

amino and nitro groups and the benzene ring.

The usual resonance inhibition by *o*-methyl substituents is not observed with the mesityl sulfones, the spectra of which are shifted toward the visible relative to the phenyl and *p*-tolyl sulfones. On the basis of these observations and of a

consideration of the geometry of penta- and hexavalent systems, it is concluded that a coplanar configuration of unsaturated atoms or groups about sulfur is not a prerequisite for resonance involving the sulfone function.

SWARTHMORE, PA.

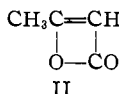
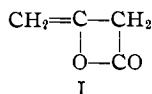
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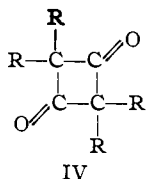
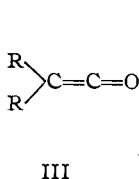
The Structure of the Acidic Dimer of Methylketene

BY R. B. WOODWARD AND GILBERT SMALL, JR.

The extraordinary chemical behavior of the ketene dimers has lent exceptional interest to that class of substances, and the controversy which has raged for decades over the structures of the compounds is without parallel in the study of small molecules. Although many expressions have been considered¹ for the dimer from ketene itself the evidence now available is conclusive in favor of the view that diketene is one or the other, or a mixture, of the β -lactones (I) and (II). It is clear that (I) can be formed by the spontaneous *asym-*



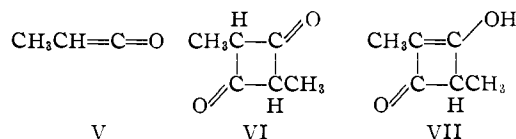
metrical dimerization of ketene, and the possibility of prototropic isomerization of (I) to (II) needs no further comment here. Dialkyl ketenes (III), on the other hand, dimerize *symmetrically* to tetraalkylcyclobutanediones (IV).²



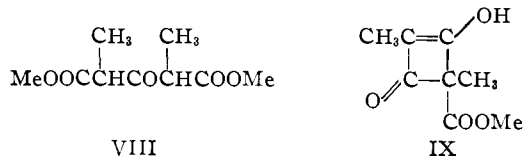
The circumstances obtaining in the intermediate case of the aldoketenes have not hitherto been defined precisely. Methylketene (V) may be considered the prototype of this class. Two dimers of

(1) Chick and Wilsmore, *J. Chem. Soc.*, **93**, 946 (1908); Staudinger and Bereza, *Ber.*, **42**, 4908 (1909); Chick and Wilsmore, *J. Chem. Soc.*, **97**, 1978 (1910); Hurd, Sweet and Thomas, *THIS JOURNAL*, **55**, 337 (1933); Angus, Leckie, Le Fevre and Wassermann, *J. Chem. Soc.*, 1751 (1935); Hurd and Williams, *THIS JOURNAL*, **58**, 962 (1936); Hurd and Roe, *ibid.*, **61**, 3355 (1939); Boese, *Ind. Eng. Chem.*, **32**, 16 (1940); Hurd and Abernethy, *THIS JOURNAL*, **62**, 1147 (1940); Hurd, Calvin and Magel, *ibid.*, **63**, 2174 (1941); Oesper and Smyth, *ibid.*, **64**, 768 (1942); Hurd and Smyth, *ibid.*, **65**, 94 (1943); Rice and Roberts, *ibid.*, **65**, 1677 (1943); Taufen and Murray, *ibid.*, **67**, 754 (1945); Whiffen and Thompson, *J. Chem. Soc.*, 1005 (1946); Bauer, Bregman and Wrightson, Abstracts April, 1946, Meeting, Am. Chem. Soc., p. 15p; Fitzpatrick, *THIS JOURNAL*, **69**, 2236 (1947); Blomquist and Baldwin, *ibid.*, **70**, 29 (1948); Miller and Koch, *ibid.*, **70**, 1890 (1948).

(2) Wedekind and Weisswange, *Ber.*, **39**, 1631 (1906); Staudinger, *ibid.*, **44**, 521 (1911); Miller, Dissertation, Cornell University, 1937; Hammick, Hampson and Jenkins, *Nature*, **136**, 990 (1935); Jenkins, *J. Chem. Soc.*, 862 (1936).



the aldoketene have been reported: (i) a *liquid* dimer, whose physical and chemical properties mirror those of diketene,^{3a,b,c} and (ii) a *crystalline*, acidic dimer, m. p. 140°. ^{3a,b} It has been claimed that the liquid dimer is convertible into the acidic isomer by the action of bases, and the suggestion has been made that the change is that of a diketene (VI) into the corresponding enol (VII).⁴ Other investigators have tentatively accepted the formulation of the acid dimer as (VII), while assuming that the liquid dimer was correctly represented by a β -lactone structure analogous to that of diketene.⁵ No unequivocal structure proof has been brought forward for either of the dimers. Although (VI) is a plausible product of the symmetrical dimerization of methylketene, and (VII) might be expected to exhibit properties consonant with those of the acidic dimer, structural features are present which are sufficiently unusual as to justify considerable skepticism in the absence of definitive evidence of the correctness of the expressions. It is true that a synthesis of the acidic dimer from dimethyl α,α' -dimethylacetonedicarboxylate (VIII), through an intermediate of the presumed structure (IX), has been adduced in support of the structure (VII),^{4b,6} but it will be



seen in the sequel that this work, while of great value in providing a ready source of the dimer, whose preparation through methylketene is tedious

(3) Staudinger, *Ber.*, **41**, 906 (1908); **44**, 533 (1911); Sauer, *THIS JOURNAL*, **69**, 2444 (1947).

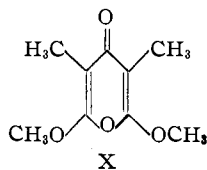
(4) Staudinger, "Die Ketene," Ferdinand Enke, Stuttgart, 1912, p. 42; Staudinger, *Ber.*, **53**, 1085 (1920).

(5) Hill, Dissertation, Cornell University, 1941; Roberts, Armstrong, Trimble and Burg, *THIS JOURNAL*, **71**, 843 (1949).

(6) Schroeter and Stassen, *Ber.*, **40**, 1604 (1907); Schroeter, *ibid.*, **49**, 2697 (1916); **59**, 978 (1926).

ous and difficult, serves only to complicate the structural problem.

In this communication, a rigorous proof of the structure (VII) for the acidic dimer of methylketene is described. We first subjected the Schroeter synthesis of the dimer to careful scrutiny. The German investigators had found that the action of strong sulfuric acid on dimethyl α,α' -dimethylacetonedicarboxylate led to two products. With acid containing excess sulfur trioxide, the major product was a substance $C_9H_{12}O_4$, formed by the abstraction of the elements of a water molecule from the ester. In view of its composition, and its pronounced *basic* properties, this substance was formulated as the γ -pyrone (X). When less concentrated sulfuric acid was used in the cyclization of the ester (VIII), an *acidic* compound,



$C_8H_{10}O_4$, was formed. When the latter was treated with hot aqueous barium hydroxide it was converted to an *acid*, $C_6H_8O_2$, identical with the acidic dimer of methylketene. Since this change corresponded empirically to the loss of a carbomethoxy group from the acidic cyclization prod-

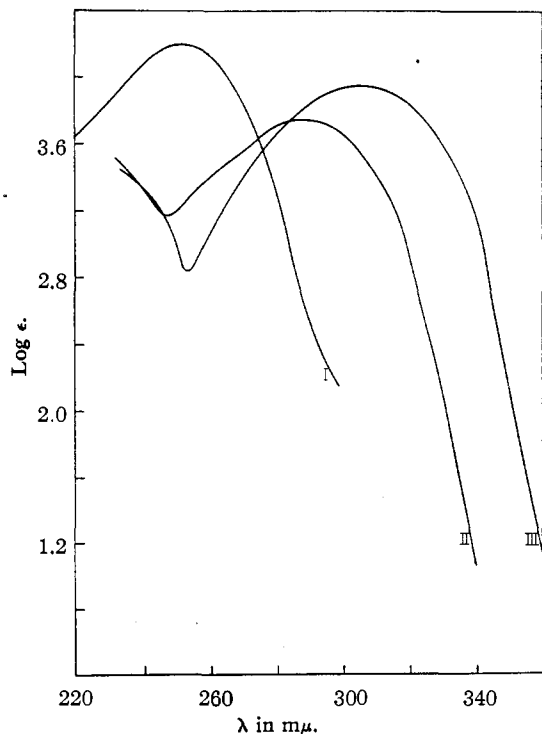
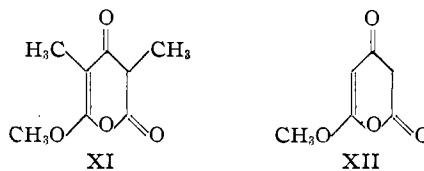


Fig. 1.—Absorption spectra in alcohol: I, 2,4-dimethyl- Δ^2 -cyclobutene-3-olone (VII); II, 6-methoxy-2,4-pyrone (XII) (enol); III, 6-methoxy-3,5-dimethyl-2,4-pyrone (XI) (enol).

uct, it was assumed that such a group was present in the latter, which was accordingly formulated as (IX). We were able to confirm these elegant experiments in detail. But we found that *the acidic substance $C_8H_{10}O_4$ was smoothly transformed by diazomethane to the basic compound $C_9H_{12}O_4$* . Further, the careful hydrolysis of the latter gave, in addition to other products, a certain amount of the acid substance. The formulation of the basic compound as (X) is not subject to question; consequently, our experiments show that *Schroeter's acidic cyclization product is the pyronone (XI)* (or, more properly, one of the corresponding enols). Confirmation of the view that the acidic compound and its hydrolysis product are not as



closely related as the formulas (VII) and (IX) imply was obtained through the measurement of the ultraviolet absorption spectra of the substances (Fig. 1); while (VII) and (IX) contain the same absorbing system, the spectrum of the dimer is very different from that of its progenitor. Further, the spectrum of the latter is very similar to that of the unsubstituted analog (XII)⁷; the small shift of the position of maximum absorption in the spectrum of (XI) as compared with that of (XII) is a consequence of the higher degree of substitution in (XI). It is now clear that the formation of methylketene dimer from (XI) cannot be construed as directly informative with respect to the constitution of the dimer; rather does it constitute a special problem, which will be considered further below.^{7a}

We turned next to the further study of the acidic dimer itself. We first confirmed the molecular formula, $C_6H_8O_2$, through analyses and molecular weight determinations.⁸ Further confirmation of the molecular size was obtained through the preparation of a liquid *monomethyl ether*, $C_7H_{10}O_2$, b. p. 83° (8 mm.) (209° , 760 mm.), and a *monobromo derivative*, $C_6H_7O_2Br$,⁹ m. p. 158° (dec.). The dimer was shown to have one active hydrogen atom in the Zerewitinov determination (*no addition*), and to possess two methyl groups bound to

(7) Prepared by the method of Litynski and Malachowski, *Roczniki Chem.*, **7**, 579 (1927).

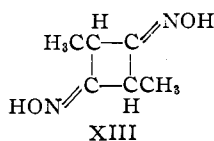
(7a) Dr. Evans B. Reid (Johns Hopkins) has very kindly informed us that he has independently reached conclusions similar to ours in regard to the structure of Schroeter's acidic condensation product.

(8) Measurements on chloroform solutions by the isothermal distillation method indicated that the dimer was highly associated in the inert solvent. On the other hand, our results for phenol solutions confirmed Schroeter's results, which were in satisfactory agreement with the formula $C_6H_8O_2$ (ref. 6b, p. 2735).

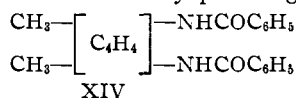
(9) Taken by itself this observation does not distinguish among formulas $(C_6H_8O_2)_n$ where n is even, but does eliminate all expressions with odd values of n except $n = 1$. Thus, the "dimer" cannot have the trimeric formula $C_9H_{12}O_3$; finally, the boiling point of the methyl ether is much too low for a compound $C_{14}H_{20}O_4$.

carbon (Kuhn-Roth method). We further satisfied ourselves that the dimer was cleaved under vigorous hydrolytic conditions to diethyl ketone and carbon dioxide. It may be observed at this point that all of these observations were consistent with the formulation of the dimer as (VII), but could not be so construed as to provide proof of the correctness of that expression.

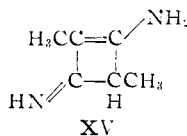
Numerous attempts to reduce the dimer, either by chemical or catalytic methods, were unsuccessful. But decisive results were obtained in the reduction of the compound $C_6H_{10}N_2O_2$, obtained by the action of hydroxylamine on the dimer. This compound had been obtained by Schroeter,^{6b} who assigned to it, without proof, the dioxime structure (XIII). When it was hydrogenated over reduced platinum oxide, two substances were



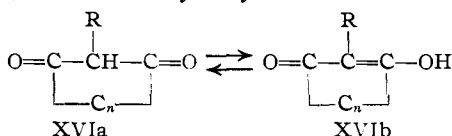
formed. The first was a volatile, crystalline very powerful base, $C_6H_{10}N_2$, m. p. 159.5–160°, which was hydrolyzable by aqueous alkalis to the dimer. It may be noted here that these facts indicate that the compound $C_6H_{10}N_2O_2$ is formed from the dimer without rearrangement or cleavage of the carbon skeleton of the latter. The other product from the hydrogenation was an amine, $C_6H_{14}N_2$, isolated as its *dibenzoyl derivative*, m. p. 272°. The latter was shown by analysis to possess the formula $C_{20}H_{22}N_2O_2$, and to contain two CH_3-C groups and two C_6H_5CONH- groups. Consequently we may formulate it as (XIV). The substance was not attacked by permanganate or by



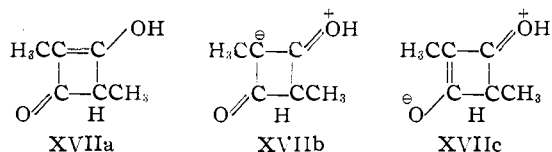
bromine water; the residue C_4H_4 is therefore saturated, and *must contain either a three- or a four-membered carbon ring*. These experiments, then, provide direct unequivocal evidence of the presence of a small carbon ring in the dimer itself, and taken with the other facts detailed above, permit no formulation but (VI) or (VII) for that substance. It is now clear that the base $C_6H_{10}N_2$ is the vinylogous amidine (XV); this view is in ac-



cord with the strongly basic properties of the substance, and with its hydrolysis to the dimer.

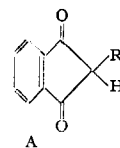


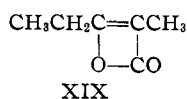
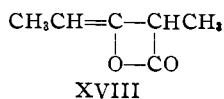
Normally, in the system (XVIa) \rightleftharpoons (XVIb), the enol is the strongly predominant species at equilibrium.¹⁰ It may be anticipated that the placing of a double bond within a cyclobutane ring would be a process of sufficient difficulty to oppose to a significant extent the enolization of a diketone such as (VI). No experimental evidence is available at present which enables us to estimate quantitatively the relative proportions of (VI) and (VII) at equilibrium. But the dimer behaves in all respects as a typical enol. It may be titrated instantaneously as a monobasic acid. In dilute alcoholic solutions it is rapidly and substantially completely dissociated to the corresponding anion (*vide infra*). It reacts rapidly and completely with bromine and with diazomethane, and immediately gives a positive ferric reaction. It gives one mole of methane in the Zerewitinov determination, and undergoes no addition; in contrast, dimedon gives 1.4 moles of methane and suffers addition of 0.6 mole of Grignard reagent. It is clear that the extra strain engendered by the placing of a double bond in the cyclobutane ring is much smaller than the stabilization resulting from electronic distribution in the enol system (*cf.* XVIIa \leftrightarrow XVIIb \leftrightarrow XVIIc), and that the



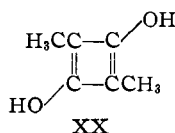
dimer, like dihydroresorcinol and other cyclic β -diketones, exists substantially completely in the enolic form (VII); the possibility is of course not excluded that the enol form (VII) predominates over the keto form (VI) at equilibrium in lesser measure than in the analogous cases. It is worthy of note at this point that in the absence of further evidence, we cannot accept the view expressed by Staudinger⁴ that the liquid dimer of methylketene is the diketone (VI), and that it is transformed into (VII) by the action of bases. In our hands, the pure liquid dimer prepared by the action of trimethylamine on propionyl chloride^{3c, b} gave no trace of (VII) on treatment with alkalis. It seems reasonable to assume, with Roberts⁵ and others, that the liquid dimer is a β -lactone (XVIII or XIX), analogous to diketene itself, and in that event the failure to observe the transformation

(10) Schwarzenbach and Lutz, *Helv. Chim. Acta*, **23**, 1151, 1155 (1940); Schwarzenbach and Felder, *ibid.*, **27**, 1044 (1944). Though no measurements of the position of equilibrium for a simple enolized 1,3-cyclopentanedione are available, the ultraviolet absorption measurements of Woodward and Blout (*THIS JOURNAL*, **65**, 562 (1943)) demonstrate that such compounds are substantially completely enolized in alcoholic solutions. Mention may be made of the observation of Schwarzenbach and Felder (*loc. cit.*) that the indanediones (A) are enolized only to the extent of 1–2%. In our view the attachment of the ends of the enolizable system to a benzene ring introduces special factors which cause these cases to be not directly comparable with the simpler models.





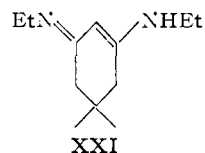
(XVIII or XIX) \rightarrow (VII) cannot be regarded as surprising. But the possibility cannot be rigorously excluded at present that there are two liquid methylketene dimers. Staudinger's experiments involved the direct dimerization of methylketene; so far as we are aware, no proof of the identity of the liquid dimer obtained in that way with the one mentioned above has been brought forward, and for the present the matter is *sub judice*. We may conclude the discussion of tautomeric phenomena by the observation that no evidence has been forthcoming in our work, or in that of other investigators, which points to the participation of the interesting cyclobutadienoid tautomer (XX) in equilibria involving the acidic dimer. The con-



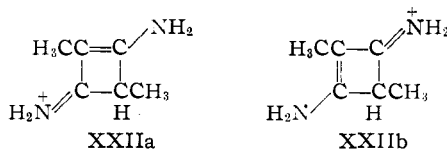
clusion may be drawn that aromatic resonance in the cyclobutadiene system cannot provide stabilization energy comparable in magnitude with that derived from the system (XVIIa \leftrightarrow XVIIb \leftrightarrow XVIIc).

While the incorporation of the enolized β -dicarbonyl system within a cyclobutane ring does not markedly disturb the tautomeric relationships normally obtaining in such systems, it does have a pronounced effect upon the characteristic acidity of the function. Indeed, the powerful acidity of the dimer is perhaps its most remarkable property. Our measurements indicate a pK of *ca.* 2.8 for the substance; *it is thus about one hundred times as strong an acid as a typical saturated carboxylic acid, and two hundred and fifty times as strong as the analogous dihydroresorcinol,*^{10a} which contains the same functional system within a six-membered ring. The strong acidity of the dimer is further mirrored in the very ready hydrolysis of its ether, in the failure of bromination to proceed beyond the stage of the monobromo derivative, in its complete resistance to the addition of the Grignard reagent, and perhaps also in its marked resistance to reduction and hydrogenation. The high acidity of the substance suggests a greater relative contribution of either or both of the ionic forms (XVIIb) and (XVIIc) to the ground state than ordinary obtains in such systems; the phenomenon then becomes explicable when it is realized that such an increase in the relative contribution of (XVIIb) is attributable to the release thereby of a certain amount of the strain devolving from the presence of a double bond within a four-membered ring (as in XVIIa and XVIIc). On the other hand, the possibility that the nuclei of the ring carbon atoms are less well shielded when present in small rings than in

open chains, or in rings in which no distortion from normal bond angles is necessary, also deserves consideration in connection with the high acidity of the dimer. Were this so, the basicity of the amine (XV) should be very much less than that of its six-ring analog. But in fact, we found that for (XV), $pK = ca.$ 12, a value very close to that for (XXI) (pK 12.13).^{10a} This result in-

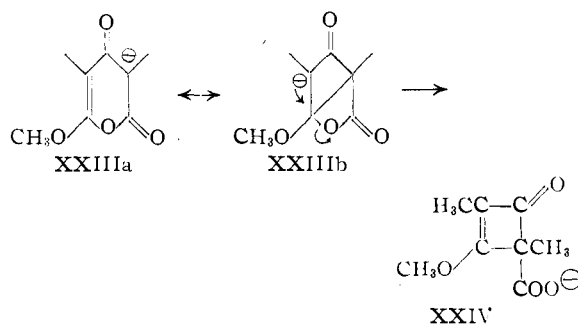


dicates that no general acid-strengthening effect of the small ring is operative. Beyond that, it may be noted that in the case of the cation (XXIIa \leftrightarrow XXIIb) from the base (XV), no singly

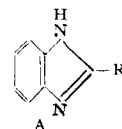


charged forms comparable to (XVIIb), in which no double bond is present in the four-membered ring, are possible; in this light, our views are compatible with the fact that the cyclobutane ring, while causing (VII) to be a very strong acid, has no marked effect on the basicity of (XV), as compared with (XXI).¹¹

We turn now to a consideration of the mechanism of the remarkable change which takes place in the formation of the dimer (VII) from the pyronone (XI). We suggest that the electronic processes (XXIIIa \leftrightarrow XXIIIb) \rightarrow (XXIV) are involved. In view of the appreciable con-



(11) It should be noted that the properties of the base (XV) would appear to require revision of Schwarzenbach's views (*cf.* ref. 10a, p. 1176) with respect to the relatively feebly basic character of the benzimidazoles (A). Thus, if symmetrical resonance in the cation from A is inhibited solely by inclusion of the system within the five-membered ring, (XV) should be a very weak base. But in any event, although the presence of two bonds of order 1.5 within the five-membered ring will undoubtedly occasion some strain in the cation from A, in our view there is no unequivocal ground for assuming that equal, or possibly even greater strain will not be present in the free base; in that case these factors should not be expected to exert a base-weakening effect.

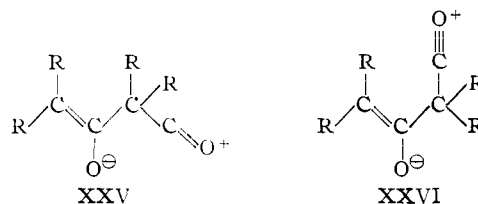


tribution of Dewar states to hybridization in benzene and like molecules,¹² a not inconsiderable contribution of structures such as (XXIIIb) will be expected even in the ground state of the pyronone anion, and the latter in that sense already contains a *quasi* four-membered ring. Beyond that it is likely that (XXIIIb) and related forms contribute to the activated state of the hybrid pyronone anion in sufficiently greater measure to permit direct degradation of the activated ion in the sense (XXIIIb)→(XXIV). The further transformation of (XXIV) by hydrolysis and decarboxylation, to the anion of (VII) requires no special hypotheses, but it may be noted that the decarboxylation might well be concerted with the change (XXIII)→(XXIV).

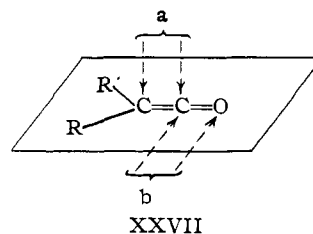
The ultraviolet absorption spectrum of the dimer deserves some further comment. The curve (Fig. 1) appears to be very similar to those observed for dihydroresorcinol, and other enolized cyclic β -diketones.¹³ However, while the position of maximum absorption in the latter case shifts 20–25 $m\mu$ to longer wave lengths in alkaline solution, as a result of conversion of the enols to the corresponding anions, the absorption spectrum of the dimer is substantially the same in neutral and in alkaline media. It is clear that the dimer is so strong an acid that in solutions sufficiently dilute to permit absorption measurements in the ultraviolet it is completely dissociated to the corresponding anion. Consequently, on comparing similar molecular species, it is found that the position of maximum absorption (λ_{max} , 252 $m\mu$) for the anion from the cyclobutane derivative (VII) is displaced 20–30 $m\mu$ to shorter wave lengths as compared with those of analogous anions containing five- (λ_{max} , 272 $m\mu$) and six-membered (λ_{max} , 282 $m\mu$) rings. It may be noted that the inclusion of a simple α,β -unsaturated carbonyl system in a five-membered ring results in a displacement, in a similar sense, of the normal spectrum for that system.¹⁴

It is now established beyond question that the dimerization of methylketene, like that of dimethylketene, leads to the formation of a cyclobutane derivative. In the case of dimethylketene, the cyclobutanedione appears to be very nearly the sole product¹⁵; the extent to which the dimerization of the aldoketene follows an analogous course is not known at present, but it is likely that the reaction takes place simultaneously by two different processes, the one leading to a cyclobutane derivative, and the other to a β -lactone. In any event, no cyclobutane derivative has been identified so far as a product of the dimerization of ketene itself. The inference is

clear that the accumulation of methyl groups favors symmetrical over unsymmetrical dimerization. We should like to point out that if the reaction involves an intermediate such as (XXV),



the steric effect of bulky R groups will favor the orientation (XXVI), which leads to cyclobutane ring formation, over the orientation (XXV), which favors the production of a β -lactone; beyond that, should the dimerization be a direct four-center combination of the two reacting molecules, the steric situation is even more clearly defined. Thus, simultaneous addition of two groups to the carbon-carbon double bond of a ketene must take place from a direction *perpendicular* to the plane in which the ketene molecule lies (arrows a, XXVII). On the other hand, addition to the carbonyl group must take place *in the plane* (arrows b, XXVII). The first



of these processes will be involved in symmetrical dimerization, and the second in the formation of the unsymmetrical dimer. Examination of models reveals that approach in the plane (b, XXVII) is substantially impossible when R = methyl, while no hindrance stands in the way of approach in the alternate direction.

Experimental

Dimethyl α,α' -Dimethylacetonedicarboxylate (VIII) (cf. ref. 6b).—Methyl bromide could be substituted for methyl iodide by conducting the reaction under the pressure exerted by methyl bromide at room temperature. The vapor pressure of the gaseous reagent was counterbalanced by compressed air. Into a five-liter ring-necked flask was poured 360 g. (2.07 moles) of dimethyl acetonedicarboxylate dissolved in an equal weight of absolute methanol. A two-liter dropping funnel was attached to the flask. From a Matheson cylinder enough methyl bromide was admitted into the flask to sweep it clear of air. Next the dropping funnel was swept clear of methyl bromide by air. The condensing agent, prepared by dissolving 95.2 g. (4.14 gram atoms) of sodium in 930 cc. of absolute methanol, was poured into the dropping funnel. The rubber stoppers were securely wired in place. Pressure was applied to the system by simultaneously admitting methyl bromide and compressed air until the full pressure of the compressed air supply (ca. 2 atm.) was exerted on the system. The flask was maintained at 25–30° by means of a water-bath. The condensing agent was gradually introduced from the dropping funnel during a

(12) Pauling and Wheland, *J. Chem. Phys.*, **1**, 362 (1933).

(13) Woodward and Blout (ref. 10, *loc. cit.*); Blout, Eager and Silverman, *THIS JOURNAL*, **68**, 566 (1946).

(14) Gillam and West, *J. Chem. Soc.*, 486 (1942).

(15) Staudinger and Klever (*Ber.*, **40**, 1149 (1907)) mention a liquid dimer of dimethylketene. Very little work was done with this substance, and other workers do not appear to have encountered it.

period of four hours while the flask was intermittently swirled to mix the components. The reaction mixture was allowed to stand overnight.

The pressure was then released. Sufficient water was added to dissolve the crystalline sodium bromide. After separation of the ester layer the aqueous layer was twice extracted with 100-cc. portions of carbon tetrachloride which were combined with the ester. The organic solution was first washed with 50 cc. of dilute hydrochloric acid and then with two 75-cc. portions of water. The carbon tetrachloride was distilled off, and the ester was purified by distillation *in vacuo*. Following a small portion of distillate passing over from 55–103° at 2 mm., 376.5 g. (90.2%) of dimethyl *sym*-dimethylacetonedicarboxylate (b. p. 105–110° at 2 mm.) was obtained.

6-Methoxy-3,5-dimethyl-2,4-pyrone (XI).—The ester was condensed by the use of a very concentrated sulfuric acid mixture according to the Schroeter procedure.⁶ Into a one-liter three-necked flask equipped with an electrically driven stirrer, thermometer and dropping funnel there was placed a concentrated sulfuric acid mixture, consisting of 126.8 g. of concd. sulfuric acid and 273.2 g. of fuming sulfuric acid (20% free sulfur trioxide). This was cooled to 5° by means of an ice-bath. Dimethyl α,α' -dimethylacetonedicarboxylate (96 g.) was added in a dropwise manner so that the temperature of the stirred solution did not rise above 7°. The reaction mixture was allowed to stand overnight.

On the following morning the acid solution was decomposed by pouring into a beaker containing 900 g. of chopped ice. The fine-grained, white precipitate was filtered with suction on a sintered glass funnel, taken up in 600 cc. of 10% sodium carbonate, washed twice with 100-cc. portions of chloroform, reprecipitated with 6 *N* hydrochloric acid, filtered with suction, rinsed three times with small portions of water, sucked as dry as possible, then transferred to a vacuum desiccator and dried over potassium hydroxide. The crude product weighed 24 g. (30%). Crystallization of 8 g. from 200 cc. of purified dioxane gave 3.5 g. of colorless crystalline material, m. p. 156.5–157.0°. Neutralization of a sample of the acid filtrate showed no indication of the presence of the basic dimethoxy-pyrone.

This condensation is particularly sensitive to the concentration of the acid used. The following runs were made according to the above procedure with 12 g. of ester in 50 g. of varied acid mixtures.

Formula (calcd.)	Fuming H ₂ SO ₄ (20% SO ₃), g.	Concd. H ₂ SO ₄ (94.5– 96.5%), g.	Product, g.	Yield, %
H ₂ SO ₄ ·1/5H ₂ O	5.3	44.7	1.5	14.9
H ₂ SO ₄ ·1/6H ₂ O	8.5	41.5	1.65	16.4
H ₂ SO ₄ ·1/8H ₂ O	12.8	37.2	1.2	12.0
H ₂ SO ₄ ·1/9H ₂ O	13.9	36.1	2.2	21.9
H ₂ SO ₄ ·1/10H ₂ O	15.0	35.0	2.2	21.9
H ₂ SO ₄ ·1/12H ₂ O	16.6	33.4	2.35	23.4
H ₂ SO ₄ ·1/15H ₂ O	18.3	31.7	1.04	10.4

It is not known why the third run deviates from the general trend of the variation in yield with concentration of the acid.

Anal. Calcd. for C₈H₁₀O₄: neut. equiv., 170. Found: neut. equiv., 173.

2,6-Dimethoxy-3,5-dimethyl- γ -pyrone (X).—Dimethyl α,α' -dimethylacetonedicarboxylate was condensed by the use of a more highly concentrated sulfuric acid mixture, according to the procedure of Schroeter.⁶

Into a 500-cc. three-necked flask equipped with an electrically driven stirrer, thermometer and dropping funnel there was placed a concentrated sulfuric acid mixture consisting of 30.2 g. of concd. sulfuric acid and 36.1 g. of fuming sulfuric acid. The acid was cooled to 5°. Then 16 g. of dimethyl α,α' -dimethylacetonedicarboxylate was added in a dropwise manner with stirring. The mixture

was allowed to stand at room temperature for twenty-four hours. The sulfuric acid mixture was poured onto 165 g. of chopped ice contained in a beaker. A small amount of flocculent white precipitate formed. This was filtered off with suction, and worked up in the above described manner to yield 1.0 g. of the crude hydroxymethoxydimethyl- γ -pyrone. Upon neutralization of the sulfuric acid filtrate with 10% sodium carbonate solution the basic dimethoxydimethyl- γ -pyrone separated as a voluminous white precipitate which was filtered with suction, dried *in vacuo* (4.0 g., 25%). Crystallization from benzene (10 cc. of benzene per gram of pyrone) yielded 2.0 g., m. p. 159–163°; recrystallization gave 1.5 g. of fat, colorless needles, m. p. 165°.

Action of Baryta on 2,6-Dimethoxy-3,5-dimethyl- γ -pyrone.—Into a 200-cc. ring-necked flask equipped with a reflux condenser 2.5 g. of recrystallized 2,6-dimethoxy-3,5-dimethyl- γ -pyrone (m. p. 164.5–165.0°) was added to a suspension of 18 g. of barium hydroxide octahydrate in 48 cc. of water. The mixture was warmed on the steam-bath for one hour and a quarter. At the end of this time the mixture was cooled in ice. Carbon dioxide was bubbled in until the solution was just acid to litmus, and then about 2 cc. of 10% sodium carbonate solution was added to make the mixture alkaline. With the aid of Johns-Manville Filter-Cel the barium carbonate was removed. The aqueous filtrate was extracted with three 20-cc. portions of ether. Upon distillation of the ether there remained about 1 cc. of a light yellow oil which possessed a sweet ketonic odor. This oil distilled between 95–102° and formed a 2,4-dinitrophenylhydrazone which after crystallization from ethanol melted 155.5–156.0°. Mixed melting point with authentic dinitrophenylhydrazone of diethyl ketone showed no depression.

The aqueous solution was then acidified with dilute hydrochloric acid and extracted four times with 20-cc. portions of ether. Evaporation of the ether left a residue of white solid particles accompanied by 1 cc. of unidentified oil. The white solid was collected (70 mg.), m. p. 125–130°. Crystallization from methanol improved the melting point to 154–157°. A mixed melting point determination with authentic 6-methoxy-3,5-dimethyl-2,4-pyrone (m. p. 156.0–157.0°) showed no depression, m. m. p. 155–157°.

2,6-Dimethoxy-3,5-dimethyl- γ -pyrone (X) from the Action of Diazomethane on 6-Methoxy-3,5-dimethyl-2,4-pyrone.—One gram of 6-methoxy-3,5-dimethyl-2,4-pyrone was placed in a 50-ml. Erlenmeyer flask and covered with a layer of methanol. The flask was cooled in an ice-salt mixture. In small portions 35 cc. of an ethereal solution of diazomethane was added. Gas bubbles were evolved and the yellow color of the diazomethane was rapidly discharged. As the reaction proceeded the solid starting material dissolved. Before complete solution had occurred a granulated, colorless solid crystallized from the cold solution. The completion of this rapid reaction was evidenced by the persistence of the yellow coloration. After standing one-half hour the solvent was evaporated, leaving 0.36 g. of colorless crystalline material, m. p. 153–160°. The product was twice crystallized from benzene to yield crystals melting at 164–165°. A mixed melting point with authentic 2,6-dimethoxy-3,5-dimethyl- γ -pyrone showed no depression, m. m. p. 164–165°.

2,4-Dimethyl- Δ^2 -cyclobutene-3-olone-1 (VII).—This compound was prepared according to Schroeter's procedure⁶ by subjecting the methoxydimethylpyrone to the action of baryta. Into a three-necked flask equipped with stirrer, thermometer and reflux condenser there was added 50 g. of the crude methoxydimethylpyrone to a suspension of 300 g. of barium hydroxide octahydrate in 750 cc. of water. The mixture was warmed on the water-bath to a temperature of 85°. Shortly a precipitate formed which was assumed to be barium carbonate. After a half-hour there was detected at the open end of the reflux condenser the sweet ketonic odor of diethyl ketone, the by-product isolated by Schroeter from this reaction. The reaction was allowed to run for a period of two to two and one-half

hours. Then carbon dioxide was passed in to precipitate excess of barium ion, the solution was filtered free of barium carbonate and concentrated to a very small volume; diethyl ketone passed off with the vapor. Usually best results were obtained by evaporating to near dryness. Spot tests were conducted with concentrated hydrochloric acid to ensure that the solution had been evaporated to a sufficient extent; for only by sufficient concentration would the white solid be formed upon acidification, and then in copious amount, accompanied by a frothing evolution of carbon dioxide. At this point the entire solution was so treated with concentrated hydrochloric acid. The white crystalline solid was then filtered, dried *in vacuo* over potassium hydroxide pellets and then extracted with hot benzene from the accompanying barium chloride. On cooling the benzene solution 5.8 g. of colorless, short needles separated, m. p. 130–131°. Repeated recrystallization from benzene raised the melting point to 138°.

Anal. Calcd. for $C_6H_8O_2$: active H (Zerewitinov), 0.90; CH_3-C , 49.1. Found: active H, 0.84; CH_3-C , 36.8, 41.2.

The compound immediately decolorized aqueous potassium permanganate, and also bromine in carbon tetrachloride. This latter reaction furnished a colorless, crystalline monobromo compound. It crystallized from glacial acetic acid in transparent prisms, m. p. 158° dec.

Anal. Calcd. for $C_6H_7O_2Br$: C, 37.72; H, 3.69; Br, 41.83; neut. equiv., 95.5. Found: C, 38.42; H, 3.87; Br, 39.93; neut. equiv., 96.4, 97.3.

Methylation of Dimethylcyclobutenolone by Diazomethane.—Into a 250-cc. Erlenmeyer flask was poured 4.27 g. (0.038 mole) of dimethylcyclobutenolone and 20 cc. of anhydrous diethyl ether. The flask was cooled in an ice-salt mixture and 100 cc. of an ether solution of diazomethane prepared from 10 g. of nitrosomethylurea (calcd. 97 millimoles of diazomethane) was added in small amounts. There was an immediate and vigorous evolution of gas bubbles. Upon addition of the last 3 cc. all the white solid had dissolved, there was no further evolution of gas and the solution retained the characteristic greenish-yellow hue of the free diazomethane in ether. The mixture stood one hour before the solvent was evaporated. The residual, brownish-yellow, clear oil was distilled at 10 mm.; 2.8 g. passed over at 85–86°. The product was clear, slightly yellow and possessed a pleasantly sweet odor; boiling point 209° (760 mm.) (Sivolobov micro determination), d_{20}^{20} 0.995, n_D^{20} 1.4719. With ferric chloride there is no coloration, although upon standing two hours the same purplish-red color characteristic of the starting material, itself, had developed.

Anal. Calcd. for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 66.61; H, 7.95.

This methylated compound undergoes ready hydrolysis. A drop of the oily product was placed with 5 drops of water in a small test-tube and allowed to stand overnight at room temperature. On the following morning clear crystals were observed. These were filtered and dried in air, m. p. 137–138° dec.; mixed melting point with dimethylcyclobutenolone showed no depression, m. m. p. 138–139°.

Dioxime of Dimethylcyclobutanedione.—There was added 1.2 g. of dimethylcyclobutenolone to a solution made up from 5 g. of hydroxylamine hydrochloride in 30 cc. of water with 20 cc. of 10% sodium hydroxide. The reaction mixture was warmed on the steam-bath for thirty minutes. The reaction mixture on standing overnight deposited small, finely-divided crystals which were filtered off and dried; amount, 1.5 g., m. p. 178–183°; twice crystallized from ethanol, m. p. 198–200° dec.

Anal. Calcd. for $C_6H_{10}O_2N_2$: active H (Zerewitinov), 1.42. Found: active H, 1.40.

Hydrogenation of the Dioxime (XIII).—In a 125-cc. hydrogenation flask there was placed 1.41 g. of the dioxime (0.01 mole) in 75 cc. of glacial acetic acid with 0.17 g. of Adams catalyst. Two and one-half moles of hydro-

gen were absorbed in the first six hours, a total of 3.3 moles in forty-eight hours, at the end of which time the reaction had ceased. The catalyst was filtered off. A portion (*ca.* 1/3) of the filtrate was evaporated to a small volume at the water-pump; the residual, brown, viscous oil was placed in a vacuum desiccator over potassium hydroxide. After a half-hour a brownish deposit was observed to form on the drying agent, so this method of purification was discontinued. The remainder of the filtrate was strongly acidified with *ca.* 10 cc. of concd. hydrochloric acid and then subjected to evaporation at the water pump. The residual solution, *ca.* 20 cc., was transferred to an evaporating dish and placed in a vacuum desiccator over potassium hydroxide. There remained a brownish, gummy solid weighing 1.8 g. which was taken up in 15 cc. of 95% ethanol. The ethanolic solution was filtered free of a small amount of an unidentified colorless, crystalline solid. To the clear ethanol solution was added, in small portions, 25 cc. of diethyl ether over a period of one hour; a suspension was thrown out of solution. After standing overnight there was precipitated a gummy deposit exhibiting some crystalline form. The supernatant liquor was decanted; the flask containing the gum was placed in a vacuum desiccator over potassium hydroxide and the material dried to a solidified froth of bubbles. The supernatant liquid was treated with more ethyl ether and a second crop of precipitated gum was isolated and dried in the same fashion. The frothed material was a light brown solid, easily pulverized, weighing 480 mg. However, a small sample became gummy during the brief exposure to air when transfer to a melting point capillary was attempted. A chloroplatinate derivative was prepared.

Anal. Calcd. for $(C_6H_{10}N_2)_2H_2PtCl_6 \cdot H_2O$: C, 22.23; H, 3.73. Found: C, 22.39; H, 3.97.

Dibenzoyl Derivative of Dimethylcyclobutanediamine (XIV).—In a small test-tube 0.15 g. of the hydrochloride mixture was dissolved in 1 cc. of water. To this solution was added 1 cc. of 20% sodium hydroxide solution. Then there was added in small portions with vigorous shaking 0.2 cc. of freshly distilled benzoyl chloride. Immediately a gummy solid formed. After ten minutes of shaking this was filtered off, washed with water and placed in a vacuum desiccator over potassium hydroxide. The solid was recrystallized three times from 50% aqueous ethanol, m. p. 272°.

Anal. Calcd. for $C_{20}H_{22}O_2N_2$: C, 74.50; H, 6.88; mol. wt., 322; CH_3-C , 16.8; $N-CO-C_6H_5$, 73.9; active H, 0.625. Found: C, 74.57; H, 7.02; mol. wt. (Rast) in camphor, 331; CH_3-C , 12.0; $N-CO-C_6H_5$, 73.51⁶; active H, 0.653. The substance did not decolorize aqueous potassium permanganate or bromine in carbon tetrachloride.

1-Amino-3-imino-2,4-dimethyl- Δ^1 -cyclobutene (XV).—Dropwise addition of 5 cc. of 5 *N* sodium hydroxide to a filtered solution containing 0.18 g. of the above hydrochloride mixture in 2 cc. of water was accompanied by the immediate separation of glistening, colorless plates. The mixture was cooled in ice for some time, and the product was then filtered off and dried *in vacuo* over potassium hydroxide (100 mg.), m. p. 153–157°. This substance is readily soluble in water. Sublimation of the crude product at the pressure afforded by the mechanical pump (bath temperature 145–150°) yielded a fine, fluffy white powder, m. p. 159.5–160.0°, decomposing to a dark red-brown oil following an initial sintering and discoloration. Even though the bath temperature was increased to 160° no further sublimation occurred; there remained a residue of yellow powder.

Anal. Calcd. for $C_6H_{10}N_2$: C, 65.41; H, 9.15. Found: C, 65.90; H, 9.30.

Hydrolysis of 1-Amino-3-imino-2,4-dimethyl- Δ^1 -cyclobutene to 2,4-Dimethyl- Δ^2 -cyclobutene-3-ol-one.—

(16) Inordinately low and non-reproducible results were experienced in using sulfuric acid, aqueous alkali or methanolic alkali as hydrolyzing agent. However, by the use of 100% phosphoric acid, which was prepared according to the method of Olivier (*Rec. trav. chim.*, **48**, 568 (1929)) the hydrolysis could be carried out smoothly.

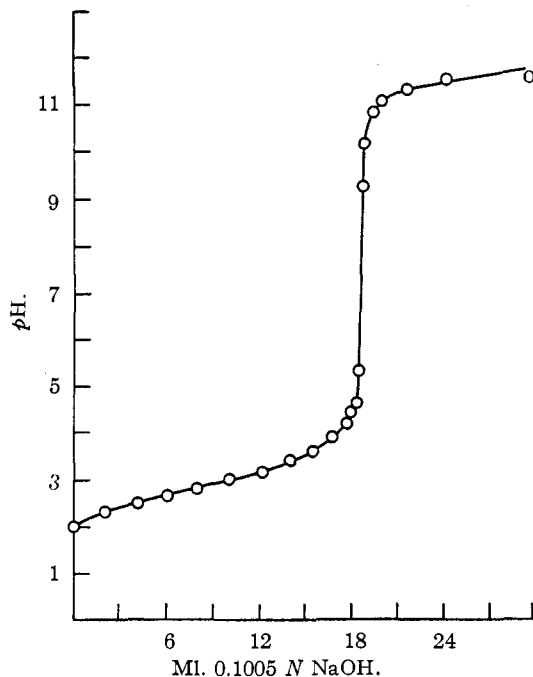


Fig. 2.—Potentiometric titration of 2,4-dimethyl- Δ^2 -cyclobutene-3-ol-one (VII).

Twenty mg. of the base, m. p. 160° , was dissolved in three drops of water. Three drops of 5 *N* sodium hydroxide was added and the solution was gently warmed on the steam-bath, then set aside to stand overnight. On the following morning the solution was acidified with two drops of concentrated hydrochloric acid and the clear solution was evaporated to dryness by a gentle stream of air. The crystalline residue was dried *in vacuo* over potassium hydroxide. A separation of the organic material from sodium chloride was accomplished by extracting with 0.25 ml. of hot benzene, filtering, evaporating the clear filtrate to one-fifth of its original volume and drying *in vacuo* over potassium hydroxide and paraffin wax (10 mg.), m. p. 129 – 130° ; mixed melting point with authentic 2,4-dimethyl- Δ^2 -cyclobutene-3-ol-one (m. p. 136°) 131 – 133° . The product also gave a violet-red ferric chloride test identical with that of dimethylcyclobutenolone.

Anal. Calcd. for $C_8H_8O_2$: neut. equiv., 112.1. Found: neut. equiv., 112.

Potentiometric Titrations.—The instrument used for these determinations was a Beckman pH meter, model G. A 0.05 *M* solution of potassium acid phthalate was used as a standard buffer.

(A) 2,4-Dimethyl- Δ^2 -cyclobutene-3-ol-one (m. p. 139° dec.) was titrated potentiometrically with 0.1005 *N* sodium

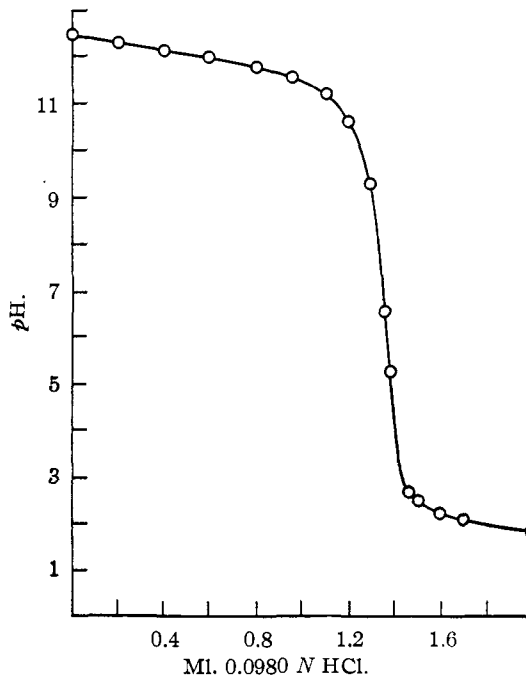


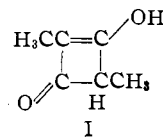
Fig. 3.—Potentiometric titration of 1-amino-3-imino-2,4-dimethyl- Δ^1 -cyclobutene (XV).

hydroxide. Dimethylcyclobutenolone, 0.2132 g. (1.9 μ moles), was dissolved in 19 cc. of water. The results of the titration are graphically represented by the accompanying curve (Fig. 2), from which we deduce pK 2.8.

(B) 1-Amino-3-imino-2,4-dimethyl- Δ^1 -cyclobutene was prepared for titration by dissolving 15.8 mg. of freshly sublimed material in 1.4 ml. of water. This solution was titrated potentiometrically with 0.0980 *N* hydrochloric acid. From the results (Fig. 3) we deduce the value pK ca. 12.

Summary

The structure (I) for the acidic dimer of methylketene is established. The consequences of the inclusion of the enolized β -diketone system



within a cyclobutane ring are discussed.

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