[From the Scientific Department, Ministry of Defence, Israel]

Basic Exchange Resins as Catalysts in the Michael Reaction. I.

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Two commercial basic resins, Amberlite IRA 400 and IRA 410, have been studied as catalysts in Michael reactions Fifteen acceptor-donor systems have been investigated, and the results are discussed.

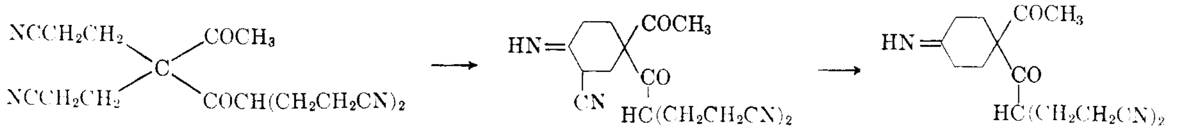
Exchange resins, both of acidic and—to a lesser degree—of basic[1–4] nature, are used widely as catalysts. It seemed of interest to investigate systematically the applicability of basic resins in the Michael reaction, as only some occasional observations in this direction have been reported.[5–7] It would appear that these resins might facilitate the kinetic analysis of the reaction and the working up of the reaction products, and help to avoid secondary reactions as they often occur in homogeneous catalysis.

In this first paper, two commercial resins, Amberlite IRA 400 ("A") and Amberlite IRA 410 ("B") have been compared systematically in a number of relatively simple systems. Both are quaternary ammonium salts on a polystyrene matrix: the second is somewhat less basic. The reactants were mixed with the resin (in its OH′-form) and the mixture was kept at room temperature. The determination of the refractive index of the liquid provided a simple means of following the course of the reaction. When the change of the refractive index became negligible, the supernatant was filtered from the catalyst and worked up by the usual methods.

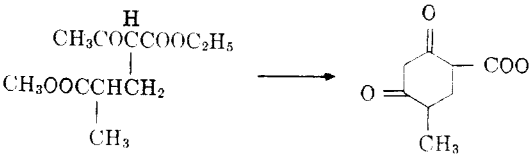
The results of these experiments are summarized in Tables I–IV.

DISCUSSION

The products obtained were the normal ones; only in two cases secondary cyclization reactions were observed. From acetylacetone and acrylonitrile (Table II, No. 6, 7) a product of the composition $C_{16}H_{21}N_3O_2$ was isolated, for which the following mechanism of formation has been assumed in analogy with known reactions:



The normal (1:1) product from ethyl acetoacetate and methyl methacrylate was in some runs converted into ethyl 4-methyl-cyclohexane-1,3-dione-6-carboxylate (Table IV, No. 3).



One of the conclusions to be drawn from the experimental data is that α-substitution in the acceptor even by a methyl group makes both the resins used inefficient as catalysts: with methyl methacrylate, only 2-nitropropane and (with resin *A* only) ethyl acetoacetate could be condensed; however, even as reactive donor molecules as acetylacetone, benzyl cyanide, or diethyl malonate did not condense. The only other reaction which could not be achieved was the condensation between diethyl malonate and acrylonitrile in the presence of resin *B*. Here, a second characteristic of the resin-catalyzed Michael reactions expresses itself. The two resins used appear to possess *specific* condensing activity in several systems, so that one may expect by the selection of a suitable resin to carry out one of a number of possible condensation reactions —a point which deserves further study. In certain cases (Table I, No. 3,4; Table III, No. 3,4; Table IV, No. 1,2), one of the resins gives considerably higher yields than the other, and it is not always the same resin which is more efficient.

The method employed makes it possible to compare semi-quantitatively different donors and acceptors in their ability to undergo Michael reactions. Using the yields as indicator, one can, *e.g.*, derive from the experiments with acrylonitrile (Table III), the following sequence: 2-nitropropane > acetylacetone > ethyl acetoacetate > benzyl cyanide > diethyl malonate. This point is now being studied in a more quantitative manner.

The yields obtained are satisfactory and in some cases exceed significantly those obtained with the classical procedures.

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(1) Durr, *Compt. rend.*, **236**, 1571 (1953).

(2) Austerweil and Pallard, *Bull. soc. chim. France*, 678 (1953).

(3) Mastagli, *et al.*, *Bull. soc. chim. France*, 693 (1953).

(4) Durr and Mastagli, *Compt. rend.*, **235**, 1038 (1952).

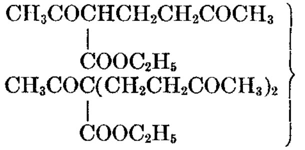
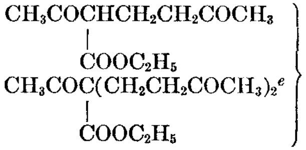
(5) Schmidle and Mansfield, *Ind. Eng. Chem.*, **44**, 1388 (1952).

(6) Schmidle and Mansfield, U. S. Patent 2,658,070 (*Chem. Abstr.*, **48**, 13715 (1954)).

(7) Howk and Langkammerer, U. S. Patent 2,579,580 (*Chem. Abstr.*, **46**, 7114 (1952)).

TABLE I

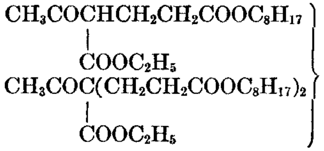
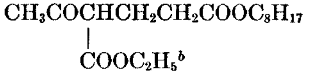
MICHAEL REACTION WITH METHYL VINYL KETONE (0.1 mole) AS ACCEPTOR
(Temperature 30°)

No.	Donor (0.1 mole)	Resin (g.)	Duration (days)	Product Formula	Product Yield	B.P., °C.	Mm.	Analysis C Calc'd	Analysis C Found	Analysis H Calc'd	Analysis H Found
1.	1-Nitropropane[a]	A (8)	30	$(CH_3)_2C(NO_2)CH_2CH_2COCH_3$	54	123	10^{cd}				
2.	2-Nitropropane[a]	B (8)	30	$(CH_3)_2C(NO_2)CH_2CH_2COCH_3$	36	118	7				
3.	Ethyl acetoacetate	A (8)	35	 $CH_3CO\underset{COOC_2H_5}{\underset{\mid}{C}}HCH_2CH_2COCH_3$		75–78	1.2	60.0	60.4	8.0	8.0
				$CH_3CO\underset{COOC_2H_5}{\underset{\mid}{C}}(CH_2CH_2COCH_3)_2$	26	125–126	1.2	62.2	62.4	8.1	7.9
4.	Ethyl acetoacetate	B (8)	35	 $CH_3CO\underset{COOC_2H_5}{\underset{\mid}{C}}HCH_2CH_2COCH_3$		68–70	0.9	60.0	60.1	8.0	8.4
				$CH_3CO\underset{COOC_2H_5}{\underset{\mid}{C}}(CH_2CH_2COCH_3)_2{}^{e}$	14	115	0.7	62.2	62.8	8.1	8.4
5.	Diethyl malonate[b]	A (8)	50	$(H_5C_2OOC)_2CHCH_2CH_2COCH_3$	38	133–135	4				
6.	Diethyl malonate[b]	B (8)	50	$(H_5C_2OOC)_2CHCH_2CH_2COCH_3$	36	74–75	0.4	57.4	57.7	7.8	7.9
				$(H_5C_2OOC)_2C(CH_2CH_2COCH_3)_2{}^{f}$		108–110	0.4	60.0	59.6	8.0	7.8

[a] Diluted with 10 ml. of dioxane. [b] Diluted with 10 ml. of ethanol. [c] DNP, m.p. 118°, while Schechter, *et al.*[d] report m.p. 130.5–131.5°. [d] Schechter, Ley, and Zeldin, *J. Am. Chem. Soc.*, **74,** 3664 (1952); British Celanese Ltd., British Patent 671,412 [*Chem. Abstr.*, **47,** 2198 (1953)]. [e] Henecka, *Ber.*, **81,** 197 (1948). [f] Kress, U. S. Patent 2,540,267 [*Chem. Abstr.*, **45,** 5720 (1951)].

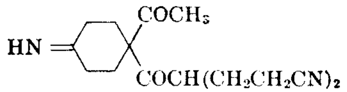
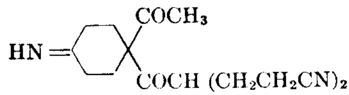
TABLE II

MICHAEL REACTIONS WITH OCTYL ACRYLATE[a] AS ACCEPTOR
(Temperature 30°, time of reaction 45 days)

No.	Donor	Mole	Resin (g.)	Product Formula	Product Yield	B.p., °C.	Mm.	Analysis C Calc'd	Analysis C Found	Analysis H Calc'd	Analysis H Found
1.	2-Nitropropane	0.1	A (8)	$(CH_3)_2C(NO_2)CH_2CH_2COOC_8H_{17}$	70	165–166	3	61.8	61.5	10.0	9.8
2.	2-Nitropropane	0.1	B (8)	$(CH_3)_2C(NO_2)CH_2CH_2COOC_8H_{17}$	70	161–163	3				
3.	Ethyl acetoacetate	0.5	A (4)	 $CH_3CO\underset{COOC_2H_5}{\underset{\mid}{C}}HCH_2CH_2COOC_8H_{17}$		152–156	0.6	65.0	65.0	9.6	9.6
				$CH_3CO\underset{COOC_2H_5}{\underset{\mid}{C}}(CH_2CH_2COOC_8H_{17})_2$	39	210	0.25	68.8	68.5	10.3	10.2
4.	Ethyl acetoacetate	0.5	B (4)	 $CH_3CO\underset{COOC_2H_5{}^{b}}{\underset{\mid}{C}}HCH_2CH_2COOC_8H_{17}$		165–170	0.9	65.0	64.8	9.6	9.8

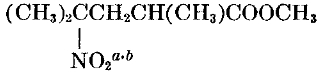
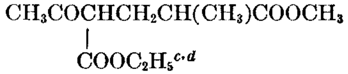
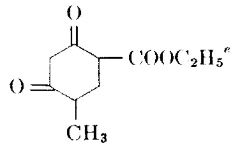
[a] B.p. 92°/0.5 mm. [b] The bis-adduct began to decompose upon distillation.

TABLE III
MICHAEL REACTIONS WITH ACRYLONITRILE AS ACCEPTOR (0.2 mole)
(Temperature 30° unless otherwise stated)

No.	Donor	Mole	Resin (8 g.)	Duration	Product Formula	Yield	B.p., °C.	Mm.	Analysis C Calc'd	C Found	H Calc'd	H Found	N Calc'd	N Found
1.	2-Nitropropane	0.1	A	2 days[a]	$(CH_3)_2C(NO_2)CH_2CH_2CN$[b]	90	122–123	4						
2.	2-Nitropropane	0.1	B	8 days[a]	$(CH_3)_2C(NO_2)CH_2CH_2CN$[b]	80	122–123	4						
3.	Ethyl acetoacetate	0.1	A	40 days	$CH_3COCHCOOC_2H_5$ | CH_2CH_2CN[c]	46	115	3						
					$CH_3COC(CH_2CH_2CN)_2$ | $COOC_2H_5$[d]	24	[p]		61.0	61.2	7.0	7.3	11.8	11.8
4.	Ethyl acetoacetate	0.1	B	40 days	$CH_3COC(CH_2CH_2CN)_2$ | $COOC_2H_5$[d,e]	22	80; 80–85	0.8						
5.	Acetylacetone	0.1	A	2 days[f]	$CH_3COCHCH_2CH_2CN$ | $COCH_3$		119–120	0.6	62.8	62.8	7.2	7.2	9.1	9.3
6.	Acetylacetone	0.1	B	30 days	$CH_3COCHCH_2CH_2CN$ | $COCH_3$[g]	15	115–116	0.7	62.8	62.3	7.2	7.5		
						15	163–165	0.8	67.0	67.9	7.3	7.0	14.7	15.0
7.	Acetylacetone	0.1	B	6 hours reflux	$CH_3COC(CH_2CH_2CN)_2$ | $COCH_3$[h,i]	18								
						28	175–180	0.9	67.0	66.9	7.3	7.1		
8.	Diethyl malonate	0.1	A	35 days	$(H_5C_2OOC)_2C(CH_2CH_2CN)_2$[l]	50	[s]							
					$(H_5C_2OOC)_2CHCH_2CH_2CN$[m]	18	130	2						
9.	Diethyl malonate	0.1	B	30 days	No reaction									
10.	Benzyl cyanide	0.3	A	3 days	$C_6H_5CH(CN)CH_2CH_2CN$[n]	43	145–148	0.8	77.5	77.6	6.0	5.8	16.5	17.0
					$C_6H_5C(CN)(CH_2CH_2CN)_2$[o]		212–215	0.8	75.3	75.6	6.0	6.1	18.7	18.5

[a] Exothermic reaction. The reaction temperature was kept below 45° by cooling and vigorous stirring. [b] Buckley, Elliott, Hunt, and Lowe, *J. Chem. Soc.*, 1505 (1947); b.p. 70°/0.09 mm. [c] Yoho and Levine, *J. Am. Chem. Soc.*, **74**, 5597 (1952). [d] Bruson and Riener, *J. Am. Chem. Soc.*, **64**, 2850 (1942) (m.p. 82°); Terentev, Kost, and Gurvich, *Chem. Abstr.*, **47**, 8663 (1953). [e] A small unidentified higher fraction, b.p. 116°/0.9 mm., was also observed. [f] At about 40°, the same reaction took place in 6 hours; it was exothermic and was kept in check by cooling and vigorous stirring. [g] A low fraction, b.p. 79–81°/0.1 mm., was also observed, which appeared to have the same composition. [h] A low fraction, b.p. 70–71°/0.9 mm., was also observed; *2,4-dinitrophenyl-hydrazone*, m.p. 145.5°. [i] This substance has been described by Zellars and Levine, *J. Org. Chem.*, **13**, 911 (1948); m.p. 180–180.4°. [k] 2,4-Dinitrophenylhydrazone, m.p. 118° (*Anal.* Calc'd for $C_{28}H_{29}N_{11}O_8$: C, 51.9; H, 4.5; N, 23.8. Found: C, 52.1; H, 4.8; N, 24.2). [l] Bruson and Riener, *J. Am. Chem. Soc.*, **65**, 23 (1943) (m.p. 62°); Mikeska, U. S. Patent 2,461,336 (*Chem. Abstr.*, **43**, 4689 (1949) (m.p. 61°); Terentev, Kost, and Gurvich, *Chem. Abstr.*, **47**, 8663 (1953). [m] Mikeska, l.c.; Albertson and Fillmann, *J. Am. Chem. Soc.*, **71**, 2818 (1949). [n] Koelsch, *J. Am. Chem. Soc.*, **65**, 437 (1943) (b.p. 198–200°/12 mm.); Rogers, U. S. Patent 2,460,536 (*Chem. Abstr.*, **43**, 3446 (1949) (b.p. 163°/1 mm.). [o] The substance did not crystallize. Bruson and Riener, *J. Am. Chem. Soc.*, **65**, 23 (1943) give m.p. 70°. Terentev, Kost and Gurvich, *Chem. Abstr.*, **47**, 8663 (1953); Kost and Terentev, *Chem. Abstr.*, **47**, 2759 (1953); Campbell, *J. Chem. Soc.*, 1377 (1954). [p] M.p. 79°. [r] M.p. 180.5°. [s] M.p. 59–60°.

TABLE IV
MICHAEL REACTIONS WITH METHYL METHACRYLATE AS ACCEPTOR (0.1 mole)

No.	Donor	Mole	Resin (8 g.)	Duration (days)	Product Formula	Yield, %	B.p., °C.	Mm.
1.	2-Nitropropane	0.3	A	50	 $\underset{\mathrm{NO_2}^{a,b}}{\underset{\vert}{(CH_3)_2C}}CH_2CH(CH_3)COOCH_3$	20	120	10
2.	2-Nitropropane	0.3	B	50	 $\underset{\mathrm{NO_2}^{a}}{\underset{\vert}{(CH_3)_2C}}CH_2CH(CH_3)COOCH_3$	62	104	4
3.	Ethyl acetoacetate	0.2	A	30	 $CH_3CO\underset{\mathrm{COOC_2H_5}^{c,d}}{\underset{\vert}{C}}HCH_2CH(CH_3)COOCH_3$ or	38		
						38	118	0.9
4.	Ethyl acetoacetate	0.2	B	30	No reaction			
5.	Acetylacetone	0.3	A	30	No reaction			
6.	Acetylacetone	0.3	B	30	No reaction			
7.	Diethyl malonate	0.3	A	30	No reaction			
8.	Diethyl malonate	0.3	B	30	No reaction			
9.	Benzyl cyanide	0.1	A	30	No reaction			
10.	Benzyl cyanide	0.1	B	30	No reaction			

[a] n_D^{18} 1.4400. [b] Kloetzel, *J. Am. Chem. Soc.*, **70**, 3571 (1948), reports b.p. 72°/13 mm. and n_D^{20} 1.4388; Leonard and Shoemaker, *J. Am. Chem. Soc.*, **71**, 1760 (1949). [c] Calc'd for $C_{11}H_{18}O_5$: C, 57.4; H, 8.0. Found: C, 57.7; H, 8.1. [d] Smrt and Sorm, *Chem. Abstr.*, **48**, 3903 (1954). [e] Calc'd for $C_{10}H_{14}O_4$: C, 60.6; H, 7.0. Found: C, 59.5; H, 7.0.