TABLE I

	Reactants											Product					
	Amine				Resin[a]			Acrylonitrile			Reaction							
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$_2$CH$_2$-CN)$_2$
1	n-C$_8$H$_{16}$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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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).

TABLE I

MAXIMUM YIELD DATA (%) FOR OXIDATION OF DIVINYLCARBINOL WITH MANGANESE DIOXIDE

Manganese dioxide	Ratio divinyl carbinol/manganese dioxide 1/5	1/10	1/15
Type A	10–20	28–50	30–50
Type B	5–12	15–26	20–27
Type C	5–15	23–41	22–40
Type D	18–20	40–49	39–50

six hours. Extended reaction periods did not greatly improve the yield of the ketone.

The 3-pentadienone was isolated by vacuum distillation in the presence of a polymerization inhibitor, hydroquinone. It was identified by elemental analysis, refractive index, and infrared spectroscopy. Vapor phase chromatography showed the isolated product to be 98–99% pure, containing a small quantity of the carbinol as an impurity in some instances.

In one reaction the ketone was isolated as the 2,4-dinitrophenylhydrazone in a 96% yield indicating that a considerable part of the product may have been lost during its isolation. Attempts to prepare the oxime and dimethyl ketal were unsuccessful using conventional methods due to polymerization of the ketone.

Experimental[8]

Divinylcarbinol was prepared by the method of Ramsden.[9] The oxidation of the carbinol was carried out as follows: To a 200-ml. three-necked flask equipped with mechanical stirrer, condenser, and thermometer (all outlets covered with Drierite tubes) was introduced 10.0 g. (0.12 mole) of divinylcarbinol in 150 ml. of dry chloroform. One hundred grams of manganese dioxide (type A) was added over a period of 15 min. and the mixture stirred rapidly at ambient temperature for 24 hr. The infrared spectrum of the solution indicated a carbonyl-containing compound and only a trace of residual carbinol. The solid material was removed by filtration and the major part of the solvent removed at reduced pressure until the volume was reduced to 25–30 ml. The liquid residue to which 0.25 g. hydroquinone had been added was then distilled through an 18-in. semimicro spinning band column to give 4.97 g. (50%) 3-pentadienone, b.p. 37–38° (50 mm.), n^{20}_{D} 1.4497 [reported[2] b.p. 41–44° (75 mm.), n^{20}_{D} 1.4485]. The infrared spectrum showed absorption at 3050 cm.$^{-}$ (C—H valence stretching absorption), 1660 cm.$^{-1}$ (C=C stretching vibration absorption) and 1672 cm.$^{-1}$ (C=O). The latter absorption band is consistent with that reported by Bellamy[10] for the carbonyl absorption in vinyl ketones (1685–1665 cm.$^{-1}$). This general procedure was used employing all four types of manganese dioxide.

Anal. Calcd. for C_5H_6O: C, 73.17; H, 7.31. Found: C, 73.10; H, 7.39.

The ketone was examined by vapor phase chromatography[11] and found to be 98–99% pure in all instances.

The 2,4-dinitrophenylhydrazone of 3-pentadienone was obtained by treating a solution of the ketone [from 2.0 g. of divinylcarbinol and 20.0 g. of manganese dioxide (type C) in 50 ml. chloroform] with a solution of 4.0 g. of 2,4-dinitrophenylhydrazine and 8.0 ml. of concentrated sulfuric acid in 90 ml. of methanol. An immediate orange precipitate appeared which was collected by filtration and recrystallized from 95% ethanol, melting with polymerization at 95–102°. The yield was 6.0 g. (96%).

Anal. Calcd. for $C_{11}H_{10}N_4O_4$: C, 50.38; H, 3.81; N, 21.37. Found: C, 50.21; H, 3.71; N, 21.49.

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[8] All melting and boiling points are uncorrected.

[9] H. E. Ramsden, *et al.*, *J. Org. Chem.*, **22**, 1602 (1957).

[10] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y., 1959, p. 136.

[11] Vapor phase chromatography was carried out on an Aerograph Gas Chromatographic Instrument, Model A-100C, employing a 5-ft. dinonylphthalate column at 75°.

Hydroxy Alkylation of Primary Aromatic Amines

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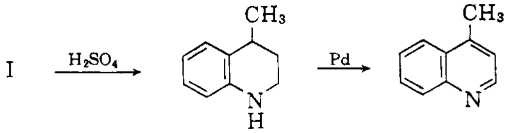
The one-step reaction of aniline with 1,3-butanediol in the presence of Raney nickel[2] furnished 4-anilino-2-butanol[3] I (R = C_6H_5) in 20% yield.

$$RNH_2 + HOCH_2—CH_2CHOHCH_3 \xrightarrow{Ni} \underset{\text{I}}{RNHCH_2CH_2CHOHCH_3}$$

o-Anisidine, *p*-anisidine, ethyl *p*-aminobenzoate, *α*-naphthylamine, and *β*-naphthylamine reacted similarly.[4] The physical properties and analyses of these products are shown in Table I.

Treatment of I (R = C_6H_5) with concentrated sulfuric acid at room temperature gave *dl*-1,2,3,4-tetrahydrolepidine in 90% yield. The latter was readily dehydrogenated in near quantitative yield to lepidine. 4-*p*-Anisidino-2-butanol I (R = *p*-$CH_3OC_6H_4$) gave *dl*-6-methoxy 1,2,3,4-tetrahydrolepidine in 60% yield.[5] Dehydrogenation furnished 6-methoxylepidine.



4-*p*-Carbethoxyanilino-2-butanol failed to undergo the intramolecular Friedal–Crafts reaction

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[1] To whom inquiries should be addressed.

[2] Raney nickel induced alkylation of primary aromatic amines with primary and secondary alcohols is described by G. N. Kao, B. D. Tilak, and K. Venkataraman, *J. Sci. Ind. Res.* (India), **14B**, 624 (1955); R. G. Rice and E. J. Kohn, *J. Am. Chem. Soc.*, **77**, 4052 (1955); C. Ainsworth, *ibid.*, **78**, 1835 (1956); J. Horyna and O. Cerny, *Chem. listy*, **50**, 381 (1956); *Collection Czech. Chem. Commun.*, **21**, 906 (1956); R. G. Rice, E. J. Kohn, and L. W. Daasch, *J. Org. Chem.*, **23**, 1352 (1958).

[3] N. V. Bringi and P. V. Deshmukh, *Hindustan Antibiotics Bull.*, **3**, 66 (1960), report the preparation of 4-anilino-1-butanol from the primary glycol.

[4] J. Lichtenberger and L. Dürr, *Bull. soc. chim. France*, 664 (1956), report the preparation of I (R = C_6H_5, and R = *o*-$CH_3OC_6H_4$) by the reaction of 1,3-butanediol cyclic sulphate and the amine followed by hydrolysis.

[5] This has been prepared previously by catalytic hydrogenation of 6-methoxylepidine; M. Levitz and M. T. Bogert, *J. Org. Chem.*, **10**, 341 (1945).