[CONTRIBUTION FROM THE CASE INSTITUTE OF TECHNOLOGY]

Catalysis by Anion Exchange Resins. Condensations of Nitroparaffins with Aldehydes and Ketones

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A quaternary ammonium hydroxide type of anion exchange resin (Amberlite IRA-400) was found to be an effective catalyst for the condensation of nitroparaffins with aldehydes and some ketones. A weak base resin (Amberlite IR-4B) was not a successful catalyst for condensations involving nitromethane or for most condensations involving nitroethane. As exceptions *n*-butyraldehyde and isobutyraldehyde were condensed with nitroethane in the presence of Amberlite IR-4B. Amberlite IR-4B was a better catalyst than Amberlite IRA-400 for the condensation of aldehydes, except for formaldehyde, with 2-nitropropane. Ketones such as acetone and cyclohexanone condensed slowly with nitromethane and nitroethane in the presence of Amberlite IRA-400.

The nitroparaffins undergo aldol condensations with aldehydes or ketones in the presence of bases. This type of reaction has received considerable attention by a number of investigators including, Vanderbilt and Hass,[2] Sprang and Degering,[3] Nightingale and Janes,[4] and Hass and Bourland.[5] The bases that have been used as catalysts include sodium carbonate, sodium hydroxide, and calcium or barium hydroxides. Schmidle and Mansfield[6] reported the condensation of nitromethane and nitroethane with propionaldehyde and butyraldehyde catalyzed by the anion exchange resins Amberlite IRA-400 and IRA-410. It was thought desirable to extend this work to include other aldehydes, ketones and nitroparaffins.

The advantages of using anion exchange resins as catalysts for organic reactions have been described previously.[7,8] The reaction product is not contaminated with the catalyst and no neutralization or separation steps are required other than decantation of the solution away from the resin.

Two resins were used in this investigation: Amberlite IRA-400, which is a strong base of a quaternary ammonium hydroxide type and Amberlite IR-4B, which is a weak base containing secondary and tertiary amino groups. These resins were prepared for use by washing in a Büchner funnel with 6 to 8 volumes of 5 per cent sodium hydroxide solution then with distilled water until the washings were neutral. The resin then was washed with alcohol and dried at room temperature. Amberlite IRA-400 must be kept in a tightly stoppered bottle because it slowly becomes deactivated in contact with air by the absorption of carbon dioxide.

EXPERIMENTAL

The condensations of nitroparaffins were carried out in essentially the same way. Freshly distilled aldehyde or ketone, nitroparaffin, and mutual solvent, such as ethanol, were charged along with the ion exchange resin (25 per cent of the weight of the carbonyl compound) into a flask and agitated by shaking at room temperature for 15 hours. In some cases longer periods of agitation were required. After the reaction was complete, the catalyst was removed by filtration and the reaction products were separated by fractional distillation.

The nitroparaffins were used in 10 to 25 per cent excess except in the case of cyclohexanone in which the ratio of ketone to nitroparaffin was 2 to 1.

The following examples illustrate the procedures used:

Formaldehyde and nitromethane. Nitromethane (112 g.), 81 g. of 37% formalin solution, and 7.5 g. of Amberlite IRA-400 along with an equal volume of ethanol were mixed in a flask, placed on a Burrell wrist action shaker, and agitated for 15 hours at room temperature. There was an initial rise in temperature to 55° when the reactants were mixed but the temperature for most of the reaction period was about 30°. At the end of the reaction period, the resin was filtered off and washed with ethanol, the washings were combined with the reaction mixture, and the products were separated by distillation at reduced pressure. There was obtained 15 g. of 2-nitroethanol boiling from 83–85° at 10 mm. In addition, 49 g. of highly colored high-boiling material was obtained which probably contained di- and tri-methylolnitromethanes. These products were not isolated.

Propionaldehyde and nitroethane. Distilled propionaldehyde (58 g.) 82.5 g. of nitroethane (10% excess), and 75 ml. of ethanol were agitated on a mechanical shaker for 15 hours at about 30° in the presence of 15 g. of Amberlite IRA-400. After the reaction was completed, the resin was filtered out and the unreacted starting materials and products were recovered by distillation. There was obtained 91 g. of 2-nitro-3-pentanol, boiling at 107–109° at 10 mm. This represents a conversion of 68.4%. No by-products could be found.

Isobutyraldehyde and 2-nitropropane. Isobutyraldehyde (72 g.), 98 g. of 2-nitropropane, 100 ml. of ethanol, and 18 g. of Amberlite IR-4B resin were mixed and agitated for 48 hours at room temperature. The resin was filtered off and the products were separated by fractional distillation to give 2-nitro-2,4-dimethyl-3-pentanol boiling at 123–125° at 100 mm. The conversion was 18.5%.

Cyclohexanone and nitromethane. Cyclohexanone (196 g.), 61 g. of nitromethane, 200 ml. of ethanol, and 25 g. of Am-

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(1) From the M. S. Thesis of Franklin P. Abbott.

(2) B. M. Vanderbilt and H. B. Hass, *Ind. Eng. Chem.*, **32**, 34 (1940).

(3) C. A. Sprang and E. Degering, *J. Am. Chem. Soc.*, **62**, 1735 (1940).

(4) Dorothy Nightingale and J. R. Janes, *J. Am. Chem. Soc.*, **66**, 352 (1944).

(5) H. B. Hass and J. F. Bourland, *J. Org. Chem.*, **12**, 704 (1947).

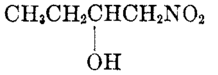
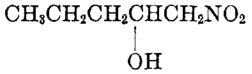
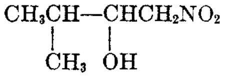
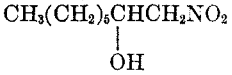
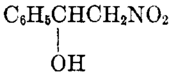
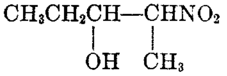
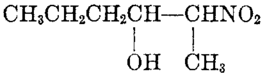
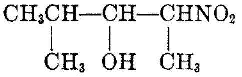
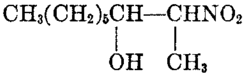
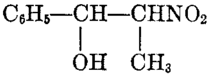
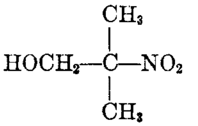
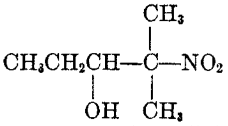
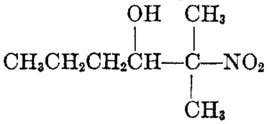
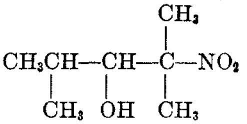
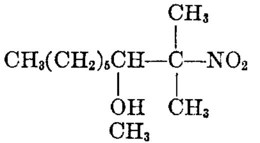
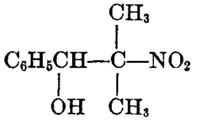
(6) C. J. Schmidle and R. C. Mansfield, *Ind. Eng. Chem.*, **44**, 1388 (1952).

(7) M. J. Astle and J. A. Zaslowsky, *Ind. Eng. Chem.*, **44**, 2867 (1952).

(8) A. Galat, *J. Am. Chem. Soc.*, **70**, 3945 (1948).

TABLE I

Condensation of Aldehydes with Nitroparaffins in the Presence of Anion Exchange Resins

Aldehyde	Product	B.P., °C./ 10 mm.	n_D^{20}	Conversion,[a] % IRA-400	Conversion,[a] % IR-4B
	NITROMETHANE				
Formaldehyde	$HOCH_2CH_2NO_2$	83–85	1.4300	16	—
Propionaldehyde	 $CH_3CH_2\underset{OH}{CH}CH_2NO_2$	102–104	1.4408	68	—
n-Butyraldehyde	 $CH_3CH_2CH_2\underset{OH}{CH}CH_2NO_2$	114–116	1.4465	69	—
Isobutyraldehyde	 $CH_3\underset{CH_3}{CH}-\underset{OH}{CH}CH_2NO_2$	111–113	1.4455	36	—
Heptaldehyde	 $CH_3(CH_2)_5\underset{OH}{CH}CH_2NO_2$	149–151	1.4520	63	—
Benzaldehyde	 $C_6H_5\underset{OH}{CH}CH_2NO_2$	155–157	1.5385	59	—
	NITROETHANE				
Formaldehyde	 $HOCH_2\underset{CH_3}{CH}NO_2$	97–99	1.4388	45	—
Propionaldehyde	 $CH_3CH_2\underset{OH}{CH}-\underset{CH_3}{CH}NO_2$	107–109	1.4467	60	—
n-Butyraldehyde	 $CH_3CH_2CH_2\underset{OH}{CH}-\underset{CH_3}{CH}NO_2$	119–121	1.4469	36	41
Isobutyraldehyde	 $CH_3\underset{CH_3}{CH}-\underset{OH}{CH}-\underset{CH_3}{CH}NO_2$	113–115	1.4473	0	36
Heptaldehyde	 $CH_3(CH_2)_5\underset{OH}{CH}-\underset{CH_3}{CH}NO_2$	154–156	1.4538	59	—
Benzaldehyde	 $C_6H_5-\underset{OH}{CH}-\underset{CH_3}{CH}NO_2$	158–160	1.5202	22	—
	2-NITROPROPANE				
Formaldehyde	 $HOCH_2-\overset{CH_3}{\underset{CH_3}{C}}-NO_2$	93–96[d]	—	12	0
Propionaldehyde	 $CH_3CH_2\underset{OH}{CH}-\overset{CH_3}{\underset{CH_3}{C}}-NO_2$	110–112	1.4523	14	30
n-Butyraldehyde	 $CH_3CH_2CH_2\overset{OH}{CH}-\overset{CH_3}{\underset{CH_3}{C}}-NO_2$	122–124	1.4497	9	15
Isobutyraldehyde	 $CH_3\underset{CH_3}{CH}-\underset{OH}{CH}-\overset{CH_3}{\underset{CH_3}{C}}-NO_2$	123–125	1.4480	0	19[b]
Heptaldehyde	 $CH_3(CH_2)_5\underset{OH}{CH}-\overset{CH_3}{\underset{CH_3}{C}}-NO_2$	162–164	1.4588	5	18
Benzaldehyde	 $C_6H_5\underset{OH}{CH}-\overset{CH_3}{\underset{CH_3}{C}}-NO_2$	165–167	—	0	14[c]

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[a] Conversions are based on aldehyde. Reaction time 15 hours at room temperature. [b] 48 hours. [c] One week. [d] This is a melting point.

berlite IRA-400 were mixed and agitated for one week at room temperature. The resin then was filtered off and the products were separated by distillation. 1-(Nitromethyl)-cyclohexanol was obtained boiling at 118–120° at 10 mm. The conversion was 26.4% based on the ketone.

DISCUSSION

The results of the reactions between aldehydes and the nitroparaffins are shown in Table I and for the reactions with ketones in Table II. Anion exchange resins do not seem to be satisfactory catalysts for the condensation of formaldehyde with nitromethane since only a nine per cent conversion to 2-nitroethanol was obtained when Amberlite IRA-400 was used.

No condensation was observed when Amberlite IR-4B was used as a catalyst and paraformaldehyde was found to be an unsatisfactory source of formaldehyde with either catalyst.

The straight chain aldehydes, propionaldehyde, *n*-butyraldehyde, and *n*-heptaldehyde as well as benzaldehyde when reacted with nitromethane were all converted to the corresponding nitroalcohols to about the same extent in 15 hours and all rates are satisfactory for synthetic purposes. The rates were comparable to those obtained with other catalysts. With a mole ratio of nitromethane to *n*-butyraldehyde of 2 to 1, an 87 per cent conversion to the nitroalcohol was obtained in 15 hours.

Isobutyraldehyde reacted with nitromethane somewhat slower than did the other aldehydes but the rate of reaction was still satisfactory. Amberlite IR-4B was not a satisfactory catalyst for any of these reactions.

Formaldehyde reacted with nitroethane much better than with nitromethane. The conversion to the nitroalcohol was about five times as great in 15 hours as was obtained with nitromethane. The rate of conversions of *n*-propionaldehyde and *n*-heptaldehyde with nitroethane in the presence of Amberlite IRA-400 were about the same as observed with nitromethane, but the condensation of both *n*-butyraldehyde and isobutyraldehyde were greatly reduced. The condensation of these two aldehydes with nitroethane could be successfully catalyzed with Amberlite IR-4B and in fact the conversions were better than could be obtained with IRA-400. This apparent anomaly cannot be explained at this time.

The condensations with 2-nitropropane with all of the aldehydes investigated were very much slower than with the other nitroparaffins. The reaction period had to be extended to 48 hours and in one case one week in order to obtain satisfactory conversion. This would be expected because of the presence of only one hydrogen on the carbon atom *alpha* to the nitro group. In every case with the exception of formaldehyde, Amberlite IR-4B was found to be a better catalyst for condensations involving 2-nitropropane than IRA-400. This confirms the work of Vanderbilt and Hass[2] who showed that strongly basic catalysts tend to reverse the aldehyde-secondary nitroparaffin condensations.

TABLE II

CONDENSATION OF NITROPARAFFINS WITH KETONES IN THE PRESENCE OF AMBERLITE IRA-400

Ketone	Product	B.P., °C./ 10 mm.	n_D^{20}	Reaction Time	Conversion, %
		NITROMETHANE			
Acetone	2-Methyl-3-nitro-2-propanol	84–86	1.3328	15 hours	19
Cyclohexanone	1-Nitromethylcyclohexanol	118–120	1.4820	1 week	27
		NITROETHANE			
Acetone	2-Methyl-3-nitro-2-butanol	95–97	1.3351	15 hours	4
Cyclohexanone	1-(1-Nitroethyl)cyclohexanol	122–124	1.4788	1 week	15

Ketones did not condense with nitroparaffins as readily as did the aldehydes, but after periods of time ranging from two to seven days, both acetone and cyclohexanone condensed with nitromethane and nitroethane in the presence of Amberlite IRA-400 (Table II). No condensation of ketones with 2-nitropropane could be obtained and Amberlite IR-4B was not a satisfactory catalyst for the condensation of ketones with any of the nitroparaffins. The rates of reaction were very slow but yields were excellent in that no by-products could be detected. Blicke[9] has condensed nitromethane with cyclohexanone in methanol in the presence of sodium hydroxide to give a 67% yield of 1-(nitromethyl)cyclohexanol.

Consistent results were obtained when the catalyst Amberlite IRA-400 was regenerated between runs. Without regeneration, the catalyst slowly lost its activity, either by reaction with the organic acids resulting from the oxidation of the aldehydes or by absorption of CO_2 between runs. These conditions could be minimized by continuous operations and by using freshly distilled aldehyde. No loss of activity of the Amberlite IR-4B

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(9) F. F. Blicke, N. J. Doorenbos, and R. H. Cox, *J. Am. Chem. Soc.*, **74**, 2924 (1952).

was observed, since the salts of the weakly basic amines with organic acids are also effective catalysts for aldol type condensations.

These procedures can be developed into continuous processes for the preparation of nitroalcohols in which the reactants are continuously passed through a column packed with the resin.[5] By recycling the unreacted starting materials, the yields of nitroalcohols should be very high.

All of the nitroalcohols obtained in this investigation had been previously prepared and their identities were confirmed by boiling point and refractive indexes.

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