

recrystallizations from carbon tetrachloride yielded 3 g. of white crystalline (V). (V) had practically no odor and melted at 113–113.5°. From analyses and molecular weight determinations, the formula of (V) was established as being C₁₀Cl₁₂.

Anal. Calcd. for C₁₀Cl₁₂: Cl, 78.00; mol. wt., 545.5. Found: Cl, 77.94; mol. wt., 537.

Summary

1. Octachloro-1,3-pentadiene (I) when treated with chlorine in the presence of direct sunlight at elevated temperatures undergoes chlorinolysis to yield hexachloroethane and carbon tetrachloride.

2. 1,1,2,3,3,4,5,5,5-Nonachloro-1-pentene (II) reacts as above but at lower temperatures to

give hexachloroethane and *s*-heptachloropropane.

3. (II) reacts with copper to yield chiefly a dehalogenated product, C₅HCl₇ (III), and a smaller amount of a coupled product, C₁₀H₂Cl₁₄ (IV).

4. No definite products were obtained through the reaction of (I) with copper.

5. (IV) is dehydrohalogenated by potassium hydroxide to give C₁₀Cl₁₂ (V).

6. Structural formulas are suggested for compounds (IV) and (V).

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The Electric Moments of Some *p*-Substituted Phenyl Selenocyanates and Thiocyanates

BY TOD W. CAMPBELL AND MAX T. ROGERS

The electric moments of a series of *para* substituted phenyl thiocyanates and phenyl selenocyanates have been studied to obtain information concerning the nature of resonance in these compounds. None of the substances whose dipole moments are reported here have been measured previously, but values have been reported for phenyl thiocyanate,¹ *p*-chlorophenyl thiocyanate,¹ *p*-tolyl selenocyanate² and *p*-chlorophenyl selenocyanate² so that group moments may be calculated for the thiocyno- and selenocyno- groups in aromatic compounds.

Experimental Part

Materials

Benzene.—Baker C. P. benzene was dried over sodium and filtered before use, *d*₄²⁵, 0.87344, *n*_D²⁰ 1.4978.

***p*-Dimethylaminophenyl Thiocyanate and *p*-Aminophenyl Thiocyanate.**—These were prepared by the method of Brewster and Schroeder³: *p*-dimethylaminophenylthiocyanate, white needles, m. p. 75°; *p*-aminophenyl thiocyanate,^{3a} m. p. 57°.

***p*-Dimethylaminophenyl Selenocyanate and *p*-Aminophenyl Selenocyanate.**⁴—These were prepared from cyanogen triselenide⁵ and, respectively, dimethylaniline (m. p. product 105°) and aniline (m. p. of product 91–92°).

***p*-Nitrophenyl Thiocyanate and *p*-Nitrophenyl Selenocyanate.**—These were prepared from diazotized *p*-nitroaniline and, respectively, ferric thiocyanate (m. p. of product 133°) and potassium selenocyanate (m. p. of product 137–138°).⁶

***p*-Selenocyanophenyl Thiocyanate** was prepared from diazotized *p*-aminophenyl thiocyanate and potassium

selenocyanate in a buffered solution.⁷ The product melted at 111.5–112° after repeated recrystallization from a ligroin–benzene mixture.

p-Methoxyphenyl selenocyanate was synthesized from diazotized anisidine and potassium selenocyanate. The product⁸ melted at 65°.

Apparatus and Method

Electric moments were measured in benzene solution at 25° using a heterodyne-beat apparatus and technique previously described.⁹ The experimental data and molar polarizations are shown in Table I; the derived values of the molar polarization at infinite dilution (*P*[∞]), the molecular refraction, MR_D, and the dipole moment, are shown in Table II. The molecular refraction of each compound was obtained from the refractive indices of the solutions² (Table I) or, in the cases of *p*-aminophenyl selenocyanate and *p*-methoxyphenyl selenocyanate, from empirical atomic and group refractions.¹⁰

Discussion of Results

The observed dipole moments are compared in Table III with the vector sums of the moments of the substituents, assuming free rotation about single bonds. The group moments and angles used are: C_{aromatic}-H, 0.4 (assumed), 180°; C_{ar}-NO₂, 3.55, 0°; C_{ar}-NH₂,¹¹ 1.86, 143°; C_{ar}-N(CH₃)₂,¹¹ 1.98, 180°; C_{ar}-OCH₃,¹¹ 1.37, 119°; C_{ar}-SCN,² 3.36, 58°30'; C_{ar}-SeCN,² 3.83, 53°30'. (The angle is 0° when the negative end of the dipole is directed away from the ring.)

There is an increase in dipole moment when an electron donating group is *para* to the selenocyno or thiocyno group and this increment may be attributed to enhancement of resonance. The effect is greater with the dimethylamino group

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(10) The group refractions of the —SCN and —SeCN groups were taken to be 13.4 and 18.0.

(11) Estimated from values of various *para* disubstituted benzene derivatives in the literature using principally the *p*-chloro-, *p*-fluoro- and *p*-methyl- compounds.

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TABLE I

DIELECTRIC CONSTANTS, DENSITIES, REFRACTIVE INDICES AND POLARIZATIONS IN BENZENE AT 25°

| f_1 | ϵ | n^{25D} | d | P_1 |
|---------------------------------------------|------------|-----------|---------|-------|
| <i>p</i> -Aminophenyl thiocyanate | | | | |
| 0.001464 | 2.328 | | 0.87422 | 588.3 |
| .001578 | 2.333 | | .87434 | 591.6 |
| .001808 | 2.343 | 1.4982 | .87431 | 600.9 |
| .002521 | 2.369 | 1.4984 | .87474 | 587.3 |
| .004182 | 2.432 | 1.4988 | .87561 | 576.2 |
| <i>p</i> -Dimethylaminophenyl thiocyanate | | | | |
| 0.001325 | 2.334 | | 0.87410 | 712.4 |
| .002818 | 2.402 | 1.4987 | .87483 | 699.7 |
| .003788 | 2.447 | 1.4988 | .87530 | 697.0 |
| .006030 | 2.549 | 1.4991 | .87626 | 682.3 |
| .007456 | 2.614 | 1.4993 | .87710 | 672.6 |
| .007979 | 2.637 | 1.4997 | .87737 | 669.7 |
| <i>p</i> -Nitrophenyl thiocyanate | | | | |
| 0.002205 | 2.303 | 1.4983 | 0.87517 | 241.0 |
| .004283 | 2.329 | 1.4988 | .87672 | 230.4 |
| .005624 | 2.350 | 1.4991 | .87780 | 235.9 |
| .007304 | 2.373 | 1.4992 | .87911 | 236.3 |
| .009116 | 2.400 | 1.4995 | .88049 | 237.7 |
| .010934 | 2.423 | 1.5000 | .88188 | 223.6 |
| <i>p</i> -Aminophenyl selenocyanate | | | | |
| 0.001147 | 2.316 | | .87471 | 584.3 |
| .001315 | 2.322 | | .87438 | 591.9 |
| .001624 | 2.335 | | .87511 | 591.1 |
| .002078 | 2.352 | | .87530 | 591.2 |
| <i>p</i> -Dimethylaminophenyl selenocyanate | | | | |
| 0.001008 | 2.318 | | 0.87453 | 703.7 |
| .001974 | 2.363 | | .87535 | 704.6 |
| .002205 | 2.376 | | .87555 | 721.7 |
| .002792 | 2.399 | 1.4982 | .87628 | 694.3 |
| .003869 | 2.449 | 1.4987 | .87726 | 692.7 |
| .004228 | 2.465 | 1.4987 | .87761 | 689.9 |
| <i>p</i> -Methoxyphenyl selenocyanate | | | | |
| 0.001645 | 2.317 | | 0.87511 | 437.0 |
| .002421 | 2.341 | | .87599 | 450.2 |
| .005249 | 2.420 | | .87879 | 441.8 |
| <i>p</i> -Nitrophenyl selenocyanate | | | | |
| 0.000993 | 2.290 | | 0.87402 | 309.2 |
| .001852 | 2.306 | 1.4983 | 0.87518 | 311.5 |
| .003631 | 2.339 | 1.4989 | .87746 | 307.7 |
| .005651 | 2.379 | 1.4992 | .88012 | 311.1 |
| .007567 | 2.417 | 1.4995 | .88237 | 313.5 |
| .010602 | 2.477 | 1.5000 | .88632 | 311.8 |
| <i>p</i> -Selenocyanophenyl thiocyanate | | | | |
| 0.003598 | 2.358 | | .87790 | 384.9 |
| .005198 | 2.392 | 1.4989 | .88011 | 370.4 |
| .009200 | 2.486 | 1.5000 | .88500 | 370.1 |

than with the amino group and is least with the methoxy group. The enhancement is larger for the thiocyanate than for the selenocyanate group for the same *para* substituent; thus, the increment (1.0) observed for *p*-dimethylaminophenylthiocy-

TABLE II

MOLAR REFRACTIONS, MOLAR POLARIZATIONS AND DIPOLE MOMENTS

| Substance | M_{RD} | P_{∞} | μ (Debye) |
|---------------------------------------------|----------|--------------|---------------|
| <i>p</i> -Aminophenyl thiocyanate | 47.0 | 592 | 5.16 |
| <i>p</i> -Dimethylaminophenyl thiocyanate | 54.0 | 720 | 5.70 |
| <i>p</i> -Nitrophenyl thiocyanate | 46.0 | 243 | 3.10 |
| <i>p</i> -Aminophenyl selenocyanate | 43.0 | 600 | 5.22 |
| <i>p</i> -Dimethylaminophenyl selenocyanate | 57.0 | 708 | 5.64 |
| <i>p</i> -Methoxyphenyl selenocyanate | 48.1 | 450 | 4.42 |
| <i>p</i> -Nitrophenyl selenocyanate | 50.5 | 312 | 3.58 |
| <i>p</i> -Selenocyanophenyl thiocyanate | 55.4 | 385 | 4.02 |

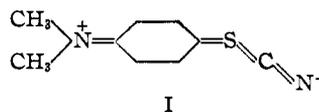
TABLE III

OBSERVED AND CALCULATED ELECTRIC MOMENTS OF SOME DISUBSTITUTED BENZENES

| Compound X | Y | $\mu_{obs.}$ | $\mu_{calcd.}$ | $\mu_{obs.} - \mu_{calcd.}$ |
|----------------------------------|------|--------------|----------------|-----------------------------|
| NH ₂ | SCN | 5.22 | 4.51 | 0.71 |
| N(CH ₃) ₂ | SCN | 5.70 | 4.71 | .99 |
| NH ₂ | SeCN | 5.16 | 5.02 | .14 |
| N(CH ₃) ₂ | SeCN | 5.64 | 5.25 | .39 |
| OCH ₃ | SeCN | 4.40 | 4.42 | -.02 |
| NO ₂ | SCN | 3.10 | 3.38 | -.28 |
| NO ₂ | SeCN | 3.58 | 3.34 | .24 |
| SCN | SeCN | 4.02 | 4.23 | -.21 |

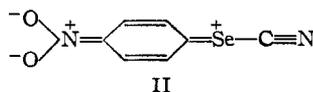
anate is almost as large as found for *p*-nitrodimethylaniline (1.35).

It is unlikely that the larger increments, at least, could be accounted for by a widening of the angles alone since the angle of the dimethylamino group is already small (or zero) and we would not expect a large change in the angle C_{ar}-SCN. It seems more likely that structures such as I are somewhat stabilized in the molecules with a strong electron-receiving group (-SCN or -SeCN) *para* to a strong electron-donating group (-N(CH₃)₂, NH₂, OCH₃) and contribute to a small extent to the ground state of the molecule. Since the charge separation is large such structures have a large effect on the dipole moment.



Selenium might be expected to be able to expand its octet more easily than sulfur since it belongs to a higher period; however, structures such as I appear to be less important in the selenocyanates, probably because of the smaller tendency of selenium to form multiple bonds.

The thiocyanate and selenocyanate groups might also act as electron donating groups and the increment observed for *p*-nitrophenyl selenocya-



nate could be due to a small contribution of structures such as II; this explanation is made doubtful by the observed decrement in the case of *p*-nitrophenyl thiocyanate.

An alternative explanation of the observed increments might be that they arise from an abnormally large vibration polarization¹² such as is found in *p*-dinitrobenzene. The large increments observed here and, especially, the large differences between the thio- and selenocyanates suggests that these are principally resonance effects.

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Summary

The electric moments of some *para* substituted phenylthiocyanates and phenylselenocyanates have been measured in benzene solution at 25°; the substituents used were the amino, dimethylamino, nitro, and methoxyl groups. A rather large enhancement of resonance is observed when the thiocyno- and, to a smaller extent, the selenocyno- group is *para* to an electron-receiving group. The results have been briefly discussed in terms of resonance.

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Properties of Polymers as Functions of Conversion. IV. Composition Studies of Rubber-like Copolymers¹

BY F. T. WALL, R. W. POWERS,² G. D. SANDS³ AND G. S. STENT

It is generally recognized that the products obtained at different stages of conversion in a polymerization reaction will exhibit wide variations in chemical and physical properties. For example, the intrinsic viscosity can show changes of several hundred per cent.,⁴ and the molecular weight can likewise vary several fold.⁵ In the case of copolymers, the composition of the product, which is generally different from that of the reaction mixture, can also change during the conversion.

Numerous copolymer systems have been investigated from a composition standpoint by Mayo,⁶ Alfrey⁷ and others. For bulk and solution polymerizations, relatively simple theories have been devised for the compositional relationships,^{6a,7a,8} but for emulsion systems, the situation is much more complicated. A considerable amount of experimental work, however, has been done on emulsion copolymerizations. For example, Meehan⁹ studied the GR-S system in some detail and observed that the styrene content varied from 17 to 25% in the course of a reaction when the initial charge was 25% styrene. Fordyce and Chapin¹⁰ also have investigated several emulsion systems. The investigations here reported deal with the de-

pendence of composition on conversion for a number of rubber-like copolymers other than GR-S.

Theory

During recent years considerable thought has been given to the theoretical aspects of the compositional relationships in copolymers.^{6a,7a,8} These theories ultimately give rise to a basic differential equation governing the relative rates of disappearance of the monomers. This differential equation, which is valid for single phase polymerizations, is

$$\frac{dM_1}{dM_2} = \frac{M_1(r_1M_1 + M_2)}{M_2(M_1 + r_2M_2)} \quad (1)$$

where M_1 and M_2 equal the number of moles of unreacted monomer and the parameters r_1 and r_2 represent the ratios of certain specific reaction rate constants for the chain growth steps.¹¹ The general validity of equation (1) has been established by many experiments, although it is not obvious that it should be valid for emulsion reactions. However, it will be seen later that an equation of the same type does empirically agree with the observations for many emulsion systems, although considerable doubt can be raised as to its full validity in some cases. Actually it is possible to derive such an equation for emulsion systems by making certain assumptions such as the following:

(1) It is first supposed that the reaction does not take place in the oil phase of the emulsion. (If the reaction occurs in the oil phase, then equation (1) would be expected to hold right off and the present discussion would be irrelevant except for the perturbing effect of the monomer solubility in water.)

(2) Secondly, it is assumed that the amount of monomeric material in the actual reaction environment (supposed not to be the oil phase) repre-

(1) This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program (first reported in March, 1947).

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