[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE COLLEGE OF ST. THOMAS]

THE PREPARATION OF THE NEOPENTYL ESTERS OF ACRYLIC AND METHACRYLIC ACIDS

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The development of interest in ester derivatives of acrylic and methacrylic acids since the original work on these compounds by Rohm (1), has been rapid. The fact that it is often observed that small proportions of acrylic monomers are sufficient to produce desirable modifications in copolymers (2) has stimulated the curiosity of workers in the field as to the effect of structure, especially branching, on the polymerization characteristics of acrylic-type polymers and copolymers. This has led to the preparation of a wide variety of acrylic esters and there is copious literature on the subject. Careful perusal of the literature, however, has failed to reveal any reference to the synthesis of the neopentyl esters of either acrylic or methacrylic acids. This is a serious omission in view of the obviously unique structural features of the neopentyl group and is doubtless due to the difficulties heretofore experienced in the preparation of neopentyl alcohol. Development by Brown (3, 4) of the lithium aluminum hydride reduction procedure for carboxylic acids has made neopentyl alcohol available from pivalic acid so the current researches were launched to supply the missing data on the neopentyl esters.

The neopentyl esters were readily prepared by the following schemes:

$$\text{(a)}\quad CH_2{=}C(R)CO_2H + (CH_3)_3CCH_2OH \xrightarrow{H^+} CH_2{=}C(R)CO_2CH_2C(CH_3)_3 + H_2O$$

$$\text{(b)}\quad CH_2{=}C(R)COCl + (CH_3)_3CCH_2OH + C_6H_5N(CH_3)_2 \rightarrow CH_2{=}C(R)CO_2CH_2C(CH_3)_3 + C_6H_5N(CH_3)_2{\cdot}HCl$$

The neopentyl alcohol required in the syntheses was made both by the method of Whitmore (5) as shown in equation (c):

$$\text{(c)}\quad (CH_3)_3CCOCl + 2\ (CH_3)_3CMgCl + H_2O \rightarrow (CH_3)_3CCH_2OH + 2\ (CH_3)_2C{=}CH_2 + MgCl_2 + Mg(OH)Cl$$

and by the method of Brown (4) using lithium aluminum hydride reduction. The latter procedure proved to be by far the more practical one and most of the neopentyl alcohol prepared in this study was made in this way.

The physical characteristics of both of the esters are presented in Table I.

EXPERIMENTAL

I. PREPARATION OF NEOPENTYL ALCOHOL

A. *From pivalyl chloride.* The acid chloride was prepared by the procedure of Stemple, Cross, and Mariella (6). To a solution of 1.5 moles of *tert*-butylmagnesium chloride in 1

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TABLE I
PHYSICAL CONSTANTS OF THE NEOPENTYL ESTERS

Neopentyl Acrylate		Neopentyl Methacrylate	
B.P., °C.	mm.	B.P., °C.	mm.
28.5	5.5	40.0	6.0
36.0	9.3	53.5	11.5
44.0	14.5	58.0	14.0
51.5	21.0	65.0	19.0
n_D	t., °C.	n_D	t., °C.
1.4190	12.5	1.4203	20.0
1.4180	17.5	1.4191	23.0
1.4166*	20.0	1.4181	25.5
1.4142	24.0		
1.4138	25.0		
d_{20}^{t}	t., °C.	d_{20}^{t}	t., °C.
0.8759	20.0	0.8775	17.0
		0.8740*	20.0
		0.8730	21.0
		0.8697	26.0

* Interpolated.

liter of dry ether was added 0.35 mole of undiluted pivalyl chloride over a period of 1½ hours with constant stirring. A 15-minute stirring period was allowed after the addition was completed and the mixture was allowed to stand overnight. The Grignard complex then was decomposed and worked up according to the directions of Whitmore (5). The product boiling at 106–112° amounted to 20.8 g. (65%). Redistillation of this material gave 19 g. of neopentyl alcohol boiling at 110–112°.

B. *From pivalic acid.* A 15-g. sample of commercial lithium aluminum hydride was dissolved in 400 ml. of anhydrous diethyl ether by refluxing the mixture, with stirring, for three hours. A solution of 30 g. of pivalic acid prepared from *tert*-butyl chloride (7) in 150 ml. of anhydrous ether was added slowly to the hydride solution over a period of five hours. The entire reaction mixture was allowed to stand at room temperature for two days and then was refluxed gently for eight hours. Excess hydride was decomposed by slow addition of water to the mixture until all evidence of reaction had ceased. Alcoholates and salts formed in the hydrolysis were dissolved by cautious addition of 36 *N* sulfuric acid to the reaction vessel until the solid phase disappeared and two clear layers resulted. The ether layer was separated and the aqueous phase was extracted with several small portions of ether, these extracts being added to the original ether layer. At this point the ether solutions from two such runs as described above were combined and worked up together. These combined ether solutions were washed with four 50-ml. portions of saturated sodium bicarbonate solution and then with three 50-ml. portions of distilled water. The ether solution was dried by refluxing for four hours with calcium oxide. The excess calcium oxide and the calcium hydroxide formed were filtered and the ether solution was fractionated. A 46.5-g. (90%) portion of product was collected from 100–112°. This material was solid at room temperature and was used directly in the subsequent preparation of neopentyl acrylate.

With one batch of lithium aluminum hydride, application of the above directions gave no isolable neopentyl alcohol but when powdered, anhydrous aluminum chloride (50 g.) was added to the ether solution of inert hydride, evidence of reduction was noted on the addition of pivalic acid. The excess hydride and aluminum chloride were decomposed with water but the customary white solid failed to appear at once in the reaction flask. On standing four days, however, some frothing of the mixture occurred and the white solid finally appeared. The mixture was worked up in the usual way and 15.3 g. (62%) of usable neopentyl alcohol was obtained.

II. PREPARATION OF NEOPENTYL ACRYLATE

A. *From acryloyl chloride.* A 1-litre 3-necked flask provided with a stirrer, thermometer, and dropping-funnel was charged with neopentyl alcohol (20 g.), freshly distilled nitrobenzene (200 ml.), and dimethylaniline (30 g.). To this mixture, which turned a deep red on introduction of the amine, a solution of acryloyl chloride (22 g.), prepared by the method of Rehberg (8), in nitrobenzene (100 ml.) was added dropwise over a period of 40 minutes. The reaction temperature rose to 42° during the addition period. After the acid chloride had been added, the mixture was stirred for 1 hour and then allowed to stand overnight. The reaction product was distilled at 35 mm. and everything boiling up to 100° at this pressure was taken. The distillate was washed with small portions of water and saturated sodium carbonate and then dried over sodium sulfate. Distillation of this product gave 21.5 g. (66%) of a colorless liquid boiling 49.5–51° at 20 mm.

B. *From acrylic acid.* A one-liter round bottom flask was charged with neopentyl alcohol (55 g.), acrylic acid (50 g., m.p. 13.4°), *p*-toluenesulfonic acid (3 g.), pyrogallol (5 g.), copper powder (0.1 g.), and benzene (300 ml.). The flask was then attached to a phase separator and cyclicly distilled for 9 hours. At this time 11.5 ml. of water, representing 97% of the total water of esterification had been separated. The benzene solution was washed with several portions of saturated sodium carbonate solution and of water, dried over sodium sulfate, and then distilled at atmospheric pressure until practically all the benzene had been removed. The residue, when distilled at reduced pressure, gave 70 g. (79%) of a colorless liquid b.p. 35–39° (14 mm.).

Several batches of neopentyl acrylate prepared as explained above were combined and distilled at reduced pressure. A sharply-boiling heart cut was analyzed.

Anal. Calc'd for $C_8H_{14}O_2$: C, 67.57; H, 9.92; Sapon. equiv., 142.2; M_D, 40.34.
Found: C, 67.32: H, 9.93; Sapon. equiv., 141.6; M_D, 40.73.

III. PREPARATION OF NEOPENTYL METHACRYLATE

A. *From methacryloyl chloride* (9, 10). A 500-ml. 3-necked flask provided with a stirrer, thermometer, and dropping-funnel was charged with neopentyl alcohol (25 g.), freshly distilled benzene (300 ml.), and dimethylaniline (34.4 g.). To this mixture 31 g. of methacryloylchloride (an excess of approximately 5%) prepared by the method of Stemple, Cross, and Mariella (6) dissolved in benzene (50 ml.) was added dropwise. No temperature rise was noted during addition of the chloride and no evidence of reaction was apparent so the mixture was gently refluxed for three hours. At the end of this time two layers were in evidence in the reaction flask. The mixture was allowed to stand 24 hours and again was refluxed for 3 hours with stirring. The two layers then were separated and the water layer was extracted with two small (25 ml.) portions of benzene. These extracts were added to the main benzene solution which was then washed alternately with three small portions each of water, 10% hydrochloric acid solution, and water. The washed benzene solution was dried with potassium carbonate and distilled to yield 32.2 g. (72.8%) of a colorless liquid boiling 61–62° at 18 mm.

B. *From methacrylic acid.* A 200-ml. boiling flask was charged with neopentyl alcohol (30 g.), 98% methacrylic acid (31.4 g., approximately a 5% excess), sulfuric acid (0.2 g.), hydrated *p*-toluenesulfonic acid (3.0 g.), pyrogallol (1.0 g.), cuprous bromide (0.5 g.), and benzene (100 ml.). The flask was attached to a phase separator and distilled until water collection ceased, a matter of 6 hours. The entire mixture was distilled to remove all volatile products and to leave the catalysts and inhibitors behind. The distillate from this operation was carefully refractionated and the low-boiling portion containing the benzene was separated and discarded. As a second fraction 45.5 g. (85.8%) of a colorless liquid, b.p. 61–64° (19 mm.) was collected.

The crude neopentyl methacrylate prepared by both methods described above was combined and carefully purified by washing with several portions of saturated sodium carbonate and then with water and dried with potassium carbonate. This material was carefully fractionated and a heart cut was analyzed.

Anal. Calc'd for $C_9H_{16}O_2$: C, 69.19; H, 10.32; Sapon. equiv., 156.2; M_D, 44.96.
Found: C, 69.57; H, 10.41; Sapon. equiv., 158.0; M_D, 44.91.

The partly hindered character of neopentyl methacrylate was definitely noted in saponification studies on this compound. The ester was not completely hydrolyzed by treatment with NaOH in diethylene glycol (11) even at temperatures as high as 145° for as long as 20 minutes. For complete saponification it was necessary to reflux the compound with concentrated alcoholic sodium hydroxide (12) for as long as 15 hours.

SUMMARY

A description is given of methods of preparation of the neopentyl esters of acrylic and methacrylic acids. Physical properties of these esters have been measured and the values are presented. The effect of the partly hindered character of neopentyl methacrylate on the saponification of this ester is pointed out.

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