TABLE 2

PERCENT OF RUPTURED C-C LINKS IN THE TOTAL PYROLYZED PART*

Polymer	Original No. of links P_0	No. of ruptured links P	$R = \frac{P \times 100}{P_0}$ %
Polystyrene	1.923N†	.634N	33.0
Polyisobutene	3.572N	.588N	16.5
Polyisoprene	5.882N	.276N	4.7
Polybutadiene	7.407N	.283N	3.8
GR-S	6.061N	.270N	4.5
Polyethylene	7.143N	.175N	2.5

* Calculated for 100 g of the polymer.
† N = Avogadro's number.

size, decomposition does not take place until a temperature of about 800° C is reached. However, the introduction of a small amount of free radicals into the system induces the rupture of C-C links to take place at temperatures as low as 300° C (*3*). Since the hydrocarbon polymers discussed here decompose on heating at temperatures of 350°–450° C, it can be assumed that here too decomposition is due to the presence of free radicals.

TABLE 3

DISTRIBUTION OF C-C LINK RUPTURES BETWEEN SMALL AND LARGE MOLECULES*

Polymer	Monomeric type molecules		Intermediate and large molecules	
	Fraction IIIA	Fraction IV	Fraction IIIB	Fraction II
	%	%	%	%
Polystyrene	64.6	0.8	...	34.6
Polyisobutene	65.4	2.4	10.7	21.5
Polyisoprene	30.1	0.5	13.4	56.0
Polybutadiene	29.1	6.7	23.0	41.2
GR-S	30.1	4.5	19.7	45.7
Polyethylene	11.9	8.5	...	79.6

* Calculated in percent of total number of ruptures.

It is also assumed that the free radicals are the ends of the macromolecules, where rupture of C-C links to give molecules of monomer size may start. These free end radicals may in addition cause rupture of C-C links at some other points throughout the chain whenever they come up against these points at random.

Three mechanisms of chain rupture can be visualized:

1. Small fragments of monomeric size break away at the ends of a macromolecular chain until the residual fragment is small enough to escape into the gaseous phase at the temperature of pyrolysis. The products of pyrolysis will consist mainly of small-sized molecules.

2. The macromolecule breaks at random until fragments are sufficiently small to vaporize. In this mechanism the larger molecules, above the monomeric size, will predominate in the vaporized product.

3. A combination of mechanisms 1 and 2 giving rise to a mixture of small and large molecules, the ratio of the two groups of fragments depending on the polymer.

Table 3 shows the relative number of C-C ruptures due to monomeric type molecules (fractions IIIA and IV) as compared with the number of ruptures due to medium- and large-sized molecules (fractions IIIB and II), on the basis of $R = R_1 = 100$. It can be seen from this table that mechanism 1 predominates in the case of polystyrene and polyisobutene; mechanism 2 predominates in the case of polyethylene; and mechanism 3 in the case of the other polymers.

Some experiments carried out in this laboratory on the pyrolysis of polymethylmethacrylate at 400° C showed that about 90% of the C-C link ruptures were due to the formation of the monomer. This, then, represents a case where ruptures of C-C links occur almost exclusively at the ends of the macromolecular chains.

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Di-(*p*-chlorophenyl)methylcarbinol, a New Miticide[1]

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In the course of a research program on synthetic organic insecticides related to 1,1-di-(*p*-chlorophenyl)-2,2,2-trichloroethane (DDT), the di-(*p*-halophenyl)alkylcarbinols $(p\text{-}XC_6H_4)_2C(OH)R$, showed high initial and residual toxicity to mites (*5*). This paper is a preliminary report on certain properties of this class of compounds.

Miticides have become indispensable since the widespread use of DDT. DDT is not only ineffective against this class of agricultural pests, but it also promotes the growth of mites by destroying predatory insects.

The di-(*p*-halophenyl)alkylcarbinols are unusual in the high specificity of their action. Although tests have been run against a wide variety of insects, only mites are affected at practical levels of concentration. Red spiders, European red mites, two-spotted mites, and Pacific mites can be controlled. There is no plant damage under ordinary spraying conditions. The mode of action has not been definitely established, but these compounds appear to be contact poisons.

Although exhaustive toxicity tests on laboratory animals have not been run, preliminary results with the di-(*p*-chlorophenyl)methylcarbinol on rats indicate acute and chronic toxicities which are not greater than DDT (*4*) and which subsequent study may show to be even lower. In the manufacture of pilot plant batches on a

[1] U. S. Patent 2,430,586, November 11, 1947, R. F. Ruthruff, Oliver Grummitt, and B. C. Dickinson, assigned to the Sherwin-Williams Company, Cleveland, Ohio.

[2] The writer wishes to acknowledge the financial support of the Sherwin-Williams Company, and the work of the following collaborators on the chemical phase of this study: A. A. Arters, R. E. Blank, Jean Fick, D. M. Marsh, and J. A. Stearns.

tonnage scale, no harmful effects have been observed on plant personnel exposed over several months.

The most important member of the class, because of its accessibility and cost, is di-(*p*-chlorophenyl)methylcarbinol,[3] $(p\text{-}ClC_6H_4)_2C(OH)CH_3$, which was first made by Bergmann and Bondi in 1931 by the action of methylmagnesium iodide on *p,p'*-dichlorobenzophenone (*1, 3*). It can also be made by other Grignard reactions such as the action of *p*-chlorophenylmagnesium bromide on ethyl acetate or on *p*-chloroacetophenone. The *p,p'*-dichlorobenzophenone, not available commercially, can be made by several Friedel-Crafts reactions, including chlorobenzene with carbon tetrachloride, with phosgene and, with *p*-chlorobenzoyl chloride. Oxidation of DDT ethyene, 1,1-di-(*p*-chlorophenyl)-2,2-dichloroethylene, yields this ketone, a reaction which first showed the structure of DDT (*2*).

Di-(*p*-chlorophenyl)methylcarbinol is a colorless, crystalline solid, melting at 69.5°–70.0° C. It cannot be vacuum-distilled at 1-mm pressure or vacuum-sublimed without decomposition. Thin films exposed to air at room temperature for 42 days volatilized less than 2%. It is insoluble in water, soluble in the common organic solvents, and most soluble in the polar type such as alcohols, ketones, etc. As a tertiary alcohol, this compound may be dehydrated to 1,1-di-(*p*-chlorophenyl)ethylene, mp 84°–86° C, by the prolonged action of heat above its melting point or by the catalytic action of strong acids in solution. Oxidation of the carbinol yields *p,p'*-dichlorobenzophenone. Catalytic reduction yields 1,1-di-(*p*-chlorophenyl) ethane. Typical alcohol derivatives such as ethers and esters are difficult to prepare because of the ease of dehydration and the sterically hindered alcohol group.

Various analytical procedures for the carbinol and related compounds have been developed. Traces of the carbinol may be estimated colorimetrically by nitration followed by treatment with alkali. The carbinol and its isomers are analyzed by measuring the water of dehydration either by Karl Fischer titration or volumetrically, if large samples are taken. Quantitative oxidation of a mixture containing carbinols and the corresponding ethylenes and ketones in which the chlorine atoms are in the *p,p'* and *o,p'* positions of the rings gives a mixture of *p,p'* and *o,p'*-dichlorobenzophenones whose composition can be estimated from setting point-composition data. From water yield and oxidation results, concentration of the most active isomer, di-(*p*-chlorophenyl)-methylcarbinol, can be calculated. Ultraviolet absorption spectra and setting point-composition diagrams are also useful in analyzing mixtures of carbinol, ethylene, and ketone.

From the preparation and testing of a number of derivatives and analogues of the di-(*p*-halophenyl)alkylcarbinols, certain conclusions on the relation of structure to activity may be drawn. For maximum activity the ring halogen atoms are necessary. Isomeric carbinols with one or both of the halogens in the ortho position are much less active. The alkyl group, R in $(p\text{-}ClC_6H_4)_2C(OH)R$, may be methyl, ethyl, etc., or cycloalkyl such as cyclohexyl, but aryl or aralkyl groups such as phenyl and benzyl give compounds of lower activity. If the alcoholic group is shifted from the tertiary carbon atom, as in the isomeric B-β-di-(*p*-chlorophenyl)ethanol, the miticidal activity is lost.

The details of these properties, syntheses, and analyses will be published at a later date.

[3] Sometimes abbreviated to DMC. Spraying compositions containing DMC have the trade-marked name of Dimite.

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Localization of C^{14} in the Tissues of Mice after Administration of C^{14} Methyl-labeled Glycine[1]

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Carbon-labeled compounds offer a wide range of experimental possibilities because of the ubiquity of carbon in living organisms. Because of its long half-life, C^{14} offers the additional advantage of an isotope that can be studied over long periods of time. However, this very fact has resulted in an understandable hesitation to use it, without more knowledge regarding the effects of prolonged exposure of living tissues to radiation. It was felt that if the radioactivity were fairly evenly distributed in the organism, the total dose could be so calculated as to keep the radiation to any one tissue or organ within a reasonably calculated safety margin.

Bloom *et al.* (*1*), using BaC^*O_3 or $NaHC^*O_3$ injected intraperitoneally into young rats, showed by means of autoradiographs that activity tended to localize in bone and remain there long after soft tissues were no longer active, although the activity in various tissues was not directly weighed and measured, so that the residual activity in bone may have been extremely small. It was felt, therefore, that further work should be done to see if use of soluble compounds resulted in radioactivity localizing in the bone.

Glycine, labeled with C^{14} in the methylene position, having an activity of 567,000 cpm (4.57 c/mg) prepared by Ostwald (*3*) was injected into the tail veins of adult, male, strain A mice. Each animal was injected with 1.728 mg of glycine*, a total activity of 1.08×10^6 cpm. Fifteen animals were injected simultaneously and sacrificed at varying time intervals from 6 hr to 43 days. Some were sealed in glass metabolic cages so that activity measurements of breath, feces, and urine could be made. Combustions, plating, corrections, etc. were carried out as described by Calvin *et al.* (*2*). The moisture removed by vacuum desiccation (in order to obtain dry tissues)

[1] The work described in this paper was sponsored by the Atomic Energy Commission.

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