Insecticidal Evaluation of Two Unsaturated Alcoholic Derivatives of a Perchlorinated Caged Ketone

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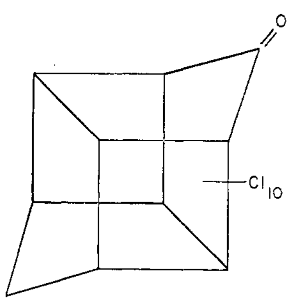
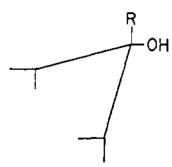
Two unsaturated alcoholic derivatives of ketone I have been prepared and evaluated as insecticides. They are considerably more active than I in nearly all cases, and on cockroaches show a faster rate of kill. The acetylenic derivative is more active than the ethylenic analog on three insects, and about equivalent on two.

The insecticide-fungicide decachlorooctahydro-1,3,4-metheno-2*H*-cyclobuta[*cd*]pentalen-2-one, or decachloropentacyclo-($5.3.0.0^{2,6}.0^{4,10}.0^{5,9}$)decan-3-one, (I) is effective on a wide variety of chewing insects (Allied Chemical Corp., 1960). (The designation "Kepone," a registered trade make of Allied Chemical Corporation, applies to I only when it is used in insecticidal or acaricidal formulations.)



I



II

IIa. R = —C≡CH
b. R = $—CH=CH_2$
c. R = $C_2H_5OCOCH_2CH_2COCH_2—$
d. R = $C_2H_5OCOCH_2NHCO—$
e. R = C_6H_5

I II

Previous studies at this laboratory (Gilbert *et al.*, 1966a, 1966b) showed, however, that modification of I at the carbonyl group could result in marked changes in insecticidal activity. Alcoholic derivatives of structure II had in many cases broader spectra of activity and/or increased rates of action. Compounds IIc and IId were among the most active compounds studied. In all cases, R was saturated aliphatic or aromatic. The purpose of the present study was to determine the effect of making R unsaturated, with the unsaturation residing on the carbon atom next to the carbinol carbon atom for maximum possible effect and with a varied degree of unsaturation. The closest approach to such compounds in the previous study was IIe, which, although promising in initial tests, was concluded to be less active than IIc, IId, and others on the basis of followup studies. However, the phenyl group of IIe is not unsaturated in the usual sense. Compounds IIa and IIb were accordingly prepared and tested.

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PREPARATION OF TEST COMPOUNDS

Compound IIa. The Grignard procedure (Gilbert *et al.*, 1966a) was followed with modifications as follows. A solution of approximately 0.1 mole of anhydrous I in xylene was prepared as usual. The xylene was removed by evaporation under reduced pressure, and the anhydrous I so obtained was immediately dissolved in dry tetrahydrofuran (*ca.* 100 ml.). To this solution was added at 0° over 15 minutes a solution of 0.1 mole ethinyl magnesium bromide in 100 ml. of dry tetrahydrofuran, prepared by a standard method (Skattebøl *et al.*, 1959). The resulting solution was refluxed for 65 hours, by which time I had completely reacted, as indicated by the infrared spectrum. The solution was cooled, acidified with 0.1 mole of H_2SO_4 in 120 ml. of water, and poured into water to separate the solid product which was filtered. The aqueous layer was extracted with two 50 ml. portions of chloroform, which were mixed with the solid product. Evaporation to dryness gave 45 grams of crude IIa (85% of theory). After sublimation at 210° (0.2 mm.), it showed m.p. 354–5° C. with darkening at 260°. *Anal.* Calcd for $C_{12}H_2Cl_{10}O$: 27.9% C, 0.4% H, 68.6% Cl, molecular weight 517. Found: 27.5%, 0.6%, 68.2%, 530. The infrared spectrum shows stretching bands at 3584 $cm.^{-1}$ for O—H, at 3311 for ≡C—H; and at 2137 for C≡C, which is consistent with formula IIa, and indicates the absence of unreacted I.

Compound IIb. In a similar manner a solution of 0.22 mole of vinyl magnesium chloride in tetrahydrofuran (purchased from Monomer-Polymer Laboratories, Philadelphia, Pa.) was reacted with anhydrous I (0.122 mole) in tetrahydrofuran. A similar workup procedure was used, giving crude IIb in 85% yield. After purification by sublimation at 210° (0.7 mm.), it was found to have a m.p. >400° C. *Anal.* Calcd for $C_{12}H_4Cl_{10}O$: 27.8% C, 0.8% H, 68.4% Cl. Found: 27.4%, 0.9%, 67.9%. The infrared spectrum shows stretching bands at 3797 $cm.^{-1}$ for O—H, and at 1642 for C=C (very weak), which is consistent with formula IIb.

BIOLOGICAL EVALUATION

Compounds I and IIa–d were compared in spray tests by procedures already described (Gilbert *et al.*, 1966a); the data are summarized in Table I. All of the compounds were ineffective on mites [*Tetranychus telarius* (Linnaeus)]. Bait formulations containing 0.125% toxicant with a 6:6:1 mixture of powdered sugar, powdered milk, and dried egg were tested on cockroaches, with the results shown in Table II.

The data show that IIa and IIb have high activity of a type generally resembling that of the other alcoholic derivatives of I. IIa is the most active of the five compounds on southern armyworms, and is the second most active on Mexican bean

Table I. Spray Test Comparison of Experimental Compounds

(Per Cent Kill)

Per Cent Toxicant in Spray, ($\times 10^3$)	Mexican Bean Beetle Larvae[a]					Pea Aphid Adults[b]					Southern Armyworm Larvae[c]					Colorado Potato Beetle Larvae[d]				
	I	IIa	IIb	IIc	IId	I	IIa	IIb	IIb	IId	I	IIa	IIb	IIc	IId	I	IIa	IIb	IIc	IId
240	100		88	100																
120	80	100	80	60	100															
60	60	80	60	40	100	0														
30		60			100					90										
15									100	80	80	100	100	80	60					
7.5							100	100	100	60	0	100	60	0	40					
3.8							80	70	100			80	0		0					
1.9							50	10								50				
0.94																	100	40	100	100
0.47																	50	20	100	100
0.23																	0	0	80	90

[a] Mexican bean beetle larvae: *Epilachna varivestis* (Mulsant).
[b] Pea aphid adults: *Macrosiphum pisi* (Harris).
[c] Southern armyworm larvae: *Prodenia eridania* (Cramer).
[d] Colorado potato beetle larvae: *Leptinotarsa decemlineata* (Say).

Table II. Bait Test Comparison on Cockroaches

(Per Cent Kill after Days Given)

Compound	American Roach Nymphs[a] 1	2	3	4	German Roach Adults[b] Sex	1	2
I	10	80	90	100	M	0	100
					F	0	100
IIa	70	100	—	—	M	40	100
					F	20	100
IIb	90	100	—	—	M	20	100
					F	40	100
IIc	70	100	—	—	M	80	100
					F	60	100
IId	0	100	—	—	M	60	100
					F	10	100

[a] American cockroach nymphs: *Periplaneta americana.*
[b] German cockroach adults: *Blattella germanica* (Linnaeus).

beetles and (like IIb) on pea aphids. IIa resembles IIc and IId in being highly effective on Colorado potato beetles. IIa is more active than IIb on three insects, and about equivalent on the other two. I is markedly less active than its derivatives, especially on pea aphids and Colorado potato beetles, and in its speed of action on roaches.

I and IIa were tested for control of subterranean termites, *Reticulitermes flavipes.* White pine stakes were soaked for 1 minute in a 1.5% solution of the toxicant in acetone-water, dried, and kept in the ground for one year. The untreated stakes showed heavy damage; those treated with I, medium to heavy; and the stakes treated with IIa, none.

LITERATURE CITED

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