melting point and comparison of its ir spectrum with that of an authentic sample.

**Isolation of p-(1,1,3,3-Tetramethylbutyl)phenyl p-[2-Hydroxy-5-(1,1,3,3-tetramethylbutyl)benzoyl]benzoate (2).**—A solution of 2.0 g of 1 in 150 ml of anhydrous dioxane was placed in a Pyrex glass test tube and irradiated with a 550-W Hanovia mercury arc for 37 hr. The yellow solution was evaporated to a paste, and the residue was taken up in acetone. The insoluble material, 1.0 g, was filtered out and the filtrate was concentrated, cooled in dry ice, and filtered. Five recrystallizations of the yellow precipitate from acetone–water produced a material, mp 156–157°, identified as 2: ir (KBr) 1631 (C=O), 1743 $cm^{-1}$ (C=O); nmr ($CDCl_3$) singlet at 11.7 ppm (1 H, OH).

*Anal.* Calcd for $C_{36}H_{46}O_4$: C, 79.68; H, 8.54; O, 11.80. Found: C, 79.68; H, 8.54; O, 11.48.

**Isolation of p-[2-Hydroxy-5-(1,1,3,3-tetramethylbutyl)benzoyl]benzoic Acid (5).**—A solution of 12.0 g of 1 in 600 ml of dioxane (0.5% water) was irradiated for 26 hr with a 2.5-W 2537-Å immersion lamp. The yellow solution was evaporated to a paste and the residue was taken up in ether. The ether solution was filtered and then shaken with a 10% sodium hydroxide solution. The yellow precipitate formed was dissolved in warm water, and the resulting solution was acidified with hydrochloric acid. The precipitate was collected and sublimed at 0.5 mm pressure and 206° bath temperature. The initial fraction was discarded and the yellow, crystalline material, mp 196–197°, was identified as 5: ir (KBr) 1628 (C=O), 1692 $cm^{-1}$ (C=O); nmr singlet at 11.8 ppm (2 H, OH and $CO_2H$).

*Anal.* Calcd for $C_{22}H_{26}O_4$: C, 74.70; H, 7.41; O, 17.89. Found: C, 74.92; H, 7.54; O, 17.54.

**Isolation of Terephthalic Acid.**—A solution of 1.0 g of 1 in 100 ml of 10:1 dioxane–water solution was irradiated for 48 hr in several Pyrex glass tubes with a 550-W Hanovia mercury arc. The solutions were combined and evaporated to dryness on a steam bath. The residue was extracted with warm sodium bicarbonate solution. The sodium bicarbonate solution was acidified with 6 *N* hydrochloric acid and filtered. The precipitate was washed with water and ether. The precipitate had a melting point greater than 300° and its ir spectrum was identical with that of a known sample of terephthalic acid.

**Photolysis of 1 in Polystyrene.**—A hot solution of 4.0 g of polystyrene and 0.08 g of 1 in 100 ml of methylene chloride was poured into a petri dish and allowed to stand until a hard film was obtained. The dish was then left overnight on a hot plate set at 50°. Half of the resulting film was irradiated in a Rayonet reactor (3100-Å lamps) for 48 hr. Samples (approximately 0.50 g) of the above films were dissolved in 50 ml of methylene chloride containing 4.0 ml of a 0.30% solution of *o*-hydroxybenzophenone (glc internal standard). The resulting solutions were cooled, diluted with 200 ml of acetone, filtered, and evaporated to dryness in a rotary evaporator. The residue was taken up in 2 ml of dioxane. A 0.2-ml portion of this solution was treated with 1.0 ml of Tri-Sil and chromatographed as previously described. As a control, a solution of 1 in benzene at the same concentration was photolyzed under the same conditions.

**Registry No.**—1, 3637-39-6; 2, 26157-65-3; 4, 26157-66-4; 5, 26157-67-5.

**Acknowledgment.**—The authors gratefully acknowledge the help of Professor David Whitten, of the University of North Carolina, with whom many fruitful discussions of this work were held.

# Photolysis of 2,2,5,5-Tetramethyldihydro-3-furanone[1,2]

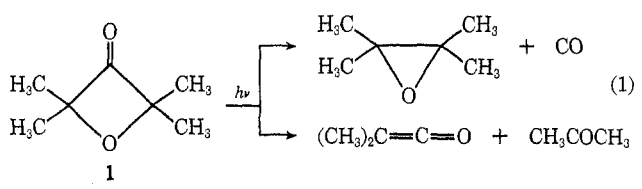
GRAHAM HAGENS, JOHN P. WASACZ, MADELEINE JOULLIÉ, AND PETER YATES*

*Departments of Chemistry of the University of Pennsylvania, Philadelphia, Pennsylvania 19104, and the University of Toronto, Toronto 5, Ontario, Canada*

*Received May 4, 1970*

The photolysis of 2,2,5,5-tetramethyldihydro-3-furanone in methanol gives methyl 3-isopropoxy-3-methylbutanoate, methyl 3-methyl-2-butenoate, isopropyl 3-methyl-2-butenoate, methyl 3-methyl-3-butenoate, and isopropyl alcohol. These products are all considered to arise *via* the ketene formed by Norrish type I cleavage of the dihydrofuranone followed by intramolecular hydrogen abstraction. Corroboration for this view is provided by the observation that photolysis of 2,2,5,5-tetramethyldihydro-3-furanone-*4*-$d_2$ in methanol gives methyl 3-(isopropoxy-*1*-*d*)-3-methylbutanoate-*2*-*d* and methyl 3-methyl-2-butenoate-*2*-*d*.

Although the photolysis of cyclic ketones has been studied extensively, the only previous investigation of the photolysis of an oxacycloalkanone appears to be that of Hammond and coworkers,[3] who found that 2,2,4,4-tetramethyl-3-oxetanone (1) undergoes both decarbonylation and cleavage to a ketene and ketone (eq 1). These reactions are closely analogous to reactions observed in the case of cyclobutanones,[4] and were interpreted as involving initial Norrish type I cleavage of the oxetanone.




(1)

1

We report now a study of the photolysis of the related 2,2,5,5-tetramethyldihydro-3-furanone (2) in methanol. This investigation was undertaken (1) to extend our knowledge of the photochemistry of oxacycloalkanones, and (2) as part of the search for new cases of the photochemical conversion of cyclic ketones to cyclic acetals.[2] With respect to the latter quest, it was considered that the absence of hydrogen atoms at the ring atoms bearing a $\beta$ relationship to the carbonyl group might inhibit alkenal formation[5] and that the circumstance that the ring is five membered might inhibit ketene formation.[6] It was hoped that if these two pathways were thus made more difficult, an oxacarbene[2] might be formed, leading to the formation of a cyclic acetal. In the event, however, this goal was not achieved.

* Author to whom correspondence should be addressed.

(1) Taken from dissertations presented by J. P. Wasacz and G. R. Hagens in partial fulfillment of the requirements of the Ph.D. degree at the University of Pennsylvania, 1969, and the University of Toronto, 1970, respectively.

(2) Part of this work was discussed at the Second IUPAC Symposium on Photochemistry, Enschede, Holland, 1967; P. Yates, *Pure Appl. Chem.*, **16**, 93 (1968).

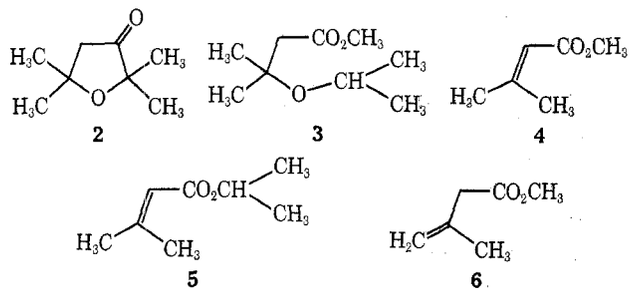
(3) P. J. Wagner, C. A. Stout, S. Searles, Jr., and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 1242 (1966).

(4) N. J. Turro and R. M. Southam, *Tetrahedron Lett.*, 545 (1967); D. R. Morton, E. Lee-Ruff, R. M. Southam, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 4349 (1970).

(5) R. Srinivasan, *ibid.*, **81**, 1546 (1959).

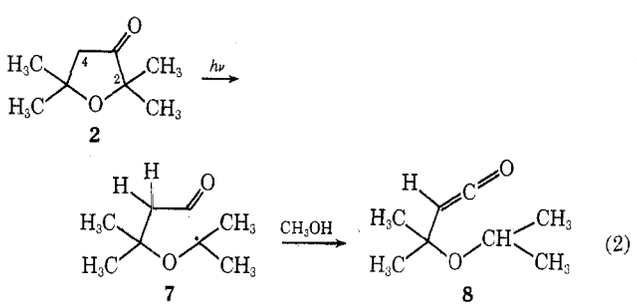
(6) G. Quinkert, *Pure Appl. Chem.*, **9**, 607 (1964).

Irradiation of dilute methanolic solutions of **2** in a Pyrex vessel with a medium-pressure mercury arc lamp gave methyl 3-isopropoxy-3-methylbutanoate (**3**), methyl 3-methyl-2-butenoate (**4**), and isopropyl 3-methyl-2-butenoate (**5**).[7] Vapor phase chromatography (vpc) indicated that the relative yields of these products were *ca.* 9:23:1; the formation of isopropyl alcohol was also detected by vpc. When the photolysis of **2** was carried out in the presence of sodium carbonate, the product mixture was greatly enriched in **3**. Photolysis of **2** in methanol containing a small amount of sulfuric acid gave **4** almost entirely. Photolysis of **2** in pentane gave **5** as the only significant volatile product. When the irrradiation of **2** in methanol was carried out by immersion of the lamp in the solution, the formation of **5** was not observed, but a new product, methyl 3-methyl-3-butenoate (**6**), was detected.



**2** **3** **4** **5** **6**

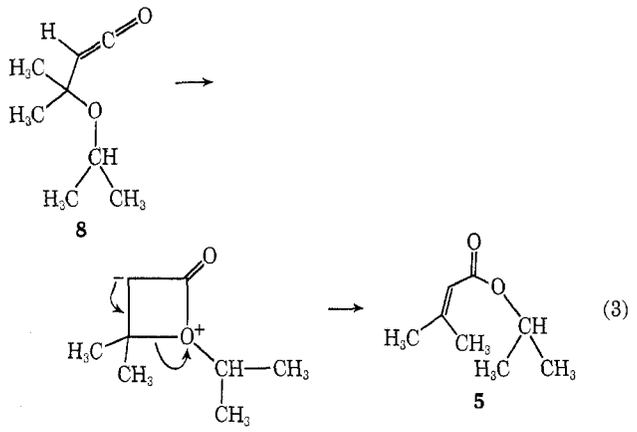
These observations can be interpreted in terms of the intermediacy of the ketene **8**, formed *via* Norrish type I cleavage of the more highly substituted[6] carbon–carbon bond adjacent to the carbonyl group of **2** to give **7** (eq 2). Reaction of this ketene with methanol in the normal fashion accounts for the formation of **3**.



**2** **7** **8** (2)

The formation of increased amounts of **4** when the reaction is carried out in the presence of acid and of increased amounts of **3** when the reaction is carried out in the presence of base indicates that **4** arises, at least in major part, by acid-catalyzed elimination of isopropyl alcohol from **3**. That such a reaction can occur in the dark was established by boiling a solution of **3** in methanol containing sulfuric acid for a brief period and demonstrating the formation of **4** and isopropyl alcohol.

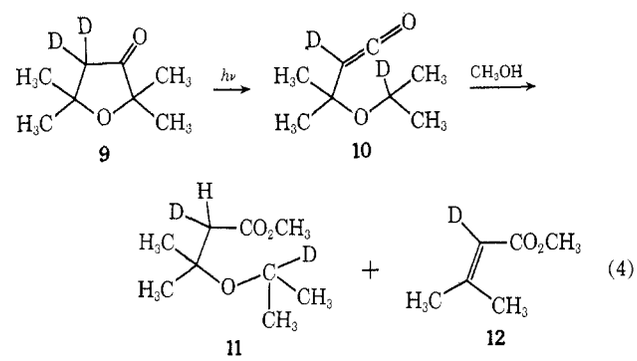
The formation of **5** from **2** in methanolic solution might result from alcoholysis of **4** by the isopropyl alcohol eliminated in the formation of the latter. However, this is unlikely to be a significant pathway in dilute methanolic solution. Its formation is best interpreted as involving intramolecular attack of the ether oxygen atom on the ketene function in **8** (eq 3). Such a route can also account for the formation of **5** as the major volatile product from **2** in pentane.



**8** **5** (3)

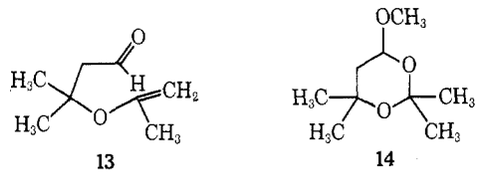
The formation of the $\beta,\gamma$-unsaturated ester **6** can be interpreted as involving the photoisomerization of the corresponding $\alpha,\beta$-unsaturated ester **4**. Such isomerization has been reported previously by Jorgenson and Gundel,[8] and its occurrence in the present case was confirmed by irradiation of **4**. The fact that formation of **6** from **2** was observed only when the ultraviolet radiation was not filtered by a Pyrex vessel is in accord with expectation in that direct excitation of the $\alpha,\beta$-unsaturated ester **3** would require radiation of shorter wavelength than that transmitted by Pyrex.

The postulated intramolecular transfer of a hydrogen atom from C-4 to C-2 in **7** in the formation of the intermediate ketene **8** (eq 2) has been confirmed by deuterium labeling at C-4. Irradiation of **9** gave **11** and **12**, the products anticipated from the ketene **10** (eq 4).



**9** **10** **11** **12** (4)

Thus, all the photoproducts obtained from **2** are most probably derived from the ketene **8**, formed by intramolecular hydrogen abstraction in the Norrish type I cleavage product **7**; no products derived *via* alternative hydrogen abstraction processes in **7**, *e.g.*, **13**, or *via* carbon–oxygen bond formation in **7**, *e.g.*, **14**, could be detected. The failure to form the unsaturated aldehyde



**13** **14**

is not surprising, since its formation requires an unfavorable hydrogen abstraction from a methyl group in

(7) See Experimental Section for identification of products.

(8) M. J. Jorgenson and L. Gundel, *Tetrahedron Lett.*, 4991 (1968).

7. The exclusive formation of **8** is noteworthy, however, since it has previously been found that the hydrogen abstraction process leading to ketene formation is unfavorable in the case of the Norrish type I cleavage products formed from five-membered cyclic ketones.[6] The failure of oxacarbene formation to compete with ketene formation in this case reveals the very unfavorable nature of this reaction relative to ketene formation and places severe structural restrictions on those cyclic ketones that may be expected to undergo this reaction.

## Experimental Section

The ultraviolet light source was a 450-W Hanovia Type L medium pressure mercury arc lamp; irradiation of solutions was carried out in Pyrex tubes placed close to the light source, unless otherwise specified. Infrared and nmr spectra were recorded in carbon tetrachloride solution. Analysis by vpc was carried out on a 10 ft × 0.25 in. column of 10% SE-30 on 80–100 Chromosorb W at 150°, unless otherwise specified. Preparative vpc was carried out on a 20 ft × 0.25 in. column of 10% silicone rubber on 45–60 Chromosorb W at 100–110° (injection port, 180°) with a helium flow rate of 120 ml/min; retention times are reported relative to air, coinjected as reference.

**Photolysis of 2,2,5,5-Tetramethyldihydro-3-furanone (2). A.**—A solution of 2,2,5,5-tetramethyldihydro-3-furanone (**2**)[9] (2.00 g) in methanol (100 ml) was irradiated for 5 days. Analysis by vpc showed that all the starting material had been consumed and that methyl 3-isopropoxy-3-methylbutanoate (**3**), methyl 3-methyl-2-butenoate (**4**), and isopropyl 3-methyl-2-butenoate (**5**) were formed in the ratio *ca.* 9:23:1; vpc analysis at 30° showed that isopropyl alcohol was also formed.

**B.**—To a solution of **2** (2.00 g) in methanol (50 ml) was added sodium carbonate (0.10 g). The mixture was irradiated for 75 hr, after which time vpc analysis revealed that 55% of **2** remained and that compounds **3** and **5** were formed in the ratio 24:1; no compound **4** was detected. Half of the methanol was distilled under reduced pressure, and the residual solution was added to a solution of Girard's-T reagent (1.00 g) in 10% acetic acid–ethanol (10 ml). The resulting solution was boiled for 30 min, after which time vpc analysis showed the complete removal of **2**. Water was added, and the mixture was extracted with ether. The ethereal solution was dried and stripped of solvent under reduced pressure, and the residual oil was molecularly distilled at 80–90° (15 mm) to give **3**.

**C.**—To a solution of **2** (2.00 g) in methanol (50 ml) was added 1 drop of concentrated sulfuric acid. The solution was irradiated for 75 hr, after which time vpc analysis revealed that 50% of **2** remained and that **4** represented 83% of the volatile photoproducts. A sample of the solution stored in the dark for several days showed no change in composition, as determined by vpc. After partial removal of methanol from the photolysis mixture, compound **2** was removed by treatment with Girard's-T reagent as in procedure B. The ether-soluble fraction was molecularly distilled at 60–80° (15 mm) to give **4**.

**D.**—A solution of **2** (3.00 g) in pentane (50 ml) was irradiated for 3 days, after which time the solution was brown in color and a gum had formed on the walls of the tube. Analysis by vpc revealed that no **2** remained and that the major volatile product was compound **5**; other products with longer retention times were present in small amount. The photolysis solution was stripped of solvent under reduced pressure, and the residual oil was molecularly distilled at 80–90° (15 mm) to give **5** (0.98 g, 33%).

**E.**—A solution of **2** (16.9 g, 0.119 mol) in methanol (300 ml) was irradiated by immersion of the lamp in the solution for 12 hr. After distillation of 290 ml of methanol, preparative vpc gave the following components of the photolysis mixture (retention times in parentheses): methanol (21 sec), isopropyl alcohol (43 sec), **6** (254 sec), **2** (415 sec), **4** (566 sec), and **3** (1667 sec).

**Identification of Products from Photolysis of 2. Methyl 3-isopropoxy-3-methylbutanoate** (**3**) gave the following: $\nu$ 1738 (ester C=O), 1379 (w), and 1364 (m) cm$^{-1}$ [$(CH_3)_2C$]; $\delta$ 1.07 [d, $J$ = 6 Hz, 6 H, $(CH_3)_2CH$–], 1.25 [s, 6 H, $(CH_3)_2C<$], 2.38 (s, 2 H, $-CH_2CO-$), 3.58 (s, 3 H, $OCH_3$), and 3.77 [septet, $J$ = 6 Hz, 1 H, $(CH_3)_2CH$–]; *m/e* 159 (M − $CH_3$), 115 [$CH_3OOCCH_2\overset{+}{C}(CH_3)_2$], 101 [$(CH_3)_2CHO\overset{+}{C}(CH_3)_2$], 85 ($CH_3CO\overset{+}{C}H_2$), 73 ($CH_3OOC\overset{+}{C}H_2$), and 43 ($CH_3\overset{+}{C}HCH_3$).

*Anal.* Calcd for $C_9H_{18}O_3$: C, 62.04; H, 10.41. Found: C, 62.37; H, 10.09.

**Methyl 3-methyl-2-butenoate** (**4**) gave the following: $\nu$ 1725 (conjugated ester C=O) and 1660 cm$^{-1}$ (C=C); $\delta$ 1.86 (d, $J$ = 1.5 Hz, 3 H, *trans*-$CH_3C$=CCO–), 2.15 (d, $J$ = 1.5 Hz, 3 H, *cis*-$CH_3C$=CCO–), 3.60 (s, 3 H, $OCH_3$), and 5.70 [septet, $J$ = 1.5 Hz, 1 H, $(CH_3)_2C$=CHCO–]; *m/e* 114 (M), 83 [$(CH_3)_2C=C\overset{+}{H}C\overset{+}{O}$], and 55 [$(CH_3)_2C=\overset{+}{C}H$].

*Anal.* Calcd for $C_6H_{10}O_2$: C, 63.14; H, 8.83. Found: C, 63.27; H, 8.63.

The infrared and nmr spectra and the vpc retention time of the photolysis product were identical with those of an authentic sample of **4**, prepared by esterification of 3-methyl-2-butenoic acid with diazomethane.

**Isopropyl 3-methyl-2-butenoate** (**5**) gave the following: $\nu$ 1712 (conjugated ester C=O) and 1664 cm$^{-1}$ (C=C); $\delta$ 1.20 (d, $J$ = 6 Hz, 6 H, $(CH_3)_2CH$–], 1.86 (d, $J$ = 1.3 Hz, 3 H, *trans*-$CH_3C$=CCO–), 2.16 (d, $J$ = 1.3 Hz, 3 H, *cis*-$CH_3C$=CCO–), 5.02 [septet, $J$ = 6 Hz, 1 H, $(CH_3)_2CHO$–], and 5.67 [m, 1 H, $(CH_3)_2C$=CH–]. The infrared and nmr spectra and the vpc retention time of the photolysis product were identical with those of an authentic sample of **5**, prepared by esterification of 3-methyl-2-butenoic acid with isopropyl alcohol in the presence of concentrated sulfuric acid.

**Methyl 3-methyl-3-butenoate** (**6**) gave the following: $\nu$ 3078 (C=$CH_2$), 1746 (ester C=O), and 1649 cm$^{-1}$ (C=C); $\delta$ 1.80 (s, 3 H, $CH_3C$=C), 2.95 (s, 2 H, $CH_2C$=C), 3.63 (s, 3 H, $OCH_3$), and 4.82 (s, 2 H, C=$CH_2$).[10]

**Isopropyl alcohol** gave the following: $\delta$ 1.13 [d, $J$ = 6 Hz, 6 H, $(CH_3)_2CH$–] and 3.92 [septet, $J$ = 6 Hz, 1 H, $(CH_3)_2CH$–O–], corresponding to signals in the spectrum of an authentic sample.

**Acid-Catalyzed Conversion of 3 to 4.**—A solution of **3** in methanol was treated with a drop of concentrated sulfuric acid, and the solution was boiled under reflux for 10 min. Analysis by vpc showed that **3** was partially converted to **4**; vpc analysis at 30° showed that isopropyl alcohol was also formed. Both products were identified by comparison of their retention times with those of authentic samples.

**Photoisomerization of 4 to 6.**—A solution of **4** in methanol was irradiated in a quartz tube for 12 hr. Analysis by vpc (10% fluorosilicone on 60–80 Chromosorb W, 8 ft × 0.25 in., 125°) showed that no **4** remained and the **6**, as identified by its retention time, had been formed. Coinjection of this photolysis mixture with that from the photolysis of **2** in methanol confirmed that **6** was present in both mixtures.

**2,2,5,5-Tetramethyldihydro-3-furanone-4-$d_2$** (**9**).—A mixture of 2,5-dimethyl-2,5-dihydroxyhex-3-yne (3.75 g, 0.026 mol), mercuric sulfate (0.75 g, 0.0025 mol), and deuterium oxide (15 ml) was stirred magnetically for 15 min and then distilled. The distillate, which separated into two layers, was saturated with potassium carbonate and the upper, organic layer was removed and dried with magnesum sulfate. This layer was distilled, and the fraction boiling at 150.5–152° was collected to give 2,2,5,5-tetramethyldihydro-3-furanone-4-$d_2$ (**9**) (3.5 g, 92%): $\nu$ 1757 cm$^{-1}$ (ester C=O); $\delta$ 1.20 [s, 6 H, 2-$C(CH_3)_2$] and 1.33 [s, 6 H, 5-$C(CH_3)_2$].[11]

*Anal.* Calcd for $C_6H_{12}D_2O_2$: C, 66.63; H and D, 11.18. Found: C, 66.24; H and D, 11.26.

**Photolysis of 2,2,5,5-Tetramethyldihydro-3-furanone-4-$d_2$** (**9**).—A solution of 2,2,5,5-tetramethyldihydro-3-furanone-4-$d_2$ (0.52 g, 0.0036 mol) in methanol (8.0 ml) was irradiated for 12 hr in a quartz tube. The methanol was removed from the reaction mixture by distillation, and the residue was subjected to preparative vpc to give **11** and **12** with retention times of 971 and 278 sec, respectively.

Analysis by vpc (10% fluorosilicone on 60–80 Chromosorb W, 8 ft × 0.25 in., 125°) showed the presence in the original photolysis mixture of 33% of **11** and 54% of **12**.

(9) H. Richet, *Ann. Chim.*, [12] **3**, 317 (1948); F. Leonard, A. Wajngurt, and H. Horn, *J. Org. Chem.*, **21**, 1400 (1956).

(10) This nmr spectrum was recorded on a solution in a microtube and fine splittings could not be observed.

(11) The assignment of the methyl proton signals are derived from those for **2**: P. M. Burke, Ph.D. Thesis, University of Toronto, 1966.

**Identification of Products from Photolysis of 9. Methyl 3-methyl-3-(isopropoxy-1-*d*)butanoate-2-*d*** (11) gave the following: $\nu$ 1733 cm$^{-1}$ (ester C=O); $\delta$ 1.07 [m, 6 H, $(CH_3)_2CD$-], 1.25 [s, 6 H, $(CH_3)_2C<$], 2.39 (m, 1 H, -CHD-), and 3.61 (s, 3 H, $OCH_3$).

*Anal.* Calcd for $C_9H_{16}D_2O_3$: C, 61.33; H and D, 11.44. Found: C, 61.54; H and D, 11.34.

**Methyl 3-methyl-2-butenoate-2-*d*** (12) gave the following: $\nu$ 1718 (conjugated ester C=O) and 1643 cm$^{-1}$ (C=C); $\delta$ 1.88 (s, 3 H, *trans*-$CH_3C$=CCO-), 2.15 (s, 3 H, *cis*-$CH_3C$=CCO-), and 3.62 (s, 3 H, $OCH_3$).

*Anal.* Calcd for $C_6H_9D_2O_2$: C, 62.53; H and D, 9.70. Found: C, 62.32; H and D, 10.08.

**Registry No.**—2, 5455-94-7; 3, 25859-48-7; 4, 924-50-5; 5, 25859-51-2; 6, 25859-52-3; 9, 25859-53-4; 11, 25907-97-5; 12, 25859-50-1.

**Acknowledgments.**—We thank the National Research Council of Canada for support of part of this research and for the award of a Fellowship (to G. H.). One of us (J. P. W.) gratefully acknowledges financial aid from the National Aeronautics and Space Administration (1965–1968) and from the National Science Foundation (1968–1969).

# Benzene Ring Substituted Indeno[1,2-*c*]pyrazol-4(1*H*)-ones

WILLIAM A. MOSHER* AND WALTER E. MEIER

*Department of Chemistry, University of Delaware, Newark, Delaware 19711*

*Received April 2, 1970*

The condensation of 4-substituted 2-acetyl-1,3-indandiones (**1a–d**) with hydrazine yielded the corresponding indandione $\alpha$-hydrazones (**2a–c**), indeno[1,2-*c*]pyrazol-4(1*H*)-ones (**3** and **6**) or indeno[1,2-*c*]pyrazol-4(1*H*)-one hydrazones (**7a–c**), depending upon the nature of the substituents and the reaction conditions. Evidence is presented that the product of the reaction of 2-acetyl-4-nitro-1,3-indandione (**1a**) with hydrazine is 3-methyl-8-nitroindeno[1,2-*c*]pyrazol-4(1*H*)-one (**6**), whereas the product from 2-acetyl-4-amino-1,3-indandione (**1b**) and hydrazine is 5-amino-3-methylindeno[1,2-*c*]pyrazol-4(1*H*)-one (**3**) and that the ring closure of the $\alpha$-hydrazones of 4-amino- and 4-acetamido-2-acetyl-1,3-indandione (**2a** and **2b**) yields 5-amino- and 5-acetamino-3-methylindeno[1,2-*c*]pyrazol-4(1*H*)-one (**3** and **4**). 2-Acetyl-5-nitro-1,3-indandione (**12**) was treated with hydrazine to give 3-methyl-6- (or 7-) nitroindeno[1,2-*c*]pyrazol-4(1*H*)-one hydrazone (**13**).

A number of indeno[1,2-*c*]pyrazol-4(1*H*)-ones with substituents in the pyrazole ring has been reported in several papers from this laboratory.[1,2] The interesting physiological properties of these compounds prompted us to investigate the syntheses and characteristics of benzene ring substituted 3-methylindeno[1,2-*c*]pyrazol-4 (1*H*)-ones **3**, **4**, **6**, **7**, and **13**, Scheme I).

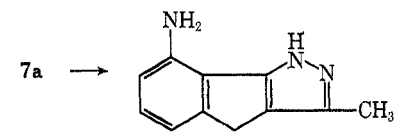
The preparation of 4- and 5-substituted 2-acetyl-1,3-indandiones (**1a–d** and **12**) necessary for this investigation was described in a previous paper.[3] The condensation of 4-amino- and 4-acetamido-2-acetyl-1,3-indandione (**1b** and **1c**) with 1 or 2 mol of hydrazine in refluxing ethanol for 0.5–1 hr yielded the $\alpha$-hydrazones of the corresponding 2-acetylindandiones (**2a** and **2b**). When these hydrazones were refluxed in ethanol (in the case of **2a** catalytic amounts of hydrochloric acid were necessary) cyclization to the corresponding indeno-[1,2-*c*]pyrazol-4(1*H*)-ones **3** and **4** occurred. Whereas when **2a** and **2b** were refluxed in acetic anhydride the $\alpha$-acetylhydrazone of 4-acetamido-2-acetyl-1,3-indandione (**5**) was formed.

The condensation of 4-amino-2-acetyl-1,3-indandione (**1b**) with hydrazine at 180–200° under the conditions of the Wolff–Kishner reaction gave directly 5-amino-3-methylindeno[1,2-*c*]pyrazol-4(1*H*)-one (**3**), whereas 4-nitro-2-acetyl-1,3-indandione (**1a**) yielded directly 8-nitro-3-methylindeno[1,2-*c*]pyrazol-4(1*H*)-one (**6**) by reacting with 1 mol of hydrazine in refluxing ethanol for 48 hr. When an excess of hydrazine was used, the nitroindandione **1a** gave the indenopyrazolone hydrazone **7a**. Under these last conditions 4-acetamido- and 4-hydroxy-2-acetyl-1,3-indandione (**1c** and **1d**) also gave the corresponding indenopyrazolone hydrazones **7b** and **7c**. All attempts to form the hydrazone of 5-amino-3-methylindeno[1,2-*c*]pyrazol-4(1*H*)-one from **1b** failed.

The hydrazono group in the indandione hydrazones **2a–c** is on the side chain carbonyl, as demonstrated by a positive Tollens test[4] and by the formation of a red solution with aqueous sodium hydroxide.[4]

In the condensation of compounds **1** with hydrazine to form **3**, **6**, and **7** and in the cyclization of compounds **2** to form **3** and **4**, only one of the two possible isomers, the 5- or 8-substituted 3-methylindeno[1,2-*c*]pyrazol-4-(1*H*)-one, was formed. Theoretical considerations would lead one to predict that these reactions would give the 8-substituted rather than the 5-substituted isomer, when R is an electron-withdrawing group and the 5 rather than the 8 isomer, when R is an electron-donating group.

Evidence for the structure of the nitro derivative **7a** was obtained by treating it with hydrazine and palladium on charcoal to form the amino-1,4-dihydro-3-methylindeno[1,2-*c*]pyrazole (**8**). The melting point and infrared spectrum of **8** were found to be different from those of an authentic sample of 5-amino-1,4-dihydro-3-methylindeno[1,2-*c*]pyrazole (**10**, see below) and therefore the 8-nitro structure was assigned to com-




**8**

* Author to whom correspondence should be addressed.

(1) R. A. Braun and W. A. Mosher, *J. Amer. Chem. Soc.*, **80**, 4919 (1958).

(2) R. A. Braun and W. A. Mosher, *J. Org. Chem.*, **24**, 648 (1959).

(3) W. A. Mosher and W. E. Meier, *ibid.*, in press.

(4) R. A. Braun and W. A. Mosher, *J. Amer. Chem. Soc.*, **80**, 2749 (1958).