pyridine (VId) and 1.0 g of chloroacetaldoxime in 2 ml of tetramethylene sulfone was allowed to react at room temperature for 8 days. On working up as above, a precipitate was obtained which crystallized from methanol–ethyl acetate as pale yellow needles, yield 2.0 g (83%), mp 169–170° dec.

Anal. Calcd for $C_{10}H_{13}ClN_2O_3$: C, 49.08; H, 5.37; N, 11.45. Found: C, 49.07; H, 5.16; N, 11.60.

2-Azaquinolizinium Chloride 2-Oxide (IXc).—A solution of 1.0 g of 1-(2-oximinoethyl)-2-(1,3-dioxolan-2-yl)pyridinium chloride (VIIId) and 10 ml of concentrated hydrochloric acid was heated on a steam bath for 4 hr. The acid was removed under reduced pressure (aspirator) and the residue crystallized from methanol as pale yellow needles, yield 0.6 g (80%). The compound turns dark at 190° and decomposes above 240°.

Anal. Calcd for $C_8H_7ClN_2O$: C, 52.61; H, 3.86; N, 15.34. Found: C, 52.62; H, 3.76; N, 15.55.

Cyclization of 1-(2-oximinoethyl)-2-(oximinomethyl)pyridinium chloride (VIIIc) by the above method yielded the same product.

The **bromide** was obtained by substituting 48% hydrobromic acid for hydrochloric acid in the cyclization procedure. It crystallized from methanol as yellow needles which decompose at 280° with previous darkening: yield 85%; λ_{max}, mμ (log ϵ), 288 (3.99), 258 (sh) (3.63), 265 (sh) (3.59), 275 (sh) (3.52), 308 (sh) (3.50), 320 (3.62), 339 (3.66), and 360 (3.32).

Anal. Calcd for $C_8H_7BrN_2O$: C, 42.31; H, 3.10; N, 12.33. Found: C, 42.09; H, 3.05; N, 12.19.

2-Azaquinolizidine (Vb).—A suspension of 1.0 g of 2-azaquinolizinium chloride 2-oxide (IXc) in 200 ml of methanol was hydrogenated at atmospheric pressure for 2 days in the presence of 0.1 g of platinum oxide catalyst. The colorless solution was concentrated under reduced pressure and the residue was treated with a dilute solution of sodium carbonate and then extracted with ether. Evaporation of the ether gave an oil which distilled at 60° (1 mm).

The dipicrate crystallized from water as yellow needles, mp 251–260° dec (lit.[6] mp 250–260° dec).

Anal. Calcd for $C_{20}H_{22}N_8O_{14}$: C, 40.14; H, 3.70; N, 18.72. Found: C, 40.51; H, 4.00; N, 18.48.

3-Methyl-2-azabenzo[*h*]quinolizinium Bromide 2-Oxide (X).—A mixture of 1.7 g of 1-oximinomethylisoquinoline[8] and 1.4 g of bromoacetone in 20 ml of acetone was refluxed for 6 hr. On working up as usual, the yellow precipitate was crystallized from methanol–ethyl acetate as yellow needles: yield 1.5 g (50%); the compound darkens at 225° and decomposes at 252°; λ_{max}, mμ (log ϵ), 245 (4.26), 251 (4.27), 290 (3.99), 352 (3.78), 367 (3.97), and 388 (4.04).

Anal. Calcd for $C_{13}H_{11}BrN_2O \cdot 0.5H_2O$: C, 52.02; H, 4.03; N, 9.33. Found: C, 51.80; H, 4.13; N, 9.26.

3-Methyl-2-azabenzo[*g*]quinolizinium Bromide 2-Oxide (XI).—A mixture of 1.7 g of 3-oximinomethylisoquinoline[9] and 1.4 g of bromoacetone in 20 ml of acetone was refluxed for 6 hr. The precipitated salt was collected, washed with ethyl acetate, and crystallized from methanol–ethyl acetate as reddish yellow needles, yield 1.65 g (55%); the compound darkens at 190° but does not melt till 405°. The bromide was not obtained pure.

The **picrate** crystallized from methanol as yellow needles, mp 224–225° dec.

Anal. Calcd for $C_{10}H_{13}N_5O_8$: C, 51.94; H, 2.98; N, 15.94. Found: C, 51.71; H, 3.02; N, 15.92.

(8) R. S. Barrows and H. G. Lindwall, *J. Am. Chem. Soc.*, **64**, 2430 (1942).

(9) F. R. Crowne and J. G. Breckenridge, *Can. J. Chem.*, **32**, 641 (1954).

Ketenes. VIII. Some Reactions of 1-(Dimethylamino)-4-methyl-1-penten-3-one[1]

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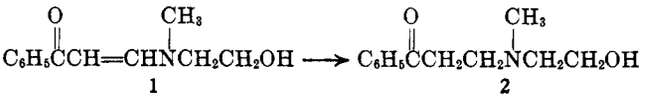
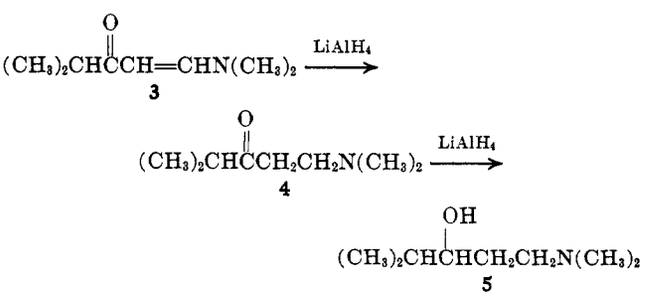
Some new reactions of 1-(dimethylamino)-4-methyl-1-penten-3-one (DMPN), which is prepared from ketene and N,N-dimethylisobutenylamine, are described. In particular, reductions, amine exchange, heterocyclic formation, and addition to dimethylketene are covered.

The recent discovery of a facile synthesis for 1-(dimethylamino)-4-methyl-1-penten-3-one (DMPN) from ketene and N,N-dimethylisobutenylamine[2] prompted us to investigate some reactions of this material. Vinylogous amides, of which DMPN is an example, are a class of materials that have received attention in recent years because of their special properties.[3-6] Because DMPN is an amide vinylog, the field position of the dimethylamino group is at δ 2.86 in the nmr spectrum, which is very close to the position reported for amides, but considerably different from that for amines.[7]

Walker reported that reduction of amide vinylogs with lithium aluminum hydride generally leads to reduction of the carbonyl group not the enamine group. He also reported that the amide vinylog **1** is reduced by lithium aluminum hydride to the saturated amino ketone **2**, and he felt that the hydroxy group contributes



to stopping the reduction at **2** because of the formation of "*noncyclic*, insoluble metallic complex salts of these products, resulting in their precipitation—*i.e.*, removal from the scene where further attack by hydride might progress."[6] In view of the work of deStevens and Halamandaris[8] and of our work with DMPN (**3**), we feel



that the hydroxy group is not necessary for the success of this reduction. DMPN when reduced with lithium aluminum hydride in ether gave 1-(dimethylamino)-4-methyl-3-pentanone (**4**) in 68% yield. This is a 1,4

(1) Paper VII in this series: J. C. Martin and R. H. Meen, *J. Org. Chem.*, **30**, 4311 (1965).

(2) R. H. Hasek and J. C. Martin, *ibid.*, **28**, 1468 (1963).

(3) S. A. Glickman and A. C. Cope, *J. Am. Chem. Soc.*, **67**, 1017 (1945).

(4) N. H. Cromwell, F. A. Miller, A. R. Johnson, R. L. Frank, and D. J. Wallace, *ibid.*, **71**, 3337 (1949).

(5) N. F. Albertson, *ibid.*, **74**, 249 (1952).

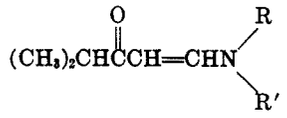
(6) G. N. Walker, *J. Org. Chem.*, **27**, 4227 (1962).

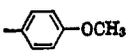
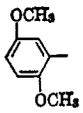
(7) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, p. 56.

(8) G. deStevens and A. Halamandaris, *J. Org. Chem.*, **26**, 1614 (1961).

TABLE I

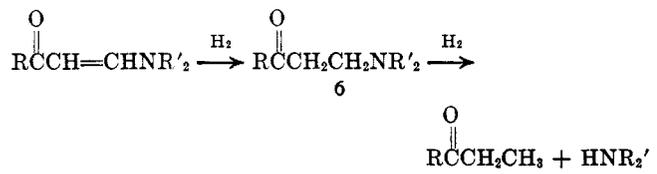
AMINE EXCHANGE REACTIONS WITH DMPN



R	R′	Bp, °C (mm)	Yield, %	Formula	Carbon, % Calcd	Carbon, % Found	Hydrogen, % Calcd	Hydrogen, % Found	Nitrogen, % Calcd	Nitrogen, % Found
C_6H_5	H	111–115 (0.3)	76	$C_{12}H_{16}NO$	76.2	76.1	8.0	8.4	7.4	7.4
C_6H_5	CH_3	133–134 (0.1)	60	$C_{13}H_{17}NO$	76.9	76.7	8.4	8.2	6.8	6.7
	H	152–157 (0.8)[a]	72	$C_{13}H_{17}NO_2$	71.2	70.9	7.8	7.8	6.4	6.4
	H	150–151 (0.07)	41	$C_{14}H_{19}NO_3$	67.5	67.5	7.7	7.5	5.6	5.7
	H	104–105 (0.1)[b]	13	$C_{11}H_{14}N_2O$	69.5	69.6	7.4	7.7	14.7	14.7
$CH_3(CH_2)_3$–	H	114.5–117 (5)	81	$C_{10}H_{19}NO$	80.0	79.8	11.3	11.1	8.3	8.2
$CH_3(CH_2)_{11}$–	H	161–163 (0.5)	83	$C_{18}H_{35}NO$	76.9	76.4	12.4	12.7	5.0	5.2

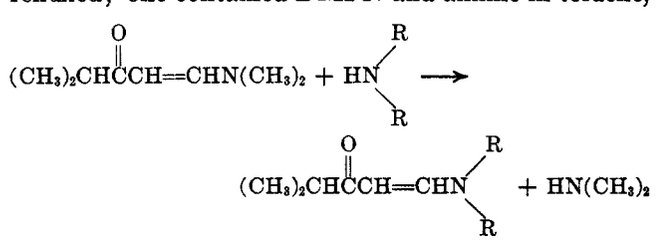
[a] Solidified on cooling; after recrystallization from hexane, it melted at 82–84°. [b] Solidified on cooling; after recrystallization from benzene, it melted at 100–105°.

reduction with the ketone group being bound as its enolate salt and released during the hydrolytic work-up. The amino ketone **4** is readily reduced to the amino alcohol **5** by another treatment with lithium aluminum hydride. Baker and Schlesinger[9] and Kochetkov[10] have shown that catalytic hydrogenation of amide vinylogs with platinum or Raney nickel results in cleavage of the molecule to an amine and a saturated ketone.



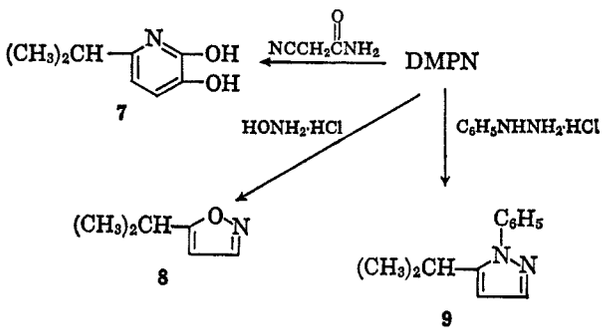
One possible explanation is that the first stage of the reduction is to the amino ketone **6**. Compounds like **6** are Mannich bases and are known to cleave or to undergo hydrogenolysis to the saturated ketone and amine.[11] The reduction of DMPN over ruthenium catalyst at 70° and 1500-psi pressure gave the amino alcohol **5** in 72% yield. The reduction of DMPN over rhodium catalyst gave **5** in 71% yield, but the use of palladium led to cleavage products.

DMPN when heated with other primary or secondary amines underwent an amine exchange reaction with the liberation of dimethylamine. This exchange seems to be general, and a list of the products produced by this reaction is given in Table I. This exchange reaction is catalyzed by acids. Two parallel mixtures were refluxed; one contained DMPN and aniline in toluene,



and the other contained in addition to these ingredients ~2% of *p*-toluenesulfonic acid. Samples were withdrawn at intervals and examined by glpc. The mixture containing the acid reacted appreciably faster than the uncatalyzed mixture.

Kochetkov[10] recognized that amide vinylogs are useful for the preparation of certain heterocyclic compounds. DMPN when used with reagents containing amino groups proved to be a versatile intermediate for the synthesis of heterocyclic compounds. The classes of materials prepared by using DMPN and reagents containing amino groups include pyridines, isoxazoles, pyrazoles, and pyrimidines. 2-Cyanoacetamide and DMPN afforded 2-hydroxy-6-isopropylnicotinonitrile (**7**) in 71% yield, and hydroxylamine hydrochloride and



DMPN gave 5-isopropylisoxazole (**8**) in 86% yield. Pyrazoles were prepared from DMPN and hydrazine, phenylhydrazine, and semicarbazide. Typical of this type of closure is the reaction of DMPN and phenylhydrazine hydrochloride to give 5-isopropyl-1-phenylpyrazole (**9**) in 65% yield. A complete list of heterocyclic compounds prepared from DMPN is given in Table II.

DMPN reacted readily with dimethylketene to afford 4-(dimethylamino)-3,4-dihydro-6-isopropyl-3,3-dimethyl-2H-pyran-2-one (**10**) in 86% yield. The structure of **10** was assigned on the basis of its nmr spectrum and on the fact that it hydrolyzed to 2,6-dimethyl-5-hepten-3-one (**11**). In a similar reaction butylethylketene and DMPN gave 3-butyl-4-(di-

(9) R. H. Baker and A. H. Schlesinger, *J. Am. Chem. Soc.*, **68**, 2009 (1946).

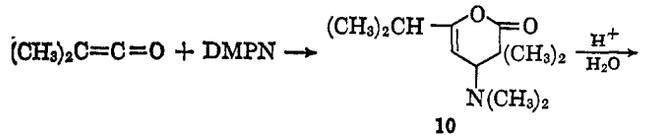
(10) N. K. Kochetkov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 47 (1954); *Chem. Abstr.*, **49**, 6090 (1955).

(11) H. Hellman and G. Opitz, "α-Aminoalkylierung," Verlag Chemie, GmbH., Wienheim, 1960, p 249.

TABLE II. HETEROCYCLIC COMPOUNDS MADE FROM DMPN

Reactant	Product	Bp, °C (mm)	Mp, °C	Yield, %	Formula	Carbon, % Calcd	Carbon, % Found	Hydrogen, % Calcd	Hydrogen, % Found	Nitrogen, % Calcd	Nitrogen, % Found
$NH_2NH_2 \cdot HCl$	$(CH_3)_2CH$	115 (12)	...	82	$C_6H_{10}N_2$	65.5	65.2	9.1	9.3	25.4	25.3
$HONH_2 \cdot HCl$	$(CH_3)_2CH$	67 (36)	...	86	C_6H_9NO	64.9	64.8	8.1	8.1	12.6	12.5
$NCCH_2CONH_2$	$(CH_3)_2CH$	... ...	208.5–210	71	$C_9H_{10}N_2O$	66.7	66.9	6.2	6.3	17.3	17.1
$\left(NH(NH_2CNH_2)_2\right)_2CO_3$	$CH(CH_3)_2$	... ...	116.5–119	54	$C_7H_{11}N_3$	61.3	60.7	8.1	7.9	30.6	31.2
$C_6H_5NHNH_2 \cdot HCl$	$(CH_3)_2CH$	80–82 (0.07)	...	65	$C_{12}H_{14}N_2$	77.4	77.0	7.6	7.6	15.0	14.8
$NH_2CONHNH_2 \cdot HCl$	$(CH_3)_2CH$	... ...	100–101	79	$C_7H_{11}N_3O$	54.9	55.4	7.2	7.7	27.4	27.0
	$(CH_3)_2CH$	... ...	70–73	36	$C_8H_{10}N_4$	59.2	59.0	6.2	6.3	34.6	34.6

methylamino)-3-ethyl-3,4-dihydro-6-isopropyl-2H-pyran-2-one in 52% yield. Although the formation of **11** is formally the result of a 1,4 cycloaddition of di-



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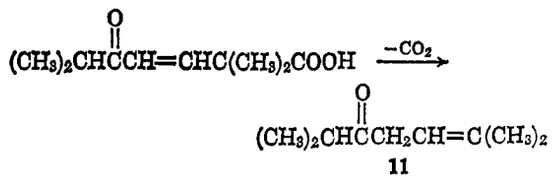
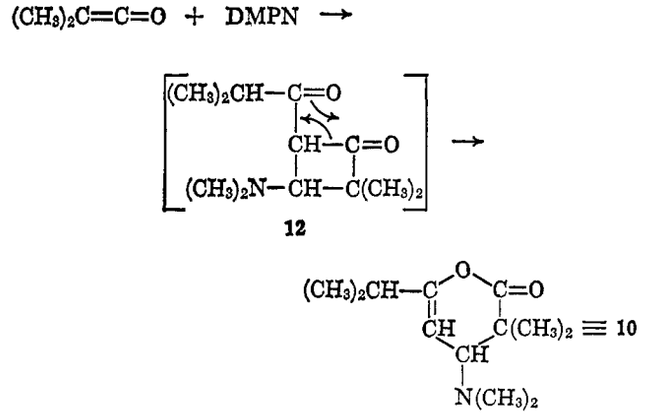


11

methylketene to the conjugated system of DMPN in a reaction reminiscent of the action of dienophiles on acrolein, there is no precedent for 1,4 cycloadditions involving ketenes. In fact ketenes and dienes have been shown to give only 1,2-cycloaddition products.[12] For this reason we feel that the path that this reaction follows is more likely a 1,2 cycloaddition of dimethylketene to DMPN, then to the intermediate cyclobutanone **12**, and followed by an intramolecular rearrangement to give **10**.



12

Experimental Section

DMPN[13] was prepared from ketene and N,N-dimethylisobutenylamine according to a method given in the literature.[2] Dimethylketene and butylethylketene were prepared by pyrolysis of the corresponding anhydrides.[16]

Reduction of DMPN with Lithium Aluminum Hydride.—DMPN (100 g, 0.71 mole) was added slowly to a stirred slurry of 19 g (0.5 mole) of lithium aluminum hydride in 250 ml of ether. The temperature was kept at 10–15° by an ice bath. As soon as the addition was complete, the reaction mixture was added rapidly to 400 ml of ethyl acetate. To this mixture was added successively 19 ml of water, 15 ml of 20% sodium hydroxide solution, and 65 ml of water. The solid was removed by filtration, and the filtrate was distilled through a 6-in. Vigreux column to give 69 g (68%) of **4**: bp 77–79° (20 mm); infrared (smear), 3.60 and 5.83 μ; nmr (neat), doublet at 1.04 (methyls of isopropyl group), singlet at 2.12 (dimethylamino group), and unresolved peaks at 2.53 (methylidyne of isopropyl group and methylene groups) ppm.

(12) J. C. Martin, P. G. Gott, V. W. Goodlett, and R. H. Hasek, *J. Org. Chem.*, **30**, 4175 (1965).

(13) DMPN had the following properties: bp 99° (1.7 mm); $n^{20}D$ 1.5305; infrared (smear),[14] 3.58, 6.05, 6.22, and 6.30 μ; nmr (neat),[15] doublet at 0.96 and septet at 2.51 (isopropyl group), singlet at 2.86 (dimethylamino group), doublets at 4.99 and 7.54 (J = 13 cps, olefinic protons) ppm.

(14) Infrared spectra were determined on a Baird AB-2 instrument.

(15) Nmr spectra were obtained with a Varian A-60 instrument operating at 60 Mc. Tetramethylsilane was used as an internal standard.

(16) R. H. Hasek and E. U. Elam (to Eastman Kodak Co.), Canadian Patent 618,772 (1961).

Anal. Calcd for $C_8H_{17}NO$: C, 67.1; H, 12.0; N, 9.8. Found: C, 67.4; H, 12.3; N, 9.6.

The picrate was prepared and recrystallized from ethyl alcohol. It melted at 144–145° (lit.[17] mp 146–147°).

Anal. Calcd for $C_{14}H_{20}N_4O_8$: C, 45.2; H, 5.4; N, 15.0. Found: C, 45.4; H, 5.6; N, 15.0.

Reduction of 4 with Lithium Aluminum Hydride.—A solution of 35.7 g (0.25 mole) of **4** in 50 ml of ether was added slowly with stirring to a slurry of 5.0 g (0.13 mole) of lithium aluminum hydride in 200 ml of ether. The reaction temperature was kept at 0–5° during the addition. Stirring was continued for 30 min after the addition was complete, and then 5 ml of ethyl acetate was added followed by 5 ml of water, 3.5 ml of 20% sodium hydroxide solution, and 18 ml of water. The solid was removed by filtration; distillation of the filtrate through a 6-in. Vigreux column gave 27.0 g (75%) of **5**: bp 79–80° (18 mm); $n^{20}D$ 1.4353; infrared (smear), 3.0–3.1 and 3.52 μ; nmr (neat), doublet at 0.88 and multiple peaks at 1.46 (isopropyl group), quartet at 1.46 (methylene group), quartet at 3.34 (methylidyne proton), singlet at 2.18 (dimethylamino group), singlet at 5.10 (hydroxy group), and multiple peaks at 2.38 (methylene group adjacent to nitrogen) ppm.

Anal. Calcd for $C_8H_{19}NO$: C, 66.2; H, 13.1; N, 9.7. Found: C, 66.4; H, 13.3; N, 9.4.

The picrate was recrystallized from ethyl alcohol and melted at 111.5–112.5°.

Anal. Calcd for $C_{14}H_{22}N_4O_8$: C, 44.9; H, 5.9; N, 15.0. Found: C, 44.7; H, 6.1; N, 14.8.

Catalytic Hydrogenation of DMPN.—A solution of 50 g of DMPN in 200 ml of water was hydrogenated in a rocking autoclave over 2 g of 5% ruthenium on carbon at 70° and 1500-psi pressure for 2 hr. The catalyst was removed by filtration. The filtrate consisted of two layers, and 400 ml of ether was added to extract the product. After the product had been dried over anhydrous magnesium sulfate, the ether solution was distilled through a 6-in. Vigreux column to give 36.3 g (72%) of 1-(dimethylamino)-4-methyl-3-pentanol (**5**), bp 104° (50 mm), $n^{20}D$ 1.4348. The infrared spectrum of this material was identical with that of **5** prepared by the action of lithium aluminum hydride on **4**. The picrate melted at 111–112°. The melting point was not depressed when this was mixed with the picrate of **5** prepared by lithium aluminum hydride reduction.

1-(Butylamino)-4-methyl-1-penten-3-one.—A solution of 21.2 g (0.15 mole) of DMPN, 33 g (0.45 mole) of butylamine, and 0.3 g of *p*-toluenesulfonic acid in 100 ml of benzene was refluxed under a water-cooled condenser for 7 hr. Dimethylamine was allowed to evolve from the system. Distillation of the reaction solution through a 6-in. Vigreux column gave 20.5 g (81%) of 1-(butylamino)-4-methyl-1-penten-3-one, bp 114.5–117° (5 mm), $n^{20}D$ 1.5056.

Anal. Calcd for $C_{10}H_{19}NO$: C, 71.0; H, 11.3; N, 8.3. Found: C, 70.8; H, 11.1; N, 8.2.

The Effect of Acid Catalysis in the Preparation of 1-Anilino-4-methyl-1-penten-3-one.—Two reaction solutions were prepared. Solution A contained 28.2 g (0.2 mole) of DMPN and 27.9 g (0.3 mole) of aniline in 150 ml of toluene, and solution B contained in addition to these ingredients 1.0 g of *p*-toluenesulfonic acid. These solutions were refluxed, and samples were withdrawn periodically and examined by glpc. The values reported in Table III are area per cent.

TABLE III

RATE OF FORMATION OF 1-ANILINO-4-METHYL-1-PENTEN-3-ONE

Time of reflux, hr	A (without catalyst), % product	B (with catalyst), % product
0.25	10	66
1.25	50	80
5.25	75	98

(17) M. Brown and W. S. Johnson, *J. Org. Chem.*, **27**, 4706 (1962).

2-Hydroxy-6-isopropylnicotinonitrile (7).—A solution containing 70.5 g (0.5 mole) of DMPN, 42 g (0.5 mole) of 2-cyanoacetamide, and 5 ml of acetic acid in 200 ml of water was refluxed for several hours. A large amount of solid came out of solution. The reaction mixture was cooled and made alkaline with sodium hydroxide solution. The solid was removed by filtration. After the solid had been dried, there was obtained 57.5 g (71%) of **7**, mp 208.5–210°.

Anal. Calcd for $C_9H_{10}N_2$: C, 66.7; H, 6.2; N, 17.3. Found: C, 66.9; H, 6.3; N, 17.1.

5-Isopropylisoxazole (8).—To a stirred solution of 70.5 g (0.5 mole)of DMPN in 30 ml of water was slowly added a solution of 35 g (0.5 mole) of hydroxylamine hydrochloride in 40 ml of water. The temperature rose to 50° during the addition. The solution was heated on a steam bath for 2 hr, cooled, and made alkaline with sodium hydroxide solution. The organic layer was taken up in ether and dried over anhydrous magnesium sulfate. Distillation through a 10-in. packed column gave 47.3 g (86%) of **8**, bp 67° (36 mm).

Anal. Calcd for C_6H_9NO: C, 64.9; H, 8.1; N, 12.6. Found: C, 64.8; H, 8.1; N, 12.5.

5-Isopropyl-1-phenylpyrazole (9).—DMPN (28.2 g, 0.2 mole) was added slowly with stirring to a solution of 21.6 g (0.2 mole) of phenylhydrazine and 9 g (0.089) mole of concentrated sulfuric acid in 22 ml of water. The temperature was kept at 34–40° during the addition and at 68° for 2 hr. The mixture was neutralized with sodium hydroxide solution and extracted with ether; the ether extract was dried over anhydrous magnesium sulfate. Distillation through a 10-in. packed column afforded 24.0 g (65%) of **9**, bp 80–82° (0.07 mm).

Anal. Calcd for $C_{12}H_{14}N_2$: C, 77.4; H, 7.6; N, 15.0. Found: C, 77.0; H, 7.6; N, 14.8.

4-(Dimethylamino)-3,4-dihydro-6-isopropyl-3,3-dimethyl-2H-pyran-2-one (10).—Dimethylketene (140 g, 2.0 moles) was added over a 30-min period to a stirred solution of 282 g (2.0 moles) of DMPN in 300 ml of benzene. The temperature of the exothermic reaction was kept at 20–30° by a water bath. After the reaction solution had been stirred for 2 hr, it was distilled through a 10-in packed column to give 360.1 g (86%) of **10**: bp 79° (1 mm); $n^{20}D$ 1.4733; infrared (smear), 5.70 and 6.00 μ; nmr (CCl_4), doublet at 1.20 and a septet at 2.50 (isopropyl group), singlets at 1.25 and 1.29 (methyl groups), singlet at 2.19 (dimethylamino group), doublet at 2.98 (methylidyne proton), and doublet at 5.14 (olefinic proton) ppm.

Anal. Calcd for $C_{12}H_{21}NO_2$: C, 68.2; H, 10.0; N, 6.6. Found: C, 67.8; H, 9.9; N, 6.5.

3-Butyl-4-(dimethylamino)-3-ethyl-3,4-dihydro-6-isopropyl-2H-pyran-2-one.—A solution of 31.4 g (0.25 mole) of butylethylketene and 35 g (0.25 mole) of DMPN in 200 ml of toluene was refluxed for 8 hr. After cooling, the reaction solution was treated with dilute hydrochloric acid. The aqueous layer was separated, made alkaline with sodium hydroxide solution, and extracted with ether; the ether extract was dried over anhydrous magnesium sulfate. Distillation of this material through a 10-in. packed column gave 34.4 g (52%) of 3-butyl-4-(dimethylamino)-3-ethyl-3,4-dihydro-6-isopropyl-2H-pyran-2-one, bp 110–113° (1.5 mm).

Anal. Calcd for $C_{16}H_{29}NO_2$: C, 71.9; H, 10.9; N, 5.2. Found: C, 71.7; H, 11.0; N, 5.2.

Hydrolysis of 10.—A solution of 21.1 g (0.1 mole) of **10** in 200 ml of water containing 24.3 ml of concentrated hydrochloric acid was heated on a steam bath for 3 hr. An oily layer separated and was extracted with ether; the ether extract was dried over anhydrous magnesium sulfate. Distillation of this material gave 2.9 g of 2,6-dimethyl-5-hepten-3-one (**11**): bp 89–91° (32 mm); infrared (smear), 5.87 and 6.02 μ; nmr (CCl_4), doublet at 1.11 and septet at 2.77 (isopropyl group), two peaks at 1.70 and 1.86 (other methyl groups), doublet at 3.27 (methylene group), and a triplet at 5.61 (olefinic proton) ppm.