

collected at each of the two main peaks. The infrared spectra (Perkin-Elmer infrared spectrophotometer, Model 21, sodium chloride optics) had characteristic α -olefin absorptions at 3070–3080 cm^{-1} (C—H stretch), 870–875 cm^{-1} (C—H out of plane deformation), and 1660–1670 cm^{-1} (C=C stretch) (6). The liquid residue from the distillation of the olefin was 2-methyl-3-acetoxymethylbornane (9.0 grams, 25% recovery). The infrared spectrum and vapor phase chromatogram were identical with those of an authentic sample.

2,3-Dimethylnorbornane. A solution of 2-methyl-3-methylenorbornane (12.5 grams, 0.1 mole) in hexane (40 ml.) was hydrogenated at 25° C. and 24–31 p.s.i.g. with platinum oxide (0.1 gram) in a Parr hydrogenator. Hydrogen (78% of the theoretical amount) was taken up during 0.75 hour. The catalyst was removed by filtration. The liquid was fractionated in a 6-inch Vigreux column to yield 2,3-dimethylnorbornane (8.6 grams, 67% yield); boiling point = 130–145° C.; $n_D^{20} = 1.4588$ (reported (2): boiling point for *trans* form = 41° C. at 20 mm. of Hg, $n_D^{20} = 1.4512$; for *endo-cis* form boiling point = 50.5° C. at 20 mm. of Hg, $n_D^{20} = 1.4643$; for *exo-cis* form boiling point = 53° C. at 25 mm. of Hg, $n_D^{20} = 1.4596$). The gas chromatogram on a 6-foot column of 10% Squalane on 35–80 mesh Chromosorb W (97° C.; 95 cc. of He per minute) had six peaks. Three of the peaks had a combined total area of 98.5%. Peak 3 had a retention time of 10.7 minutes (28.1%). Peak 4 had a retention time of 14.4 minutes (32.5%) and peak 5 had a retention time of 16.2 minutes (37.9%). A sample was

collected at each of the peaks. The infrared spectrum of peak 3 was identical with that of authentic *trans*-2,3-dimethylnorbornane, that of peak 4 was identical with that of authentic *exo-cis*-2,3-dimethylnorbornane, and that of peak 5 was identical with that of authentic *endo-cis*-2,3-dimethylnorbornane (1).

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Cyanoethyl Esters of Halocarboxylic Acids

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THE 2-CYANOETHYL TRICHLOROACETATE was reported recently (1) to be a selective herbicide. This note concerns some additional esters of ethylene cyanohydrin with halogen-containing carboxylic acids which also possess varying degrees of herbicidal activity. An analogous product, 2-cyanoethyl α -chloroacrylate, was reported earlier (2) but no indication of its biological activity was given.

The esters described in the table were prepared by direct

esterification of the acid (A), transesterification of an ethyl ester (B), acid chloride-pyridine method (C) and chlorination of an unsaturated acid (D).

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- (2) Lichty, J., (to Wingfoot Corp.), U.S. Patent 2,322,035 (1943).

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Table I. 2-Cyanoethyl Esters of Halocarboxylic Acids, $\text{RCO}_2\text{CH}_2\text{CH}_2\text{CN}$

R	Formula	Yield, %	% B.P. ^a /mm.	n_D^{20}	D_{20}^{20}	Calcd., %			Found, %			
						C	H	N	C	H	N	
$\text{Cl}_3\text{C}-^d$	$\text{C}_3\text{H}_4\text{NO}_2\text{Cl}_3$	43	99	0.5	1.4758	1.4774	27.7	1.8	6.5	27.9	1.8	6.3
$\text{Cl}_2\text{HC}-^f$	$\text{C}_5\text{H}_8\text{NO}_2\text{Cl}_2$	19	128	6	1.4673	1.3831	33.0	2.7	7.7	33.4	2.7	7.4 ^b
$\text{ClH}_2\text{C}-^e$	$\text{C}_5\text{H}_8\text{NO}_2\text{Cl}$	64	123	3.5	1.4527	1.2582	40.7	4.1	9.5 ^c	40.9	4.7	9.1 ^c
$\text{BrH}_2\text{C}-^e$	$\text{C}_5\text{H}_8\text{NO}_2\text{Br}$	79	133	5	1.4760	1.5740	31.3	3.1	7.3	31.9	3.2	7.7
$\text{CH}_2\text{CCl}_2-^d$	$\text{C}_8\text{H}_7\text{NO}_2\text{Cl}_2$	20	92	1	1.4570		36.7	3.6	7.1	37.3	3.8	7.0
$\text{ClCH}_2\text{CHCl}-^e$	$\text{C}_8\text{H}_7\text{NO}_2\text{Cl}_2$	92	Residue		1.4730	1.3484	36.9	3.6	7.1	36.9	3.6	7.0
$\text{ClCH}_2(\text{CH}_2)_4-^e$	$\text{C}_9\text{H}_{14}\text{NO}_2\text{Cl}$	79	165	5.5	1.4564	1.1096	53.0	6.9	6.9	53.2	6.9	7.0
$p\text{-Cl-C}_6\text{H}_4-^e$	$\text{C}_{10}\text{H}_9\text{NO}_2\text{Cl}$	55	160	4	m.p. 41°		57.3	3.8	6.7	56.8	3.8	7.1
$\text{Cl}_2\text{C}_6\text{H}_4-^e$	$\text{C}_{10}\text{H}_8\text{NO}_2\text{Cl}_2$	63	Residue		1.5010	1.2422	48.0	5.2	5.6	48.5	5.6	5.2
$\text{Cl}_2\text{C}_6\text{H}_3\text{-OCH}_2-^e$	$\text{C}_{11}\text{H}_9\text{NO}_2\text{Cl}_2$	98			m.p. 91–94°		48.2	3.3	5.1	48.4	3.0	5.4
$\text{Cl}_2\text{C}_6\text{H}_3\text{-O}(\text{CH}_2)_3-^e$	$\text{C}_{13}\text{H}_{13}\text{NO}_2\text{Cl}_2$	98	Residue		1.5269		51.6	4.3	4.6	51.7	4.2	5.1
$\text{CH}_3(\text{CH}_2)_7\text{-CH-ClCHCl}(\text{CH}_2)_7-^e$	$\text{C}_{21}\text{H}_{37}\text{NO}_2\text{Cl}_2$	86	Residue		1.4853	0.9330						2.9

^aAll temperatures are uncorrected. ^b% Cl = 37.9. ^c% Cl = 37.9. ^d% Cl = 24.0. ^e% Cl = 24.4. ^fBy Method A. ^gBy Method B. ^hBy Method C. ⁱBy Method D.