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

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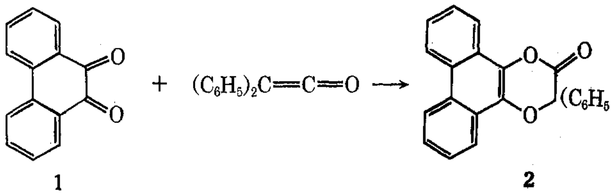
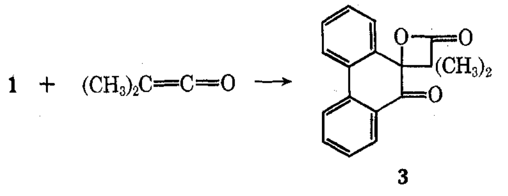
Reaction of dimethylketene with benzil and its mono-p-tolylimine gave 4,4-dimethyl-1,5-diphenyl-2,6-dioxabicyclo[3.1.0]hexan-3-one (**8**) and 4,4-dimethyl-1,5-diphenyl-2-p-tolyl-6-oxa-2-azabicyclo[3.1.0]hexan-3-one (**18**), respectively. These adducts underwent hydrolysis to afford derivatives of 3-phenylhydracrylic 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**

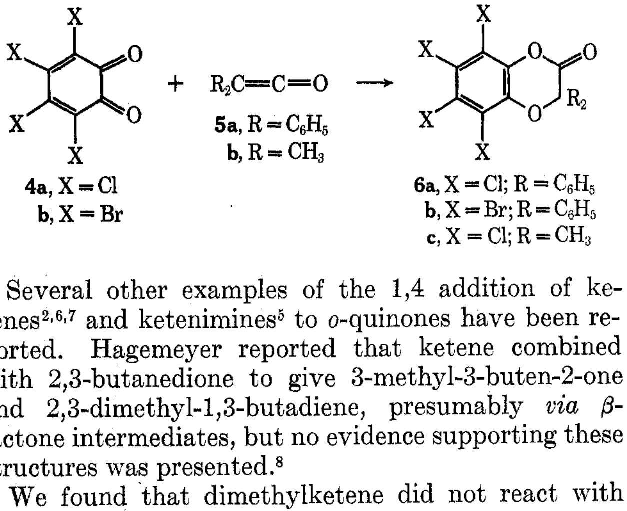


and found that the addition did not require ultraviolet light but proceeded smoothly using a Lewis acid catalyst. Dimethylketene and **1** in the presence of zinc chloride did not react in an analogous fashion but gave the mono β-lactone **3**. Structure **3** was assigned on the



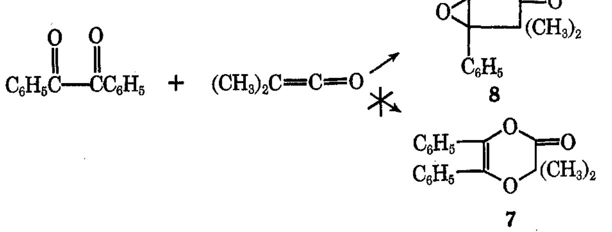
basis of its infrared spectrum which showed bands at 5.49 μ (β-lactone carbonyl) and 5.9 μ (ketone carbonyl).

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]



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-



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[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).

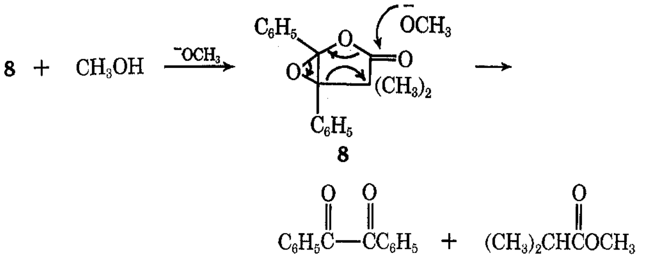
[6] L. Horner, E. Spietschka, and A. Gross, *ibid.*, **573**, 17 (1951).

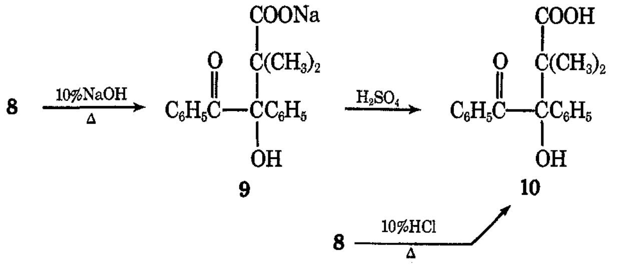
[7] J. L. E. Erickson and J. M. Dechary, *J. Amer. Chem. Soc.*, **74**, 2644 (1952).

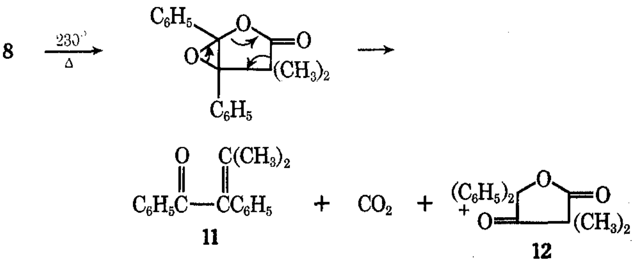
[8] H. J. Hagemeyer, *Ind. Eng. Chem.*, **41**, 765 (1949).

pound **8** in 84% yield. Structure **8** was assigned on the basis of spectral and chemical evidence. In the nmr spectrum the methyl groups of **8** appeared as two singlets at δ 1.20 and 1.47 which did not coalesce on heating in the nmr probe. The methyl groups of **7** would have been expected to appear as a singlet. The uv spectrum of **8** showed reasonable agreement with that reported for *cis*-α,α′-epoxybibenzyl[9] but not for stilbene itself.

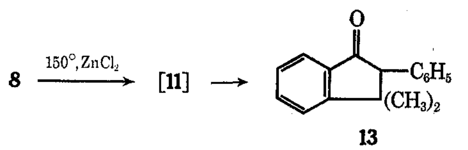
When heated with methanol in the presence of a catalytic amount of sodium methoxide, **8** gave benzil and methyl isobutyrate. The same products could have arisen from structure **7**; however, aqueous base and acid hydrolysis gave products **9** and **10**, respectively, which can only arise from **8**. The sodium salt **9** was extremely insoluble in water, and hot 50% sulfuric acid was necessary to liberate the free acid **10**. Hydrolysis of **8** with 10% lithium hydroxide followed by treatment with hydrochloric acid at room temperature gave a 95% yield of **10**. On thermolysis in the absence of a catalyst, **8** evolved CO_2 and gave 3-methyl-2-phenylcrotonophenone (**11**) as the main product, together with small amounts of 3,3-dimethyl-5,5-diphenyl-2,4(3*H*,5*H*)-furandione (**12**) and benzil.





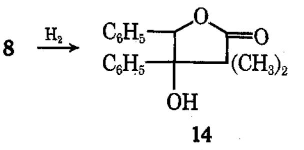


Thermolysis of **8** in the presence of zinc chloride gave 3,3-dimethyl-2-phenyl-1-indanone (**13**) which probably arose from ring closure of **11**.



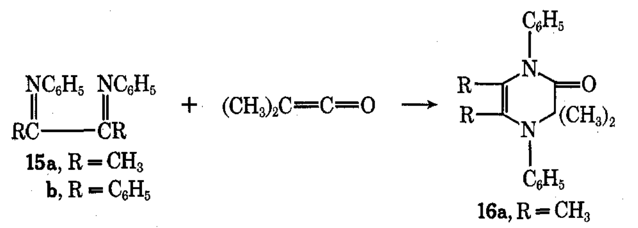
When the reaction of benzil with dimethylketene was carried out in the presence of boron trifluoride instead of zinc chloride, **12** was obtained in 70% yield; however, **8** is probably an intermediate since it is also rearranged to **12** by boron trifluoride.

Hydrogenation of **8** over Raney nickel gave **14** in modest yield.

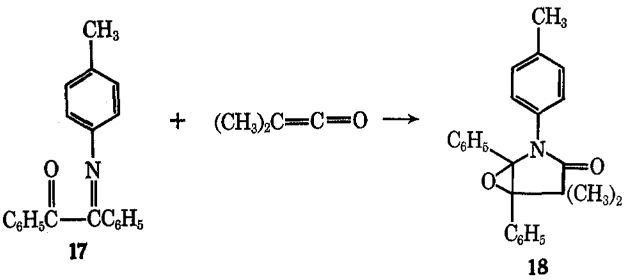


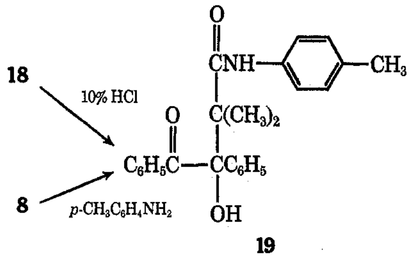
Ketene and diphenylketene did not react with benzil in the presence of zinc chloride. Dimethylketene reacted with 2,3-butanedione in the presence of either zinc chloride or boron trifluoride to give intractable mixtures.

The reaction of the dianils **15a** and **15b** with dimethylketene gave pyrazinones **16a** and **16b**, respectively. No catalyst was necessary. Pfleger and Jäger[10] reported similar results from the 1,4 cycloaddition of phenylketene and diphenylketene to the dianil **15a**.



The α-ketoanil, 2-phenyl-2-(*p*-tolylimino)acetophenone (**17**), reacted with dimethylketene to give 4,4-dimethyl-1,5-diphenyl-2-*p*-tolyl-6-oxa-2-azabicyclo[3.1.0]hexan-3-one (**18**) in 87% yield. The structure assignment for **18** was based on spectral evidence and on the fact that hydrolysis with 10% hydrochloric acid gave **19**, which was also obtained by treatment of **8** with *p*-toluidine.





The reaction of ketenes with α-dicarbonyl compounds is obviously not general but varies with the ketene, the structure and reactivity of the α-dicarbonyl compound, and the catalyst used.

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[9] L. A. Strait, D. Jambotkar, R. Ketcham, and M. Hrenoff, *J. Org. Chem.*, **31**, 3976 (1966).

[10] R. Pfleger and A. Jäger, *Chem. Ber.*, **90**, 2460 (1957).

Experimental Section

3,3-Diphenylphenanthro[9,10-*b*]-*p*-dioxin-2-one (2).[2]—Phenanthrenequinone (5.2 g, 0.025 mol) was added to a solution of 4.8 g (0.025 mol) of diphenylketene in 100 ml of tetrahydrofuran containing 0.5 g of zinc chloride. The solution was stirred overnight and filtered to remove 2.3 g of **2**. The filtrate, when concentrated, gave an additional 4.8 g of **2** (total yield: 7.1 g, 71%): mp 233–235° (lit.[2] mp 227–230°); ir (KBr) 5.61 μ; uv max (CH_2Cl_2) 255 mμ (ϵ 40,737) and 225 (27,158).

3,3-Dimethylspiro[oxetane-2,9′(10′*H*)-phenanthrene]-4,10′-dione (3).—Dimethylketene (2.9 g, 0.034 mol) was added to a solution of 5.2 g (0.025 mol) of phenanthrenequinone in 200 ml of tetrahydrofuran containing 0.5 g of zinc chloride. The mixture was stirred overnight at room temperature and yielded 8 g of viscous oil when the solvent was removed *in vacuo*. A 3-g sample of this crude product was purified by column chromatography; a 500 × 25 mm column packed with 120 g of Grace silica gel, grade 12, 28–200 mesh was used. The elution solvent was an 85:15 petroleum ether–ethyl acetate solution. Twelve 125-ml fractions were collected; fractions 4–12 were combined and yielded 2 g of solid when the solvent was removed *in vacuo*. Recrystallization of this solid from cyclohexane gave 1.62 g (62%) of **3**: mp 108–109°; ir (KBr) 5.49 and 5.9 μ; nmr ($CDCl_3$) δ 0.92 (s, 3), 1.20 (s, 3), and 7.2–8.1 (m, 8); uv max (CH_3OH) 244 mμ (ϵ 53,388) and 204 (41,914).

Anal. Calcd for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07. Found: C, 77.35; H, 5.15.

4,4-Dimethyl-1,5-diphenyl-2,6-dioxabicyclo[3.1.0]hexan-3-one (8).—Dimethylketene (53 g, 0.76 mol) was added in 10-ml portions to a slurry of 105 g (0.5 mol) of benzil in 300 ml of ether containing 1 g of zinc chloride. The reaction was slightly exothermic and the temperature rose to a maximum of 30.5°. The solution was stirred overnight and washed with a 10% K_2CO_3 solution, and the ether was removed *in vacuo*. The residue, when recrystallized from acetonitrile, gave 118 g (84%) of **8**: mp 91–92°; ir (KBr) 5.59 μ; ir (Nujol) 5.61 μ; nmr ($CDCl_3$) δ 1.20 (s, 3), 1.47 (s, 3), and 7.23 (m, 10); uv max (CH_3OH) 208 mμ (ϵ 22,774) and 256 (651).

Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 76.96; H, 5.72.

Treatment of 8 with Methanolic Sodium Methoxide.—**8** (5 g, 0.018 mol) was combined with 15 ml of methanol containing 0.1 g of sodium methoxide, and the solution was refluxed for 2.5 hr. Glpc showed the presence of methyl isobutyrate. The methanol and methyl isobutyrate were removed by distillation, and the residue, when treated with petroleum ether, yielded 3 g (80%) of benzil.

Sodium 3-Benzoyl-2,2-dimethyl-3-phenylhydracrylate (9).—**8** (14 g, 0.05 mol) was combined with a solution of 150 ml of aqueous 10% NaOH, and the mixture was refluxed for 22 hr. The solution was cooled and the product filtered and dried to give 13.5 g (85%) of **9**: mp (as a DTA endotherm) 258°; ir (KBr) 6.0 and 6.4 μ; nmr (CD_3SOCD_3) δ 0.97 (s, 3), 1.20 (s, 3), 7.64 (m, 2), 7.3 (m, 3), and 9.8 (s, 1). An analytical sample was recrystallized from dimethylformamide. Heating 4.75 g of **9** with 75 ml of concentrated HCl gave 4.4 g of recovered **9**. It was necessary to heat the salt with 50% H_2SO_4 in order to obtain the free acid **10**.

3-Benzoyl-2,2-dimethyl-3-phenylhydracrylic Acid (10).—**8** (14 g, 0.05 mol) was combined with 200 ml of aqueous 10% HCl, and the slurry was stirred and refluxed for 2.5 hr. The mixture was cooled and filtered, and the white solid was washed with water and dried to give 14.7 g (99%) of **10**: mp 209.5–210.5°; ir (KBr) 5.96 and 6.03 μ; nmr ($CDCl_3$, CD_3SOCD_3) δ 1.21 (s, 3), 1.26 (s, 3), 6.3 (s, 1), 7.64 (m, 2), 7.3 (m, 3), and 11.4 (s, 1); uv max (CH_3OH) 252 mμ (ϵ 7336). Recrystallization from ethyl acetate gave an analytical sample with mp 210–211°.

Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.55; H, 6.14.

10 was also prepared from **8** and aqueous lithium hydroxide as follows. **8** (14 g, 0.05 mol) was combined with 200 ml of 10% lithium hydroxide solution, and the slurry was stirred and refluxed for 20.5 hr. The resulting lithium salt was collected by filtration and stirred overnight with 100 ml of concentrated HCl. The solid was removed by filtration, washed with water, and dried; the yield of **10** was 14.2 g (95%).

3-Methyl-2-phenylcrotonophenone (11) by Thermolysis of 8.—**8** (14 g, 0.05 mol) was placed in a flask and heated in an oil bath at *ca.* 230° for 2.3 hr. Carbon dioxide, detected by ir, was evolved during the early part of the heating period. The residual oil weighed 12.1 g: ir (neat) 5.58, 5.7, and 6.03 μ. Samples collected by preparative glpc showed the oil to be a mixture of *ca.* 75% **11**, 15% **12**, and 10% benzil.

11: ir (neat) 6.03 μ; nmr ($CDCl_3$) δ 1.75 (s, 3), 1.83 (s, 3), 7.9 (m, 2), and 7.3 (m, 8).

Anal. Calcd for $C_{17}H_{16}O$: C, 86.41; H, 6.82. Found: C, 85.91; H, 6.79.

12: mp 78–80°; ir (neat) 5.58 and 5.7 μ; nmr ($CDCl_3$) δ 1.42 (s, 6), and 7.35 (m, 10).

Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 76.92; H, 5.81.

3,3-Dimethyl-5,5-diphenyl-2,4(3*H*,5*H*)-furandione (12).—Dimethylketene (7.7 g, 0.11 mol) was added in three portions to a solution of 21 g (0.1 mol) of benzil in 150 ml of ether containing 3 ml of boron trifluoride etherate. The mixture was allowed to stand overnight, and removal of the ether *in vacuo* left an oil that crystallized. The crude product, after recrystallization from a mixture of cyclohexane and petroleum ether, gave 19.6 g (70%) of **12**. Glpc showed it to be contaminated with *ca.* 10% **11**.

The rearrangement of **8** to **12** was carried out by treatment of 2.8 g (0.01 mol) of **8** in 10 ml of $CHCl_3$ with 5 drops of boron trifluoride etherate. Removal of the solvent *in vacuo* left 2.8 g of crude **12** contaminated with benzil and **11**, as shown by glpc.

3,3-Dimethyl-2-phenyl-1-indanone (13) by Thermolysis of 8 in the Presence of Zinc Chloride.—**8** (14 g, 0.05 mol) was placed in a flask along with 0.2 g of $ZnCl_2$ and the flask immersed in an oil bath at 150°. Vigorous evolution of gas began immediately and ceased in less than 5 min. The bath temperature was raised to 225° and kept there for 1 hr. The resulting oil crystallized on cooling. Recrystallization from benzene gave 6.2 g (53%) of **13**.

An analytical sample was recrystallized from $CHCl_3$: mp 157–158°; ir (KBr) 5.86 μ; nmr ($CDCl_3$) δ 0.87 (s, 3), 1.53 (s, 3), 3.70 (s, 1), and 6.8–7.8 (m, 9).

Anal. Calcd for $C_{17}H_{16}O$: C, 86.41; H, 6.82. Found: C, 86.39; H, 6.89.

Dihydro-4-hydroxy-3,3-dimethyl-4,5-diphenyl-2(3*H*)-furanone (14).—**8** (14 g, 0.05 mol) was hydrogenated in 200 ml of cyclohexane at 100°, 1500 psi of H_2, over 2 g of Raney nickel for 2 hr. Removal of the catalyst by filtration and removal, *in vacuo*, of the solvent from the filtrate left 14.8 g of a mixture of **14** and **8**. Recrystallization from ethanol gave 4.7 g (42%) of **14**. Concentration of the filtrate gave 3.5 g of **8**. An analytical sample of **14** was obtained by recrystallization from benzene: mp 210–212°; ir (KBr) 5.75 μ; nmr ($CDCl_3$, CD_3SOCD_3) δ 0.86 (s, 3), 1.50 (s, 3), 5.75 (s, 1), 5.90 (s, 1), and 6.8–7.4 (m, 10).

Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.20; H, 6.51.

3,4-Dihydro-3,3,5,6-tetramethyl-1,4-diphenyl-2(1*H*)-pyrazinone (16a).—Dimethylketene (9.8 g, 0.14 mol) was added in six portions to a solution of 23.6 g (0.1 mol) of *N*,*N*′-(dimethylethanediylidene)dianiline (**15a**)[10] in 300 ml of ether. The product began to separate during the addition. The solution was stirred overnight and the ether evaporated to give 29 g (95%) of **16a**. An analytical sample was recrystallized from cyclohexane: mp 160–161°; ir (KBr) 5.71 and 5.99 μ; nmr ($CDCl_3$) δ 1.38 (s, 3), 1.42 (s, 3), 1.82 (s, 6), and 6.5–7.6 (m, 10); uv max (CH_3OH) 203 mμ (ϵ 38,872) and 250 (16,201).

Anal. Calcd for $C_{20}H_{22}N_2O$: C, 78.40; H, 7.25; N, 9.14. Found: C, 78.51; H, 7.30; N, 9.09.

3,4-Dihydro-3,3-dimethyl-1,4,5,6-tetraphenyl-2(1*H*)-pyrazinone (16b).—Dimethylketene (7.0 g, 0.1 mol) was added to a solution of 18 g (0.05 mol) of *N*,*N*′-(diphenylethanediylidene)-dianiline (**15b**)[11] in 100 ml of tetrahydrofuran. The solution, stirred overnight and filtered, yielded 7.3 g of **16b**. Evaporation of the filtrate solvent gave an additional 10.3 g of **16b** (total yield: 17.6 g, 82%). An analytical sample was recrystallized from acetonitrile: mp 198–199°; ir (KBr) 5.69 and 6.09 μ; nmr ($CDCl_3$) δ 0.92 (s, 3), 1.73 (s, 3), and 6.4–7.7 (m, 20); uv max (CH_3OH) 203 mμ (ϵ 50,724).

Anal. Calcd for $C_{30}H_{26}N_2O$: C, 83.69; H, 6.09; N, 6.51. Found: C, 83.68; H, 6.20; N, 6.51.

2-Phenyl-2-(*p*-tolylimino)acetophenone (17).—Benzil (84 g, 0.4 mol) and 51 g of *p*-toluidine were combined and heated at 170–220° for 2.5 hr with slow removal of water. The resulting

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(11) J. S. Walia, J. Singh, M. S. Chattha, and M. Satyanarayana, *Tetrahedron Lett.*, 195 (1969).

oil was cooled and added to ethanol, and the crystals were collected by filtration. The yield of **17** was 72 g (60%): mp 113–114°; ir (KBr) 6.0 and 6.18 μ; nmr ($CDCl_3$) δ 2.27 (s, 3) and 6.4–8.0 (m, 14).

Anal. Calcd for $C_{21}H_{17}NO$: C, 84.25; H, 5.72; N, 4.68. Found: C, 84.13; H, 5.84; N, 4.59.

4,4-Dimethyl-1,5-diphenyl-2-*p*-tolyl-6-oxa-2-azabicyclo[3.1.0]-hexan-3-one (18).—Dimethylketene (7.7 g, 0.11 mol) was added in two portions to a solution of 30 g (0.1 mol) of **17** in 250 ml of ether. The temperature rose to 34°, and product began to separate after about 0.5 hr. The mixture, stirred overnight and filtered, gave 26 g (71%) of **18**: mp 183–184°; ir (KBr) 5.75 μ; nmr ($CDCl_3$) δ 1.21 (s, 3), 1.43 (s, 3), 2.05 (s, 3), and 6.8–7.5 (m, 14).

Anal. Calcd for $C_{25}H_{23}NO_2$: C, 81.27; H, 6.27; N, 3.79. Found: C, 81.26; H, 6.41; N, 3.51.

3-Benzoyl-2,2-dimethyl-3-phenyl-*p*-hydracrylotoluidide (19).—**18** (5 g, 0.014 mol) was combined with 75 ml of aqueous 10% HCl and the mixture refluxed with stirring for 4 hr. An ir spectrum of the crude material showed a band at 5.73 μ (starting material). The solid was dried, ground in a mortar, and refluxed for an additional 2 hr in 75 ml of aqueous 10% HCl. Filtration of the cooled solution gave 4.6 g (88%) of crude **19**. An analytical sample was recrystallized from xylene: mp 216–217°; ir (Nujol) 6.0 μ; nmr ($CDCl_3$, CD_3SOCD_3) δ 1.02 (s, 3), 1.60 (s, 3), 2.24 (s, 3), 5.17 (s, 1), 7.45 (m, 2), and 6.6–7.3 (m, 12).

Anal. Calcd for $C_{25}H_{25}NO_3$: C, 77.49; H, 6.50; N, 3.61. Found: C, 77.49; H, 6.58; N, 3.30.

19 was also obtained by treatment of **8** with *p*-toluidine. **8** (14 g, 0.05 mol) and 5.35 g (0.05 mol) of *p*-toluidine were combined and heated at 100° for 1 hr. The ir spectrum showed a new band at 6.0 μ. An additional 0.05 mol of *p*-toluidine was added and the mixture heated at 150° for 2 hr. The oil was cooled and treated with cyclohexane to give 5.9 g (31%) of **19**.

Registry No.—**3**, 29689-76-7; **8**, 29689-77-8; **9**, 29689-78-9; **10**, 29689-79-0; **11**, 29689-80-3; **12**, 29689-81-4; **13**, 29689-82-5; **14**, 29689-83-6; **16a**, 29689-84-7; **16b**, 29689-85-8; **17**, 29689-86-9; **18**, 29784-79-0; **19**, 29784-80-3; dimethylketene, 598-26-5.

Some Reactions of Tetramethylallene

JAMES C. MARTIN,* PHILIP L. CARTER, AND JAMES L. CHITWOOD

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

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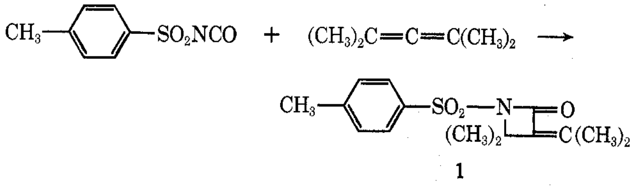
Tetramethyllallene (TMA) reacted with sulfonyl isocyanate *via* a 2 + 2 cycloaddition to give the azetidinone **1**. Trichloroacetyl isocyanate and TMA reacted *via* a 4 + 2 cycloaddition to give **2**, which rearranged readily to the acyclic product **3**. TMA reacted thermally with acrylonitrile to give a mixture of the cyclobutane **4** and the acyclic diene **5**. Dimethyl acetylenedicarboxylate and TMA reacted to afford a mixture of the isomeric trienes **9** and **10**.

The purpose of this paper is to report some of the reactions of tetramethylallene (TMA) with activated isocyanates, electron-deficient olefins, and acetylenes.

TMA undergoes facile cycloaddition reactions with heterocumulenes. The reactions of TMA with dimethylketene and diphenylketene have been reported.[1] Moriconi and Kelly[2,3] have reported the cycloaddition of chlorosulfonyl isocyanate to TMA and other allenes. In agreement with Moriconi's work, we found that activated isocyanates react readily with TMA. *p*-Tolylsulfonyl isocyanate and TMA, when warmed in benzene, gave 3-isopropylidene-4,4-dimethyl-1-(*p*-tolylsulfonyl)-2-azetidinone (**1**) in 67% yield.



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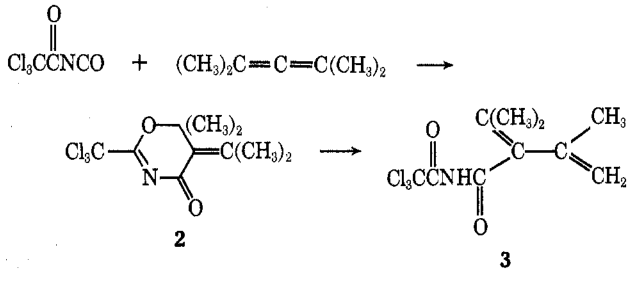
Interestingly, replacement of the *p*-tolylsulfonyl moiety by a trichloroacetyl group results in facile formation of **2**, a 1,4 cycloadduct of a type not available from sulfonyl isocyanates. The reaction between trichloroacetyl isocyanate and TMA in carbon tetrachloride at ambient temperature was followed by nmr. The complete conversion to **2** required about 18 hr and was evidenced by the disappearance of the TMA singlet and the appearance of three singlets characteristic of the methyl groups of **2**.



After 9 days at room temperature, **2** had completely rearranged to **3**, as evidenced by the disappearance of the spectrum of **2** and the appearance of a new spectrum characteristic of **3**. A preparative run gave **3** in 82% yield.

The thermal reaction of TMA with electron-deficient olefins was reported to yield six-membered-ring products, resulting from a preliminary isomerization of the allene to 2,4-dimethyl-1,3-pentadiene (**7**) followed by a Diels–Alder reaction.[4] Instead, we found that the reaction of TMA and acrylonitrile at 150° gave a 73% conversion to a 3:2 mixture of 3-isopropylidene-2,2-dimethylcyclobutanecarbonitrile (**4**) and 4-isopropenyl-5-methyl-4-hexenenitrile (**5**). None of the reported product (**6**) was found, but, when TMA was deliberately isomerized to the conjugated diene **7** and then heated with acrylonitrile, the cyclohexene **6** was the exclusive product.

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[1] J. C. Martin, P. G. Gott, V. W. Goodlett, and R. H. Hasek, *J. Org. Chem.*, **30**, 4175 (1965).

[2] E. J. Moriconi and J. F. Kelly, *J. Amer. Chem. Soc.*, **88**, 3657 (1966).

[3] E. J. Moriconi and J. F. Kelly, *J. Org. Chem.*, **33**, 3036 (1968).

[4] D. R. Taylor and D. B. Wright, *Chem. Commun.*, 434 (1968).