which white needles of pure **3c** (X = Cl) were obtained after three crystallizations from cyclohexane.

Reaction of the Aziridines 1a and b with Thiophenol.—Thiophenol (1 equiv) and 1 equiv of **1a** or **b** were heated under reflux in carbon tetrachloride for 24 hr. The reaction mixture was washed (aqueous Na_2CO_3), dried (Na_2SO_4), and concentrated. The products could not be distilled without decomposition.

Reaction of the Aziridines 1a–c with *p*-Nitrobenzoic Acid.—A solution of 2 equiv of *p*-nitrobenzoic acid and 1 equiv of the aziridine **1a** or **b** was heated under reflux in chloroform for 16 hr. The solvent was removed and the resulting solid was recrystallized from benzene. The products were complexes of *p*-nitrobenzoic acid with the adducts. Equimolar quantities of *p*-nitrobenzoic acid and aziridine would produce the complex and unreacted aziridine after 16 hr. The ultraviolet spectrum of the complex from **1a** in ethanol exhibited λ_{max} 262 mμ (ϵ 21,500); the complex from **1b**, λ_{max} 263 mμ (ϵ 22,100). Treatment of a methylene chloride solution of the complex with aqueous sodium carbonate produced the corresponding adduct **2a** (X = *p*-nitrobenzoyloxy) or **2b** (X = *p*-nitrobenzoyloxy), which was recrystallized from benzene. Compound **2a** (X = *p*-nitrobenzoyloxy) exhibited λ_{max} 258 mμ (ϵ 12,400); **2b** (X = *p*-nitrobenzoyloxy), λ_{max} 258 mμ (ϵ 13,600). Treatment of **1c** with *p*-nitrobenzoic acid (2 equiv) produced an oil which was washed (aqueous Na_2CO_3) to remove any unreacted or complexed *p*-nitrobenzoic acid. The organic phase was dried (Na_2SO_4) and evaporated. The residue was diluted with ether and N,N-dimethyl-*p*-nitrobenzamide was deposited (0.96 g from 2.05 g of **1c**). Identification was made by mixture melting point and infrared comparison with an authentic sample.

Reaction of the Aziridines 1a–c with Pyrrolidine.—The aziridine **1a**, **b**, or **c** was heated in pyrrolidine under reflux for 16 hr (**1a** and **b**), or for 96 hr (**1c**). The first two adducts could be distilled under reduced pressure, although considerable decomposition occurred with **2b** (X = 1-pyrrolydinyl). A small forerun of unreacted **1b** was obtained when the reaction time was 16 hr. Compound **2c** (X = 1-pyrrolidinyl) was obtained as a mushy solid when the crude product was kept at 0.2 mm for 24 hr; **2c** (X = 1-pyrrolidinyl) was further purified by dissolving it in pentane and chilling (ice–methanol bath). The process was repeated four times and white needles, mp 48.5–50°, were obtained.

Reaction of the Aziridines 1a–c with Methanol Containing Sodium Methoxide.—Sodium (1 equiv) in excess methanol and 1 equiv of the aziridine **1a**, **b**, or **c** was heated under reflux for 16 hr (**1a** and **b**), or 92 hr (**1c**). After cooling to room temperature, sufficient acetic acid was added to neutralize the sodium methoxide, and the methanol was evaporated *in vacuo*. The product was taken up in ether, filtered, and concentrated. Distillation under reduced pressure produced **2a** (X = OCH_3) and **2b** (X = OCH_3). A forerun of unreacted aziridine was obtained from the reactions of **1b** and **c**. In the latter case, once the unreacted aziridine had been removed, pure **2c** (X = OCH_3) was obtained from the residue by sublimation at 80–85° (0.025 mm).

Acknowledgment.—The authors are indebted to Dr. T. M. Valega for helpful discussions in the preparation of this manuscript and to Mr. E. L. Gooden for obtaining the nmr spectra reported in Table II.

Ketenes. X. Heterocyclic Systems Derived from Dimethylmalonyl Chloride[1]

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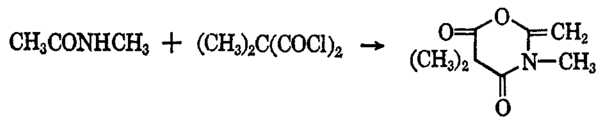
Dimethylmalonyl chloride was found to react with a number of N-monosubstituted amides to afford dihydro-2-methylene-4H-1,3-oxazine-4,6(5H)-diones and with N-monosubstituted thioamides and N,N'-disubstituted amidines to give the corresponding thiazine and pyrimidine analogs. Several reactions producing these heterocycles are described. The dihydro-2-methylene-4H-1,3-oxazine-4,6(5H)-diones were found to rearrange to 3-oxoglutarimides if the methylene group was substituted with one or two groups other than hydrogen. The reaction of dimethylmalonyl chloride with aromatic amides unsubstituted on the nitrogen gave 4H-1,3-oxazine-4,6(5H)-diones. A similar reaction with aliphatic amides unsubstituted on the nitrogen gave dihydro-2-methylene-4H-1,3-oxazine-4,6(5H)-diones; however, if triethylamine was used as an acid acceptor, dihydro-3-isobutyryl-2-methylene-4H-1,3-oxazine-4,6(5H)-diones resulted. Imines having at least one α-methylene group and dimethylmalonyl chloride gave substituted 2,4(1H,3H)-pyridinediones.

Ziegler and Meindl[2,3] have described the reactions of monosubstituted malonyl chlorides with aromatic amides and also with certain enamines. We have examined the reaction of dimethylmalonyl chloride[4] with a number of amides, thioamides, and enamines, and the present paper is a report of this work.

Dimethylmalonyl chloride was found to react with N-methylacetamide in the presence of triethylamine to produce a compound subsequently identified as dihydro-3,5,5-trimethyl-2-methylene-4H-1,3-oxazine-4,6(5H)-dione (**1**). The structural assignment of **1** was based on its elemental analysis, on its infrared and nmr spectra, and on some of its chemical reactions which are described later in the paper.



1

This ring closure was found to be a general reaction for a number of N-monosubstituted amides and thioamides with dimethylmalonyl chloride. Variations in the R groups from H to CH_3 to C_6H_5 did not affect the course of the reaction or greatly influence the ultimate yield. Table I affords a list of the amides which combined with dimethylmalonyl chloride to give cyclic compounds. N-Methylcrotonamide afforded a butadiene-type product (**2a**) in 84% yield, and 2-pyrrolidinone gave the bicyclic product (**2b**) in 65% yield. The alternate carbon–nitrogen closure leading to the 3-oxoglutarmides **3** was not observed in any case.

The use of a tertiary amine as a hydrogen chloride acceptor was unnecessary when R' and R'' were not hydrogen. N-Methylisobutyramide and dimethylmalonyl chloride when refluxed in ethylene dichloride afforded a 90% yield of dihydro-2-isopropylidene-3,5,-5-trimethyl-4H-1,3-oxazine-4,6(5H)-dione (**2c**). How-

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[1] Paper IX in this series: R. H. Hasek, P. G. Gott, and J. C. Martin, *J. Org. Chem.*, **31**, 1931 (1966).

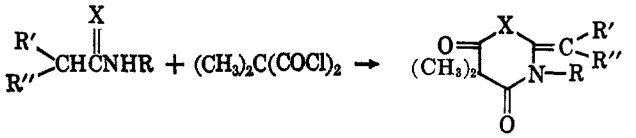
[2] E. Ziegler and H. Meindl, *Monatsh. Chem.*, **95**, 1318 (1964).

[3] E. Ziegler, F. Hradetzky, and K. Belegratis, *ibid.*, **96**, 1347 (1965).

[4] R. G. Nations and K. C. Brannock (to Eastman Kodak Co.), U. S. Patent 3,220,935 (1965).

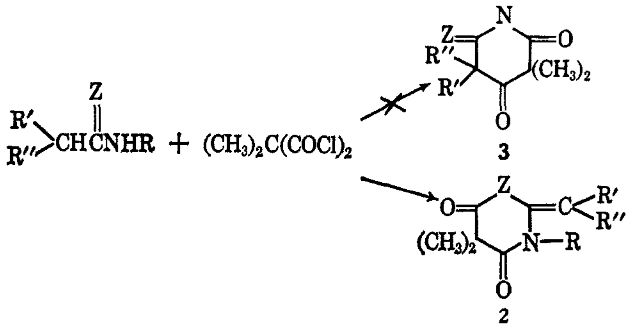
TABLE I

PRODUCTS FROM THE REACTION OF DIMETHYLMALONYL CHLORIDE WITH AMIDES[a]



R	R′	R″	X	Mp or bp (mm), °C	Recrystn solvent	Yield, %	Formula	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found
CH_3	H	H	O	52–55.5 78–80 (1)		72	$C_8H_{11}NO_3$	56.8	56.9	6.6	6.8	8.3	8.5
C_6H_5	H	H	O	108.5–109	Hexane–benzene	21	$C_{13}H_{13}NO_3$	67.5	67.0	5.6	5.9	6.1	6.8
CH_3	CH_3	H	O	69–71 81–85 (0.5)	Hexane	80	$C_9H_{13}NO_3$	59.0	59.4	7.2	7.3	7.7	7.7
CH_3	CH_3	CH_3	O	57–58	Ethyl ether	69	$C_{10}H_{15}NO_3$	60.9	60.8	7.7	7.6	7.1	7.0
C_4H_9	CH_3	CH_3	O	116–119 (1)		67	$C_{13}H_{21}NO_3$	65.2	65.3	8.9	8.9	5.8	5.5
C_6H_5	CH_3	CH_3	O	129–130 (0.07)		50	$C_{15}H_{17}NO_3$	69.8	69.6	6.6	6.8	5.4	5.4
$C_{12}H_{25}$	CH_3	CH_3	O	167 (0.07)		55	$C_{21}H_{37}NO_3$	71.8	71.7	10.6	10.7	4.0	4.1
CH_3	H	$CH_2{=}CH$[b]	O	90–92 100–115 (0.3)	Toluene	84	$C_{10}H_{13}NO_3$	61.5	61.3	6.7	6.8	7.2	7.4
CH_3	C_6H_5	H	O	111–113	Ethyl alcohol	75	$C_{14}H_{15}NO_3$	68.6	68.7	6.2	5.7	5.7	5.7
CH_3	C_6H_5	C_6H_5	O	132–136	Ethyl alcohol	98	$C_{20}H_{19}NO_3$	74.7	74.8	6.0	6.1	4.4	4.6
CH_3	$-(CH_2)_2-$[c]	H	O	203–206	Ethyl ether	82	$C_{18}H_{24}N_2O_6$	59.3	59.3	6.6	6.6	7.7	7.9
$-(CH_2)_2-$		H	O	71–72		65	$C_9H_{11}NO_3$	59.7	59.7	6.1	6.1	7.7	8.0
C_6H_5	H	H	S	114–116	Hexane–benzene	75	$C_{13}H_{13}NO_2S$	63.1	63.4	5.3	5.7	5.7	5.4
CH_3	CH_3	CH_3	S	103–106 (0.1)		81	$C_{10}H_{15}NO_2S$	56.3	56.5	7.1	7.2	6.6	6.3
C_6H_5	H	H	NC_6H_5	198.5–200	Ethyl acetate	67	$C_{19}H_{18}N_2O_2$	74.5	74.7	5.9	6.1	9.1	9.2

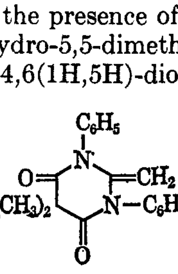
[a] These products were all made using triethylamine. [b] Starting amide was $CH_3CH{=}CH\overset{O}{\overset{\|}{C}}NHCH_3$. [c] Bisadduct.



2a, $R = CH_3$; $R' = CH{=}CH_2$; $R'' = H$; $Z = O$
b, R and $R' = CH_2CH_2$; $R'' = H$; $Z = O$
c, $R = R' = R'' = CH_3$; $Z = O$
d, $R = C_6H_5$; $R' = R'' = H$; $Z = S$

ever, N-methylacetamide and dimethylmalonyl chloride under the same conditions gave no 1 but produced a large amount of viscous, undistillable product. Thioacetanilide and dimethylmalonyl chloride in the presence of triethylamine gave a 75% yield of dihydro-5,5-dimethyl-2-methylene-3-phenyl-4H-1,3-thiazine-4,6-(5H)-dione (**2d**).

Amidines also reacted with dimethylmalonyl chloride; *e.g.*, N,N-diphenylacetamidine and dimethylmalonyl chloride in the presence of triethylamine gave a 67% yield of dihydro-5,5-dimethyl-2-methylene-1,3-diphenylpyrimidine-4,6(1H,5H)-dione (**4**).



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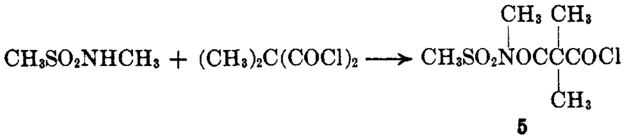
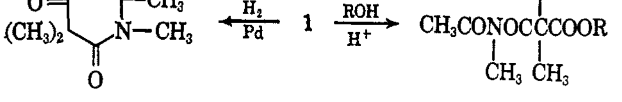
The monosubstituted sulfonamide, N-methylmethanesulfonamide, when treated with dimethylmalonyl chloride in the presence of triethylamine, reacted only on the nitrogen to give N,2,2-trimethyl-N-(methylsulfonyl)malonamoyl chloride (**5**) in 99% yield.



$$CH_3SO_2NHCH_3 + (CH_3)_2C(COCl)_2 \longrightarrow CH_3SO_2\overset{CH_3}{N}OC\overset{CH_3}{\underset{CH_3}{C}}COCl$$

5

Several reactions of the oxazinedione 1 were explored. When 1 was stirred with water at room temperature, it hydrolyzed to give a 70% yield of N-acetyl-N,2,2-trimethylmalonamic acid (**6a**), which at room temperature slowly decarboxylated to N-acetyl-N-methylisobutyramide. Catalytic hydrogenation of 1 over palladium afforded an 84% yield of dihydro-2,3,5,5-tetramethyl-4H-1,3-oxazine-4,6(5H)-dione (**7**). In the presence of *p*-toluenesulfonic acid catalyst at room temperature, methanol and 1 gave a 97% yield of methyl N-acetyl-N,2,2-trimethylmalonamate (**6b**). When refluxed with 1 in toluene, aniline gave 2,2-dimethyl-N,N′-diphenylmalonamide and methylamine gave N,N′,2,2-tetramethylmalonamide.



7

6a, R = H
b, R = CH_3

Rearrangement to N,2,2,4,4-pentamethyl-3-oxoglutarimide (**8**) in 92% yield was effected by treating **2c** with a small amount of sodium methoxide. Analytical data of 3-oxoglutarimides are given in Table II. With weaker bases such as potassium carbonate, heating at 200–250° was necessary to promote the reaction. Passing **2c** over Vycor chips at 600° caused the same rearrangement in 68% yield. A marked resemblance can be seen between this rearrangement and that of certain dihydro-4H-1,3-oxazin-6(5H)-ones to 2,4-piperidinediones.[5] When the dihydro-4H-1,3-oxazine-4,6-

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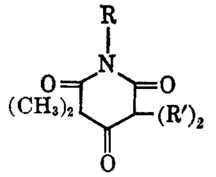
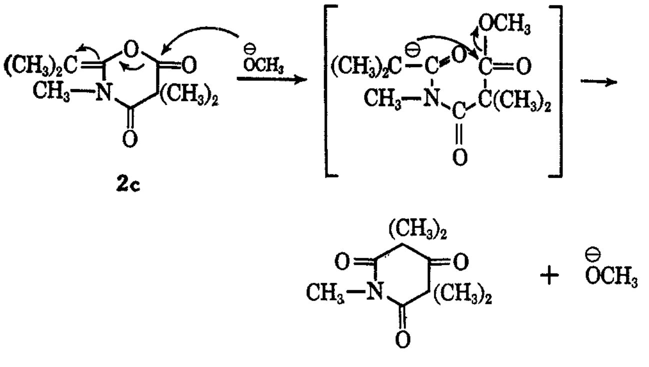
[5] J. C. Martin, V. A. Hoyle, Jr., and K. C. Brannock, *Tetrahedron Letters*, **No. 40**, 3589 (1965).

TABLE II

3-OXOGLUTARIMIDES

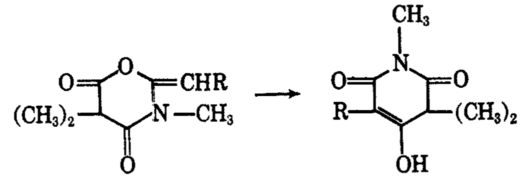


R	R′	Mp or bp (mm), °C	Recrystn solvent	Yield, %	Method	Formula	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found
CH_3	CH_3	75.5–76.5	Toluene	68	A	$C_{10}H_{15}NO_3$	60.9	61.0	7.7	7.4	7.1	7.2
				92	B							
C_4H_9	CH_3	139 (10)		68	A	$C_{13}H_{21}NO_3$	65.2	65.5	8.9	8.9	5.9	5.7
C_6H_5	CH_3	99–102	Ethyl alcohol	48	B	$C_{15}H_{17}NO_3$	69.5	70.1	6.6	6.7	5.4	5.5
$C_{12}H_{25}$	CH_3	160–162 (0.07)		87	B	$C_{21}H_{37}NO_3$	71.8	72.0	10.6	10.8	4.0	3.5
CH_3	C_6H_5	137–138.5	Ethyl alcohol	45	B	$C_{20}H_{19}NO_3$	74.7	74.8	6.0	6.0	4.4	4.1



2c **8**

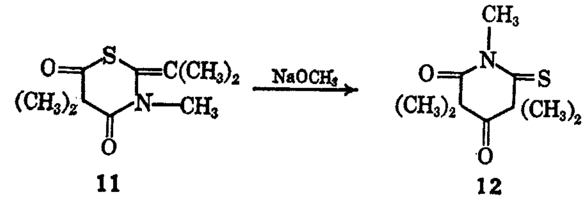
(5H)-dione contained only one group on the exocyclic double bond, the rearrangement did not take place with sodium methoxide but could be effected by using a hot tube. The resulting glutarimides existed in the enol form. At 600° over Vycor chips, 2-ethylidenedihydro-3,5,5-trimethyl-4H-1,3-oxazine-4,6(5H)-dione (**9a**) and 2-benzylidenedihydro-3,5,5-trimethyl-4H-1,3-oxazine-4,6(5H)-dione (**9b**) rearranged to 3-hydroxy-N,2,4,4-tetramethylglutaconimide (**10a**) and 3-hydroxy-N,4,4-trimethyl-2-phenylglutaconimide (**10b**), respectively.



9a, R = CH_3
b, R = C_6H_5

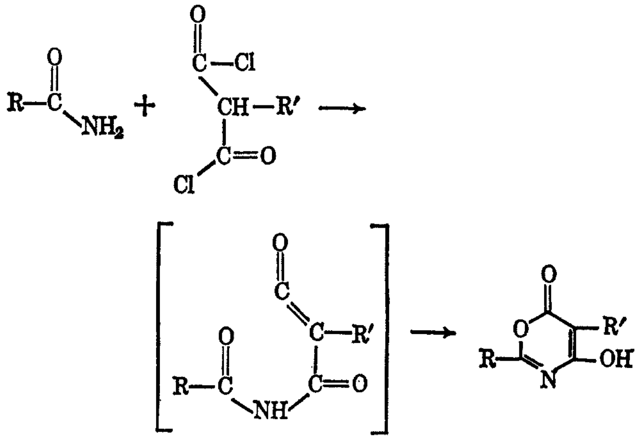
10a, R = CH_3
b, R = C_6H_5

When the dihydro-4H-1,3-oxazine-4,6(5H)-dione had an unsubstituted exocyclic methylene group (**2**, where R′ and R″ = H), the rearrangement did not take place either with sodium methoxide or in the vapor phase at 620°. It was also observed that **2d** and **4** did not rearrange under these conditions, but that dihydro-2-isopropylidene-3,5,5-trimethyl-4H-1,3-thiazine-4,6(5H)-dione (**11**) did rearrange smoothly to N,2,2,4,4-pentamethyl-3-oxo-1-thioglutarimide (**12**) on treatment with sodium methoxide.



11 **12**

Ziegler and Meindl[2] described the reaction of monosubstituted malonyl chlorides with aromatic amides to give the enol forms of certain 4H-1,3-oxazine-4,6(5H)-diones. They invoked a mechanism involving a ketene intermediate **13** to explain the reaction. Their main justification for this mechanism was based on the failure of the disubstituted malonyl chlorides to enter into a similar reaction. The absence of a hydrogen atom on the central carbon atom in the disubstituted malonyl chlorides would make a structure like **13** impossible. They reasoned that, since the disubstituted malonyl chlorides could not form a ketene and since they observed no reaction, then a ketene was an essential intermediate in the mechanism.



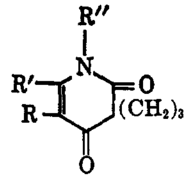
13

However, we have now found that dimethylmalonyl chloride does react with aromatic amides in the absence of triethylamine to give 4H-1,3-oxazine-4,6(5H)-diones in good yields. This means that the ketene intermediate is not necessary to explain the reaction of Ziegler and Meindl.

Benzamide and dimethylmalonyl chloride were refluxed in ethylene dichloride to give 5,5-dimethyl-2-phenyl-4H-1,3-oxazine-4,6(5H)-dione (**14a**) in 62% yield. In a similar fashion, *o*-toluamide gave 5,5-dimethyl-2-*o*-tolyl-4H-1,3-oxazine-4,6(5H)-dione (**14b**) in 76% yield, and thiobenzamide gave 5,5-dimethyl-2-phenyl-4H-1,3-thiazine-4,6(5H)-dione (**14c**) in 88% yield. The structural assignment for **14a** was based on its elemental analysis, on its infrared and nmr spectra,

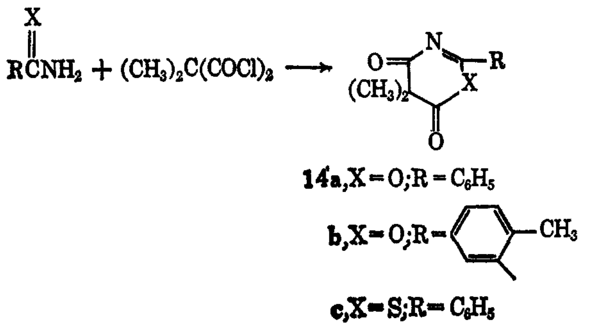
TABLE III

REACTION PRODUCTS FROM IMINES AND DIMETHYLMALONYL CHLORIDE



R	R′	R″	Bp (mm), °C	Yield, %	Formula	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found
C_2H_5	H	$CH(CH_3)_2$	90–100 (0.6)[a]	91	$C_{12}H_{19}NO_2$	68.9	68.6	9.2	8.9	6.7	6.8
$-(CH_2)_3-$		C_3H_7	135–138 (1.0)	76	$C_{13}H_{19}NO_2$	70.5	70.3	8.7	8.5	6.3	6.2
$-(CH_2)_4-$		C_3H_7	124–126 (0.3)[b]	81	$C_{14}H_{21}NO_2$	71.5	71.7	9.0	8.7	6.0	6.1

[a] Solidified on cooling. Sample recrystallized from carbon tetrachloride melted at 59–61°. [b] Solidified on standing. Sample recrystallized from hexane melted at 44–46°.

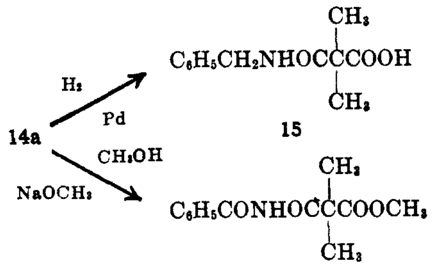


14a, X = O; R = C_6H_5

b, X = O; R =

c, X = S; R = C_6H_5

and on the facts that its hydrogenation afforded N-benzyl-2,2-dimethylmalonamic acid (**15**) and that its reaction with methanol gave methyl N-benzoyl-2,2-dimethylmalonamate (**16**). When dimethylmalonyl chloride and benzamide were combined in the presence of triethylamine, benzonitrile in 63% yield and **14a** in 8% yield were obtained.



$$14a \xrightarrow{H_2,\ Pd} C_6H_5CH_2NHOC\overset{CH_3}{\underset{CH_3}{C}}COOH$$

15

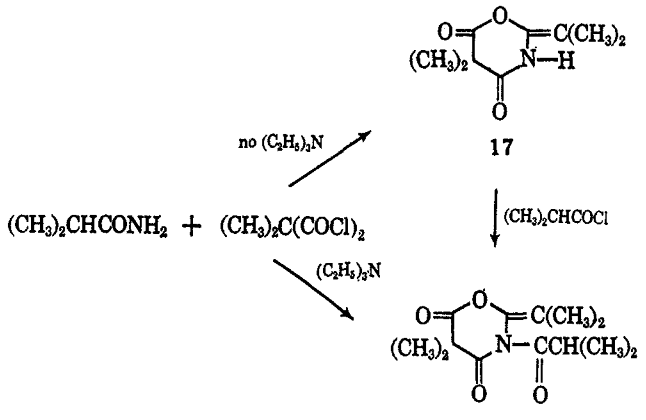
$$14a \xrightarrow{CH_3OH,\ NaOCH_3} C_6H_5CONHOC\overset{CH_3}{\underset{CH_3}{C}}COOCH_3$$

16

The reaction of dimethylmalonyl chloride with aliphatic amides unsubstituted on the nitrogen was exemplified by the combination of isobutyramide and dimethylmalonyl chloride in refluxing ethylene dichloride to afford dihydro-2-isopropylidene-5,5-dimethyl-4H-1,3-oxazine-4,6(5H)-dione (**17**) in the absence of triethylamine. When the same reactants were combined in the presence of triethylamine, dihydro-3-isobutyryl-2-isopropylidene-5,5-dimethyl-4H-1,3-oxazine-4,6(5H)-dione (**18**) was produced in 43% yield. The action of isobutyryl chloride converted **17** to **18**.

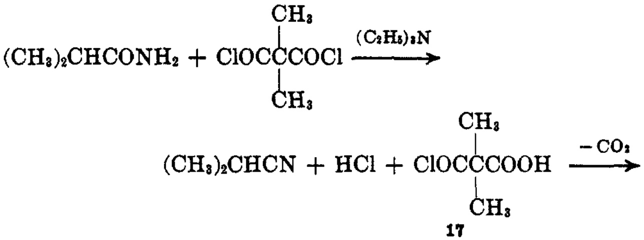
When acetamide and dimethylmalonyl chloride were combined in the absence of triethylamine, only tars resulted, but, in the presence of triethylamine, dihydro-3-isobutyryl-5,5-dimethyl-2-methylene-4H-1,3-oxazine-4,6(5H)-dione (**19**) was obtained in 52% yield.

The unexpected presence of the isobutyryl group on the nitrogen atom in **18** and **19** can be rationalized by several reaction paths, one being the reaction of dimethylmalonyl chloride with isobutyramide to form isobutyronitrile and the half acid chloride of dimethylmalonic acid. Decarboxylation of the latter would produce isobutyryl chloride which in turn would combine with **17** to produce **18**. The presence of a considerable amount of isobutyronitrile was detected in the reaction mixture when dimethylmalonyl chloride and isobutyramide were combined in the presence of triethylamine.



17

18

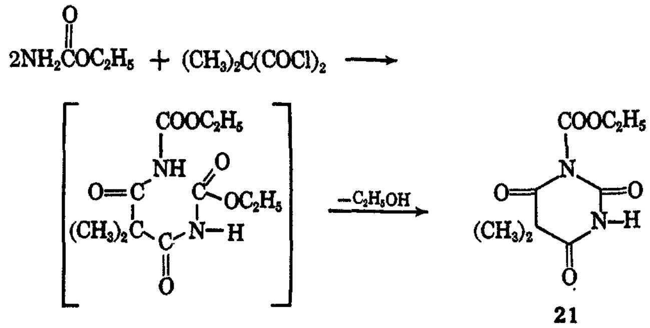


$$(CH_3)_2CHCONH_2 + ClOC\overset{CH_3}{\underset{CH_3}{C}}COCl \xrightarrow{(C_2H_5)_3N}$$

$$(CH_3)_2CHCN + HCl + ClOC\overset{CH_3}{\underset{CH_3}{C}}COOH \xrightarrow{-CO_2}$$

$$ClOCCH(CH_3)_2 \xrightarrow{17} 18$$

Ethyl carbamate reacted with dimethylmalonyl chloride differently from other primary amides. From two molecules of ethyl carbamate and one molecule of dimethylmalonyl chloride, ethyl hexahydro-5,5-dimeth-

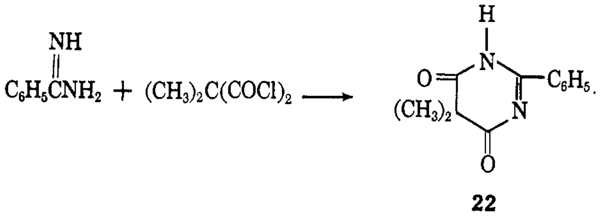


20

21

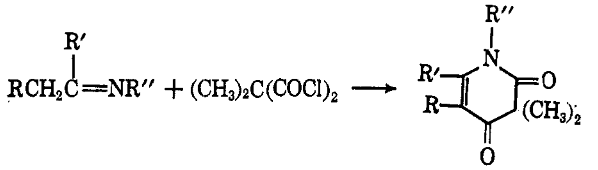
yl-2,4,6-trioxo-1-pyrimidinecarboxylate (**21**) was produced, possibly *via* the intermediate bisamide **20**. No triethylamine was used.

Amidines unsubstituted on the nitrogens also reacted quite readily with dimethylmalonyl chloride. Benzamidine hydrochloride and dimethylmalonyl chloride when combined in the presence of aqueous sodium hydroxide afforded 5,5-dimethyl-2-phenyl-4,6-(1H,5H)-pyrimidinedione (22) in 49% yield.



22

Imines having a least one α-methylene group condensed with dimethylmalonyl chloride in the presence of triethylamine to give substituted 2,4-(1H,3H)-pyridinediones (see Table III for analytical data). N-Butylideneisopropylamine, N-cyclohexylidenepropyl amine, and N-cyclopentylidenepropylamine gave 5-ethyl-1-isopropyl-3,3-dimethyl-2,4-(1H,3H)-pyridinedione (**23a**), 5,6,7,8-tetrahydro-3,3-dimethyl-1-propyl-2,4-(1H,3H)-quinolinedione (**23b**), and 6,7-dihydro-3,3-dimethyl-1-propyl-5H-1-pyrindine-2,4(1H,3H)-dione (**23c**), respectively.



23a, R = C_2H_5; R′ = H; R″ = $CH(CH_3)_2$
b, R and R′ = $\{CH_2\}_4$; R″ = C_3H_7
c, R and R′ = $\{CH_2\}_3$; R″ = C_3H_7

Experimental Section

Dihydro-3,5,5-trimethyl-2-methylene-4H-1,3-oxazine-4,6(5H)-dione (1).—Dimethylmalonyl chloride (84.5 g, 0.5 mole) was added rapidly to a stirred solution of 36.5 g (0.5 mole) of N-methylacetamide and 152 g (1.5 moles) of triethylamine in 500 ml of toluene. The reaction temperature rose to 90°, and a large amount of solid precipitated. After the mixture was stirred for 2 hr, the solid was removed by filtration and washed several times with ether. The solid material consisted of 135.3 g (98.5%) of triethylamine hydrochloride. Distillation of the filtrates through a 6-in. Vigreux column gave 60.5 g (72%) of **1**, bp 78–80° (1 mm), which solidified on cooling: mp 52–55.5°; infrared absorptions[6] (smear), 5.67, 5.9–6.15 μ (broad); nmr spectrum[7] (neat), singlet at 1.38, 6 H (*gem*-dimethyl groups), singlet at 3.22, 3 H (methyl group attached to nitrogen), and quartet at 4.28 ppm, 2 H (terminal methylene group); ultraviolet spectrum[8] (isopropyl alcohol), 233 mμ (log ε 4.08).

Anal. Calcd for $C_8H_{11}NO_3$: C, 56.8; H, 6.6; N, 8.3. Found: C, 56.9; H, 6.8; N, 8.5.

Dihydro-5,5-dimethyl-2-methylene-3-phenyl-4H-1,3-thiazine-4,6(5H)-dione (2d).—Under the same general conditions used for the preparation of **1**, 27.8 g (0.165 mole) of dimethylmalonyl chloride, 25 g (0.165 mole) of thioacetanilide, 50 g (0.5 mole) of triethylamine, and 300 ml of toluene gave 38.2 g (100%) of crude **2d**. Recrystallization of this material from a mixture of hexane and benzene gave 28.6 g (75%) of **2d**: mp 114–116°; infrared absorptions (KBr), 5.98, 6.06, and 6.30 μ; nmr spectrum (CCl_4), singlet at 1.55, 6 H (*gem*-dimethyl group), doublets (J = 2.1 cps) at 4.60, 1 H, and 4.91, 1 H (terminal methylene group), and multiple peaks at 7.28 ppm, 5 H (aromatic protons); ultraviolet spectrum (isopropyl alcohol), 244 mμ (log ε 3.98).

Anal. Calcd for $C_{13}H_{13}NO_2S$: C, 63.1; H, 5.3; N, 5.7. Found: C, 63.4; H, 5.7; N, 5.4.

Dihydro-5,5-dimethyl-2-methylene-1,3-diphenylpyrimidine-4,6-(1H,5H)-dione (**4**).—To a stirred solution of 25 g (0.12 mole) of N,N′-diphenylacetamidine and 30.3 g (0.3 mole) of triethylamine in 150 ml of toluene was added rapidly 20.3 g (0.12 mole) of dimethylmalonyl chloride. The temperature rose to 90°, and a large amount of solid precipitated. After the mixture was stirred for 2 hr, it was filtered to give 57.7 g of solid which was stirred with 150 ml of water to remove triethylamine hydrochloride. The insoluble material **4** melted at 198.5–199.5° and weighed 24.5 g (67%). A sample was recrystallized from ethyl acetate to give a product with mp 198.5–200°; infrared absorptions (KBr), 5.84, 5.96, and 6.22 μ; nmr spectrum ($CHCl_3$), singlet at 1.62, 6 H (*gem*-dimethyl group), singlet at 3.58, 2 H (terminal methylene group), and multiple peaks at 7.49 ppm 10 H (aromatic protons); ultraviolet spectrum (ethyl alcohol), 248 mμ (log ε 4.15).

Anal. Calcd for $C_{19}H_{18}N_2O_2$: C, 74.5; H, 5.9; N, 9.1. Found: C, 74.7; H, 6.1; N, 9.2.

Reaction of Dimethylmalonyl Chloride with N-Methylisobutyramide in the Absence of a Catalyst.—A solution of 20.1 g (0.2 mole) of N-methylisobutyramide and 37.2 g (0.22 mole) of dimethylmalonyl chloride in 125 ml of ethylene dichloride was refluxed for 4 hr. Hydrogen chloride evolved rapidly. The reaction solution was distilled through a 6-in. Vigreux column to give 35.6 g (90%) of dihydro-2-isopropylidene-3,5,5-trimethyl-4H-1,3-oxazine-4,6(5H)-dione (**2c**): bp 85–86° (0.3 mm), $n^{20}D$ 1.4960. This material solidified on standing, and a sample after recrystallization from cold ether had mp 57–58°; infrared absorptions (smear), 5.62 and 5.95 μ; nmr spectrum (CCl_4), singlet at 1.38, 6 H (*gem*-dimethyl group), singlet at 1.86, 6 H (methyl groups on double bond), and singlet at 3.26 ppm, 3 H (methyl group attached to nitrogen); ultraviolet spectrum (isopropyl alcohol), 204 mμ (log ε 3.98) and 232 mμ (log ε 3.96).

Anal. Calcd for $C_{10}H_{15}NO_3$: C, 60.3; H, 7.6. Found: C, 60.5; H, 7.7.

Reaction of Dimethylmalonyl Chloride with N-Methylmethanesulfonamide.—Dimethylmalonyl chloride (25.4 g, 0.15 mole) was added rapidly with stirring to a solution of 16.4 g (0.15 mole) of N-methylmethanesulfonamide and 31 g (0.3 mole) of triethylamine in 100 ml of tetrahydrofuran. The mixture was refluxed for 3 hr before the triethylamine hydrochloride (21.2 g) was removed by filtration. Vacuum concentration of the filtrate gave 36.0 g (99%) of crude N,2,2-trimethyl-N-(methylsulfonyl)-malonamoyl chloride (**5**), mp 72–76°. A sample recrystallized from carbon tetrachloride had mp 74–76°; infrared absorptions (KBr), 5.60 and 5.96 μ; nmr spectrum (CCl_4), singlet at 1.62, 6 H (*gem*-dimethyl group) and singlets at 3.18, 3 H, and 3.22 ppm, 3 H (CH_3SO_2– and >NCH_3).

Anal. Calcd for $C_7H_{12}ClNO_4S$: C, 34.8; H, 5.0; N, 5.8; Cl, 14.7. Found: C, 35.1; H, 5.5; N, 5.9; Cl, 14.6.

Hydrolysis of 1.—After 10 g (0.059 mole) of **1** and 20 ml of water were stirred together for 2.5 hr, the resulting mixture was cooled to 5° and filtered to obtain 7.8 g (70%) of **6a**: mp 113–114° dec; infrared absorptions (KBr), 5.9, 5.95, and 6.0 μ; nmr spectrum ($CHCl_3$), singlet at 1.53, 6 H (*gem*-dimethyl group), singlet at 2.40, 3 H (acetyl group), singlet at 3.33, 3 H (methyl attached to nitrogen), and singlet at 11.72 ppm, 1 H (acid proton).

Anal. Calcd for $C_8H_{13}NO_4$: C, 51.3; H, 7.0; N, 7.5. Found: C, 51.3; H, 7.2; N, 7.7.

On standing at room temperature for several days, **6a** (7.5 g) changed with the evolution of carbon dioxide into a mobile liquid (5.7 g). Distillation through a 6-in. Vigreux column afforded 5.2 g (86%) of N-acetyl-N-methylisobutyramide: bp 62–64° (3 mm); $n^{20}D$ 1.4515; infrared absorptions (smear), 5.8 to 6.0 μ; nmr spectrum (neat), doublet at 1.10, 6 H, and septet at 3.31, 1 H (isopropyl group), singlet at 2.31, 3 H (acetyl group), and singlet at 3.20 ppm, 3 H (methyl group attached to nitrogen).

Anal. Calcd for $C_7H_{13}NO_2$: C, 58.7; H, 9.1; N, 9.8. Found: C, 58.4; H, 9.1; N, 10.0.

Dihydro-2,3,5,5-tetramethyl-4H-1,3-oxazine-4,6(5H)-dione (**7**).—A solution of 33.8 g (0.2 mole) of **1** in 150 ml of toluene was

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[6] Infrared spectra were recorded on a Baird AB-2 instrument.

[7] Nmr spectra were recorded on a Varian A-60 instrument at 60 Mc. Field position values are referred to tetramethylsilane as an internal standard.

[8] Ultraviolet spectra were determined on a Cary instrument, Model 14 MS, Serial No. 11, operating from 200 to 400 mμ.

hydrogenated over 8 g of 5% palladium on carbon at 30° and 40 psi for 30 min in a stirred pressure bottle. The hydrogen absorbed was 0.20 mole. The catalyst was removed by filtration, and the filtrate was concentrated *in vacuo* to give a crystalline residue which was washed with hexane and dried to give 28.6 g (84%) of 7, mp 69–73°. A sample was recrystallized twice from toluene to give a material with mp 70–72°; infrared absorptions (KBr), 5.72 and 6.03 μ; nmr spectrum (CCl_4), singlet at 1.45, 6 H (*gem*-dimethyl group), doublet at 1.69, 3 H (methyl group), singlet at 3.01, 3 H (methyl attached to nitrogen), and quartet at 5.69 ppm, 1 H (methylidyne proton).

Anal. Calcd for $C_8H_{13}NO_3$: C, 56.1; H, 7.7; N, 8.2. Found: C, 56.4; H, 7.5; N, 8.3.

Reaction of 1 with Aniline.—A solution of 16.9 g (0.1 mole) of 1 and 9.3 g (0.1 mole) of aniline in 20 ml of toluene was refluxed for 20 hr. The solid that separated on cooling was removed by filtration and washed with cold hexane to give 1.7 g (12%) of crude 2,2-dimethyl-N,N′-diphenylmalonamide, mp 190–199°. One recrystallization from ethyl alcohol gave a product melting at 203–204° (lit.[9] mp 202.5–203°). The infrared spectrum of this material was identical with that of a sample of 2,2-dimethyl-N,N′-diphenylmalonamide prepared from dimethylmalonyl chloride and aniline.

Reaction of 1 with Methylamine.—Methylamine was passed into a stirred solution of 19.6 g (0.116 mole) of 1 in 50 ml of toluene until the reaction ceased to be exothermic. The solvent was removed *in vacuo* to give 25 g of residue, which was then washed with cold toluene and hexane to give 16.4 g (90%) of crude N,N′,2,2-tetramethylmalonamide, mp 69–114°. Recrystallization from ethyl alcohol gave a product melting at 122–126° (lit.[10] mp 123°). The infrared spectrum of this material was identical with that of a sample of N,N′,2,2-tetramethylmalonamide prepared from methylamine and dimethylmalonyl chloride.

Reaction of 1 with Methanol Using Acid Catalyst.—*p*-Toluenesulfonic acid (0.02 g) was added to a chilled solution of 10 g (0.059 mole) of 1 in 15 ml of methanol. The reaction was exothermic and the temperature rose to 50°. After 15 min the excess methanol was removed *in vacuo* to give 11.5 g (97%) of crude methyl N-acetyl-N,2,2-trimethylmalonamate (6b), mp 57–62°. Recrystallization from toluene afforded 8.7 g of 6b: mp 69–72°; infrared absorptions (KBr), 5.70 and 6.05 μ; nmr spectrum (CH_2Cl_2), singlet at 1.46 6 H (*gem*-dimethyl group), singlet at 1.81, 3 H (acetyl group), singlet at 2.92, 3 H (methyl attached to nitrogen), and singlet at 3.28 ppm, 3 H (methoxy group).

Anal. Calcd for $C_9H_{15}NO_4$: C, 53.7; H, 7.5; N, 7.0. Found: C, 53.3; H, 7.5; N, 7.0.

N,2,2,4,4-Pentamethyl-3-oxoglutarimide (8) by Method A.—Dihydro-2-isopropylidene-3,5,5-trimethyl-4H-1,3-oxazine-4,6-(5H)-dione (2c, 33.0 g) was added over a period of 6 hr to a 1 × 10 in. Vycor tube packed with Vycor chips and kept at 590–610°. The pyrolysate (31.0 g) was distilled rapidly through a 6-in. Vigreux column to give 28.0 g of crude 8, bp 82–90° (1 mm). Recrystallization from toluene gave 22.3 g (68%) of 8: mp 75.5–76.5°; infrared spectrum (KBr), 5.90 and 6.0 μ; nmr spectrum (CCl_4), singlet at 1.41, 12 H (*gem*-dimethyl groups), and singlet at 3.19 ppm, 3 H, (methyl attached to nitrogen); ultraviolet spectrum (cyclohexane), 210 mμ (log ε 4.09), 259 (2.20), 269 (2.18), 300 (1.28), and 311 (1.18).

Anal. Calcd for $C_{10}H_{15}NO_3$: C, 60.9; H, 7.7; N, 7.1. Found: C, 61.0; H, 7.4; N, 7.2.

Preparation of 8 by Method B.—A mixture of 25 g of 2c, 2 g of sodium methoxide, and 40 ml of toluene was refluxed for 30 min. The mixture, after cooling, was filtered and concentrated *in vacuo* to give 25 g of solid residue, mp 72–76°. This material was distilled through a 6-in. Vigreux column to afford 23 g (92%) of 8, bp 87–90° (2 mm), mp 72–77°. The infrared spectrum of this material was identical with that of 8 prepared by method A.

3-Hydroxy-N,2,4,4-tetramethylglutaconimide (10a).—2-Ethylidenedihydro-3,5,5-trimethyl-4H-1,3-oxazine-4,6(5H)-dione (32.0 g) was treated according to method A at 635–660°. The collected pyrolysate was distilled rapidly through a 6-in. Vigreux column at 72–106° (0.1 mm). The distillate solidified and was recrystallized from toluene to give 15.1 g (47%) of 10a: mp 137–138°; infrared absorptions (KBr), 5.95, 6.05, and 6.85 μ; nmr spectrum (CH_2Cl_2), singlet at 1.51, 6 H (*gem*-dimethyl group), singlet at 1.90, 3 H (methyl group attached to olefinic linkage), singlet at 3.19, 3 H (methyl group attached to nitrogen), and broad singlet at 8.01 ppm, 1 H (enolic-OH proton); ultraviolet spectrum (CH_2Cl_2), 259 mμ (log ε 3.55).

Anal. Calcd for $C_9H_{13}NO_3$: C, 59.0; H, 7.2; N, 7.7. Found: C, 58.9; H, 7.0; N, 7.7.

3-Hydroxy-N,4,4-trimethyl-2-phenylglutaconimide (10b).—Under conditions similar to those used for preparing 10a, a solution of 60 g of 2-benzylidenedihydro-3,5,5-trimethyl-4H-1,3-oxazine-4,6(5H)-dione in 180 ml of benzene afforded 40.0 g (67%) of 10b, which melted at 145–147° after recrystallization from ethyl alcohol: infrared absorptions (KBr), 5.90, 6.05, and 6.15 μ; nmr (CH_2Cl_2), singlet at 1.44, 6 H (*gem*-dimethyl group), singlet at 3.01, 3 H (methyl group attached to nitrogen), and multiplet at 7.25 ppm, 6 H (aromatic protons and enolic-OH proton); ultraviolet spectrum (cyclohexane), 256 mμ (log ε 3.72) and 204 mμ (log ε 4.39).

Anal. Calcd for $C_{14}H_{15}NO_3$: C, 68.6; H, 6.2; N, 5.7. Found: C, 68.4; H, 6.4; N, 5.8.

N,2,2,4,4-Pentamethyl-3-oxo-1-thioglutarimide (12).—Dihydro-2-isopropylidene-3,5,5-trimethyl-4H-1,3-thiazine-4,6(5H)-dione (16, 9 g), when treated according to method B, gave 4.4 g (49%) of 12: bp 71–75° (0.7 mm); n^{20}_D 1.5425; infrared absorptions (smear), 5.79, 5.90, 6.80, 7.60, 9.08, and 9.30 μ; nmr spectrum (CCl_4), singlet at 1.38, 6 H (methyl groups at position 4), singlet at 1.51, 6 H (methyl groups at position 2), and singlet at 3.61 ppm, 3 H (methyl group attached to nitrogen); ultraviolet spectrum (cyclohexane), 232 mμ (log ε 3.29), 287 (4.24), and 439 (1.55).

Anal. Calcd for $C_{10}H_{15}NO_2S$: C, 56.3; H, 7.1; N, 6.6; S, 15.0. Found: C, 56.9; H, 7.6; N, 6.2; S, 15.0.

5,5-Dimethyl-2-phenyl-4H-1,3-oxazine-4,6(5H)-dione (14a).—A solution of 24.2 g (0.2 mole) of benzamide and 37.2 g (0.22 mole) of dimethylmalonyl chloride in 125 ml of ethylene dichloride was refluxed for 13 hr. The solvent was removed *in vacuo* to give 54 g of crude product, which was recrystallized from carbon tetrachloride to give 27 g (62%) of 14a: mp 132–135°; infrared absorptions (KBr), 5.60, 5.82, and 6.23 μ; nmr spectrum (CH_2Cl_2), singlet at 1.53, 6 H (*gem*-dimethyl group), and multiplets at 7.55, 3 H, and 8.22 ppm 2 H (aromatic protons); ultraviolet spectrum (C_2H_5OH), 205 mμ (log ε 4.00) and 234 mμ (log ε 3.96).

Anal. Calcd for $C_{12}H_{11}NO_3$: C, 66.4; H, 5.1; N, 6.5. Found: C, 66.2; H, 5.2; N, 6.3.

5,5-Dimethyl-2-phenyl-4H-1,3-thiazine-4,6(5H)-dione (14c).—A solution of 27.4 g (0.2 mole) of thiobenzamide and 37.2 g (0.22 mole) of dimethylmalonyl chloride in 125 ml of ethylene dichloride was refluxed for 3 hr. Removal of the solvent *in vacuo* afforded 52 g of crude product. Recrystallization of this material from carbon tetrachloride gave 41 g (88%) of 14c: mp 56–58°; infrared absorptions (KBr), 5.79, 5.90, 6.26, and 6.35 μ; nmr spectrum (CCl_4), singlet at 1.48, 6 H (*gem*-dimethyl group), and multiplets at 7.60, 3 H, and 8.05 ppm, 2 H (aromatic protons).

Anal. Calcd for $C_{12}H_{11}NO_2S$: C, 61.8; H, 4.8; N, 6.0. Found: C, 61.8; H, 4.4; N, 5.6.

N-Benzyl-2,2-dimethylmalonamic Acid (15).—A solution of 5 g (0.023 mole) of 14a in 200 ml of toluene was hydrogenated in a magnetically stirred pressure bottle at 40 psi and 25° over 2 g of 5% palladium on carbon. The catalyst was removed by filtration and washed with 75 ml of acetone. All filtrates and extracts were combined and evaporated *in vacuo* to give 3.1 g (60%) of crude 15. Recrystallization of the crude 15 from toluene gave a material with mp 112–114°; infrared absorptions (KBr), 3.00, 3.6–4.4, 5.83, 6.23, and 6.50 μ; nmr spectrum ($C_2H_2Cl_4$), singlet at 1.49, 6 H (methyl groups), doublet at 4.46, 2 H (methylene group), broad peak at 7.00, 1 H (-NH-), singlet at 7.29, 5 H (aromatic protons), and singlet at 11.23 ppm, 1 H (-COOH).

Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.1; H, 6.8; N, 6.3. Found: C, 65.4; H, 6.9; N, 7.0.

Methyl N-Benzoyl-2,2-dimethylmalonamate (16).—A mixture of 2.17 g (0.01 mole) of 19a, 0.1 g of sodium methoxide, and 15 ml of methanol heated spontaneously, and the solid went into solution. After the mixture had been allowed to stand for 12 hr at room temperature, the solvent was removed *in vacuo*. The viscous residue was treated with 6 ml of water to effect crystallization. Filtration gave 1.2 g (48%) of 16. A sample recrystallized from carbon tetrachloride had mp 69–71°; infrared absorptions (KBr), 3.0, 5.75, 5.90 and 6.0 μ; nmr spectrum ($CHCl_3$), singlet at 1.56, 6 H (*gem*-dimethyl group), singlet at 3.81, 3 H (methoxy group), multiplets at 7.53, 3 H, and 7.95,

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[9] M. Freund and K. Fleischer, *Ann. Chem.*, **399**, 182 (1913).

[10] A. P. N. Franchimont, *Rec. Trav. Chim.*, **4**, 206 (1885).

2 H (aromatic protons), and broad singlet at 10.15 ppm, 1 H (-NH-).

Anal. Calcd for $C_{13}H_{15}NO_4$: C, 62.6; H, 6.1; N, 5.6. Found: C, 62.8; H, 6.2; N, 5.3.

Dihydro-2-isopropylidene-5,5-dimethyl-4H-1,3-oxazine-4,6-(5H)-dione (17).—A solution of 17.4 g (0.2 mole) of isobutyramide and 37.2 g (0.22 mole) of dimethylmalonyl chloride in 125 ml of ethylene dichloride was refluxed for 3.5 hr. The solvent was removed *in vacuo*, and the residue was recrystallized from toluene to give 23.5 g of impure **17**, mp 128–153°. By repeated recrystallizations from methanol, pure **17**, mp 153–158°, was obtained: infrared absorptions (KBr), 2.96, 5.63, 5.70, 5.88, and 6.0 μ; nmr spectrum ($CHCl_3$), singlet at 1.43, 6 H (*gem*-dimethyl group), singlet at 1.76, 6 H (isopropylidene group), and broad peak at 10.12 ppm, 1 H (-NH-).

Anal. Calcd for $C_9H_{13}NO_3$: C, 59.0; H, 7.2; N, 7.7. Found: C, 59.0; H, 7.3; N, 7.5.

Dihydro-3-isobutyryl-2-isopropylidene-5,5-dimethyl-4H-1,3-oxazine-4,6(5H)-dione (18).—To a stirred solution of 43.5 g (0.5 mole) of isobutyramide and 151 g (1.5 mole) of triethylamine in 500 ml of toluene was added slowly 84.5 g (0.5 mole) of dimethylmalonyl chloride. The temperature was kept at 60° during the addition; later, the mixture was stirred at room temperature for 5 hr. The triethylamine hydrochloride was removed by filtration, and the filtrate was distilled through a 6-in. Vigreux column to give a fraction containing solvent and low-boiling materials. This fraction contained a considerable amount of isobutyronitrile, which was isolated by vapor phase chromatography and identified by its infrared spectrum. The high-boiling material gave 27.5 g (43%) of **18**, bp 110–114° (0.07 mm), which crystallized on cooling. A sample recrystallized from toluene had mp 92–93°; infrared absorptions (KBr), 5.62, 5.80, and 5.90 μ; nmr spectrum (CH_2Cl_2), doublet at 1.14, 6 H, and septet at 3.43, 1 H (isopropyl group), singlet at 1.45, 6 H (*gem*-dimethyl group), and singlets at 1.49, 3 H, and 1.84 ppm, 3 H (methyl groups on olefinic linkage).

Anal. Calcd for $C_{13}H_{19}NO_4$: C, 61.6; H, 7.6; N, 5.5. Found: C, 62.3; H, 7.7; N, 5.5.

Reaction of Isobutyryl Chloride with 17.—To a stirred solution of 1.83 g (0.01 mole) of **22** in 5 ml of toluene and 5 ml of pyridine was added 1.2 g (0.01 mole) of isobutyryl chloride. After stirring for 6 hr at room temperature, the reaction mixture was filtered. The filtrate was concentrated *in vacuo* to give 2.9 g of residue, which was washed with hexane to give 1.7 g (67%) of **18**, mp 85–88°. A mixture melting point with **18** prepared by the method explained in the previous section was 85–89°, and the infrared spectra of the two materials were identical.

Dihydro-3-isobutyryl-5,5-dimethyl-2-methylene-4H-1,3-oxazine-4,6(5H)-dione (19).—To a stirred solution of 59 g (1.0 mole) of acetamide and 303 g (3.0 moles) of triethylamine in 1 l. of toluene was added slowly 169 g (1.0 mole) of dimethylmalonyl chloride. The temperature was kept at 60–70° during the addition; then the mixture was stirred at room temperature for 12 hr. The triethylamine hydrochloride (263 g, 96%) was removed by filtration, and the filtrate was distilled through a 6-in. Vigreux column to give 59 g (52%) of **19**: bp 83–87° (0.07 mm); $n^{20}{}_D$ 1.4850; infrared absorptions (KBr), 5.60, 5.80, and 6.05 μ; nmr spectrum (CCl_4), doublet at 1.18, 6 H, and septet at 3.49, 1 H (isopropyl group), singlet at 1.48, 6 H (*gem*-dimethyl group), and pair of doublets at 4.79 ppm, 2 H (terminal methylene group).

Anal. Calcd for $C_{11}H_{15}NO_4$: C, 58.7; H, 6.7; N, 6.2. Found: C, 58.8; H, 7.1; N, 6.2.

Ethyl Hexahydro-5,5-dimethyl-2,4,6-trioxo-1-pyrimidinecarboxylate (21).—A solution of 17.8 g (0.2 mole) of ethyl carbamate and 37.2 g (0.22 mole) of dimethylmalonyl chloride in 100 ml of tetrachloroethane was refluxed for 3 hr. The solution was concentrated *in vacuo* to give 10.6 g (46%) of **21**. A sample recrystallized from butyl acetate had mp 156–158°; infrared absorptions (KBr), 2.96, 5.68, 5.75, and 5.88 μ; nmr spectrum ($C_2H_2Cl_4$), triplet at 1.41, 3 H, and quartet at 4.46, 2 H (ethoxy group), singlet at 1.59, 6 H (*gem*-dimethyl group), and broad singlet at 8.75 ppm, 1 H (-NH-).

Anal. Calcd for $C_9H_{12}N_2O_5$: C, 47.4; H, 5.3; N, 12.3. Found: C, 47.4; H, 5.2; N, 12.4.

5,5-Dimethyl-2-phenyl-4,6(1H,5H)-pyrimidinedione (22).—A solution of 7.8 g (0.05 mole) of benzamidine hydrochloride in 20 ml of 20% aqueous sodium hydroxide and 60 g of ice was stirred for 2 min in a Waring Blendor. Then a solution of 8.5 g (0.05 mole) of dimethylmalonyl chloride in 80 ml of chloroform was added, and the mixture was stirred vigorously for 10 min. The organic layer was separated, and 5.3 g (49%) of **22** crystallized out of the solution. A sample recrystallized from chloroform had mp 162–163°; infrared absorptions (KBr), 3.0, 5.80, and 6.01 μ; nmr spectrum (CH_2Cl_2), singlet at 1.49, 6 H (methyl groups), multiplets at 7.55, 3 H, and 8.14, 2 H (aromatic protons), and broad peak at 10.30 ppm, 1 H (-NH-); ultraviolet spectrum (C_2H_5OH), 203 mμ ($\log \epsilon$ 4.02) and 257 mμ ($\log \epsilon$ 4.14).

Anal. Calcd for $C_{12}H_{12}N_2O_2$: C, 66.7; H, 5.6; N, 13.0. Found: C, 66.8; H, 6.3; N, 13.0.

5-Ethyl-1-isopropyl-3,3-dimethyl-2,4(1H,3H)-pyrindinedione (23a).—To a stirred solution of 62 g (0.55 mole) of butylideneisopropylamine and 168 g (1.65 moles) of triethylamine in 600 ml of toluene was added rapidly 93 g (0.55 mole) of dimethylmalonyl chloride. The resulting mixture was refluxed for 5 hr and cooled. After triethylamine hydrochloride was removed by filtration, the filtrate was distilled through a 6-in. Vigreux column to give 105.0 g (91%) of **23a**, bp 99–100° (0.6 mm), which solidified on cooling. A sample recrystallized from carbon tetrachloride had mp 59–61°; infrared absorptions (KBr), 5.98 and 6.12 μ; nmr spectrum (CCl_4), triplet at 1.04, 3 H, and quartet at 2.21, 2 H (ethyl group), doublet at 1.28, 6 H, and septet at 4.82, 1 H (isopropyl group), singlet at 1.31, 6 H (*gem*-dimethyl groups) and singlet at 7.18 ppm, 1 H (olefinic proton); ultraviolet spectrum (cyclohexane), 311 mμ ($\log \epsilon$ 3.97).

Anal. Calcd for $C_{12}H_{19}NO_2$: C, 68.9; H, 9.2; N, 6.7. Found: C, 68.6; H, 8.9; N, 6.8.