Synthesis, spectral properties, and herbicidal activity of 2,4-dinitro-3-methyl-6-bromophenyl carboxylates

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The synthesis of new 2,4-dinitro-3-methyl-6-bromophenyl carboxylates and interpretation of their i.r. spectra are described. Linear correlation was found between $\nu(C=O)$ and the σ^* constants of the substituents in 2,4-dinitro-3-methyl-6-bromophenyl alkanoates and haloalkanoates. The preemergent activity of the synthesized compounds was found to be low while the postemergent herbicidal activity was significantly higher.

Описывается синтез и интерпретация ИК спектров новых 2,4-динитро-3-метил-6-бромфениловых эфиров карбоксильных кислот. Волновые числа полос $\nu(C=O)$ были коррелированы с константами σ^* заместителей 2,4-динитро-3-метил-6-бромфениловых эфиров алкан- и галогеналканкарбоксильных кислот. Было обнаружено слабое доэмергентное и более существенное послеэмергентное гербицидное действие.

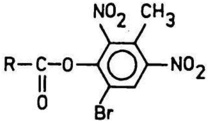
Of nitroaryl acetates, Aretit (2-*sec*-butyl-4,6-dinitrophenyl acetate) is used as herbicide in practice [1]. Numerous compounds of 2-alkyl-4,6-dinitrophenol [2—13] and halonitrophenols [14—18] are known as herbicides. Literature knowledge prompted us to prepare a new group of 2,4-dinitro-3-methyl-6-bromophenyl carboxylates (Table 1) and examine these compounds for herbicidal activity. The structures of the prepared compounds were verified by their i.r. spectra.

The starting 2,4-dinitro-3-methyl-6-bromophenol was prepared after [19] by nitration of *m*-cresol, crystallization of the formed 2,4-dinitro-*m*-cresol, and subsequent bromination with bromine in aqueous medium after [20]. The synthesis was carried out by treatment of sodium 2,4-dinitro-3-methyl-6-bromophenolate with the appropriate acyl chloride in toluene or acetone. The obtained products were yellow solids which were purified by crystallization from ethanol or cyclohexane. The compounds *III* and *IX* were liquids and were purified by separating the starting 2,4-dinitro-3-methyl-6-bromophenol with 5% sodium carbonate.

In the i.r. spectra a strong band corresponding to the stretching vibration $\nu(C=O)$ was found in the region of 1752—1816 cm^{-1}. As can be seen, the substituent R affects significantly the position of this band. We have found linear

Table 1

Characterization of the synthesized compounds



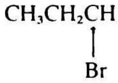
Compound	R	Formula	*M*	Calculated/found			Yield %	M.p., °C n_D^{20}
				% N	% Br	% Cl		
I	CH_3	$C_9H_7BrN_2O_6$	319.06	8.78 8.94	25.02 25.18	—	65.3	85—87
II	C_2H_5	$C_{10}H_9BrN_2O_6$	333.09	8.41 8.72	23.95 24.12	—	93.0	73—75
III	$(CH_3)_2CHCH_2$	$C_{12}H_{13}BrN_2O_6$	361.95	7.76 8.09	22.20 22.52	—	83.3	1.5611
IV	$(CH_3)_2C=CH$	$C_{12}H_{11}BrN_2O_6$	359.12	7.80 7.93	22.26 22.37	—	91.5	81—83
V	$ClCH_2$	$C_9H_6BrClN_2O_6$	353.51	7.84 8.14	22.71 22.60	10.02 9.84	80.8	69—71
VI	$BrCH_2CH_2$	$C_{10}H_8Br_2N_2O_6$	412.00	6.80 6.63	38.80 38.46	—	84.0	84—85
VII	$ClCH_2CH_2CH_2$	$C_{11}H_{10}BrClN_2O_6$	381.56	7.35 7.55	21.00 20.98	9.30 8.96	80.0	47—49
VIII	$Cl_3CCH=CH$	$C_{11}H_6BrCl_3N_2O_6$	448.43	6.25 6.10	17.81 18.19	23.74 24.12	81.0	86—88
IX	 $CH_3CH_2CH(Br)$	$C_{11}H_{10}Br_2N_2O_6$	424.16	6.56 6.80	37.50 38.10	—	73.6	1.5855
X	$4\text{-}I\text{—}C_6H_4$	$C_{14}H_8BrIN_2O_6$	507.02	5.48	15.78	24.95[a]	81.3	138—140

Table 1 (Continued)

Compound	R	Formula	*M*	Calculated/found			Yield %	M.p., °C n_D^{20}
				% N	% Br	% Cl		
				5.67	16.09	25.10		
XI	4-NO_2—C_6H_4	$C_{14}H_8BrN_3O_8$	426.13	9.86	18.76	—	87.5	146—148
				10.05	19.00			
XII	3-NO_2—C_6H_4	$C_{14}H_8BrN_3O_8$	426.13	9.86	18.76	—	60.8	89—91
				10.10	19.10			
XIII	$C_6H_5CH_2$	$C_{15}H_{11}BrN_2O_6$	395.16	7.08	20.21	—	87.0	108—109
				6.78	20.65			
XIV	$C_6H_5CH=CH$	$C_{16}H_{11}BrN_2O_6$	407.16	6.85	19.66	—	87.7	135—137
				7.09	19.61			
XV	4-NO_2—C_6H_4—OCH_2	$C_{15}H_{10}BrN_3O_9$	456.19	9.21	17.80	—	72.2	110—112
				9.35	18.00			
XVI	2-CH_3-4-Cl-C_6H_3—OCH_2	$C_{16}H_{12}BrClN_2O_7$	459.62	6.11	17.39	7.73	91.0	134—136
				6.34	17.21	8.04		

a) % I.

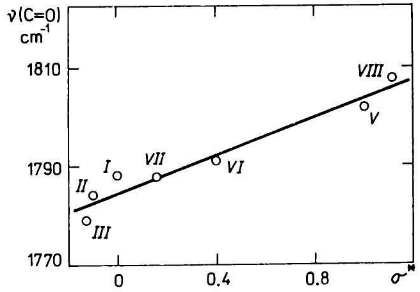


Fig. 1. Correlation of $\nu(C=O)$ with σ^* of some compounds.

correlations between $\nu(C=O)$ and the σ^* constants of the substituents R in cases when R was alkyl or haloalkyl ($\varrho = 18.18$; $r = 0.97$) (Fig. 1).

Only one band belonging to symmetric and asymmetric, respectively, stretching vibrations of the nitro group was observed in the i.r. spectra in spite of the fact that two nitro groups were present on the phenyl ring, moreover, in the compounds *XI*, *XII*, and *XV* a third nitro group was present on the second phenyl ring. The band belonging to $\nu_s(NO_2)$ was observed in the region of 1332—1341 cm^{-1} and that belonging to $\nu_{as}(NO_2)$ at 1531—1539 cm^{-1}. Both bands were very strong (Table 2).

Table 2

Infrared spectral data of the investigated compounds

Compound	ν/cm^{-1}		
	$\nu(C=O)$	$\nu_s(NO_2)$	$\nu_{as}(NO_2)$
I	1788	1341	1531
II	1784	1340	1532
III	1779	1339	1534
IV	1756	1339	1536
V	1802	1336	1536
VI	1791	1341	1538
VII	1788	1340	1538
VIII	1808	1332	1537
IX	1788	1341	1539
X	1763	1332	1538
XI	1771	1346	1538
XII	1769	1341	1538
XIII	1761	1340	1535
XIV	1752	1339	1534
XV	1808	1332	1537
XVI	1816	1338	1538

The compounds were little or not active at all when tested for preemergent herbicidal activity in 5 kg/ha and 1 kg/ha doses, therefore, the results are not presented. Majority of compounds showed high postemergent herbicidal activity in 2.5 kg/ha and 1 kg/ha doses. From the results given in Table 3 it can be seen that the compounds *VII* and *X* were least active. Of the used test objects — cultures, maize, oat, and panic were found to be most resistant, narrow-leaved vetch was medium resistant and sugar beet and flax were least resistant. Of the test objects — weeds, buckwheat and mustard were least resistant while cress and amaranth were somewhat more resistant. Of the tested compounds *XIII* was most active on weeds, while on cultures had no effect mainly when the dose was lower (1 kg/ha). There was a possibility of applying this compound on sugar beet plantations, however, its selectivity was not safe mainly when some overdoses were considered (Table 3).

Table 3

Herbicidal activity of compounds

Compound	Dose kg/ha	*Zea mays* L.	*Vicia sativa* L.	*Beta vulgaris* L.	*Linum usitatissimum* L.	*Avena sativa* L.	*Panicum miliaceum* L.	*Amaranthus retroflexus* L.	*Fagopyrum sagitatum* L.	*Sinapis arvensis* L.	*Lepidium sativum* L.
I	2.5	1	3	5	5	2	2	5	5	5	5
	1	0	1	5	2	1	1	1	4	4	4
II	2.5	1	3	5	5	2	2	5	4	5	5
	1	0	1	5	3	1	1	1	2	5	3
III	2.5	2	3	2	4	0	0	5	5	3	0
	1	0	0	0	0	0	0	0	0	0	0
IV	2.5	2	1	5	5	0	1	1	5	5	4
	1	0	0	2	0	0	0	0	4	4	0
V	2.5	1	4	5	5	2	1	5	5	5	5
	1	0	3	5	4	1	0	1	5	3	0
VI	2.5	1	3	5	4	2	1	3	5	5	5
	1	0	2	5	2	0	1	0	5	4	2
VII	2.5	1	1	1	1	0	1	1	2	3	1
	1	0	0	0	0	0	0	0	0	2	0
VIII	2.5	3	3	5	5	3	3	5	5	5	5
	1	2	1	5	3	1	2	4	3	5	4
IX	2.5	1	3	5	5	1	2	1	5	5	3
	1	0	0	0	0	0	0	0	1	3	1

Table 3 (Continued)

Compound	Dose kg/ha	*Zea mays* L.	*Vicia sativa* L.	*Beta vulgaris* L.	*Linum usitatissimum* L.	*Avena sativa* L.	*Panicum miliaceum* L.	*Amaranthus retroflexus* L.	*Fagopyrum sagitatum* L.	*Sinapis arvensis* L.	*Lepidium sativum* L.
X	2.5	0	0	0	0	1	0	0	2	3	1
	1	0	0	0	0	0	0	0	1	1	0
XI	2.5	2	3	2	4	1	2	5	4	4	5
	1	0	0	0	0	0	1	0	2	3	4
XII	2.5	2	3	5	5	1	2	5	3	5	3
	1	0	0	0	0	0	1	0	2	4	2
XIII	2.5	3	4	5	5	2	2	5	5	5	5
	1	1	0	1	2	0	1	5	5	4	2
XIV	2.5	0	1	5	2	0	0	1	4	4	0
	1	0	0	0	0	0	0	0	1	1	0
XV	2.5	1	3	5	5	2	2	5	5	5	5
	1	0	0	1	1	0	0	0	3	5	2
XVI	2.5	2	5	5	5	2	3	5	5	5	5
	1	0	4	5	3	0	2	5	5	5	4
2,4-D	2.5	0	5	5	5	0	2	5	5	5	5
Standard	1	0	5	4	3	0	1	4	4	5	5
DNOK	2.5	0	0	5	0	1	2	5	5	5	5
Standard	1	0	0	4	0	0	0	5	5	5	5

Experimental

Physical constants and the data of elemental analysis of the synthesized compounds are presented in Table 1.

Infrared spectra (Table 2) were measured on a UR-20 (Zeiss, Jena) spectrophotometer in carbon tetrachloride (concentration ~0.1—0.05 M; thickness of the NaCl cell 0.11 mm) in the region of 400—2000 cm^{-1}. The apparatus was calibrated by polystyrene foil.

Correlation of the bands $\nu(\text{C}=\text{O})$ with the σ^* constants of the substituents (Fig. 1) was carried out on a Hewlett—Packard 9100 B computer.

Herbicidal activity was determined by preemergent (into the soil) and postemergent (on the leaf) application using the test objects: *Zea mays* L. (maize), *Vicia sativa* L. (narrow-leaved vetch), *Beta vulgaris* L. (sugar beet), *Linum usitatissimum* L. (flax), *Avena sativa* L. (oat), *Panicum miliaceum* L. (panic), *Amaranthus retroflexus* L. (amaranth), *Fagopyrum sagitatum* L. (buckwheat), *Sinapis arvensis* L. (mustard), and *Lepidium sativum* L. (cress) after the described methods [21] and was evaluated as follows: 0 — no activity, 1 — 0—20% activity, 2 — 20—40% activity, 3 — 40—60% activity, 4 — 60—80% activity, 5 — 80—100% activity.

Preparation of the compounds

To sodium 2,4-dinitro-3-methyl-6-bromophenolate (0.05 mol) in acetone (80 ml) acyl chloride (0.05 mol) was added continuously at 0 to 5°C under stirring. Stirring was continued for 1 h at laboratory temperature and for 2 h at 40°C. After cooling to 10°C the reaction mixture was poured into ice water (300 ml). The precipitated solid was separated and purified by crystallization from ethanol or cyclohexane.

When the product was an oil this was dissolved in toluene (100 ml) and washed with 5% aqueous solution of sodium carbonate (100 ml). After drying with sodium sulfate, toluene was distilled off under reduced pressure.

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