvents,[8] and indeed in the polymerization of vinyl benzoate,[9] in order to account for the ready gelation of the latter. We believe, however, that ours is the first direct proof of its occurrence in a polymerizing system. From a general comparison of transfer activity in styrene and vinyl acetate systems,[2] we estimate the reactivity-ratio (to normal propagation) of reaction (3) for a styrene radical with benzene or with styrene monomer to be not less than 10^{-5} at 60°.

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[6] Obtained from Tracerlab, Inc., on allocation from the United States Atomic Energy Commission.

[7] C. C. Price and D. A. Durham, THIS JOURNAL, **65**, 757 (1943).

[8] F. R. Mayo, *ibid.*, **65**, 2324 (1943).

[9] G. E. Ham and E. L. Ringwald, *J. Polymer Sci.*, **8**, 91 (1952).

THE RELATIONSHIP BETWEEN METALLIC RADII IN BODY-CENTERED CUBIC AND CLOSE-PACKED STRUCTURES

Sir:

In the first of two recent papers dealing with the resonance-bond theory of metals Pauling[1] develops an empirical correction for the conversion of the atomic radius corresponding to the shorter of the two bond lengths in the body-centered cubic structure to that appropriate to coördination number 12. This correction is derived from a comparison of the body-centered cubic radii with the face-centered cubic or hexagonal close-packed radii of iron, titanium, zirconium and thallium, respectively.

In every instance except that of iron, however, Pauling has compared two radii the values of which are measured at different temperatures and has not allowed for the differences which arise on account of thermal expansion. In the case of iron he appears to have used an unreliable extrapolated room temperature value for γ-Fe obtained by Jette and Foote[2] from a series of Ni–Fe alloys. This value has, therefore, been rejected by the present author and the high temperature values of the cell dimensions have been used in all cases. When allowance is made for thermal expansion, it becomes apparent that the correction, ΔR, given by Pauling's equation

$$R(1) - R(n) = 0.300 \log n$$

needs little or no modification. There is, in each instance, a small difference between the calculated and observed values of ΔR but the differences are not systematic and in any case may well arise from the uncertainties associated with the temperature corrections involved.

The cell dimensions on which the calculations are based, the values of the thermal expansion coefficients used and the resulting values of the radii for C.N. 12 at 20° are given in Table I. The cell dimensions are those given by Barrett[3] but are quoted in kX. units to conform with Pauling's usage.[4] The calculated and observed values of the

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[1] L. Pauling, THIS JOURNAL, **69**, 542 (1947).

[2] E. R. Jette and F. Foote, *Metals Technology*, **3**, 1 (1936).

[3] C. S. Barrett, "Structure of Metals," 2nd Edition, McGraw-Hill Book Co., New York, N. Y., 1953.

[4] In the case of iron there is yet another reported value available for the cell dimension of γ-Fe; Wyckoff, "Crystal Structures," Vol. I, Interscience Publishers, New York, N. Y., (1948) gives a_0 = 3.63 kX. at 1100°. This makes iron an unfortunate choice for the present purpose.

correction, ΔR, are given in Table II. The results are, of course, quite independent of any assumptions that may be made concerning the valencies of the elements concerned.

TABLE I

DATA USED

Element	Form	a_0, kX.	c_0, kX.	Temp., ° C.	Coefficient of thermal expansion × 10^{-6}	R(C.N.12) at 20°, kX.
Fe	α	2.861	..	20		1.273
	γ	3.649	..	950	12[5]	1.276
Ti	α	2.945	4.674	25		1.459
	β	3.32	..	900	9[6]	1.463
Zr	α	3.223	5.123	room		1.597
	β	3.61	..	867	7.5[7]	1.594
Tl	α	3.449	5.520	room		1.713
	β	3.874		262	30[8]	1.708

Room temperature taken as 20°.

TABLE II

VALUES OF ΔR

Element	Value of ΔR		Difference in ΔR
	Calcd.	Obs.	
Fe	0.033	0.036	+0.003
Ti	0.036	0.032	−0.004
Zr	0.039	0.042	+0.003
Tl	0.041	0.046	+0.005

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(5) E. A. Owen and E. L. Yates, *Phil. Mag.*, **15**, 472 (1933); A. Kochanovska, *Physica*, **15**, 191 (1949).

(6) G. L. Miller, *Ind. Chemist*, **27**, 483 (1951).

(7) R. B. Russell, M.I.T. report No. 1073, October 1951.

(8) Fizeau (1869) quoted in "Handbook of Chemistry and Physics," 33rd Edition, Chem. Rubber Publishing Co. (1951–1952), p. 1852.

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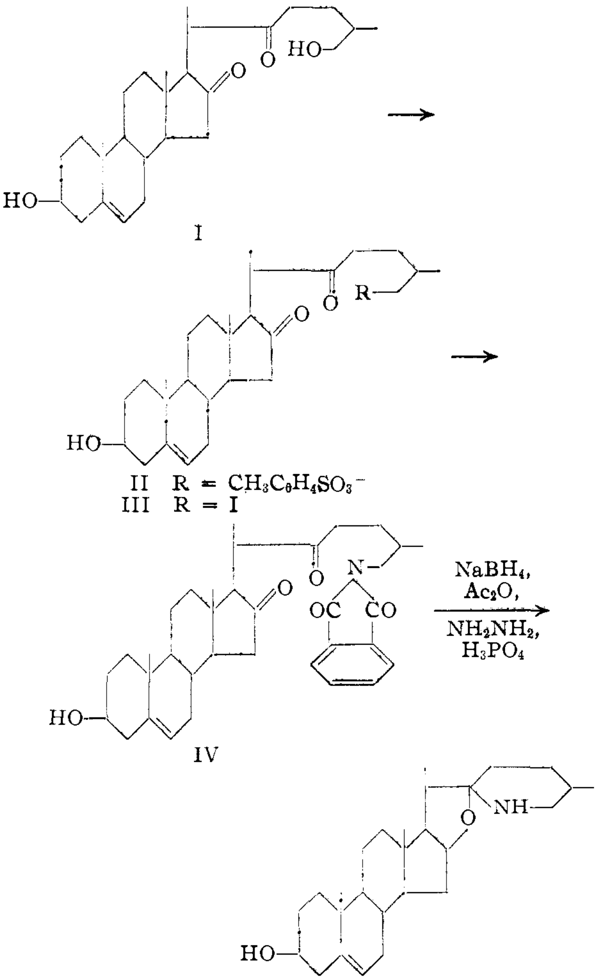
THE TRANSFORMATION OF KRYPTOGENIN TO SOLASODINE

Sir:

Inasmuch as the secondary veratrum and solanum alkaloids yield nitrogenous degradation products identical with those derived from their tertiary congeners, the secondary alkamines may be presupposed not remotely allied in skeletal structure to the octahydropyrrocoline nucleus characteristic of solanidine,[1] rubijervine, isorubijervine, and, presumably, of cevine, germine, protoverine and zygadenine. While jervine and veratramine have been categorized as complex 2-substituted-5-methylpiperidine derivatives[2] and steroid C_{20} piperidine derivatives of this type have become available by partial synthesis,[3] a further skeletal variation consonant with the chemical behavior of other members of these series finds expression as a hexacyclic aminoketal formulation related to that which characterizes the well known spiroketal sapogenins. This representation was first considered as a theoretical possibility in earlier studies on the chemistry of jervine[4] and has more recently been incorporated into the structural postulates advanced for solasodine,[5] tomatidine,[6] and solanocapsine.[7] Solasodine has now been obtained by partial synthesis from non-nitrogenous, naturally occurring steroids.

Kryptogenin, I, has been converted to the mono-*p*-toluenesulfonate II, m.p. 165–166°, $[\alpha]^{25}\mathrm{D}$ −144° ($CHCl_3$), *Anal.* Calcd. for $C_{34}H_{48}SO_6$: C, 69.82; H, 8.27; S, 5.48. Found: C, 69.82; H, 8.20; S, 5.28, which, in turn, has been transformed through the iodide III, m.p. 141–142°, $[\alpha]^{25}\mathrm{D}$ −161° ($CHCl_3$), *Anal.* Calcd. for $C_{27}H_{41}O_3I$: C, 59.99; H, 7.65; I, 23.48. Found: C, 60.20; H, 7.76; I, 23.20, to the corresponding phthalimido-derivative IV, m.p. 213–214°, *Anal.* Calcd. for $C_{35}H_{45}NO_5$: C, 75.10; H, 8.10; N, 2.50. Found: C, 74.91; H, 8.01; N, 2.60. Reduction of IV with sodium borohydride, followed by treatment with acetic anhydride and subsequent cleavage with hydrazine and phosphoric acid, has afforded solasodine, V, m.p. 200–201°, $[\alpha]^{24.8}\mathrm{D}$ −102°


I

II R = $CH_3C_6H_4SO_3^-$
III R = I

IV

V

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(1) F. C. Uhle and W. A. Jacobs, *J. Biol. Chem.*, **160**, 243 (1945).

(2) J. Fried, O. Wintersteiner, M. Moore, B. M. Iselin and A. Klingsberg, THIS JOURNAL, **73**, 2970 (1951); O. Wintersteiner and N. Hosansky, *ibid.*, **74**, 4474 (1952).

(3) F. C. Uhle, *ibid.*, **73**, 883 (1951).

(4) W. A. Jacobs and C. F. Huebner, *J. Biol. Chem.*, **170**, 635 (1947).

(5) L. H. Briggs, W. E. Harvey, R. H. Locker, W. A. McGillivray and R. N. Seeyle, *J. Chem. Soc.*, 3013 (1950).

(6) T. D. Fontaine, J. S. Ard and R. M. Ma, THIS JOURNAL, **73**, 878 (1951); R. Kuhn, I. Löw and H. Trischmann, *Chem. Ber.*, **85**, 416 (1952).

(7) E. Schlittler and H. Uehlinger, *Helv. Chim. Acta*, **35**, 2034 (1952).