THE JOURNAL OF Organic Chemistry®

Volume 36, Number 16

August 13, 1971

Ketenes. XIII. Reactions of Ketenes with Heterocumulenes[1a]

James C. Martin,* Robert D. Burpitt, P. Glenn Gott, Melvin Harris,[1b] and Ronald H. Meen

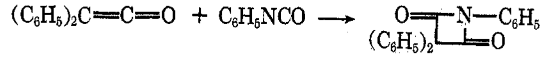
Research Laboratories, Tennessee Eastman Company, Division of Eastman Kodak Company, Kingsport, Tennessee 37662

Received June 11, 1970

Ketenes underwent cycloaddition reactions with several different heterocumulenes. Dialkylketenes and isocyanates gave malonimides, and diisocyanates gave bis(malonimides). Acyl isocyanates and ketenes generally underwent a 4 + 2 cycloaddition to give oxazinediones. Carbodiimides and ketenes gave azetidinones *via* a 2 + 2 cycloaddition. Carbon dioxide and carbon disulfide, when catalyzed by triphenylphosphine, gave 2 + 2 + 2 cycloaddition products containing 2 equiv of dialkylketenes. A ketenimine and a dialkylketene gave as the major component a 2 + 2 + 2 cycloaddition product involving two ketenimine molecules and one dialkylketene molecule.

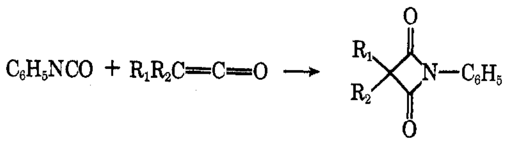
Ketenes belong to a class of compounds known as heterocumulenes.[2] The reactions of ketenes with themselves to form dimers or trimers are well documented. In this paper we report our work on reactions of ketenes with other heterocumulenes.

Isocyanates.—Staudinger reported that diphenylketene reacted with phenyl isocyanate at 220° *via* a 1:1 cycloaddition to give the malonimide **1** in low yield.[3] Similar reactions of diphenylketene with methyl and cyclohexyl isocyanates have been reported.[4] The adduct of pentamethyleneketene, generated *in situ* from the acid chloride, with phenyl isocyanate also has been reported.[5]



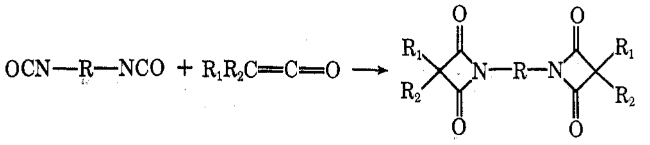
1

The reaction of monomeric dialkylketenes with isocyanates to give malonimides has not been reported. We found that, when butylethylketene was heated with phenyl isocyanate, 2-butyl-2-ethyl-*N*-phenylmalonimide (**2b**) was formed in 70% yield. Dimethylketene, in spite of its reactive nature, gave low yields of malonimides because the ketene dimerized rapidly. At 25°, dimethylketene and phenyl isocyanate afforded 2,2-dimethyl-*N*-phenylmalonimide (**2a**) in 10% yield; at 60°, the yield of **2a** was 30%.



2a, $R_1 = R_2 = CH_3$
b, $R_1 = C_2H_5$; $R_2 = C_4H_9$

The only bis(malonimide) described in the literature was prepared by a ring-closure method.[4] We readily prepared several of these bifunctional compounds by heating diethylketene or butylethylketene with diisocyanates at 180°. The aromatic diisocyanates gave much better yields than the aliphatic analogs; with diethylketene, *p*-phenylene diisocyanate gave the bis(malonimide) **3a** in 92% yield, but hexamethylene diisocyanate gave the bis(malonimide) **3b** in 30% yield. The malonimides prepared in this work are listed in Table I.



3a, $R_1 = p\text{-}C_6H_4$; $R_1 = R_2 = C_2H_5$
b, $R = (CH_2)_6$; $R_1 = R_2 = C_2H_5$

Mundlos and Graf[6] observed that *p*-toluenesulfonyl isocyanate reacted with ketene at −10° in methylene chloride solution to give *N*-(*p*-tolylsulfonyl)malonimide (**4a**) (yield of crude **4a**, 42%; purified, 12.5%) plus a large amount of polymeric material. We observed that, if the reaction was run in a dipolar aprotic solvent (such as acetonitrile) at 30–40°, the yield of crude **4a**

---

[1] (a) Paper XII in this series: J. C. Martin, P. G. Gott, and H. U. Hostettler, *J. Org. Chem.*, **32**, 1654 (1967). (b) Ciba A.-G., 4000 Basel 7, Switzerland.

[2] H. Ulrich, "Cycloaddition Reactions of Heterocumulenes," Academic Press, New York, N. Y., 1967.

[3] H. Staudinger and R. Endle, *Justus Liebigs Ann. Chem.*, **401**, 263 (1913).

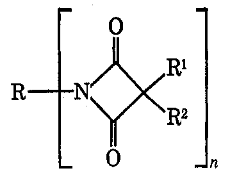
[4] A. Ebnöther, E. Jucker, E. Rissi, J. Rutschmann, E. Schreier, R. Steiner, R. Süss, and A. Vogel, *Helv. Chim. Acta*, **42**, 918 (1959).

[5] A. C. Poshkus and J. E. Herweh, *J. Org. Chem.*, **30**, 2466 (1965).

[6] E. Mundlos and R. Graf, *Justus Liebigs Ann. Chem.*, **677**, 108 (1964).

TABLE I

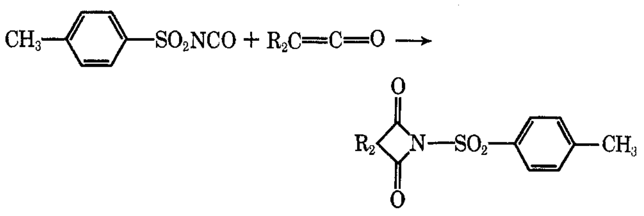
MALONIMIDES FROM KETENES AND ISOCYANATES[a]



R	R^1	R^2	Yield, %	Mp or bp (mm), °C	Registry no.
		Monomalonimides (n = 1)			
C_6H_5	CH_3	CH_3	30	36 71-74 (0.01)[b]	
C_6H_5	C_2H_5	C_4H_9	70	86-88 100-105 (0.05)[b]	29682-92-6
		Bis(malonimides) (n = 2)			
p-($CH_2C_6H_4CH_2$)	C_2H_5	C_2H_5	75	130	29682-93-7
p-($CH_2C_6H_4CH_2$)	C_2H_5	C_4H_9	50	110	29682-94-8
p-C_6H_4	C_2H_5	C_4H_9	78	75	29682-95-9
p-C_6H_4	C_2H_5	C_2H_5	92	130	
-$(CH_2)_6$-	C_2H_5	C_2H_5	20	81-82	29682-96-0
-$(CH_2)_6$-	C_2H_5	C_4H_9	10	68	29682-97-1
2,4-Tolyl	C_2H_5	C_2H_5	85	89-91	29682-98-2
2,4-Tolyl	C_2H_5	C_4H_9	80	210-220[b]	29682-99-3
2,4-Tolyl	C_6H_5	C_6H_5	30	178-179	29683-00-9
p-($C_6H_4CH_2C_6H_4$)	C_2H_5	C_2H_5	80	104-105	29683-01-0
p-($C_6H_4CH_2C_6H_4$)	C_2H_5	C_4H_9	65	42	29683-02-1

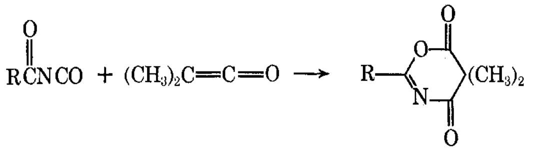
[a] Satisfactory analytical data (±0.3% for C, H, and N) were reported for all compounds: Ed. [b] Boiling point.

was quantitative; the yield of purified **4a** was 54%. Dimethylketene in this reaction gave 2,2-dimethyl-*N*-(*p*-tolylsulfonyl)malonimide (**4b**) in 94% yield.



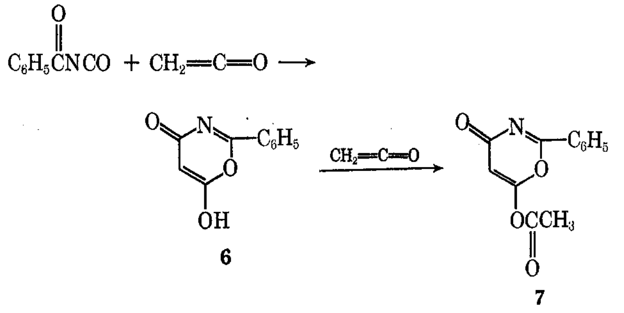
4a, R = H
b, R = CH_3

Acyl isocyanates and dimethylketene did not react to give the expected cycloaddition to a malonimide, but a product involving a 1,4 cycloaddition to the acyl isocyanate. Dimethylketene reacted with trichloroacetyl isocyanate to give 5,5-dimethyl-2-trichloromethyl-4*H*-1,3-oxazine-4,6(5*H*)-dione (**5a**) in 77% yield, and with benzoyl isocyanate to give 5,5-dimethyl-2-phenyl-4*H*-1,3-oxazine-4,6(5*H*)-dione (**5b**) in 25% yield. **5b** was identical with the reaction product from benzamide and dimethylmalonyl chloride reported previously.[7]

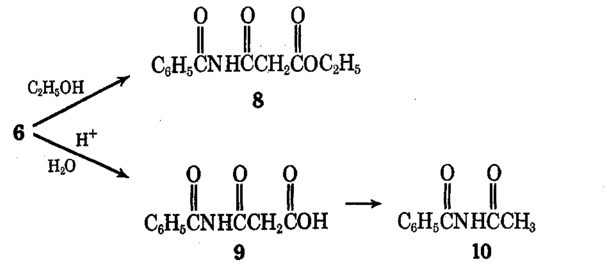


5a, R = CCl_3
b, R = C_6H_5

Ketene reacted with benzoyl isocyanate to give the adduct **6**, presumably formed *via* a 4 + 2 cycloaddition followed by enolization. In cold ether, **6** was formed in 62% yield, but in benzene at 30-40° the acetylated product **7** (51%) was obtained. When preformed **6** was treated with ketene in benzene, **7** was formed.



Ethanolysis of **6** gave **8** in 90% yield. The acidic hydrolysis of **6** gave **9** in 87% yield. **9** decarboxylated on warming to give **10** in 77% yield.



Carbodiimides.—During the course of our work, Hull[8] and Brady, *et al.*,[9] reported the reactions of several ketenes with carbodiimides. We found that diphenylketene in acetonitrile reacted readily with dicyclohexylcarbodiimide to give the 1:1 adduct, 1-cyclohexyl-4-(cy-

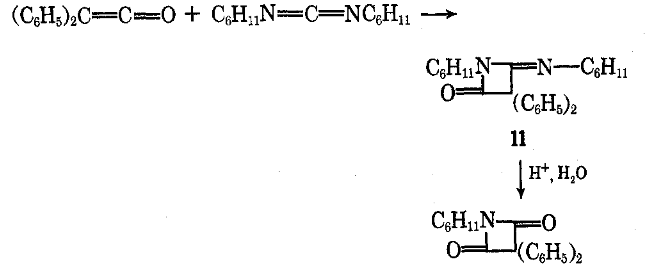
---

(7) J. C. Martin, K. C. Brannock, and R. H. Meen, *J. Org. Chem.*, **31**, 2966 (1966).

(8) R. Hull, *J. Chem. Soc.*, 1154 (1967).

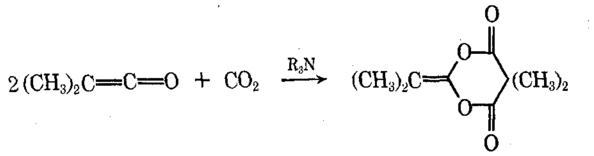
(9) W. T. Brady, E. D. Dorsey, and F. H. Parry, III, *J. Org. Chem.*, **34**, 2846 (1969).

clohexylimino)-3,3-diphenyl-2-azetidinone (**11**). The structure of **11** was established by spectral means and by hydrolysis to the malonimide **12**. No 2:1 was obtained, even when excess diphenylketene in polar solvents was used.



12

Carbon Dioxide.—Carbon dioxide does not react with ketenes in the absence of a catalyst; however, Staudinger, *et al.*,[10] found that, with trimethylamine as catalyst, dimethylketene and carbon dioxide reacted to give a mixture of several products. One of these products was a compound (mp 78°) which Staudinger identified as 2,2,4,4-tetramethyl-3-oxoglutaric anhydride. Bestian and Günther later made the same compound by a different route and correctly identified it as cyclic 2-isopropylidene-5,5-dimethyl-*m*-dioxane-4,6-dione (**13**).[11]

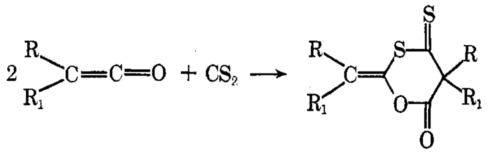


13

Our work showed that triphenylphosphine as catalyst gave **13** directly from dimethylketene and carbon dioxide in yields (68%) substantially better than those obtained with trimethylamine as catalyst. When dimethylketene and carbon dioxide were mixed in ether containing tributylphosphine, a rapid reaction gave a copious amount of a white solid. This product was unstable, and, on attempted work-up, it decomposed with evolution of dimethylketene. Triethyl phosphite as catalyst in the dimethylketene–carbon dioxide reaction gave only the lactone dimer of dimethylketene.[12]

Carbon Disulfide.—Carbon disulfide is like carbon dioxide in that it does not react with ketenes alone. Staudinger, *et al.*,[13] observed a reaction between dimethylketene and carbon disulfide when trimethylamine was added as catalyst; the polymeric product contained dimethylketene and carbon disulfide combined in a molar ratio of 5:2.

With triphenylphosphine as catalyst, dimethylketene and carbon disulfide gave a 2:1 adduct, 2-isopropylidene-5,5-dimethyl-4-thio-1,3-oxathiane-4,6-dione (**14a**) in 70% yield. The structure of **14a** was established by its uv, ir, and nmr spectra, by its reactions and derivatives, and by analogy with the dimethylketene–CO_2 reaction.



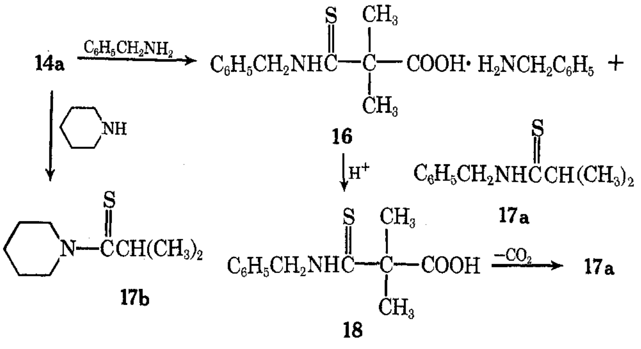
14a, $R = R_1 = CH_3$
b, $R = C_2H_5$; $R_1 = C_4H_9$

With triethyl phosphite as catalyst, **14a** was obtained in 54% yield. Other potential catalysts were tested: resinous products were obtained with sodium methoxide or tributylphosphine, and no reaction occurred with *p*-toluenesulfonic acid, boron trifluoride, or *N*,*N*-dimethylaniline.

The reaction of butylethylketene with carbon disulfide was catalyzed by tributylphosphine, but not by triphenylphosphine. The dark red product had an infrared spectrum similar to that of **14a**, and presumably had the homologous structure **14b**. It decomposed on attempted molecular distillation.

The adduct **14a** decomposed vigorously with liberation of carbon dioxide at temperatures above 120°. If the decomposition was done neat, only a dark, resinous material resulted, but, when **14a** was decomposed in refluxing toluene, 5-isopropyl-3-methyl-2-thiophenethiol (**15**) was obtained in 40% yield. No dimethylthioketene was found. The possible mechanism shown in Scheme I is suggested for the formation of **15**.

14a reacted readily with amines to give eventually 2 mol of the corresponding thioisobutyramide and carbon dioxide. The reaction proceeded stepwise to give first 1 mol of thioisobutyramide and 1 mol of the thiomalonamic acid. Subsequent decarboxylation of the thiomalonamic acid afforded the second mole of thioisobutyramide. This stepwise reaction was illustrated by the treatment of **14a** with benzylamine to give 83% of *N*-benzyl-2,2-dimethyl-3-thiomalonamic acid (**18**) and 54% of *N*-(benzylthio)isobutyramide (**17a**). Piperidine reacted with **14a** to give 1-thioisobutyrylpiperidine (**17b**).



When **14a** and other selected reagents were combined, the products either decomposed on attempted distillation or the reaction mixtures were intractable. Reagents that reacted with **14a**, but behaved as described, were *N*,*N*-dimethylisobutenylamine, 4,4′-vinylidenedimorpholine, sodium methoxide in methanol, tetramethyllallene, dimethyl acetylenedicarboxylate, hexachlorocyclopentadiene, and isobutyl alcohol.

---

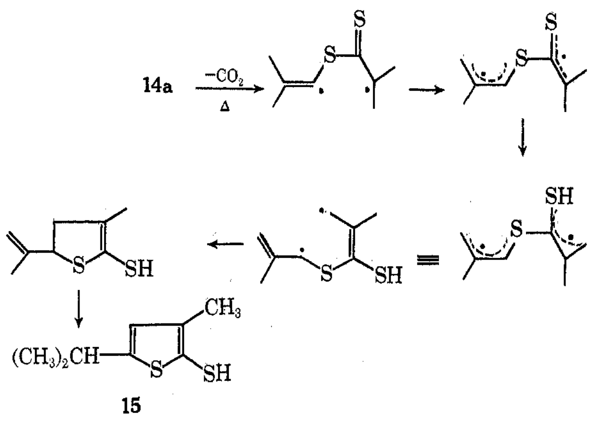
[10] H. Staudinger, F. Felix, and H. Harder, *Helv. Chim. Acta*, **8**, 306 (1925).

[11] H. Bestian and D. Günther, *Angew. Chem., Int. Ed. Engl.*, **2**, 612 (1963).

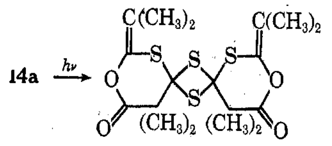
[12] E. U. Elam, *J. Org. Chem.*, **32**, 215 (1967), reported the same reaction in the absence of carbon dioxide.

[13] H. Staudinger, F. Felix, and E. Geiger, *Helv. Chim. Acta*, **8**, 314 (1925).

SCHEME I



When **14a** was exposed to sunlight or ultraviolet light, it dimerized to the tricyclic derivative **19**.



19

Carbonyl sulfide and dimethylketene reacted in the presence of triphenylphosphine to give a high yield of a material presumed to be the 2:1 adduct analogous to **13** and **14a**. The product was unstable and could not be purified satisfactorily. The crude material reacted with piperidine to give approximately equal amounts of 1-isobutyrylpiperidine and 1-thioisobutyrylpiperidine (**17b**).

Ketenimines.—The reactions of ketenimines and ketenes have not been previously reported. When dimethylketene and *N*-(2-ethylbutenylidene)methylamine were combined in acetonitrile, two products were formed: 4-(1-ethylpropylidene)dihydro-2,6-diisopropylidene-5-methyl-4*H*-1,3,5-dioxazine (**20**) in 32% yield and tetrahydro-2,4-diisopropylidene-3,5,5-trimethyl-6*H*-1,3-oxazin-6-one (**21**) in 14% yield. The formation of **20** was unusual because it represented the first time that dimethylketene formed a 2:1 adduct in which *both* ketene molecules were incorporated through the carbonyl group. In the usual 2:1 adduct with C=N compounds, one molecule of dimethylketene is combined through the olefinic group, and the other through the carbonyl group.[14] Besides the usual spectral evidence, the quantitative hydrolysis under mild conditions confirmed the structure of **20**; stirring with water for several hours at room temperature produced a mixture of **22** and **23**. Complete hydrolysis of **21** to **24** required refluxing in water for several hours. (See Scheme II.)

Experimental Section

Materials.—Ketene was generated by pyrolysis of diketene,[15] and dimethylketene by pyrolysis of isobutyric anhydride or tetramethyl-1,3-cyclobutanedione. Diethylketene was prepared from diethylmalonic acid by the technique of Bestian and Günter,[11] but without isolation of an intermediate cyclic acylal. Diphenylketene was prepared from diphenylacetyl chloride.

p-Toluenesulfonyl isocyanate was obtained from the Upjohn Co. Trichloroacetyl and benzoyl isocyanates were prepared according to the methods of Speziale and Smith.[16]

Malonimides. A. General Procedure.—**2b** was prepared by heating butylethylketene with excess phenyl isocyanate (1:3 molar ratio) for 5 hr at 180° in a bomb tube. Bis(malonimides) were synthesized under the same conditions, but excess ketene was added to the diisocyanate (3:1 molar ratio). **2a** was prepared from dimethylketene and phenyl isocyanate at a much lower temperature. Properties of the malonimides are summarized in Table I. Infrared spectra of all malonimides showed strong, sharp absorptions at 5.71–5.75 μ.

B. **2,2-Dimethyl-*N*-phenylmalonimide (2a).**—Dimethylketene (28.1 g, 0.43 mol) was added in portions to a refluxing solution of 80 g (0.67 mol) of phenyl isocyanate in 250 ml of acetonitrile. Reflux was continued for 3 hr, and the resulting solution was then distilled through a 4-in. Vigreux column to give 24.4 g (30%) of **2a**: bp 70° (0.2 mm); nmr ($CDCl_3$) δ 1.40 (s, 6) and 7.40 (m, 5).

C. ***N*,*N*′-*p*-Phenylenebis(2,2-diethylmalonimide) (3a).**—A solution of 3.92 g (0.04 mol) of diethylketene and 2.13 g (0.013 mol) of *p*-phenylene diisocyanate in 18 ml of toluene was heated for 5 hr in a sealed glass tube at 180°. The reaction mixture was evaporated to dryness, taken up in an ether–petroleum ether mixture, filtered, and evaporated to give 2 g of crude brown product. Treatment with carbon and recrystallization from methanol gave colorless crystals of **3a** (0.6 g): mp 131–132°; ir (CCl_4) 5.72 μ.

In another run, a solution of 8 g (0.05 mol) of *p*-phenylene diisocyanate and 14.7 g (0.15 mol) of diethylketene in 100 ml of toluene was inadvertently heated for 16 hr in a sealed glass tube at 180°. The reaction mixture was evaporated to dryness, and the crystalline residue was washed with cyclohexane. The yield of crude **3a** was 16.3 g (91%). Recrystallization from ethanol gave a product melting sharply at 130°.

***N*-(*p*-Tolylsulfonyl)malonimide (4a).**—Ketene was passed into a solution of 50 g (0.254 mol) of *p*-toluenesulfonyl isocyanate in 150 ml of acetonitrile to a weight increase of 11 g. The reaction mixture was cooled intermittently in ice, and the reaction temperature ranged from 28 to 40°. After being stirred for 30 min, the mixture was filtered to give 46 g of crude **4a**. Evaporation of the filtrate gave an additional 15 g of crude product. The yield of combined products, mp 125–130°, was quantitative. Recrystallization from ethyl acetate yielded 33 g (54%) of **4a**: mp 144–147° dec (lit.[6] mp 125°); ir (Nujol) 5.65 μ; nmr (CH_3NO_2) δ 2.48 (s, 3), 3.80 (s, 2), and 7.70 (typical aromatic AA′, BB′ pattern, 4).

2,2-Dimethyl-*N*-(*p*-tolylsulfonyl)malonimide (4b).—Dimethylketene (14 g, 0.2 mol) was added to a stirred solution of 39.4 g (0.2 mol) of *p*-toluenesulfonyl isocyanate in 200 ml of benzene under an atmosphere of nitrogen. The reaction was exothermic, and the temperature was kept at 10–20° by cooling with ice. The mixture was stirred for 2 hr, and the solvent was then removed under reduced pressure. The residue immediately crystallized to give 50 g (94%) of crude **4b**. A sample was recrystallized from benzene–hexane: mp 108–110°; ir (KBr) 5.60 μ; nmr (CH_2Cl_2) δ 1.32 (s, 6), 2.46 (s, 3), and 7.70 (typical aromatic AA′, BB′ pattern, 4).

Anal. Calcd for $C_{12}H_{13}NO_4S$: C, 54.0; H, 4.9; N, 5.2. Found: C, 54.0; H, 5.1; N, 5.1.

5,5-Dimethyl-2-trichloromethyl-4*H*-1,3-oxazine-4,6(5*H*)-dione (5a).—Dimethylketene (2.1 g, 0.03 mol) was added to a stirred solution of 5.7 g (0.03 mol) of trichloroacetyl isocyanate in 30 ml of benzene. The exothermic reaction was kept at 25–40° by a cooling bath. The solid that formed was removed by filtration and dried to give 6.0 g (77%) of **5a**. A sample was recrystallized from benzene–hexane: mp 152–155°; ir (KBr) 5.50, 5.73, and 6.12 μ; nmr ($C_2H_2Cl_4$) 1.60 (s).

Anal. Calcd for $C_7H_6Cl_3NO_3$: C, 32.5; H, 2.3; N, 5.4. Found: C, 32.8; H, 2.4; N, 5.2.

5,5-Dimethyl-2-phenyl-4*H*-1,3-oxazine-4,6(5*H*)-dione (5b).—Dimethylketene (11.9 g, 0.17 mol) was added to a stirred solution of 14.7 g (0.1 mol) of benzoyl isocyanate in 150 ml of benzene. The temperature of the exothermic reaction was held at 25–39° by an ice bath. Distillation of the solvent through a short Vigreux column yielded some crude solid material along with unchanged benzoyl isocyanate. The solid was recrystallized from benzene–hexane mixture to give 5.5 g (25%) of **5b**: mp 133–135°

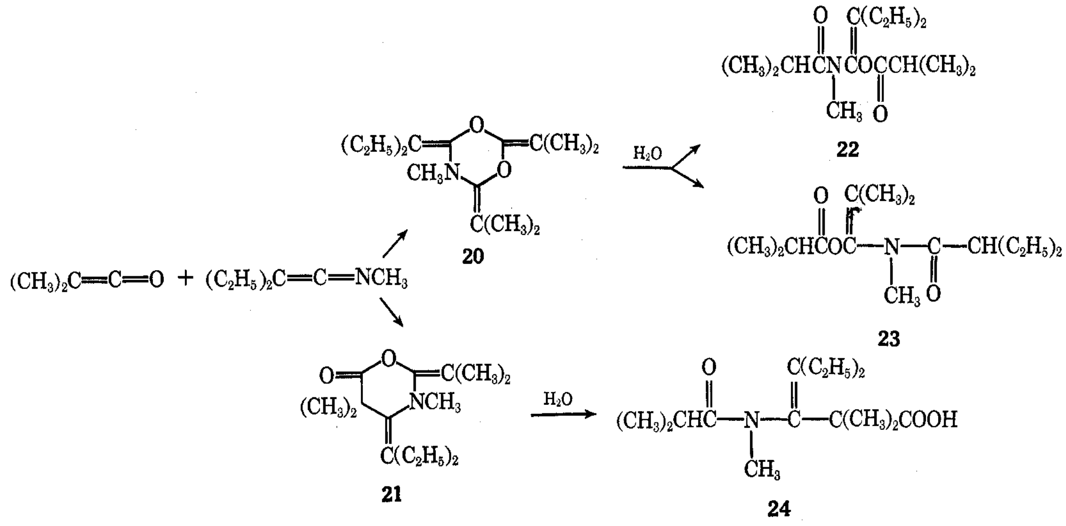
---

[14] J. C. Martin, V. A. Hoyle, Jr., and K. C. Brannock, *Tetrahedron Lett.*, 3589 (1965).

[15] S. Andreades and H. D. Carlson, *Org. Syn.*, **45**, 50 (1965).

[16] A. J. Speziale and L. R. Smith, *J. Org. Chem.*, **27**, 3742 (1962).

SCHEME II



(lit.[7] 132–135°). The infrared spectrum of **5b** was identical with that of **5b** prepared by the literature method.[7]

6-Methyl-3-benzoyl-2*H*-1,3-oxazine-2,4(3*H*)-dione (**7**).—Ketene was bubbled into a stirred solution of 14.7 g (0.1 mol) of benzoyl isocyanate in 50 ml of benzene, under a nitrogen atmosphere, until a weight increase of 5 g was obtained. The reaction temperature was controlled at 30–40° by an ice bath. The solid that precipitated was removed by filtration and recrystallized from hexane to give 7.0 g (51%) of **7**: mp 86–88.5°; ir (KBr) 5.68 and 5.71 μ; nmr (CH_2Cl_2) δ 2.50 (s, 3), 6.40 (s, 1), and two multiplets at 8.04 and 8.73 (5, aromatic protons).

Anal. Calcd for $C_{12}H_9NO_4$: C, 62.3; H, 3.9; N, 6.1. Found: C, 62.6; H, 4.0; N, 6.3.

Five grams of **7** was obtained as insoluble material from the hexane recrystallization.

6-Hydroxy-2-phenyl-4*H*-1,3-oxazin-4-one (**6**).—Ketene (5.7 g, 0.135 mol) was passed into a solution of 20 g (0.135 mol) of benzoyl isocyanate in 100 ml of ether at 5 to 10°. A white solid separated rapidly. The reaction mixture was stirred for 15 hr at room temperature and then filtered to give 15.8 g (62%) of **6**, mp 175–178° dec. A sample was recrystallized from tetrahydrofuran: mp 176–178° (dec); ir (Nujol) 3.60–4.5, 6.05, and 6 18 μ; nmr (CD_3SOCD_3) δ 3.78 (s, 1), 7.72 (m, 5), and 12.9 (s, 1).

Anal. Calcd for $C_{10}H_7NO_3$: C, 63.5; H, 3.7; N, 7.4. Found: C, 63.3; H, 4.3; N, 7.3.

Ethyl *N*-Benzoylmalonamate (**8**).—A solution of 5.0 g of **6** in 30 ml of ethyl alcohol was refluxed for 1 hr. The solvent was removed *in vacuo*, and the solid residue was recrystallized from a mixture of benzene and hexane to give 5.5 g (90%) of **8**: mp 114.5–115.5°; ir (KBr) 5.78, 5.86, and 5.95 μ; nmr (CH_2Cl_2) δ 1.32 (t, 3), 4.12 (s, 3), 4.45 (q, 2), 8.30 (m, 5), and 10.1 (s, 1).

Anal. Calcd for $C_{12}H_{13}NO_4$: C, 61.3; H, 5.6; N, 6.0. Found: C, 61.5; H, 5.8; N, 6.0.

***N*-Benzoylmalonamic Acid** (**9**).—A mixture of 3.0 g (0.016 mol) of **6** and 75 ml of 5% hydrochloric acid was stirred for 20 hr at room temperature. Filtration of the mixture gave 2.4 g (73%) of **9**. A sample was recrystallized from acetonitrile: mp 139–140° dec; ir (Nujol) 3.8–4.2, 5.86, 6.00, and 6.12 μ; nmr (deuteriopyridine) δ 3.95 (s, 2), 7.58 (m, 5), 11.6 (s, 1), and 13.0 (s, 1).

Anal. Calcd for $C_{10}H_9NO_4$: C, 58.0; H, 4.4; N, 6.8. Found: C, 58.3; H, 4.4; N, 6.7.

***N*-Acetylbenzamide** (**10**).—**9** (1 g, 0.0048 mol) was heated in a small test tube at 150° for 5 min. A gas evolved, and the oily residue crystallized on cooling. Recrystallization from benzene–cyclohexane gave 0.6 g (77%) of **10**: mp 114–115° (lit. 116–118°[17] and 117°[18]); ir (KBr) 3.03, 5.71, and 5.91 μ.

Anal. Calcd for $C_9H_9NO_2$: C, 66.3; H, 5.6; N, 8.6. Found: C, 66.3; H, 5.7; N, 8.7.

1-Cyclohexyl-4-(cyclohexylimino)-3,3-diphenyl-2-azetidinone (**11**).—A mixture of 42.5 g (0.22 mol) of diphenylketene, 44.5 g (0.216 mol) of dicyclohexylcarbodiimide, and 300 ml of acetonitrile was prepared. An exothermic reaction started and the temperature rose to 45°. The white solid that precipitated was removed by filtration after 3 hr. This solid was recrystallized from ethyl acetate to give 75.4 g (84%) of **11**: mp 160.5–162° (lit.[9] 158–159°); ir (KBr) 5.53 and 5.94 μ; nmr ($CDCl_3$) δ 1.55 (m, 20), 3.55 (m, 2), and 7.30 (s, 10).

Anal. Calcd for $C_{27}H_{32}N_2O$: C, 81.0; H, 8.1; N, 7.0. Found: C, 80.7; H, 8.1; N, 7.1.

***N*-Cyclohexyldiphenylmalonimide** (**12**) **by Hydrolysis of 11**.—A mixture of 30 g (0.075 mol) of **11** and 150 ml of 10% HCl was refluxed with stirring for 3 hr. The mixture was cooled, taken up in ether, washed with water, and dried ($MgSO_4$). Distillation through a 3-in. Vigreux column gave 18.2 g (76%) of **12**, bp 210–215° (1.5 mm). This material solidified on cooling and was recrystallized from methyl alcohol to give **11**: mp 81–82°; ir (KBr) 5.75 μ; nmr ($CDCl_3$) δ 1.56 (m, 10), 3.62 (m, 1), and 7.34 (m, 10).

Anal. Calcd for $C_{21}H_{21}NO_2$: C, 79.0; H, 6.6; N, 4.4. Found: C, 78.7; H, 6.4; N, 4.7.

2-Isopropylidene-5,5-dimethyl-*m*-dioxane-4,6-dione (**13**).—A solution of 2 g of triphenylphosphine in 275 ml of ether was chilled to −60° and saturated with CO_2. To this stirred solution was added 70 g (1.0 mol) of dimethylketene. A white solid precipitated rapidly, and a slow stream of carbon dioxide was passed through the solution while it warmed to room temperature. The solvent was removed *in vacuo* to give 92 g (100%) of crude product. Recrystallization from hexane gave 57 g (62%) of **13**, mp 75–77°. A sample was recrystallized from petroleum ether: mp 77–79° (lit. 78°[10] and 80°[11]); nmr ($CHCl_3$) δ 1.50 (s, 6) and 1.74 (s, 6).

Anal. Calcd for $C_9H_{12}O_4$: C, 58.6; H, 6.6. Found: C, 58.7; H, 6.6.

2-Isopropylidene-5,5-dimethyl-4-thio-1,3-oxathiane-4,6-dione (**14a**).—Dimethylketene (127.5 g, 1.85 mol) was added to a stirred solution of 2 g of triphenylphosphine in 500 g (6.6 mol) of carbon disulfide under a nitrogen atmosphere. The temperature of the exothermic reaction was kept at 25–37° by an ice bath. After 2 hr the reaction solution was transferred to a large evaporating dish, and the excess carbon disulfide was allowed to evaporate at room temperature. The resulting crystalline residue was recrystallized from hexane to give 138 g (70%) of **14a**: mp 75–78°; ir (KBr) 5.75 and 6.10 μ; nmr ($CHCl_3$) δ 1.62 (s, 6), 1.85 (s, 3), and 1.93 (s, 3); uv max (hexane) 244 mμ (ϵ 6630) and 344 (10,775).

Anal. Calcd for $C_9H_{12}O_2S_2$: C, 50.0; H, 5.6; S, 29.6. Found: C, 50.2; H, 5.5; S, 29.1.

5-Isopropyl-3-methyl-2-thiophenethiol (**15**) **by Thermolysis of 14a**.—A solution of 15.0 g (0.069 mol) of **14a** in toluene was refluxed for 4 hr. Carbon dioxide evolved during this period. The toluene was removed *in vacuo* and the residue was distilled to give crude **15**, bp 52–78° (0.2–0.5 mm). A glpc assay indicated that this fraction contained 4.8 g (40% yield) of **15**. A

---

[17] S. D. Work, D. R. Bryant, and C. R. Hauser, *J. Amer. Chem. Soc.*, **86**, 872 (1964).

[18] J. B. Polya and T. M. Spotswood, *Rec. Trav. Chim. Pays-Bas*, **67**, 927 (1948).

sample was purified by glpc; n^{20}_D 1.5588; nmr (CCl_4) δ 1.23 (d, 6), 3.27 (septet, 1), 1.90 (s, 3), 2.47 (s, 1), and 6.38 (s, 1).

Anal. Calcd for $C_8H_{12}S_2$: C, 55.8; H, 7.0; S, 37.2. Found: C, 56.3; H, 6.8; S, 37.1.

N-Benzylthioisobutyramide (17a) and N-Benzyl-2,2-dimethyl-3-thiomalonamic Acid (18) from Benzylamine and 14a.—A solution of 17.2 g (0.16 mol) of benzylamine in 25 ml of toluene was added with stirring and ice cooling to a solution of 10.8 g (0.05 mol) of **14a** in 150 ml of toluene. The addition was controlled so that the temperature of the exothermic reaction did not rise above 30°. Filtration gave 14.2 g (83%) of the benzylamine salt **16**, mp 130–131°. Recrystallization from warm ethanol gave 11.1 g (65%) of **16** as white needles: mp 134–135° dec; nmr (acetone) δ 1.50 (s, 6), 4.11 (s, 2), 4.86 (d, 2), and 5.85 (s, 4).

Anal. Calcd for $C_{12}H_{15}NO_2S \cdot C_7H_9N$: C, 66.3; H, 7.0; N, 8.1; S, 9.3. Found: C, 66.0; H, 7.0; N, 7.8; S, 9.6.

The solution that remained after isolation of the benzylamine salt was distilled through a short Vigreux column to give 66 g (60%) of **17a**: bp 141–147° (0.7 mm), 87% purity by glpc. A sample was purified by glpc: nmr (CCl_4) δ 1.18 (d, 6), 2.82 (septet, 1), 4.70 (d, 2), 7.22 (s, 5), and 8.67 (s, 1).

Anal. Calcd for $C_{11}H_{15}NS$: C, 68.3; H, 7.8; N, 7.3; S, 16.6. Found: C, 68.8; H, 7.9; N, 7.4; S, 16.4.

Trituration of the benzylamine salt **16** with 10% HCl gave **18**: mp 100–102° dec; nmr ($Cl_2CHCHCl_2$) δ 1.60 (s, 6), 4.82 (d, 2), 7.33 (s, 5), 8.25 (broad s, 1), and 10.8 (s, 1).

Anal. Calcd for $C_{12}H_{15}NO_2S$: C, 60.7; H, 6.4; N, 5.9; S, 13.5. Found: C, 61.0; H, 6.5; N, 6.3; S, 13.5.

1-Thioisobutyrylpiperidine (17b) from Piperidine and 14a.—Piperidine (5.1 g, 0.06 mol) was added slowly to 6.48 g (0.03 mol) of **14a**. CO_2 evolved and the mixture was cooled intermittently to keep the temperature at 50–60°. After the exothermic reaction was over, the reaction solution was warmed for 1 hr on the steam bath and then distilled through a 4-in. Vigreux column to give 5.8 g (57%) of **17b**: bp 100–102° (0.8 mm); nmr ($CDCl_3$) δ 1.22 (d, 6), 3.20 (septet, 1), and 1.73, 3.20, 3.80, 4.30 (multiplets, 10).

Anal. Calcd for $C_9H_{17}NS$: C, 63.1; H, 10.0; S, 18.7. Found: C, 62.9; H, 10.0; S, 18.8.

2,10-Diisopropylidene-5,5,13,13-tetramethyl-3,11-dioxa-1,7,9,14-tetrathiadispiro[5.1.5.1]tetradecane-4,12-dione (19) by Dimerization of 14a.—**14a** (3.5 g, 0.016 mol) was placed in a petri dish and covered with a watch glass. The sample was irradiated with a Hanovia high-pressure mercury-vapor lamp for 24 hr. The solid changed from orange to white during irradiation. The material was washed with hexane and recrystallized from benzene to give 2.0 g of **19**: mp 213°; ir (KBr) 5.73 and 6.10 μ; nmr ($CDCl_3$) δ 1.75 (s, 12) and 1.82 (s, 12).

Anal. Calcd for $C_{18}H_{24}O_4S_4$: C, 50.0; H, 5.6; S, 29.6; mol wt, 432. Found: C, 50.3; H, 5.5; S, 29.8; mol wt (ebullioscopic in benzene), 446.

N-(2-Ethylbutenylidene)methylamine.—This compound was prepared by dehydrohalogenation of N-(1-chloro-2-ethylbutylidene)methylamine according to the method of Stevens and French.[19] It had the following properties: bp 55–57° (50 mm); ir (neat) 4.95 μ; nmr (neat) δ 1.00 (t, 6), 1.93 (q, 4), and 3.07 (s, 3).

Anal. Calcd for $C_7H_{13}N$: C, 75.6; H, 11.8; N, 12.6. Found: C, 75.4; H, 11.8; N, 12.6.

4-(1-Ethylpropylidene)dihydro-2,6-diisopropylidene-5-methyl-4H-1,3,5-dioxazine (20) and Tetrahydro-2,4-diisopropylidene-3,5,5-trimethyl-6H-1,3-oxazin-6-one (21).—Dimethylketene (64 g, 0.91 mol) was added rapidly to a stirred solution of 44.4 g (0.4 mol) of N-(2-ethylbutenylidene)methylamine in 200 ml of acetonitrile under a nitrogen atmosphere. The reaction was slightly exothermic, and the temperature was held at 20–30° by periodic use of an ice bath. The reaction solution was stirred for 12 hr at room temperature and then distilled through a 6-in. Vigreux column to give 61 g of a mixture boiling from 85 to 148° (8 mm). Glpc indicated this mixture to be mostly **20** and **21**.

The mixture was fractionated through a 24-in. spinning band column to give 24 cuts. Cuts 5–19, bp 78–79° (0.7 mm), weighed 31.7 g and consisted mainly of **20**: ir (neat) 5.88, 5.92, 8.35, and 8.60 μ; nmr ($CDCl_3$) δ 1.00 (t, 6), 1.60 (s, 6), 1.63 (s, 6), 2.08 (q, 4), and 2.84 (s, 3).

Anal. Calcd for $C_{15}H_{25}NO_2$: C, 71.7; H, 10.0; N, 5.6. Found: C, 71.1; H, 9.7; N, 5.4.

Cuts 20–24, bp 90–94° (0.7 mm), weighed 8.8 g and consisted mainly of **21**: ir (neat) 5.53 (w), 5.70, 5.85, 6.03, 8.80, and 9.43 μ; nmr (CCl_4) δ 1.00 (t, 6), 1.49 (s, 6), 1.64 (s, 3), 1.72 (s, 3), 2.18 (q, 2), 2.35 (q, 2), and 2.59 (s, 3).

Anal. Calcd for $C_{15}H_{25}NO_2$: C, 71.7; H, 10.0; N, 5.6. Found: C, 71.6; H, 10.3; N, 5.6.

1-(N,2-Dimethylpropionamido)-2-ethyl-1-butenyl Isobutyrate (22) and 1-(2-Ethyl-N-methylbutyramido)-2-methylpropenyl Isobutyrate (23) by Hydrolysis of 20.—A mixture of 2.1 g of **21** and 5 ml of water was refluxed with stirring for 1 hr. The organic layer afforded quantitative yields of **22** and **23**. These two components were separated by glpc.

22: ir (neat) 5.70, 6.00, 8.92, and 9.30 μ; nmr ($CDCl_3$) δ 1.00 (t, 6), 1.08 (d, 6), 1.20 (d, 6), 1.95 (q, 2), 2.04 (q, 2), 2.50 (septet, 1), 2.72 (septet, 1), and 3.02 (s, 3).

Anal. Calcd for $C_{15}H_{27}NO_3$: C, 66.9; H, 10.1; N, 5.2. Found: C, 67.1; H, 10.3; N, 4.9.

23: ir (neat) 5.71, 6.01, 8.95, and 9.32 μ; nmr ($CDCl_3$) 0.83 (t, 6), 1.17 and 1.21 (2 doublets, 6), 1.45 (broadened quartet, 4), 1.60 (s, 3), 1.68 (s, 3), 2.50 [m, 2 $(CH_3)_2CH$ and $(C_2H_5)_2CH$], and 3.04 (s, 3).

Anal. Calcd for $C_{15}H_{27}NO_3$: C, 66.9; H, 10.1; N, 5.2. Found: C, 66.3; H, 10.2; N, 4.9.

4-Ethyl-2,2-dimethyl-3-(N-methylisobutyramido)-3-hexenoic Acid (24) by Hydrolysis of 21.—One gram of **21** was refluxed with 5 ml of water for 12 hr. The organic layer was extracted, dried ($MgSO_4$), and evaporated to give 0.8 g of **24** as a viscous oil that crystallized on standing. A sample was recrystallized from cyclohexane: mp 87–88°; ir (KBr) 3.85 (broad), 5.79, and 6.30 μ; nmr ($CDCl_3$) δ 0.92 (t, 3), 1.02 (t, 3), 1.22 (s, 3), 1.46 (s, 3), 1.22 (d, 6, J = 7.0 Hz), 2.00 (q, 2), 2.16 (q, 2), 2.92 (septet, 1), 3.20 (s, 3), and 12.80 (s, 1).

Anal. Calcd for $C_{15}H_{27}NO_3$: C, 66.9; H, 10.1; N, 5.2 Found: C, 66.9; H, 10.0; N, 5.2.

Registry No.—**2a**, 29682-67-5; **3a**, 29682-68-6; **4a**, 1888-29-5; **4b**, 29682-70-0; **5a**, 18006-60-5; **6**, 29682-72-2; **7**, 29682-73-3; **8**, 14212-68-1; **9**, 29682-75-5; **10**, 1575-95-7; **11**, 20452-63-5; **12**, 29682-78-8; **13**, 4858-67-7; **14a**, 21876-29-9; **15**, 29682-81-3; **16**, 29682-82-4; **17a**, 29682-83-5; **17b**, 17975-09-6; **18**, 29682-82-4; **19**, 29682-86-8; **20**, 29682-87-9; **21**, 29682-88-0; **22**, 29682-89-1; **23**, 29682-90-4; **24**, 29682-91-5; N-(2-ethylbutenylidene)methylamine, 29784-70-1.

Acknowledgment.—We wish to thank Professor Donald Farnum, whose comments helped us to establish the correct structure for **7**.

---

[19] C. L. Stevens and J. C. French, *J. Amer. Chem. Soc.*, **76**, 4398 (1954).