TABLE I

O—H STRETCHING FREQUENCIES OF CYCLIC GLYCOLS AND ARYLALKYL ALCOHOLS (CM.$^{-1}$)

Compound	Free	OH...π	OH...O	Ref.
Benzyl alcohol	3632	3615	...	4
β-Phenylethanol	3631	3604	...	5
cis-Cyclohexane-1,2-diol	3626	...	3587	3b
trans-Cyclohexane-1,2-diol	3634	...	3602	3b
cis-Tetrahydronaphthalene-1,2-diol	...	3618	3575	3b
trans-Tetrahydronaphthalene-1,2-diol	...	3615	3582	3b
cis-Cyclopentane-1,2-diol	3633	...	3572	3b
trans-Cyclopentane-1,2-diol	3620	...	...	3b
exo-cis-Bicycloheptane-2,3-diol	3632	...	3529	6
endo-cis-Bicycloheptane-2,3-diol	3633	...	3531	6
cis-Flavan-3,4-diol (m.p. 160°)	...	3606	3578	
trans-Flavan-3,4-diol (m.p. 145°)	...	3608	...	

atom of the 4-hydroxyl group which is weakly bonded to the oxygen atom in the 3-position. These two frequencies superimpose to give a single sharp band.

Cyanoethylation of Fatty Amines Using Acidic Ion Exchange Catalysis[1]

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Received July 9, 1962

The uncatalyzed addition of acrylonitrile to activated hydrogen bearing molecules is employed to yield the corresponding cyanoethyl substituted derivative. Ionic catalysis aids this addition to less activated centers. Cyanoethylation of weakly basic amines (for example secondary amines already bearing a deactivating cyanoethyl group) has been aided by organic acids such as acetic, propionic, benzoic, or *p*-toluenesulfonic.[2] A mixture of acetic and phosphoric acids has been employed in the direct addition of two moles acrylonitrile to primary fatty amines.[3] Reference 2 suggests use of the organic acid to 10–50% of the combined amine–acrylonitrile weight and the product yield varies from 40–70%.

Acidic ion exchange resins have been found effective in the dicyanoethylation of fatty amines. Since they remain insoluble throughout the reaction, simple filtration removes the resin or resin–amine salt from the final reaction solution. Reuse of the resin has been demonstrated, but a moderate decrease in catalytic activity was noted.

The resins were obtained water-wet and several repeated suspensions in absolute methanol removed most of the water leaving a methanol-wet resin. Similar treatment was given the three types of resins used: Dowex 50W (sulfonic acid type); Rohm & Haas XE-89 (carboxylic acid type); and Chemical Process Co. Duolite C-63 (phosphoric acid type).

Table I (p. 4116) indicates that the sulfonic resin was most active in catalyzing this reaction and the phosphoric acid resin least active.

Experiment 6 represents the repeated usage of the Dowex resin. The weight increase from A to B indicates that some amine–resin salt is combined from the first reaction. The recovered resin was washed twice in absolute methanol and reused immediately. A notable decrease in conversion of primary amine to N,N-dicyanoethyl fatty amine was observed—from 84 to 72%. When used still a third time, no further activity decrease was recorded.

The degree of resin cross linking and the mesh size also appear to affect the degree of dicyanoethylation. Dowex 50W cross linked with 1% divinylbenzene is more effective than resin cross linked with 4, 8, or 12% DVB. Likewise the smaller particle size (50–100 mesh) resin aids this reaction.

Experimental

(Table I, Run 5).—The following materials were placed in a 500-ml. three-neck round-bottom flask with mechanical stirrer, thermometer, and reflux condenser: 177 g. (0.64 mole) of octadecylamine (total amine #205, 97% primary and 0.3% secondary amine, IV 3.5, containing approximately 7% hexadecylamine), 75 g. (1.4 mole) of acrylonitrile, 5 g. of absolute methanol, and 20 g. of methanol-wet Dowex 50W-IX (50–100 mesh) H$^+$ form. An initial exothermic reaction occurred and then external heat was required to maintain the reaction at the reflux temperature of 70–75°. Samples and final reaction mixture were filtered to remove ion exchange resin. The solvent and excess acrylonitrile were removed from the filtrate under reduced pressure and finally at 60° under high vacuum. Nearly quantitative total recovery was achieved.

Hours	Total amine no.	Tertiary amine no.
2	170	22.8
7	161	65
22	157	109
29.5	150	134.7

Theoretical amine no.: dicyanoethyl derivative 149.2; monocyanoethyl derivative 174.0.

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[1] Journal Series Number 312, Central Research Laboratories, General Mills, Inc.

[2] G. W. Fowler and J. W. Lynn, U. S. Patent 3,020,310 (February 6, 1962).

[3] R. Nordgren, U. S. Patent 3,028,415, (April 3, 1962).

TABLE I

	Reactants										Reaction		Product					
	Amine				Resin[a]			Acrylonitrile										
Run no.	Name	Amine no.	G.	Mole	Name	Size	G.	G.	Mole	MeOH, g.	Temp., °C.	Time, hr.	Wt., g.	Total amine no.[d]	Tertiary amine no.[e]	Secondary amine no.[f]	Theor. tertiary amine no.	% R—N—$(CH_2CH_2CN)_2$
1	n-$C_8H_{16}NH_2$	433.7	22	0.17	Dowex 50W-4X	(20–50)	10	21	0.396	4	70–76	22	39	236	234	1.4	238.7	100
2	$C_{12}H_{24}NH_2$	303	91	0.49	Dowex 50W-4X	(20–50)	20	62	1.17	5	70–74	17	132	192.9	182	10.0	192.4	95
3	$C_{18}H_{36}NH_2$	205	276	1.0	Dowex 50W-4X	(20–50)	30	125	2.35	10	72	26	365	155.4	102	50	149.2	65
4	$C_{18}H_{36}NH_2$	205	276	1.0	Dowex 50W-4X	(50–100)	30	125	2.35	10	72	24	352	150.6	125	23	149.2	85
5	$C_{18}H_{36}NH_2$	205	177	0.64	Dowex 50W-1X	(50–100)	20	75	1.41	5	70–75	29	218	150.2	134.7		149.2	90
6a	$C_{18}H_{36}NH_2$[b]	206	273	1.0	Dowex 50W-1X	(50–100)	27	116	2.19	15	70–78	25	346	150.5	126.4		148	84
b	$C_{18}H_{36}NH_2$[b]	206	273	1.0	Dowex 50W-1X	(50–100)	37[c]	116	2.19	15	70–78	24	363	152	110		148	72
c	$C_{18}H_{36}NH_2$[b]	206	233	0.85	Dowex 50W-1X	(50–100)	35[c]	95	1.79	13	70–80	24	311	153.5	109.6		148	71
7	$C_{12}H_{24}NH_2$	303	91	0.49	XE-89		15	62	1.17	5	72	18	136	195.6	167	29	192	85
8	$C_{12}H_{24}NH_2$	303	91	0.49	Duolite C-63		15	62	1.17	5	72	18	132	209	109	100	192	50

[a] Weight–methanol-wet. [b] Mixed tall oil fatty amines. [c] Reused from previous run. [d] Total amine number: mg. potassium hydroxide equiv. to total amine in 1-g. sample (method: potentiometric titration using perchloric acid in glacial acetic acid solvent). [e] Tertiary amine number: mg. potassium hydroxide equiv. to tertiary amine in 1-g. sample (method: potentiometric titration using perchloric acid after sample treated to acetylate primary and secondary amine). [f] Secondary amine number: mg. potassium hydroxide equiv. to secondary amine in 1-g. sample (method: determine secondary + tertiary by titration after addition of salicylaldehyde; subtract tertiary).

3-Pentadienone[1]

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Received July 16, 1962

In connection with other studies in progress in this laboratory it was desired to have a source of 3-pentadienone (divinyl ketone). 3-Pentadienone has previously been prepared by the dehydrochlorination of di(β-chloroethyl) ketone[2] and by the thermal cracking of di(β-methoxyethyl)ketone.[3] Both methods were rejected due to a number of inconveniences connected with the various reactions involved. A route which appeared promising was the oxidation of divinylcarbinol under the mild conditions exemplified in the manganese dioxide oxidation of allylic alcohols, a reaction which has been studied in some detail with satisfactory results being reported in numerous instances.[4]

Various factors exert an influence on the rate of the reaction and the ultimate yield of the oxidized product. The type of manganese dioxide employed appears to be the most important single factor. It was found that divinylcarbinol could be oxidized to 3-pentadienone in moderate yields employing manganese dioxide of four different types. Manganese dioxide (type A) was purchased commercially[5] and used as received. Manganese dioxides (types B and C) were prepared according to the procedure of Harfenist[6] by pyrolysis of manganese carbonate (type B) followed by washing with dilute nitric acid and thorough drying (type C). More consistent yields of the ketone were obtained employing a grade of manganese dioxide (type D) prepared by the method of Attenburrow and coworkers.[7]

The oxidations were carried out in chloroform or methylene chloride solutions with equal results employing ratios of divinylcarbinol to manganese dioxide of from 1/5 to 1/15. The yield data is presented in Table I. Although the yields varied considerably even with oxidations carried out using a single type of manganese dioxide a ratio of 1/10 was found to give near optimum yields. The extent of the reaction was followed by infrared spectroscopy which showed in most instances that the reaction was essentially complete within four to

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[1] This work was performed under sponsorship of the U. S. Army under Contract No. DA-01-021 ORD-11878.

[2] Johannes Nelles, U. S. Patent 2,105,792 (January 18, 1938).

[3] I. N. Nazarov and I. V. Torgov, *Bull. Acad. Sci. URSS Classe Sci. Chim.*, 495 (1946); *Chem. Abstr.*, **42**, 7735 (1948).

[4] For leading reference see R. M. Evans, *Quart. Rev.*, **13**, 61 (1959).

[5] Leco manganese dioxide obtained from E. H. Sargent and Co.

[6] N. Harfenist, A. Bavley, and W. A. Lazier, *J. Org. Chem.*, **19**, 1608(1954).

[7] J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.*, 1094 (1952).