Preparation and Polymerization of Cycloalkyl Acrylates[1,2]

BY C. E. REHBERG AND W. A. FAUCETTE[3]

In our earlier work[3] it was found that all the alkyl polyacrylates studied had brittle points near room temperature, or lower. It was known that the presence of the cyclohexyl ring in the molecule caused a large rise in the softening point of polymethacrylates.[4] Hence, it appeared of interest to prepare some cycloalkyl polyacrylates in the hope that they might be of use as rigid plastics.

The monomeric acrylates (Table I) were prepared by the alcoholysis of methyl or ethyl acrylate,[4] and were polymerized in emulsion. Brittle points were determnied as previously described.[3] The one methacrylate was prepared (from methyl methacrylate) for comparison with the corresponding acrylate.

TABLE I

YIELDS, PHYSICAL CONSTANTS AND ANALYSES OF CYCLOALKYL ACRYLATES

Acrylate	Yield, %	Boiling pt. °C.	Boiling pt. Mm.	$n^{20}D$	d^{20}_4	Mol. refraction Calcd.	Mol. refraction Found	Sapon. equiv. Calcd.	Sapon. equiv. Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Brittle pt. of polymer, °C.
Cyclohexyl	77	75	11	1.4600	0.9796	42.75	43.12	154.2	155.0	70.1	70.2	..	..	16
Cyclohexyl[a]	..	182–184	Atm.	1.4673	1.0275	42.75	41.66	...	...	..	..	..	..	...
2-Methylcyclohexyl	70	69	5	1.4560	.9546	47.37	47.90	168.2	170.5	71.4	71.0	..	..	32
3-Methylcyclohexyl	78	74	6	1.4550	.9541	47.37	47.84	168.2	168.1	71.4	70.9	..	..	31
4-Methylcyclohexyl	85	55	2	1.4550	.9537	47.37	47.86	168.2	167.8	71.4	71.6	..	..	35
3,3,5-Trimethylcyclohexyl[b]	89	72	2	1.4542	.9292	56.60	57.31	196.3	204.1	73.4	73.6	10.3	10.4	48
3,3,5-Trimethylcyclohexyl[c]	50	40	0.2	1.4560	.9346	56.60	57.09	196.3	205.3	73.4	73.3	10.3	10.5	50
4-*t*-Amylcyclohexyl	85	95	1	1.4705	.9490	65.84	66.00	224.3	222.8	75.0	75.0	10.8	10.8	−8
4-Cyclohexylcyclohexyl[d]	86	115	1	1.4810[e]	.9500[e]	68.26	70.80[e]	236.3	234.0	76.2	76.0	10.2	9.9	35
Hydroabietyl	25	177	0.3	1.5172	1.0181	102.53	102.42	344.5	349.2	..	..	..	..	28
3,3,5-Trimethylcyclohexyl[f]	88	79	1	1.4560	.9255	61.22	61.77	210.3	213.9	74.2	74.5	10.6	10.7	140

[a] Reported by Ipatov, *J. Gen. Chem.* (*USSR*), **15**, 639 (1945) [*C. A.*, **40**, 5697 (1946)]. [b] Made from alcohol of m. p. 35°. [c] Made from alcohol of m. p. 51°. [d] M. p., 41°. [e] At 50°. [f] Methacrylate made from alcohol of m. p. 35°.

The two isomeric forms of 3,3,5-trimethylcyclohexanol (m. p. 35° and 51°) formed monomeric esters which showed small, but probably significant, differences in refractive index and density (Table I). Attempts to determine their melting points were indecisive; both samples became glass-like at about −50° without passing through any sharp transition point. The small difference in the brittle points of the polymers is not considered significant.

The 4-cyclohexylcyclohexyl ester was a colorless solid, melting at 41°. Excepting monomeric hydroabietyl acrylate, which was slightly colored and exceedingly viscous, the esters were colorless, mobile, or slightly oily liquids having mild, pleasant, terpene-like odors.

The hydroabietyl and the 4-*t*-amyl- and 4-cyclohexylcyclohexyl polyacrylates appeared to be of low molecular weight. They were discolored and were extremely soft and tacky. Abnormally large amounts of catalyst were required to initiate their polymerization, indicating that some inhibitor remained in the monomer. All the other polymers were hard, white, granular solids, which were readily molded to form clear, colorless sheets.

3,3,5-Trimethylcyclohexyl polymethacrylate has been evaluated as a coating for optical lenses. It is reported to have outstanding resistance to water and to outdoor weathering.[5]

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[2] Presented before the Organic Chemistry Division of the American Chemical Society at the 117th National Meeting, Philadelphia, Pa., April, 1950.

[3] Rehberg and Fisher, *Ind. Eng. Chem.*, **40**, 1429 (1948).

[4] E. I. du Pont de Nemours and Co., *ibid.*, **28**, 1160 (1936).

[5] Coles, Schulz, Levy and Wheatley, *Modern Plastics*, **25**, No. 11, 123 (1948).

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Formation of *m*-Toluidine by a New Synthetic Route

BY DAVID A. SALZBERG

In setting up a research program in this Laboratory on the metabolism of carcinogenic azo dyes, interest was centered on the greatly enhanced carcinogenic activity of 3′-methyl-*p*-dimethylaminoazobenzene[1] over the parent compound *p*-dimethylaminoazobenzene. It was felt that much could be learned by incorporating isotopic carbon (C^{14}) in the 3′-methyl group of the former dye and determining its metabolic fate in the rat, where diets containing 0.06% of the dye result in liver tumors in ten to twelve weeks.

The dye is readily prepared by coupling diazotized *m*-toluidine with dimethylaniline and thus the problem was to synthesize *m*-toluidine labeled with C^{14} in the methyl group. Benzoic acid containing C^{14} in the carboxyl group is obtainable by

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[1] Miller and Baumann, *Cancer Research*, **5**, 227 (1945).

Grignard reaction of bromobenzene and C^{14} labeled carbon dioxide.[2] As esterification of benzoic acid and meta nitration[3] of the resulting ester are readily effected, direct reduction of the methyl and ethyl *m*-nitrobenzoates to *m*-toluidine was attempted.

In 1948, Huang-Minlon[4] reported a modification of the Wolff–Kishner reaction in which nitrobenzaldehydes were reduced to toluidines by hydrazine hydrate in diethylene glycol, this solvent permitting a high refluxing temperature. The success of this reaction and the report by McFadyen and Stevens[5] that certain esters are reduced to aldehydes *via* formation of their benzenesulfonyl hydrazides prompted the present investigation of the effect of hydrazine on *m*-nitrobenzoate esters. This has resulted in a new reductive method whereby *m*-toluidine is prepared by simple distillation of an alkaline solution of the methyl or ethyl *m*-nitrobenzoate and hydrazine in diethylene glycol.

In the belief that the reaction might go through a hydrazidine intermediate which is competitively hydrolyzed and reduced by the alkali, an attempt was made to improve the yield by distilling off excess water from the initial mixture of glycol, nitroester and hydrazine hydrate, and then replacing the potassium hydroxide solution with an equivalent amount of sodium diethylene glycolate, prepared by the reaction of metallic sodium with diethylene glycol. After fifteen minutes of refluxing, the flask was allowed to cool, 2 ml. of water added, and steam distillation carried out as described below. However, this resulted in no increase in yield.

To attempt to extend the scope of this reaction, it was tried on several other compounds (Table I). On the unsubstituted aromatic and aliphatic esters, ethyl benzoate and methyl laurate, the method was unsuccessful, resulting only in hydrolysis to the corresponding acid. Attempted reduction of an equimolar mixture of nitrobenzene and ethyl benzoate gave only aniline and benzoic acid. Two grams each of the methyl *o*- and *p*-nitrobenzoates gave only approximately 0.05 g. of the corresponding *o*- and *p*-toluidines. Attempted reduction of methyl salicylate and methyl *m*-hydroxybenzoate, resulted in no reduction product.

TABLE I

EFFECT OF HYDRAZINE ON VARIOUS ESTERS

Compound	Redn. product	% yield
Ethyl benzoate	None	
Methyl laurate	None	
Methyl *o*-hydroxybenzoate	None	
Methyl *m*-hydroxybenzoate	None	
Methyl *o*-nitrobenzoate	*o*-Toluidine	Appx. 4
Methyl *m*-nitrobenzoate	*m*-Toluidine	25
Methyl *p*-nitrobenzoate	*p*-Toluidine	Appx. 4
Ethyl *m*-nitrobenzoate	*m*-Toluidine	25

Reduction of methyl *m*-nitrobenzoate labeled with C^{14} in the carboxyl group gave C^{14} labeled *m*-toluidine containing the same molar specific activity as the nitro ester.

Experimental

***m*-Toluidine.**—All procedures unless otherwise indicated followed that described below for the preparation of *m*-toluidine, and used the same mole ratios of materials.

In a 200-ml., round-bottom, standard glass-taper flask 2 g. of methyl *m*-nitrobenzoate was dissolved in 12 ml. of diethylene glycol and 3 ml. of 85% hydrazine hydrate was added. After one minute of gentle heating and swirling of the flask to ensure complete mixing, a concentrated aqueous solution containing 2 g. of potassium hydroxide was added and the flask attached to a 20-cm. Vigreux column whose side arm extended to the bottom of an ice-bath cooled receiver.

The mixture was heated over a small bunsen flame so that vapor began to condense in the side arm in five to ten minutes and shortly thereafter droplets of the *m*-toluidine appeared in the distillate. This steam distillation was continued until no water remained in the reaction mixture, as evidenced by the rise of distillation temperature from the initial 99–100°.

The organic material in the distillate was separated from the aqueous phase by ether extraction. Removal of the ether by evaporation left 0.30 g. (25%) of *m*-toluidine, b. p. 201° at 756 mm., which readily reacted with acetic anhydride to give a white solid of m. p. 65°, not depressed on mixture with an authentic sample of N-acetyl-*m*-toluidine; literature: *m*-toluidine b. p. 203°, acetamide, deriv. m. p. 65°.

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[2] Dauben, Reid and Yankwich, *Ind. Eng. Chem., Anal. Ed.*, **19**, 828 (1947).

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[4] Huang-Minlon, THIS JOURNAL, **70**, 2802 (1948).

[5] McFadyen and Stevens, *J. Chem. Soc.*, 584 (1936).

Hydrogen Peroxide Vapor Explosions—Determination of Explosive Composition[1]

BY CHARLES N. SATTERFIELD, GEORGE M. KAVANAGH, RALPH N. KINGSBURY AND HYMAN RESNICK

The occurrence of a homogeneous gas decomposition in hydrogen peroxide vapor, a reaction easily obscured by the heterogeneous decomposition on the walls, has recently been deduced by McLane.[2] His experiments, conducted at high temperature, under low pressure, and with carefully prepared surfaces, indicate that the usual wall decomposition is accompanied by some homogeneous reaction. Direct observation of explosions and flames in vapor containing hydrogen peroxide has been reported by Hart.[3] In an investigation of the nature of the decomposition reaction, measure-

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[1] This work is supported by funds from the Office of Naval Research.

[2] C. K. McLane, *J. Chem. Phys.*, **17**, 379 (1949).

[3] A. B. Hart, *Nature*, **63**, 876 (1949).