Ketenes. XV. Synthesis and Reactions of 3,3-Dimethyl-1-oxaspiro[3.5]nona-5,8-diene-2,7-dione[1]

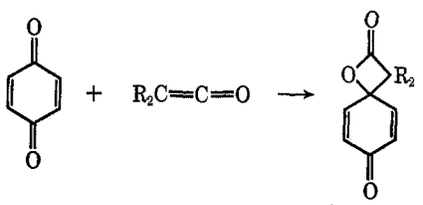
JAMES L. CHITWOOD, P. GLENN GOTT, JAMES J. KRUTAK, SR., AND JAMES C. MARTIN*

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

Received June 11, 1970

3,3-Dimethyl-1-oxaspiro[3.5]nona-5,8-diene-2,7-dione (2) was formed from 1 equiv of dimethylketene and 1 equiv of *p*-benzoquinone in ether solvents at 0 to 25°. The chemistry of this spiro lactone was investigated and compared with that of an analogous compound 1 made from diphenylketene and *p*-benzoquinone. The spiro lactone 2 was found to undergo an acid-catalyzed rearrangement, thermal and photochemical loss of carbon dioxide, and addition reactions such as halogenation, hydrogenation, and Diels–Alder addition.

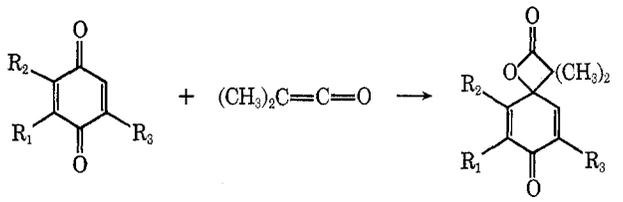
Staudinger and coworkers reported that 1 equiv of *p*-benzoquinone reacted with 1 equiv of diphenylketene at room temperature to give the mono-β-lactone **1**.[2]



1, R = C_6H_5
2, R = CH_3

We found that dimethylketene and *p*-benzoquinone reacted at room temperature in an analogous manner to give 3,3-dimethyl-1-oxaspiro[3.5]nona-5,8-diene-2,7-dione (**2**). The purpose of our work was to study the reactions of the parent compound **2**.

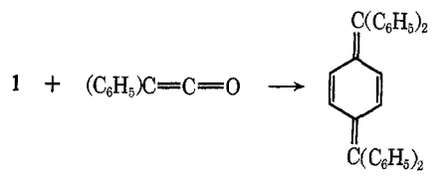
The reaction between dimethylketene and *p*-benzoquinone appears to be general for monoalkyl- and dialkyl-substituted *p*-benzoquinones as shown by the formation of **3** (see Table I); however, tetramethyl-*p*-benzoquinone did not react.



3

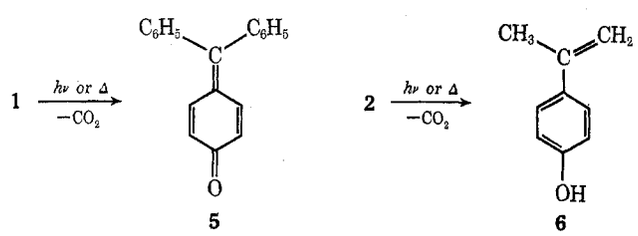
The spiro systems **3** are rich in reactive sites held in a fairly rigid array; therefore, it was of interest to investigate the interaction and reactivity of these sites. Furthermore, the fully substituted β-lactone rings of **1** and **2** might be sterically prevented from reacting as simple β-lactones. It was also desirable to ascertain any differences in reactivity due to variations of steric and electronic properties as a result of dialkyl *vs.* diaryl substitution on the β-lactone ring.

Staudinger found that a second equivalent of diphenylketene reacted with **1**, and by decarboxylation 3,6-bis(diphenylmethylene)-1,4-cyclohexadiene (**4**) was formed in low yields.[2] When a second equivalent of dimethylketene was added to **2**, only polymeric material was obtained.



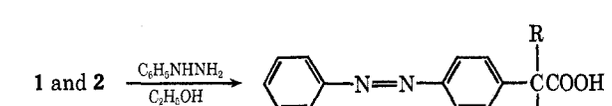
4

Both β-lactones **1** and **2** liberated CO_2 under uv irradiation and upon thermolysis. β-Lactone **1** gave 4-(diphenylmethylene)-2,5-cyclohexadien-1-one (**5**), and **2** gave *p*-isopropenylphenol (**6**) presumably *via* a transient quinonemethide.[3]



5 **6**

Staudinger reported that **1** reacted with phenylhydrazine in dichloromethane at 0° to give the phenylhydrazone derivative.[2] We found that in a protic solvent, ethyl alcohol, either **1** or **2** reacted with phenylhydrazine to give the azo compounds **7** and **8**, respectively. Although both β-lactones, **1** and **2**, lost carbon dioxide, it was reported by Staudinger that **1** reacted with glacial acetic acid to give the lactone **9**;[2] however, our interpretations of nmr and ir spectra indicate that the correct structure of the product is **10**. This assignment is supported by Staudinger's own observation that the reaction product was insoluble in sodium carbonate but soluble in sodium hydroxide and was decomposed by hot alkali into benzilic acid and hydroquinone.



7, R = C_6H_5
8, R = CH_3

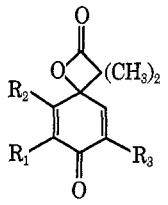
(1) Paper XIV in this series: J. C. Martin, K. C. Brannock, R. D. Burpitt, P. G. Gott, and V. A. Hoyle, Jr., *J. Org. Chem.*, **36**, 2211 (1971).

(2) (a) H. Staudinger, *Justus Liebigs Ann. Chem.*, **356**, 51 (1907); (b) H. Staudinger, *Ber.*, **41**, 1355, 1493 (1908); (c) H. Staudinger and S. Bereza, *Ann Chem.*, **380**, 243 (1911).

(3) This transient quinonemethide can be detected by irradiation of **2** at liquid nitrogen temperature. In the uv spectrum, a 320-mμ band (ε 18,000) can be seen at this temperature.

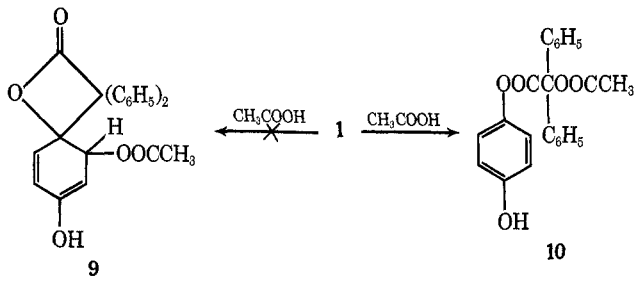
TABLE I

β-LACTONES PREPARED FROM DIMETHYLKETENE AND *p*-BENZOQUINONES[a]

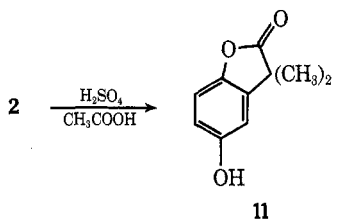


R1	R2	R3	Mp, °C	Yield, %	Nmr (CDCl3), δ H1	H2	H3	H4	CH3	Registry No.
H	H	H	107-109	64	6.49, d	7.26, d	6.49, d	7.26, d	1.48, s, 6	
tert-C_4H_9	H	H	98-99			6.88, m	6.20, d	6.88, m	1.36, s, 3 1.40, s, 3	29818-32-4
-C_4H_4-		H	110-113	70			6.52, d	7.33, d	0.92, s, 3 1.38, s, 3	29818-33-5
CH_3	H	CH_3	135-137	84		6.82, m	6.10, m		1.28, s, 3 1.33, s, 3	29818-34-6

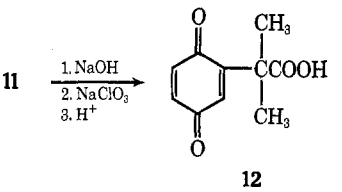
[a] Satisfactory analytical values (±0.35% for C and H) were reported for all compounds in the table: Ed.



Pure β-lactone **2** did not react with glacial acetic acid; however, when a catalytic amount of concentrated H_2SO_4 was added, the γ-lactone **11** was formed in 95% yield. In the infrared spectrum of **11** a shift of the

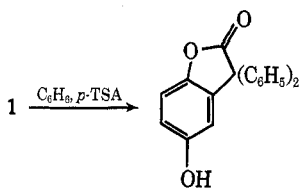


5.66-μ band toward 5.5 μ with increasing dilution in carbon tetrachloride was observed; this shift indicated intermolecular H bonding. The spectral data for this rearrangement product are in agreement with structure **11** or the isomer with the oxygens in a meta relationship. Structure **11** is the correct one because base-promoted opening of the lactone ring gave a substituted hydroquinone which was oxidized to the *p*-benzoquinone derivative **12**. The γ-lactone **11** can be produced directly



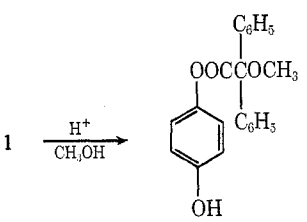
from dimethylketene and *p*-benzoquinone when the solution of **2** is acidified before isolation of the adduct.

We obtained a compound, **13**, analogous to **11** by refluxing **1** in benzene with a trace of *p*-toluenesulfonic acid (*p*-TSA). This rearrangement was reported by Staudinger who also synthesized the product **13** from

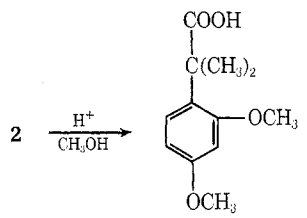


hydroquinone, benzilic acid, and tin(IV) chloride in benzene. Staudinger stated that the rearrangement occurred in refluxing benzene in the presence of light; however, in our work only decarboxylation occurred in benzene (no catalyst) at reflux, under irradiation at room temperature, or under irradiation at reflux.

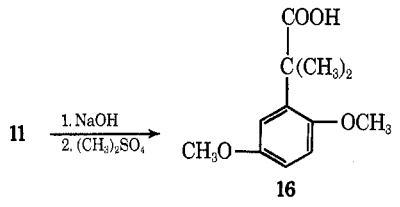
Staudinger reported that methanol reacted with **1** under acid catalysis to give an adduct analogous to **9** which was decomposed by hot alkali into methoxydiphenylacetic acid and hydroquinone.[2] The ir and nmr spectra indicated that the actual structure was **14**, a compound analogous to **10**.



The acid-catalyzed addition of methanol to **2** proceeded in a different fashion to give **15**. The elemental



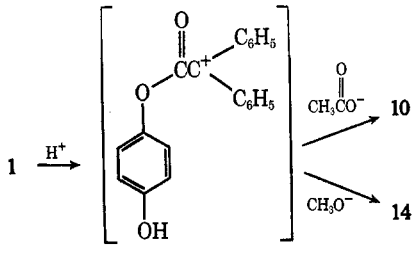
analysis and spectral data were consistent with this assignment. Again, both **15** and one of its isomers, **16**,



fit the spectral data. Compound **16**, synthesized from **11** with dimethyl sulfate, was easily distinguishable from **15** by ir and nmr spectroscopy.

Although both β-lactones, **1** and **2**, lost carbon dioxide upon heating and uv irradiation, and gave similar adducts with phenylhydrazine, the different electronic properties of the two systems fostered divergent reaction pathways under the other reaction conditions studied. The reactions of **1** and **2** in acetic acid and in methanol indicated that the active sites of the β-lactone rings of both systems are sterically hindered. Therefore, the initial attack must occur on the six-membered ring.[4] The possible pathways for these reactions appear in Schemes I and II. For compound **1** (Scheme

SCHEME I



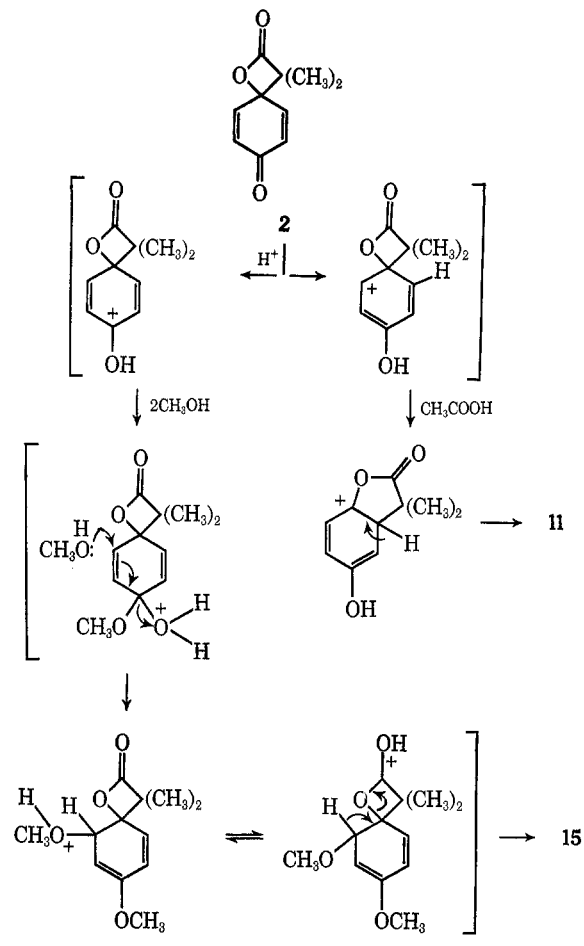
I), the two phenyl groups sufficiently stabilize the positive charge α to the carbonyl to allow the β-lactone ring to open. The cation is then trapped by either an acetate or a methoxide ion to form **10** or **14**, respectively. In benzene, a solvent of low nucleophilicity and low dielectric constant, compound **1** rearranges to relieve ring strain, and the potential cationic center is trapped intramolecularly to give **13**.

For compound **2**, the two methyl groups do not stabilize the cationic center sufficiently to allow ring opening by a pathway analogous to that for **1**. Instead, as shown in Scheme II, a rearrangement occurred in acetic acid with a mineral acid catalyst to give the more stable γ-lactone **11**. Methanol is more nucleophilic than acetic acid, and, in the presence of acid catalyst, it trapped the protonated β-lactone to give **15**.

The remainder of this paper is devoted to the reactions of β-lactone **2**. The halogenation of **2** and the reactions of these halogenated products are summarized in Scheme III. One equivalent of bromine added rapidly to **2** at room temperature to give the dibromide **17**. The second equivalent of bromine added at a much slower rate to give the tetrabromide **18**. These structural assignments are based primarily upon ir and nmr spectral data. The ir spectrum of **17** showed a β-lactone ring (5.48 μ) and an enone (5.90 μ). The nmr spectrum of **17** showed nonequivalent methyl groups as

(4) The normal reaction pathways for simple β-lactones are reviewed by H. E. Zaugg, *Org. React.*, **8**, 305 (1954).

SCHEME II



singlets at δ 1.72 and 1.42. The two vinyl protons appeared as a doublet of doublets at δ 6.68 (1 H) and a doublet of doublets at δ 6.23 (1 H).[5] The higher field signal is due to the vinyl proton adjacent to the carbonyl group since compound **3**, where R_1 = *tert*-C_4H_9 and $R_{2,3}$ = H, has two hydrogen atoms at the lower field position and only one at the higher field position. The protons on the carbons bearing bromine also appeared as doublets at δ 5.06 and 4.70. The δ 4.70 methylidyne proton is coupled to the vinyl proton α to the carbonyl by a coupling constant of 1.5 Hz, indicating that the higher field methylidyne proton is also α to the carbonyl. The β-vinyl proton is coupled to the β-methylidyne proton by a coupling constant of 2.5 Hz. The coupling constant between the two protons on the carbons bearing bromine is 2.5 Hz, indicating that the bromines are either equatorial–axial or axial–axial.[6,7] Since bromination generally proceeds in a trans manner, the bromines are assigned to axial–axial positions. The methyl groups of **18** are also nonequivalent; they appear as two singlets. One pair of adjacent ring protons is

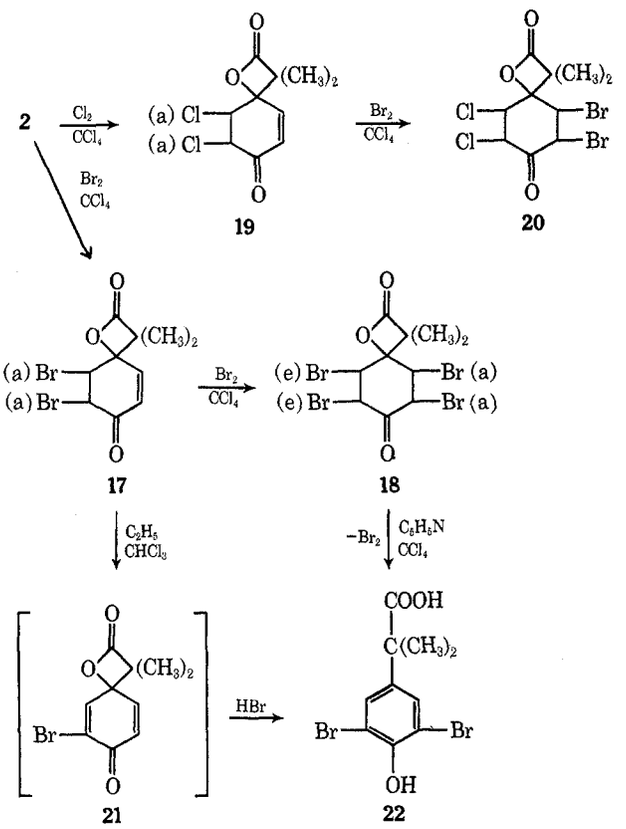
(5) Similar field positions were reported for 4,4-disubstituted-2,5-cyclohexadienones. For a discussion see W. Regel and W. von Philipsborn, *Helv. Chim. Acta*, **52**, 1354 (1969).

(6) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, pp 193, 390.

(7) One reviewer felt that only cis and trans terminology (not axial or equatorial) was relevant in cyclohexenones; however, examination of molecular models suggests that axial and equatorial terms are relevant with the cyclohexenone preferring a monoplaner (half-chair) conformation: E. Toromanoff in "Topics in Stereochemistry," Vol. 2, N. L. Allinger and E. L. Eliel, Ed., Interscience Publishers, New York, N. Y., 1967, p 157.

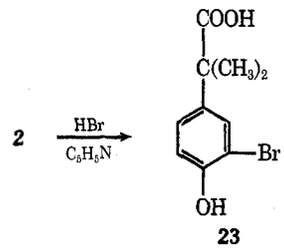
coupled by 3.0 Hz and the other by 11.0 Hz. This coupling suggests that one bromine pair is axial–axial and the other is equatorial–equatorial. In an attempt to obtain additional information about this halogenation reaction, β-lactone **2** was chlorinated to give **19** which was brominated to give **20**; however, the chemical shifts of the protons on the carbons bearing halogen were not sufficiently sensitive to halogen type to determine if the chlorines were equatorial or if the entering bromines were equatorial.[8]

SCHEME III

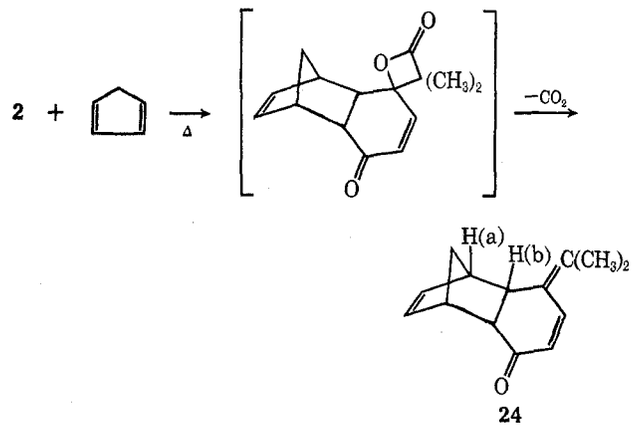


When a few drops of pyridine was added to an nmr tube containing **17** in chloroform-*d*, an elimination–addition reaction took place that could be monitored by nmr. Compound **17** rapidly lost HBr to give **21**. Hydrogen bromide then added to **21** (conjugate addition to the β-lactone ring) to give 3,5-dibromo-4-hydroxy-α-methylhydratropic acid (**22**). This reaction was also run on a preparative scale to give a 75% isolated yield of **22**. This compound also resulted from the rearrangement of **18** in the presence of pyridine. The observation of the readdition of HBr to **21** suggested that under similar conditions HBr might add to the parent β-lactone, **2**. It was found by ir and nmr that HBr did indeed add to **2** to give **23**. The halogen compounds had low thermal stabilities which made mass spectral and elemental analyses difficult.

Even though **2** decarboxylated rapidly at temperatures around 100° and slowly at room temperature, **2** underwent a Diels–Alder addition with cyclopentadiene

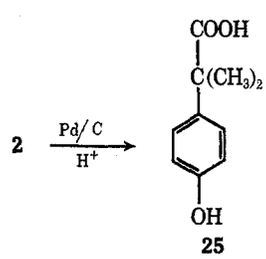


at 40° followed by the loss of CO_2 to give the bicyclic adduct **24**. The six-membered ring appeared to be



exclusively endo to the norbornene system since the coupling constant between protons a and b (4.0 Hz) was of the correct magnitude for the endo configuration.[9]

When **2** was hydrogenated over a palladium/carbon catalyst, the ring-opened product **25** was obtained.



This reaction can be viewed formally as a 1,6 addition of hydrogen.

In conclusion, the differences in the reactivities of β-lactones **1** and **2** can be explained by the greater stability of a positive charge on the tertiary carbon atom α to the carbonyl group for compound **1** (benzylic cation) compared with the stability of the corresponding cation of the dimethyl compound **2**. It was found that the enone system of **2** could react independently of the β-lactone ring but that reactions of the β-lactone ring always involved the enone system with the concomitant energy gain of aromatization.

Experimental Section

Melting points were determined with a calibrated Uni-Melt (Thomas-Hoover) apparatus. The nmr spectra were obtained on a Varian A-60 spectrometer with tetramethylsilane as an internal standard; ir spectra were recorded with Perkin-Elmer Models 137 and 421 spectrometers; uv spectra were provided by a Cary 14 MS spectrophotometer; and mass spectra were obtained on a Consolidated 21-110B mass spectrometer.

(8) One reviewer suggested that the *gem*-dimethyl part of the β-lactone will be preferentially equatorial (over the acyloxy group) once the tetrahalo compound is formed; thus, the stereochemistry of the initial two halogens relative to the β-lactone will determine which halogens are axial or equatorial in the final product.

(9) P. Laszlo and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1171 (1964)

3,3-Dimethyl-1-oxaspiro[3.5]nona-5,8-diene-2,7-dione (2).[10]—Dimethylketene (12.0 ml, 0.14 mol) was added to a stirred solution of 15.0 g (0.14 mol) of *p*-benzoquinone in 100 ml of tetrahydrofuran at 0° under an atmosphere of nitrogen. After 2 hr, the solution was allowed to warm to room temperature. A Dry Ice–acetone condenser prevented the loss of dimethylketene. After 15 hr, the solvent was removed by a rotary evaporator at room temperature and reduced pressure to give a yellow residue. The residue was repeatedly slurried with cold ether–petroleum ether (4:1) and filtered until 13.0 g (52%) of **2** remained as a pure white powder: mp 109° dec; ir (KBr) 5.45, 5.98, and 6.15 μ; nmr ($CDCl_3$) δ 6.68 (d, 2, J = 10 Hz), 6.30 (d, 2, J = 10 Hz), and 1.40 (s, 6); uv max (95% C_2H_5OH) 238 mμ (ϵ 12,254).

Anal. Calcd for $C_{10}H_{10}O_3$: C, 67.41; H, 5.66. Found: C, 67.73; H, 5.77.

Substituted β-Lactones 3.—The procedures employed in the syntheses of these compounds (Table I) were essentially identical with the procedure for the preparation of **2**.

Decarboxylation of 1 to Give 4-(Diphenylmethylene)-2,5-cyclohexadien-1-one (5).—A stirred solution of 1.0 g of **1** in 250 ml of benzene was flushed with helium for 30 min prior to and during an 11-hr irradiation (450-W Hanovia lamp, Pyrex filter). Irradiation occurred through a double-walled quartz immersion well which was cooled by flowing chilled water between the walls to avoid localized heating of the reaction mixture. A thermometer immersed in the benzene solution detected no temperature increase with irradiation. The solution became intensely yellow as the starting material was converted to **5** (ir verification). The solvent was removed at room temperature and reduced pressure to give a quantitative yield of **5**, mp 153–158°. A small sample was recrystallized from benzene–ether to give orange needles: mp 167.5–169.0° (lit.[11] 168°); ir (KBr) 3.30, 6.20, and 6.69 μ; nmr ($CDCl_3$) δ 7.5–7.0 (complex, 12 H) and 6.35 (d, 2, J = 10.0 Hz).

A solution of 1.0 g of **1** in 150 ml of benzene was refluxed for 8 hr. The solution became intensely yellow. The benzene was removed at room temperature and reduced pressure to give a quantitative yield of **5**.

An additional decarboxylation in refluxing benzene under uv light gave only **5**.

Decarboxylation of 2 to Give *p*-Isopropenylphenol (6).—A 400-mg portion of **2** was pyrolyzed through a Vycor tube at 500° under an atmosphere of nitrogen. The effluent was trapped in a liquid nitrogen cooled collection vessel. A 50% yield (150 mg) of **6** was isolated: mp 82–85° (lit.[12] 83–84°); ir (Nujol) 3.05 and 11.25 μ; nmr ($CDCl_3$) δ 7.33 (d, 2, J = 8.5 Hz), 6.75 (d, 2, J = 8.5 Hz), 5.25 (broad s, 1), 5.10 (broad s, 1, OH), 4.96 (m, 1, J = 1.5 Hz), and 2.12 (m, 3, J = 1.0 Hz).

When **2** was irradiated under conditions similar to those employed in the photolysis of **1**, high yields of **6** were obtained.

2-Methyl-2-{*p*-[(*p*-nitrophenyl)azo]phenyl}propionic Acid.—One gram (5.62 mmol) of **2** was added to a solution of 0.861 g (5.62 mmol) of (*p*-nitrophenyl)hydrazine in 40 g of anhydrous ethyl alcohol. The solution was stirred at room temperature for 16 hr and filtered to remove a small amount of insoluble material. The orange filtrate was concentrated *in vacuo*, and the solid that formed was removed by filtration and recrystallized from methanol–chloroform to give 1.3 g (74%) of 2-methyl-2-{*p*-[(*p*-nitrophenyl)azo]phenyl}propionic acid: mp 195–199° dec; ir (KBr) 2.96 (broad), 3.30, 3.42, 5.92, 6.61, and 7.50 μ; nmr ($CDCl_3$) δ 10.9 (broad s, 1), 9.37–7.53 (m, 8), and 1.73 (s, 6); uv max (CH_2Cl_2) 344 mμ (ϵ 26,538); visible max (CH_2Cl_2) 443 mμ (ϵ 1122); mass spectrum (70 ev) m/e 313 (molecular ion).

Anal. Calcd for $C_{16}H_{15}N_3O_4$: C, 61.34; H, 4.83; N, 13.14. Found: C, 61.42; H, 5.00; N, 13.66.

By a similar procedure, the reaction of phenylhydrazine with **1** and **2** gave diphenyl[*p*-(phenylazo)phenyl]acetic acid (**7**) and 2-methyl-2-[*p*-(phenylazo)phenyl]propionic acid (**8**), respectively.

7, 82% yield: mp 199.5–200.5° dec; ir (KBr) 2.97, 3.33, 3.88, 5.93, and 6.3 μ; nmr ($CDCl_3$) δ 9.88 (broad s, 1) and 8.0–7.1 (m, 19); uv max (CH_2Cl_2) 327 mμ (ϵ 22,290); visible max (CH_2Cl_2) 440 mμ (ϵ 948).

Anal. Calcd for $C_{26}H_{20}N_2O_2$: C, 79.57; H, 5.14; N, 7.14. Found: C, 78.19; H, 5.18; N, 6.95.

Esterification of **7** with diazomethane gave the corresponding methyl ester in quantitative yield: mp 164–166°; ir (KBr) 3.28, 3.39, 5.77, and 6.24 μ; nmr ($CDCl_3$) δ 8.00–7.13 (m, with strong line at 7.22, 19) and 3.75 (s, 3); uv max (CH_2Cl_2) 327 mμ (ϵ 21,001); visible max (CH_2Cl_2) 441 mμ (ϵ 894); mass spectrum (70 ev) m/e 406 (molecular ion).

Anal. Calcd for $C_{27}H_{22}N_2O_2$: C, 79.78; H, 5.46; N, 6.89. Found: C, 79.65; H, 5.54; N, 6.78.

8, 60% yield: mp 150.5–152.5°; ir (KBr) 2.75–3.7 (broad), 3.8, 5.9, and 6.25 μ; nmr ($CDCl_3$) δ 10.25 (broad s, 1), 8.01–7.34 (m, 9), and 1.63 (s, 6); uv max (CH_2Cl_2) 324 mμ (ϵ 20,973); visible max (CH_2Cl_2) 440 mμ (ϵ 859).

Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.82; H, 6.17; N, 10.66.

Reaction of 3,3-Diphenyl-1-oxaspiro[3.5]nona-5,8-diene-2,7-dione (1) with Acetic Acid to Give *p*-Hydroxyphenyl Acetoxydiphenylacetate (10).—A slurry of 3.0 g (9.2 mmol) of **1**[2] and 10 ml of glacial acetic acid was stirred for 3 days at room temperature. The slurry was filtered to give 2.9 g (84%) of **10**: mp 158–163° (lit.[2] 163°). A small sample was recrystallized from acetic acid and washed with ether and hexane: mp 165.5–167.5°; ir (KBr) 2.93 (broad), 5.65, and 5.85 μ; nmr ($CDCl_3$) δ 10.3 (broad s, 1), 7.85–7.55 (complex, 5), 7.40–7.00 (complex, 5), 6.82 (s, 4), and 2.05 (s, 3).

Anal. Calcd for $C_{22}H_{18}O_5$: C, 72.92; H, 5.01. Found: C, 72.69; H, 5.08.

Catalyzed Rearrangement of 2 to 3,3-Dimethyl-5-hydroxy-2-(3*H*)-benzofuranone (11).—To a stirred slurry of 1.0 g (5.6 mmol) of **2** in 10 ml of glacial acetic acid was added 8 drops of concentrated H_2SO_4 (pH of slurry ~1). The slurry was stirred for 16 hr at room temperature. The solvent was removed by rotary evaporation at room temperature and reduced pressure. The residue was taken up in ether, washed with a saturated aqueous solution of $NaHCO_3$, and dried ($MgSO_4$). Evaporation of the ether gave 0.95 g (95%) of **11** as a white powder, mp 138–143°. After sublimation at 120° (0.1 mm) the melting point was 149–152°; ir (KBr) 2.95, 5.66, and 6.20 μ (the 5.66 μ bond shifts to lower λ on dilution in CCl_4); nmr ($CDCl_3$) δ 6.9–6.7 (complex, 3), 6.35 (broad s, 1), and 1.50 (s, 6).

Anal. Calcd for $C_{10}H_{10}O_3$: C, 67.40; H, 5.60. Found: C, 67.39; H, 5.94.

Oxidation of 11 to α,α′-Dimethyl-3,6-dioxocyclohexadiene-1-acetic Acid (12).—A 1.0-g (5.6 mmol) portion of **11** was added to a stirred solution of 0.5 g (12.5 mmol) of NaOH in 3 ml of water. The reaction was exothermic and gave a dark red solution. All of **11** went into solution within a few minutes. After the basic solution of **11** cooled to room temperature, an oxidant, made by dissolving 0.34 g (3.1 mmol) of sodium chlorate in 30 ml of 2% aqueous H_2SO_4 and adding *ca.* 100 mg of vanadium oxide,[13] was added with stirring. The resulting solution was basic, and concentrated H_2SO_4 was added dropwise until the solution became acidic. The solution was dark green. Within 4 hr, a large quantity of yellow solid had precipitated. The reaction mixture was stirred an additional 15 hr. The slurry was filtered and the residue was washed with water and a small amount of ether. The pale yellow residue (0.5 g, 46%) was then sublimed at 135° (0.3 mm) to give **12** as a pale yellow powder: mp (sealed capillary) 180–181° dec; ir (KBr) 5.85, 6.02, and 6.25 μ; nmr [$(CD_3)_2SO$] δ 8.3 (broad s, 1), 6.79 (d, 1, J = 1.5 Hz), 6.78 (s, 1), 6.60 (d, 1, J = 1.5 Hz), and 1.36 (s, 6); uv max (95% C_2H_5OH) 244 mμ (ϵ 14,200) and 290 (1300).

Anal. Calcd for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19. Found: C, 61.91; H, 5.17.

Acid-Catalyzed Rearrangement of 1 in Benzene to Give 3,3-Diphenyl-5-hydroxy-2(3*H*)-benzofuranone (13).—A solution of 1.0 g of **1** and 100 mg of *p*-toluenesulfonic acid hydrate in 150 ml of benzene was maintained at reflux for 24 hr. The ir spectrum indicated that all the starting material had been consumed. The solvent was removed by rotary evaporation at room temperature and reduced pressure to give a viscous, dark oil. A red oil was removed from this residue in a sublimation apparatus at 140° (0.1 mm), and 0.85 g (85%) of **13** was left as a tan powder:

(10) Caution! A 100-g portion of **2** which had been stored for 3 days at room temperature in a loosely capped glass jar decomposed violently. We recommend that large-scale preparation of **2** be avoided and that the neat material be stored in small quantities (10 g or less), preferably under refrigeration.

(11) A. Baeyer and V. Villiger, *Ber.*, **36**, 2792 (1903).

(12) B. B. Corson, W. J. Heintzelman, L. H. Schwartzman, H. E. Tiefenthal, R. J. Lokken, J. E. Nickels, G. R. Atwood, and F. J. Pavlik, *J. Org. Chem.*, **23**, 544 (1958).

(13) "Organic Syntheses," Collect Vol. II, Wiley, New York, N. Y., 1943, p 553.

mp 192–195° (lit.[2] 196°); ir (KBr) 2.95 and 5.68 μ; nmr ($CDCl_3$) δ 7.45 (s, 10) and 6.85–6.55 (complex, 4).

Acid-Catalyzed Rearrangement of 1 in Methanol to Give *p*-Hydroxyphenyl Methoxydiphenylacetate (14).—To a stirred slurry of 2.0 g (6.2 mmol) of 1 in 20 ml of methanol was added 6 drops of concentrated H_2SO_4. The resulting solution was stirred 15 hr. The acid was neutralized with a saturated $NaHCO_3$ solution, and the solvent was removed at room temperature and reduced pressure by rotary evaporation. The oil obtained was dissolved in ether and washed with water. The ether layer was separated, dried ($MgSO_4$), and evaporated to give 1.9 g (86%) of a pale yellow solid, mp 117–120°. A small sample was recrystallized from ether acetate–cyclohexane to give 14 as a white solid: mp 121–123° (lit.[3] 122–123°); ir (KBr) 3.00, 5.67, and 5.78 μ; nmr ($CDCl_3$) δ 8.3 (broad s, 1), 7.70–7.20 (complex, 10), 6.78 (s, 4), and 3.22 (s, 3).

Anal. Calcd for $C_{21}H_{18}O_4$: C, 75.43; H, 5.43. Found: C, 75.34; H, 5.54.

Acid-Catalyzed Rearrangement of 2 in Methanol to Give 2,4-Dimethoxy-α-methylhydratropic Acid (15).—To a stirred solution of 2.0 g (11.2 mmol) of 2 in 20 ml of methanol was added 4 drops of concentrated H_2SO_4. The solution was stirred at room temperature for 16 hr. Work-up similar to that for 14 gave 1.2 g (48%) of 15, mp 94–104°. A small sample was recrystallized from ethyl acetate–petroleum ether to give tan crystals: mp 107.5–109°; ir (KBr) 3.4 (broad) and 5.98 μ; nmr ($CDCl_3$) δ 10.7 (broad s, 1), 7.10 (d, 1, J = 9.0 Hz), 6.40 (m, 2, J = 2.0 Hz), 3.72 (s, 3), 3.69 (s, 3), and 1.50 (s, 6).

Anal. Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.09; H, 7.06.

2,5-Dimethoxy-α-methylhydratropic Acid (16).—A 3.0-g (17 mmol) portion of 7 was dissolved in a NaOH solution (4.5 g of NaOH in 30 ml of H_2O). The solution was cooled in an ice bath and 3 ml of dimethyl sulfate was added. After 1 hr, a second 3-ml portion was added. After 10 min, the solution was heated on a steam bath for 2 hr. A solution of 7.0 g of NaOH in 6 ml of water was added, and the mixture was refluxed for 1.5 hr. The solution was cooled, acidified with 10% aqueous HCl, and extracted with three portions of ether. The ether layers were combined, and the ether was evaporated. The residue was dissolved in warm, aqueous $NaHCO_3$, washed with ether, and acidified with 10% aqueous HCl. A solid separated which was collected by filtration and washed with cold pentane to give 2.3 g (61%) of 16, mp 108–111°. A small sample was sublimed at 100° (0.1 mm): mp 110–113°; ir (KBr) 3.4 (broad) and 5.88 μ; nmr ($CDCl_3$) δ 11.1 (broad s, 1), 6.75 (complex, 3), 3.70 (s, 3), 3.65 (s, 3), and 1.50 (s, 6).

Anal. Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.06; H, 7.23.

8,9-Dibromo-3,3-dimethyl-1-oxaspiro[3.5]non-5-ene-2,7-dione (17) from Reaction of 2 with Bromine.—Bromine (3.2 g, 20 mmol) was added in small portions with stirring to a slurry of 3.6 g (20 mmol) of 2 in 50 ml of CCl_4. Near the end of the addition the bromine color began to linger, and the slurry was red after all the bromine had been added. The slurry was filtered and the residue washed with petroleum ether to give 5.9 g (87%) of 17: mp 111.5–112° dec; ir (KBr) 5.45 and 5.90 μ; nmr ($CDCl_3$) δ 6.68 (d of d, 1, J = 11.0 and 2.5 Hz), 6.23 (d of d, 1, J = 11.0 and 1.5 Hz), 5.06 (t, 1, J = 2.5 Hz), 4.70 (d of d, 1, J = 2.5 and 1.5 Hz), 1.72 (s, 3), and 1.42 (s, 3).

Anal. Calcd for $C_{10}H_{10}Br_2O_3$: C, 35.53; H, 2.98; Br, 47.31. Found: C, 35.29; H, 3.05; Br, 47.38.

5,6,8,9-Tetrabromo-3,3-dimethyl-1-oxaspiro[3.5]nonane-2,7-dione (18) from Reaction of 17 with Bromine.—Bromine (1.43 g, 9 mmol) was added with stirring to a slurry of 2.8 g (8.3 mmol) of freshly prepared 17 in 25 ml of CCl_4. Stirring was continued at room temperature for 20 hr. The red slurry was filtered, and the resulting solid was washed with ether–petroleum ether to give 3.1 g (75%) of 18 as a pale yellow powder: mp 129.5–131° dec; ir (Nujol) 5.45 and 5.73 μ; nmr ($CDCl_3$) δ 5.65 (d, 1, J = 11.0 Hz), 5.05 (d, 1, J = 11.0 Hz), 4.92 (d, 1, J = 3.0 Hz), 4.80 (d, 1, J = 3.0 Hz), 1.75 (s, 3), and 1.65 (s, 3); mass spectrum (70 eV) m/e 293 (B), no molecular ion.

Anal. Calcd for $C_{10}H_{10}Br_4O_3$: C, 24.13; H, 2.02. Found: C, 24.29; H, 2.13.

An additional 0.9 g of solid (approximately 1:1 mixture of 17 and 18) was recovered by evaporation of the filtrate. Compound 17 was unstable at room temperature and slowly decomposed with evolution of Br_2 and HBr.

8,9-Dichloro-3,3-dimethyl-1-oxaspiro[3.5]non-5-ene-2,7-dione (19) from Reaction of 2 with Chlorine.—A slurry of 2.0 g (11.2 mmol) of 2 in 25 ml of CCl_4 was stirred under an atmosphere of chlorine for 1.5 hr. After 15 min a yellow-green solution formed, followed by re-formation of a slurry. The solid was filtered to give 2.15 g (77%) of 19: mp 123–125°; ir (KBr) 5.45 and 5.88 μ; nmr ($CDCl_3$) δ 6.78 (d of d, 1, J = 11.0 and 2.5 Hz), 6.26 (d of d, 1, J = 11.0 and 1.5 Hz), 4.96 (d of d, 1, J = 2.5 and 4.0 Hz), 4.46 (d of d, 1, J = 1.5 and 4.0 Hz), and 1.70 (s, 3).

Anal. Calcd for $C_{10}H_{10}Cl_2O_3$: C, 48.3; H, 4.04. Found: C, 48.87; H, 4.12.

5,6-Dibromo-8,9-dichloro-3,3-dimethyl-1-oxaspiro[3.5]nonane-2,7-dione (20) from Reaction of 19 with Bromine.—Bromine (1.43 g, 9 mmol) was added to a stirred slurry of 1.60 g (0.4 mmol) of 19 in 20 ml of CCl_4. The slurry was stirred for 16 hr at room temperature, filtered, and washed with ether–petroleum ether (1:1) to give 2.45 g (93%) of 20 as a white solid: mp 151–155° dec; ir (KBr) 5.46 and 5.72 μ; nmr ($CDCl_3$) δ 5.49 (d, 1, J = 11.0 Hz), 4.96 (d, 1, J = 11.0 Hz), 4.85 (d, 1, J = 2.5 Hz), 4.77 (d, 1, J = 2.5 Hz), 1.75 (s, 3), and 1.58 (s, 3).

Anal. Calcd for $C_{10}H_{10}Br_2Cl_2O_3$: C, 29.4; H, 2.47. Found: C, 29.9; H, 2.56.

3,5-Dibromo-4-hydroxy-α-methylhydratropic Acid (22) by Base-Catalyzed Rearrangement of 17.—A solution of 0.5 g of 17 and 100 μl of pyridine in 24 ml of chloroform was heated at reflux for 15 min. The solvent was removed at reduced pressure. The residue was taken up in ether and extracted with a saturated aqueous $NaHCO_3$ solution. The organic layer gave 0.1 g of 17. The aqueous layer was acidified with concentrated HCl and extracted with ether. The ether layer was dried ($MgSO_4$) and evaporated to give 0.3 g (80% yield at 75% conversion) of 22: mp 166–176°; ir (Nujol) 3.00, 3.5 (broad), and 5.97 μ; nmr ($CDCl_3$) δ 9.6 (broad s, 2), 7.56 (s, 2), and 1.59 (s, 6). High-resolution mass spectrum. Calcd for $C_{10}H_{10}Br_2O_3$: 335.8998. Found: 335.9002.

This rearrangement was also run and monitored in an nmr tube. Compound 17 lost HBr before the first scan could be completed to give 6-bromo-3,3-dimethyl-1-oxaspiro[3.5]nona-5,8-diene-2,7-dione (21): nmr ($CDCl_3$) δ 7.55 (d, 1, J = 3.0 Hz), 7.20 (d of d, 1, J = 3.0 and 10.0 Hz), 6.45 (d, 1, J = 10.0 Hz), 1.46 (s, 3), and 1.42 (s, 3). Compound 21 reacted rapidly with HBr to give 22.

3-Bromo-4-hydroxy-α-methylhydratropic Acid (23) from Reaction of 2 with HBr.—Gaseous HBr was bubbled through a stirred solution of 1.0 g of 2 in 25 ml of chloroform. After the HBr addition was started, 250 μl of pyridine was added and the solution was refluxed for 5 min. The solvent was removed at room temperature and reduced pressure. The residue contained starting material and an acid identified by ir. The residue was dissolved in saturated aqueous $NaHCO_3$, washed with ether, acidified with 10% aqueous HCl, and extracted with ether. The ether solution was dried ($MgSO_4$), and the ether was removed at room temperature and reduced pressure to give 0.8 g (55%) of 23: mp 108–109°; ir (KBr) 3.5 (broad), 3.02, and 5.85 μ; nmr ($CDCl_3$) δ 7.75 (broad s, 2), 7.50–6.65 (complex, 3), and 1.51 (s, 6). High-resolution mass spectrum. Calcd for $C_{10}H_{11}BrO_3$: 257.9904. Found: 257.9908.

endo-**1,4,4a,8a-Tetrahydro-8-isopropylidene-1,4-methanonaphthalen-5-one (24).**—Cyclopentadiene (9.0 g, 0.135 mol) was added to a stirred slurry of 24.0 g (0.135 mol) of 2 in 125 ml of benzene. The slurry was maintained at 40° for 48 hr. A total of 12 ml of solution was withdrawn during the 48-hr period in order to monitor the reaction. The solvent was removed at room temperature and reduced pressure to give 23.0 g (75%) of 24, mp 70–75°. Small amounts of the product were purified by recrystallization from petroleum ether and by sublimation at 75° (0.1 mm): mp 74–75°; ir (Nujol) 6.10 and 6.24 μ; nmr ($CDCl_3$) δ 7.25 (d, 1, J = 10.0 Hz), 5.92 (t, 2, J = 1.5 Hz), 5.57 (d, 1, J = 10.0 Hz), 3.50–3.15 (complex, 3), 2.96 (d of d, 1, J = 4.0 and 9.5 Hz), 2.03 (s, 3), 1.92 (s, 3), and 1.35 (finely split s, 2); uv max (95% C_2H_5OH) 319 (ε 14,234) and 225 (7032); mass spectrum (70 eV) m/e 134 (B), no molecular ion.

Anal. Calcd for $C_{14}H_{10}O$: C, 83.96; H, 8.05. Found: C, 84.14; H, 8.15.

4-Hydroxy-α-methylhydratropic Acid (25).—A solution of 10 g (0.056 mol) of 2 in 100 ml of ethyl acetate was hydrogenated at room temperature over 1.0 g of 5% palladium-on-carbon catalyst at 2.7 atm of hydrogen. The catalyst was removed by filtration and the solvent by evaporation. The residue was slurried in hexane and filtered to give 8.1 g (80%) of 25, mp 149.5–

152.0°. Recrystallization from benzene–ethyl acetate gave 6.0 g of **25** as a white solid: mp 154–155°; ir (KBr) 3.00, 3.4 (broad), and 6.00 μ; nmr [$(CD_3)_2CO$] δ 9.0 (broad s, 2), 7.30 (d, 2, J = 9.0 Hz), 6.75 (d, 2, J = 9.0 Hz), and 1.55 (s, 6).

Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71; mol wt, 180.2. Found: C, 66.28; H, 6.69; mol wt, 178 (ebullioscopic in acetone).

Registry No.—**2**, 29818-35-7; **7**, 29818-36-8; **7** methyl ester, 29818-37-9; **8**, 29818-38-0; **10**, 29818-39-1; **11**, 26172-13-4; **12**, 29818-40-4; **14**, 29843-54-7; **15**, 29913-54-0; **16**, 29913-55-1; **17**, 29913-56-2; **18**, 29818-41-5; **19**, 29818-42-6; **20**, 29818-43-7; **22**, 29818-44-8; **23**, 29818-45-9; **24**, 29818-30-2; **25**, 29913-51-7; 2-methyl-2-{*p*-[(*p*-nitrophenyl)azo]phenyl}propionic acid, 29818-31-3.

Acknowledgment.—We are indebted to Professor Glenn Berchtold for helpful discussions and suggestions during the course of this work.

Ketenes. XVI. The Reactions of Dimethylketene with α-Dicarbonyl and Related Compounds[1]

ROBERT D. BURPITT, KENT C. BRANNOCK, RONALD G. NATIONS, AND JAMES C. MARTIN*

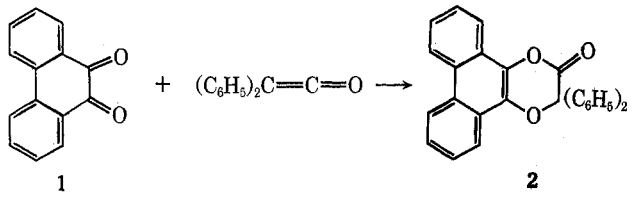
Research Laboratories, Tennessee Eastman Company, Division of Eastman Kodak Company, Kingsport, Tennessee 37662

Received June 11, 1970

Reaction of dimethylketene with benzil and its mono-*p*-tolylimine gave 4,4-dimethyl-1,5-diphenyl-2,6-dioxabicyclo[3.1.0]hexan-3-one (**8**) and 4,4-dimethyl-1,5-diphenyl-2-*p*-tolyl-6-oxa-2-azabicyclo[3.1.0]hexan-3-one (**18**), respectively. These adducts underwent hydrolysis to afford derivatives of 3-phenylhydracrylic acid. Treatment of **8** with boron trifluoride gave 3,3-dimethyl-5,5-diphenyl-2,4(3*H*,5*H*)-furandione (**12**). Dimethylketene reacted with α-dianils to give pyrazinones.

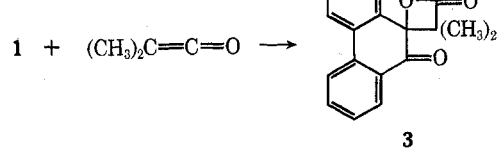
The reactions of ketenes with isolated carbonyl groups to give β-lactones is well known, but their reactions with α-dicarbonyl groups have received little attention. This paper describes the reactions of dimethylketene with α-diketones, α-ketoanils, and α-dianils.

In 1947 Schönberg and Mustafa obtained the cycloadduct **2** from diphenylketene and phenanthrenequinone (**1**) in the presence of sunlight.[2] We also obtained **2**



1 **2**

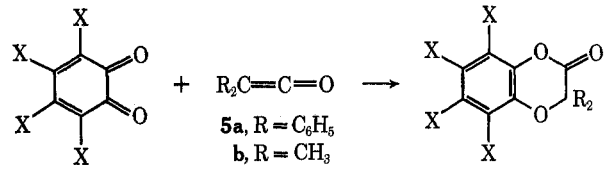
and found that the addition did not require ultraviolet light but proceeded smoothly using a Lewis acid catalyst. Dimethylketene and **1** in the presence of zinc chloride did not react in an analogous fashion but gave the mono β-lactone **3**. Structure **3** was assigned on the



3

basis of its infrared spectrum which showed bands at 5.49 μ (β-lactone carbonyl) and 5.9 μ (ketone carbonyl).

Ried and Radt reported that diphenylketene (**5a**) underwent a 1,4 cycloaddition reaction with the halogenated *o*-quinones **4a** and **4b** to give **6a** and **6b**.[3–5] Dimethylketene (**5b**) reacted similarly to give **6c**.[6]



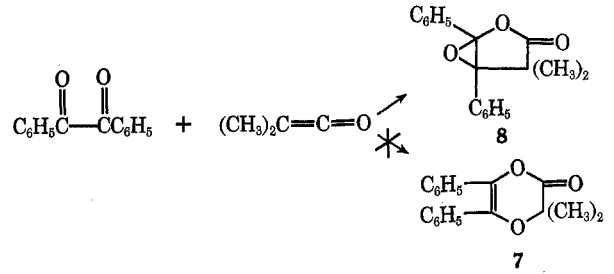
4a, X = Cl; **b**, X = Br

5a, R = C_6H_5; **b**, R = CH_3

6a, X = Cl; R = C_6H_5; **b**, X = Br; R = C_6H_5; **c**, X = Cl; R = CH_3

Several other examples of the 1,4 addition of ketenes[2,6,7] and ketenimines[5] to *o*-quinones have been reported. Hagemeyer reported that ketene combined with 2,3-butanedione to give 3-methyl-3-buten-2-one and 2,3-dimethyl-1,3-butadiene, presumably *via* β-lactone intermediates, but no evidence supporting these structures was presented.[8]

We found that dimethylketene did not react with benzil in the absence of a Lewis acid catalyst. In the presence of zinc chloride reaction occurred, not to give the expected 1:4 cycloadduct **7**, but the bicyclic com-



8

7

(1) Paper XV in this series: J. L. Chitwood, P. G. Gott, J. J. Krutak, Sr., and J. C. Martin, *J. Org. Chem.*, **36**, 2216 (1971).

(2) A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 997 (1947).

(3) W. Ried and W. Radt, *Angew. Chem., Int. Ed. Engl.*, **2**, 397 (1963).

(4) W. Ried and W. Radt, *Justus Liebigs Ann. Chem.*, **676**, 110 (1964).

(5) W. Ried and W. Radt, *ibid.*, **688**, 170 (1965).

(6) L. Horner, E. Spietschka, and A. Gross, *ibid.*, **573**, 17 (1951).

(7) J. L. E. Erickson and J. M. Dechary, *J. Amer. Chem. Soc.*, **74**, 2644 (1952).

(8) H. J. Hagemeyer, *Ind. Eng. Chem.*, **41**, 765 (1949).