123-124° at 1.38 mm., was obtained. Identification of isomers was made by catalytic reduction to a mixture of *cis*- and *trans*-2-*o*-tolylcyclohexanol[6] and subsequent v.p.c. as described for the identification of 5 and 6.

trans-**2-*o*-Tolyl-5-cyclohexen-1-ol** (**7**).—This compound was prepared in 76% yield by the lithium aluminum hydride reduction of **10** according to the procedure described for the preparation of **5** from **9**, b.p. 88-89° at 0.23-0.24 mm.

Anal. Calcd. for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.55; H, 8.42.

trans-**2-*o*-Tolyl-5-cyclohexenyl Benzoate** (**10**).—A mixture of 15.10 g. (0.08 mole) of **7** and **8** (60% **7**, 40% **8**), 16.9 g. (0.120 mole) of benzoyl chloride, and 50 ml. of anhydrous pyridine were heated for 1.5 hr. at 140°. A white precipitate formed and heat was evolved upon addition of the benzoyl chloride to the pyridine. This precipitate dissolved upon heating. At the end of the heating, two layers were present. The mixture was hydrolyzed by pouring into 200 ml. of 10% hydrochloric acid. The resulting mixture was extracted with ether, and the ethereal extracts were washed with 10% hydrochloric acid, 5% sodium bicarbonate solution, and water. After drying by passage through anhydrous sodium sulfate and standing over Drierite, the solution was filtered and solvent was removed. The crude reddish product was treated with activated charcoal and recrystallized from a hexane-benzene mixture to give a 34% yield of white crystals, m.p. 81-81.5°. (The per cent yield was based on the amount of **7** in the starting material, 9.06 g.) Lithium aluminum hydride reduction of **10** gave pure **7**.

Anal. Calcd. for $C_{20}H_{20}O_2$: C, 82.16; H, 6.90. Found: C, 82.49; H, 6.92.

trans-**2-*o*-Tolyl-*trans*-5,6-epoxycyclohexyl Benzoate** (**13**) **and** *trans*-**2-*o*-Tolyl-*cis*-5,6-epoxycyclohexyl Benzoate** (**14**).—These compounds were prepared by the epoxidation of **10** with perbenzoic acid as described for the preparation of **11** and **12** from **9**. Recrystallization from a hexane-benzene mixture resulted in the crystallization of two different crystal structures, one needles and the other rock-like. The different crystal structures were separated with forceps. Recrystallization afforded **13** as needles, m.p. 128.5-129.5°, and **14**, rock-like, m.p. 105-106°.

Anal. Calcd. for $C_{20}H_{20}O_3$: C, 77.90; H, 6.54. Found: **13**, C, 77.82; H, 6.64; **14**, C, 78.20; H, 6.47.

trans-**2-*o*-Tolyl-*cis*-4-hydroxycyclohexanol** (**15**).—This compound was prepared by the lithium aluminum hydride reduction of **11**. To a stirred mixture of 0.75 g. (0.020 mole) of lithium aluminum hydride in 10 ml. of anhydrous ether was added slowly 3.12 g. (0.011 mole) of **11** in 30 ml. of anhydrous ether. Heat was evolved during the addition. The mixture was stirred for 1.5 hr., and hydrolyzed by pouring into 42 ml. of 30% Rochelle salt solution, and the ether layer separated. The aqueous layer was extracted with ether and the combined ethereal extracts were dried by passage through anhydrous sodium sulfate. Solvent removal afforded white crystals which were recrystallized from benzene, m.p. 149.5-150°.

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.55; H, 8.60.

trans-**2-*o*-Tolyl-*trans*-5-hydroxycyclohexanol** (**16**).—This compound was prepared by the lithium aluminum hydride reduction of **12** and by the similar reduction of **13** as described for the preparation of **5** from **11**. The product from the reduction of **12** was isolated by elution chromatography over 10 g. of neutral alumina using 25-ml. portions of eluent. The eluents used were petroleum ether-benzene mixture (50:50) and benzene. Recrystallization from a benzene-petroleum ether mixture gave white crystals, m.p. 117-119°. The reduction of **13** gave a 72% yield, m.p. 118-119°. A mixture melting point of the two products showed no depression and their infrared spectra were identical. The analytical sample had m.p. 119-119.5°.

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.85; H, 8.72.

trans-**2-*o*-Tolyl-*cis*-6-hydroxycyclohexanol** (**17**).—This compound was prepared by the lithium aluminum hydride reduction of **14** as previously described for the preparation of **15** from **11**. Recrystallization from a hexane-benzene mixture afforded white crystals, m.p. 116.8-117.3°.

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.38; H, 8.75.

Acknowledgment.—The authors wish to express their sincere appreciation to Mr. B. J. Nist, Department of Chemistry, University of Washington, for obtaining the n.m.r. spectra.

Ketenes. III. Cycloaddition of Ketenes to Acetylenic Ethers[1]

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

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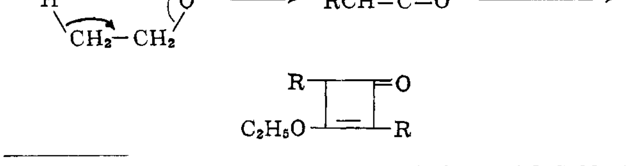
Dialkylketenes add to ethoxyacetylene to give 4,4-dialkyl-3-ethoxy-2-cyclobuten-1-ones and to 1-buten-3-ynyl methyl ether to give 4,4-dialkyl-3-(2-methoxyvinyl)-2-cyclobuten-1-ones. Some new reactions of these cyclobutenones are described.

The cycloaddition of ketenes to alkoxyacetylenes was first suggested by Nieuwenhuis and Arens,[3] whose interpretation of Ficini's earlier work[4] showed that pyrolysis of ethoxyacetylenes gave ethoxycyclobutenones. This reaction apparently involves a concerted elimination of an aldoketene from the ethoxyacetylene, followed by cycloaddition of the ketene and acetylenic ether.



Proof of this mechanism, by addition of diphenylketene to ethoxyacetylene, was obscured by the formation of rearrangement products,[5,6] and by a peculiar mode of addition involving a benzene nucleus of the diphenylketene.[7,8] Unequivocal evidence for the formation of a cyclobutenone has been presented,[9] however, and the addition of ketene to several acetylenic ethers has been described.[10,11]

Dimethylketene, presumably less reactive than di-

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(1) Paper II in this series: R. H. Hasek, P. G. Gott, and J. C. Martin' *J. Org. Chem.*, **29**, 1239 (1964).

(2) To whom inquiries should be sent.

(3) J. Nieuwenhuis and J. F. Arens, *Rec. trav. chim.*, **77**, 761 (1958).

(4) J. Ficini, *Bull. soc. chim. France*, 1367 (1954).

(5) J. Nieuwenhuis and J. F. Arens, *Rec. trav. chim.*, **77**, 1153 (1958).

(6) J. F. Arens, "Advances in Organic Chemistry: Methods and Results," Vol. 2, R. A. Raphael, E. C. Taylor, and H. Wynberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p. 193.

(7) E. F. Jenny, K. Schenker, and R. B. Woodward, *Angew. Chem.*, **73**, 756 (1961).

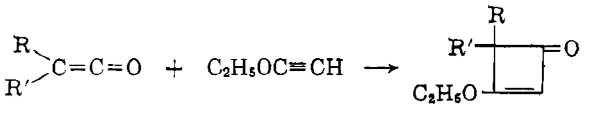
(8) D. H. R. Barton, J. N. Gardner, R. C. Petterson, and O. A. Stamm, *Proc. Chem. Soc.*, 21 (1962).

(9) J. Druey, E. F. Jenny, K. Schenker, and R. B. Woodward, *Helv. Chim. Acta*, **45**, 600 (1962).

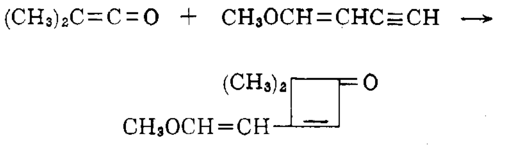
(10) H. Wasserman and E. Dehmlow, *Tetrahedron Letters*, **23**, 1031 (1962).

(11) B. Rosebeek and J. F. Arens, *Rec. trav. chim.*, **81**, 549 (1962).

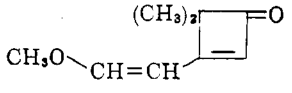
phenylketene in thermal cycloaddition reactions,[12] combined with ethoxyacetylene in acetonitrile to form 3-ethoxy-4,4-dimethyl-2-cyclobuten-1-one (Ia) in 83% yield. In hexane, the yield of Ia was 57%. Butylethylketene and ethoxyacetylene (in hexane) afforded the adduct Ib in 51% yield.



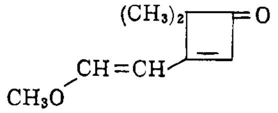
The acetylenic ether vinylog, 1-buten-3-ynyl methyl ether, combined with dimethylketene in acetonitrile to give a 38% yield of 3-(2-methoxyvinyl)-4,4-dimethyl-2-cyclobuten-1-one (II). It is noteworthy that the cycloaddition takes place on the acetylenic rather than the olefinic bond. The n.m.r. spectrum of II indicated a mixture of *cis* and *trans* isomers. A freshly distilled sample of II was approximately 55% *cis*-II and 45% *trans*-II, but, after standing for several days, it changed to 10% *cis*-II and 90% *trans*-II.



II



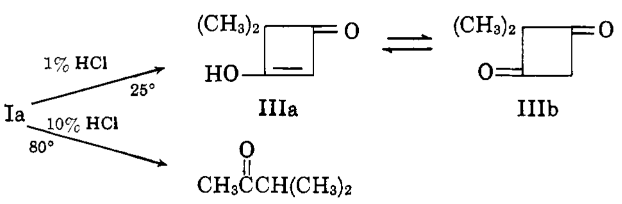
cis-II



trans-II

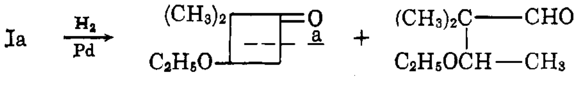
Unlike the ketene and diphenylketene adducts of ethoxyacetylene, Ia is stable at temperatures up to 150°, at which point a mildly exothermic reaction starts. The high-boiling products of this reaction have not been identified.

The hydrolysis of Ia in 1% hydrochloric acid solution gave 3-hydroxy-4,4-dimethyl-2-cyclobuten-1-one (IIIa) in 73% yield. More vigorous hydrolysis in hot 10% hydrochloric acid solution gave only 3-methyl-2-butanone.



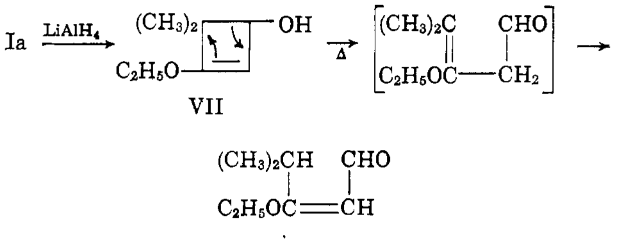
Compound III, in the solid state or dissolved in polar solvents (dimethylformamide, dimethyl sulfoxide, pyridine, acetone), exists as the enol IIIa; in chloroform solutions it exists as 2,2-dimethyl-1,3-cyclobutanedione (IIIb). N.m.r. and infrared spectral evidence show that IIIb (chloroform solution) is the preferred form. III, in effect, is a mixed dimer of ketene and dimethylketene and, like the isomeric solid dimer of methylketene,[13,14] is a relatively strong acid (pK_a 2.6). It is interesting to note, however, that the acidic dimer of methylketene, according to its n.m.r. spectrum, is always observed in the enolic form, even in chloroform solution.

The hydrogenation of Ia over palladium catalyst yielded 67% of 3-ethoxy-2,2-dimethylcyclobutanone (V) and 22% of 3-ethoxy-2,2-dimethylbutyraldehyde (VI). The latter product probably is formed by a hydrogenolysis reaction, with cleavage of bond a in V; when V was subjected to hydrogenation over palladium catalyst, a substantial amount (25%) of VI was produced.



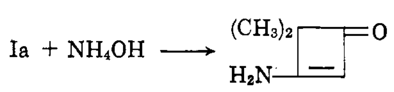
V VI

Reduction of Ia with lithium aluminum hydride gave a 70% yield of 3-ethoxy-4,4-dimethyl-2-cyclobuten-1-ol (VII), which on attempted distillation was transformed into 3-ethoxy-4-methyl-2-pentenal (VIII). A sample of VII, after standing at room temperature for 2 months, showed (infrared spectrum) extensive rearrangement to VIII. This change of VII to VIII probably occurs by a cyclobutene rearrangement.[15]

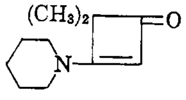


VIII

Ia may be regarded as the ethyl ester of the strongly acidic enol IIIa, and as such undergoes ammonolysis and aminolysis reactions in which the ethoxy group is replaced by an amine moiety. The aminocyclobutenone IX is formed readily by stirring Ia with ammonium hydroxide at room temperature. IX melts at high temperatures and decomposes near 213°. It is relatively insoluble in water, but dissolves readily in hydrochloric acid solution and can be regenerated by the

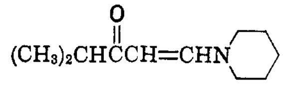


IX



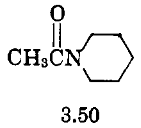
3.33

X



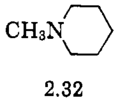
3.20

XI[17]



3.50

XII



2.32

XIII

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[12] J. D. Roberts and C. M. Sharts, *Org. Reactions*, **12**, 27 (1962).

[13] R. B. Woodward and G. Small, *J. Am. Chem. Soc.*, **72**, 1297 (1950).

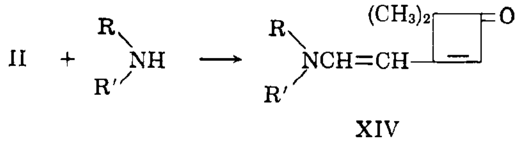
[14] Woodward and Small[13] reported pK_a 2.8 for methylketene dimer; we found pK_a 3.0.

[15] E. F. Jenny and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 2005 (1956).

[16] N.m.r. spectra were obtained with a Varian A-60 instrument at 60 Mc. with tetramethylsilane as an internal standard.

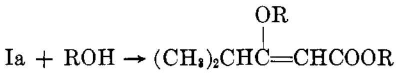
addition of sodium hydroxide. X was formed by the action of piperidine on Ia. The n.m.r. field position for the methylene groups attached to N in the piperidine ring of X is 3.33, compared with 2.32 for the normal piperidine ring in XIII. This unusual shift is comparable with that observed for the amide XII and the amide vinylog XI, and indicates that structures such as X are "amide-like."[16]

The methoxyvinylcyclobutenone II reacts with amines such as morpholine and aniline to replace the methoxy group with an amine moiety.



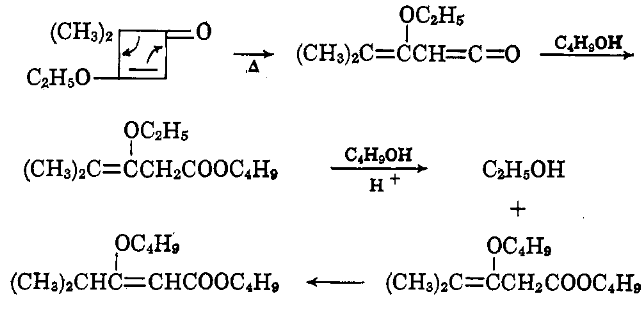
XIV

Ia reacted slowly with ethyl alcohol at 80° to give ethyl 3-ethoxy-4-methyl-2-pentenoate (XVa) in 73% yield. In the presence of an acid catalyst, Ia reacted rapidly with butyl alcohol at 130°; ethyl alcohol was evolved, and butyl 3-butoxy-4-methyl-2-pentenoate (XVb) was formed. If the acid catalyst was omitted, no ethyl alcohol was evolved, but the infrared spectrum of the reaction mixture indicated that the starting material Ia had disappeared. Addition of the catalyst at this stage gave the theoretical amount of ethyl alcohol. These facts suggest the following mechanism.



$$\text{Ia} + \text{ROH} \rightarrow (CH_3)_2CH\overset{OR}{\overset{|}{C}}{=}CHCOOR$$

XVa, R = C_2H_5
b, R = C_4H_9



Experimental

Dialkylketenes were prepared by pyrolysis of the corresponding anhydrides.[18] 3-Ethoxy-2,2-dimethylcyclobutanone was prepared by addition of dimethylketene to ethyl vinyl ether.[19] Ethoxyacetylene was obtained from Pfister Chemical Works and 1-buten-3-ynyl methyl ether from Chemische Werke Hüls.

3-Ethoxy-4,4-dimethyl-2-cyclobuten-1-one (Ia).—Dimethylketene (700 g., 10.0 moles) was added to a stirred solution of 700 g. (10.0 moles) of ethoxyacetylene in 1200 ml. of acetonitrile under a nitrogen atmosphere over a period of 4.5 hr. The reaction was exothermic and the temperature rose to 45° even with cooling by ice. The solution was stirred for 3 hr. after addition was complete and then distilled through a 12-in. packed column to give 1160 g. (83%) of Ia, b.p. 62–63° (2.5 mm.), $n^{20}D$ 1.4583; infrared absorptions (smear) at 5.69 and 6.35 μ.[20] The n.m.r. spectrum (neat) showed the following peaks: singlets at 4.80 (C=CH) and 1.15 (CH_3), and a quartet at 4.23 and a triplet at 1.40 p.p.m. (C_2H_5O).

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.5; H, 8.6. Found: C, 68.6; H, 8.5.

4-Butyl-3-ethoxy-4-ethyl-2-cyclobuten-1-one (Ib).—A solution of 92 g. (0.73 mole) of butylethylketene and 51 g. (0.73 mole) of ethoxyacetylene in 150 ml. of hexane was refluxed for 12 hr. Distillation through a 10-in. Vigreux column gave some low-boiling materials, identified as unchanged butylethylketene and ethoxyacetylene, and 73 g. (51%) of Ib, b.p. 88° (0.8 mm.), $n^{20}D$ 1.4665; infrared absorptions (smear) at 5.68, 6.0, and 6.3 μ.

Anal. Calcd. for $C_{12}H_{22}O_2$: C, 73.4; H, 10.3. Found: C, 73.2; H, 10.1.

In addition, 11 g. of an unknown compound, b.p. 129–132° (0.6 mm.), was obtained. It had infrared absorptions (smear) at 5.90, 6.46, and 6.81 μ.

3-(2-Methoxyvinyl)-4,4-dimethyl-2-cyclobuten-1-one (II).—A solution of 123 g. (1.5 moles) of 1-buten-3-ynyl methyl ether in 300 ml. of ether was stirred at room temperature under a nitrogen atmosphere while 105 g. (1.5 moles) of dimethylketene was added over a period of 30 min. The temperature of the exothermic reaction was kept at 20–25° by a cooling bath. Distillation of this solution through a 10-in. packed column gave tetramethyl-1,3-cyclobutanedione, unchanged 1-buten-3-ynyl methyl ether, and 60.5 g. (26%) of II, b.p. 89–92° (1.2 mm.); infrared absorptions (smear) at 5.8, 6.25, and 6.55 μ. The n.m.r. spectrum of II contained peaks attributed to *cis* and *trans* isomers of II: *cis*, singlets at 6.95 (OCH=C), 5.88 (OC=CH), 3.85 (CH_3O), and 1.15 (CH_3), and a doublet at 5.42 p.p.m. (ring H); *trans*, doublets at 7.90 (OCH=C), 6.0 (ring H), and 5.88 (OC=CH), and singlets at 3.72 (CH_3O) and 1.30 p.p.m. (CH_3). The *cis–trans* ratio of freshly distilled II was approximately 55:45; after the material stood for 10 days at room temperature, the ratio was about 10:90.

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.1; H, 8.0. Found: C, 70.9; H, 8.2.

3-Hydroxy-4,4-dimethyl-2-cyclobuten-1-one (IIIa).—A mixture of 250 g. (1.78 moles) of Ia and 500 ml. of 1% hydrochloric acid solution was stirred rapidly at room temperature for 20 hr. The solid product was removed by filtration, washed with water, and dried in an oven at 105°. The yield of crude IIIa, m.p. 128–130°, was 146.3 g. (73%). A sample recrystallized from benzene melted at 131–132°.

The infrared spectrum (KBr) showed two broad bands at 4.22 and 5.31, a sharp band at 5.88, and broad multipe bands from 6.6 to 7.5 μ. The infrared spectrum of a chloroform solution showed no absorption at 4.22, 5.31, 5.88, or 6.6 to 7.5, but did show a new absorption at 5.70 μ. The n.m.r. spectrum of a 20% solution of IIIa in dimethylformamide showed single peaks at 10.23 (enolic OH), 4.55 (C=CH), and 1.22 p.p.m. (CH_3). The spectrum of a chloroform solution was characteristic of IIIb and showed peaks at 3.88 (CH_2) and 1.42 p.p.m. (CH_3).

Anal. Calcd. for $C_6H_8O_2$: C, 64.3; H, 7.2. Found: C, 64.1; H, 7.0.

Hydrogenation of 3-Ethoxy-4,4-dimethyl-2-cyclobuten-1-one (Ia) over Palladium.—A solution of 40 g. of Ia in 100 ml. of cyclohexane was hydrogenated over 5 g. of 5% palladium on powdered carbon in a stainless steel rocking autoclave at 60° and 1500 p.s.i. for 4 hr. The reaction mixture was filtered to remove the catalyst and the filtrate was distilled through a 10-in. packed column to give 36.4 g. of material which boiled at 48–53° (6.5 mm.). This material was redistilled through a 24-in. spinning-band column to give 7.2 g. of 3-ethoxy-2,2-dimethylbutyraldehyde (VI), b.p. 45–47° (6.7 mm.), $n^{20}D$ 1.4157, and 19.2 g. of 3-ethoxy-2,2-dimethylcyclobutanone (V). VI was identified by comparison of its infrared spectrum with that of an authentic sample[21] (infrared absorption at 5.63 μ). V was also identified in the same manner.[19]

Hydrogenation of 3-Ethoxy-2,2-dimethylcyclobutanone (V) over Palladium.—One hundred grams of V was hydrogenated over 5 g. of 5% palladium on powdered carbon in a stainless steel rocking autoclave at 75° and 1500 p.s.i. for 6 hr. Hydrogen absorption was rapid for a short time and then stopped abruptly. The reaction mixture was filtered, 5 g. of fresh catalyst was added, and the hydrogenation was continued. Again, the initial hydrogen absorption was rapid but stopped abruptly. Examination of the reaction mixture by g.l.c. (20% Carbowax 20M on Chromosorb P) showed V and VI in a ratio of approximately

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(17) R. H. Hasek and J. C. Martin, *J. Org. Chem.*, **28**, 1468 (1963).

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

(19) See Ref. 1.

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

(21) K. C. Brannock, *J. Org. Chem.*, **25**, 258 (1960).

3:1. These materials were separated with an Aerograph Autoprep Model A-700 (Wilkens Instrument and Research) and identified by comparison of their infrared spectra with those of authentic compounds.

Reduction of Ia with Lithium Aluminum Hydride.—A solution of 50 g. (0.36 mole) of Ia in 75 ml. of dry ether was added slowly to a stirred slurry of 9.5 g. (0.25 mole) of lithium aluminum hydride in 500 ml. of dry ether. The reaction temperature was controlled at 15–20° by an ice bath. The reaction mixture was stirred for 1 hr. after the addition was complete. Water (10 ml.) was added slowly, followed by 8 ml. of 20% sodium hydroxide solution and an additional 36 ml. of water. The alumina was removed by filtration and washed several times with ether. The combined filtrates were dried over anhydrous magnesium sulfate and low-boiling materials were removed at room temperature *in vacuo*. The n.m.r. spectrum of the residue (35 g.) was characteristic of VII. Distillation of this material through a 10-in. Vigreux column gave 28 g. of 3-ethoxy-4-methyl-2-pentenal (VIII), b.p. 70–72° (3 mm.).

Infrared absorptions (smear) for VII were at 2.98, 6.1, and 6.21 μ. The n.m.r. spectrum (neat) of VII showed singlets at 2.98, 6.1, and 6.21 μ. The n.m.r. spectrum (neat) of VII showed singlets at 4.42 (C=CH), 4.10 (OCH), and 3.23 (OH), a quartet at 3.73, a triplet at 1.10 (C_2H_5O), and a doublet at 1.22 p.p.m. (CH_3). Infrared absorptions (smear) for VIII were at 3.62, 6.02, and 6.22 μ. The n.m.r. spectrum (neat) of VIII showed doublets at 9.82 (CHO) and 5.45 (C=CH), a quartet at 3.75 and a triplet at 1.42 (C_2H_5O), and a septet at 2.88 and a doublet at 1.02 p.p.m. [$(CH_3)_2CH$].

Anal. Calcd. for $C_8H_{14}O_2$ (VIII): C, 67.6; H, 9.9. Found: C, 67.3; H, 9.9.

3-Amino-4,4-dimethyl-2-cyclobuten-1-one (IX).—A mixture of 20 g. (0.14 mole) of Ia and 40 ml. of 28% ammonium hydroxide was stirred at room temperature for 4 hr. The resulting solid was isolated by filtration, washed with water, and dried in air to give 13.9 g. (89%) of IX which melted at 213° with decomposition. An analytical sample, recrystallized from ethyl alcohol, had m.p. 213° with decomposition; infrared absorptions (KBr) at 3.16, 5.98, and 6.4 to 6.9 μ (broad). The n.m.r. spectrum of IX showed a broad peak at 8.50 (NH_2) and singlets at 4.22 (C=CH) and 1.15 p.p.m. (CH_3).

Anal. Calcd. for C_6H_9NO: C, 64.8; H, 8.2; N, 12.6. Found: C, 65.0; H, 8.3; N, 12.6.

3-Piperidino-4,4-dimethyl-2-cyclobuten-1-one (X).—A solution of 40 g. (0.28 mole) of 3-ethoxy-4,4-dimethyl-2-cyclobuten-1-one and 24.3 g. (0.28 mole) of piperidine in 100 ml. of benzene was refluxed for 5 hr. Most of the benzene was removed by distillation at atmospheric pressure. The residue crystallized on cooling to give 50.4 g. (98%) of crude X, m.p. 101.5–104°. A sample recrystallized twice from a mixture of benzene and hexane had m.p. 104–104.5°; infrared absorptions (KBr) at 5.75 and 6.28 μ. The n.m.r. spectrum showed singlets at 4.32 (C=CH) and 3.33 (methylenes attached to N of piperidine), a broad peak at 1.75 (remaining methylenes of piperidine), and a doublet at 1.22 p.p.m. (CH_3).

Anal. Calcd. for $C_{11}H_{17}NO$: C, 73.7; H, 9.6; N, 7.8. Found: C, 74.0; H, 9.8; N, 7.7.

3-(2-Anilinovinyl)-2,2-dimethyl-3-cyclobuten-1-one (XIV).—A mixture of 7.6 g. (0.05 mole) of II and 4.65 g. (0.05 mole) of aniline was allowed to stand for several days at room temperature. The crystalline product was washed with cold benzene and recrystallized from ethyl alcohol to give 6.3 g. of XIV, m.p. 169–170°. XIV showed significant infrared absorptions at 6.12, 6.3, 6.45, 6.55, and 6.9 μ. The n.m.r. spectrum (dimethylformamide) showed singlets at 1.38 (CH_3) and 4.50 (ring H), a doublet at 5.92 (C=CH), and a complex multiplet at 7.25 p.p.m. ($C_6H_5NHCH=C$).

Anal. Calcd. for $C_{14}H_{15}NO$: C, 78.8; H, 7.1; N, 6.6. Found: C, 79.1; H, 7.2; N, 6.7.

Reaction of Ia with Ethyl Alcohol (XVa).—A solution of 28.0 g. (0.2 mole) of Ia in 50 ml. of ethyl alcohol was refluxed for 36 hr. Periodic examinations of the reaction solution by infrared showed a steady decrease in the amount of starting material. Distillation of this solution through a 6-in. Vigreux column gave 27.1 g. (73%) of XVa, b.p. 80–81° (6 mm.), n^{20}_D 1.4468; infrared absorptions (smear) at 5.82, 6.08, 8.7, and 9.07 μ.

Anal. Calcd. for $C_{10}H_{18}O_3$: C, 64.5; H, 9.7. Found: C, 64.7; H, 10.1.

Reaction of Ia with Butyl Alcohol (XVb).—A solution of 28.0 g. (0.2 mole) of Ia in 59 g. (0.8 mole) of butyl alcohol was refluxed under a short, packed column for 3 hr. The temperature at the head of the column remained at 115° during this period. The solution was cooled and examination of its infrared spectrum indicated that all of Ia was gone. To this solution was added 0.1 g. of *p*-toluenesulfonic acid and refluxing was continued. The head temperature rose to 77° and 10 ml. of ethyl alcohol distilled at 77–81°. The excess butyl alcohol was removed *in vacuo* and the residue was taken up in ether, washed with sodium bicarbonate solution and then with water, and finally dried over anhydrous magnesium sulfate. Distillation of this solution through a 10-in. packed column gave 25.8 g. (53%) of XVb, b.p. 97–101° (0.7 mm.), n^{20}_D 1.4522; infrared absorptions (smear) at 5.87 and 6.21 μ. The n.m.r. spectrum (neat) showed a singlet at 4.82 (C=CH), a multiplet at 3.70 (two OCH_2's and CH), and a complex region between 1.55 and 0.95 p.p.m. (all remaining protons). These areas were in the proportions of 1:5:20.

Anal. Calcd. for $C_{14}H_{26}O_3$: C, 69.4; H, 10.8. Found: C, 69.6; H, 10.9.

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Ketenes. IV. Reactions of Ketenes with Ketene O,N-Acetals and Ketene N,N-Acetals[1]

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Ketene O,N-acetals and N,N-acetals having olefinic hydrogen atoms are converted by dimethylketene into isobutyryl O,N-acetals and N,N-acetals. However, reaction with ketene gives 2:1 adducts, 4-(dialkylamino)-2H-pyran-2-ones.

In view of the facile addition of ketenes to enamines and vinyl ethers to form cyclobutanones,[3,4] an investigation into the reactions of ketenes with such highly nucleophilic olefins as ketene O,N-acetals and ketene N,N-acetals seemed warranted. Ketene N,N-acetals I with hydrogen atoms on the olefinic carbon reacted vigorously with dimethylketene to form acylketene N,N-acetals II. No infrared spectral evidence of intermediate cyclobutanone formation could be found when a reaction was carried out below 0°.

As attempts to prepare a dimethylketene N,N-acetal were unsuccessful, the action of a "blocked" ketene

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