The Reaction of Benzil with Methylsulfinyl Carbanion. II. A Study of the Reaction Mechanism

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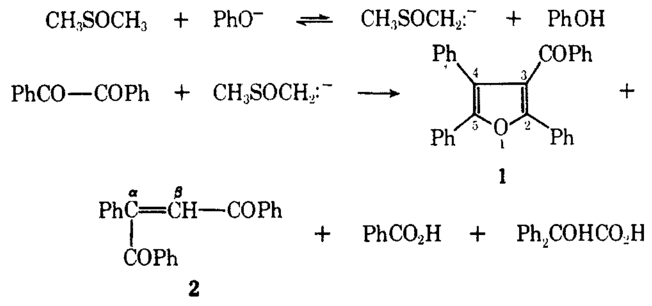
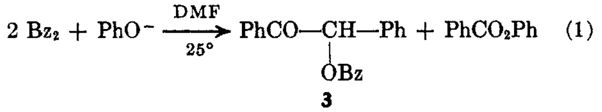
A mechanism for the reaction of benzil with methylsulfinyl carbanion is proposed. It is demonstrated that initial reaction results in the formation of acetophenone which condenses with benzil to form *cis*-α,β-dibenzoylstyrene (**2**). Compound **2** is shown to react with benzil under the influence of a variety of bases to yield 3-benzoyl-2,4,5-triphenylfuran (**1**) and an equivalent quantity of benzoic acid. The preparation and characterization of several new compounds which became necessary during the course of the investigation are described.

Recently, it was discovered in this laboratory that benzil and sodium phenoxide, when heated in dimethyl sulfoxide (DMSO), result in the formation of 3-benzoyl-2,4,5-triphenylfuran (**1**), *cis*-α,β-dibenzoylstyrene (**2**), benzoic acid, and benzilic acid.[2] It was concluded that phenoxide ion is basic enough under the conditions employed to generate methylsulfinyl carbanion (dimsyl ion) in low concentration and that the reaction observed was actually one between benzil and dimsyl ion (Scheme I). Support for this idea was found in the observation that the same reaction products are obtained when benzil is reacted directly with dimsyl ion.

SCHEME I



The initial phase of the present investigation was designed to demonstrate more conclusively the necessity of DMSO to the formation of **1** and **2** from benzil and sodium phenoxide. In other solvents that have been tested, either no reaction occurs or products are obtained which are apparently unrelated to those obtained in DMSO. Thus, in the ethereal solvents dimethoxyethane (DME) and diglyme, benzil and sodium phenoxide are unreactive, even after extended periods at elevated temperatures. On the other hand, a reaction occurs in N,N-dimethylformamide (DMF) to form benzoin benzoate (**3**) and phenyl benzoate in near-quantitative yields (eq 1).[3] Unlike the reaction in DMSO, where heating for an extended period of time is necessary,[2] this reaction progresses very rapidly at or below room temperature.

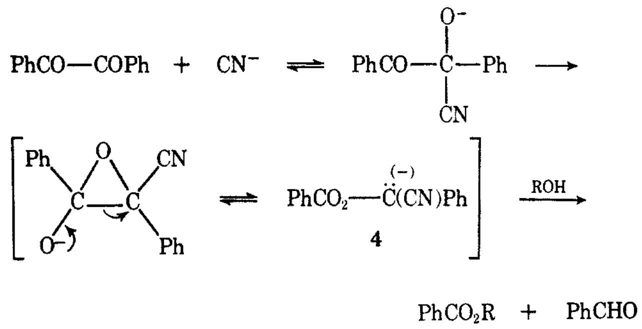


$$2\,Bz_2 + PhO^- \xrightarrow[25°]{DMF} \underset{\textstyle\underset{\textstyle \mathbf{3}}{OBz}}{PhCO{-}\overset{}{C}H{-}Ph} + PhCO_2Ph \quad (1)$$

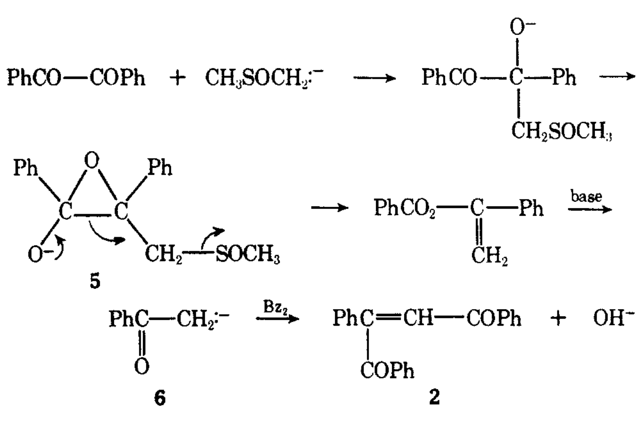
That DMSO is required in the formation **1** and **2** from benzil and sodium phenoxide is also suggested from a structural consideration of these products. For example, it is apparent that the carbon skeleton of **2** consists of three Ph–C units (from benzil) in addition to the β-carbon atom. Likewise, **1** is made up from four Ph–C units and the 3-carbon atom. In each case, the most likely source of this extra carbon is the solvent, DMSO. Derivation of additional carbon from benzil necessarily involves cleavage of the stable Ph–C bond and is therefore rejected.

Product **2**, in addition to being the less complex of the two neutral products (Scheme I), is later shown to be the precursor to **1**, and its formation in the reaction will be considered first. The compound contains an odd number of Ph–C units and its generation obviously necessitates cleavage of the central C–C bond of benzil in at least one step. If the type of reaction proposed by Kwart and Baevsky[4] to explain the cleavage of benzil by cyanide ion is invoked (Scheme II), an explanation for the formation of **2** is available (Scheme III). The

SCHEME II



SCHEME III



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[1] Taken in part from the M.S. thesis of J. M. R.

[2] J. C. Trisler, C. S. Aaron, J. L. Frye, and J. Y. Park, *J. Org. Chem.*, **33**, 1077 (1968).

[3] Unpublished results obtained with J. D. Cheng.

[4] H. Kwart and M. Baevsky, *J. Amer. Chem. Soc.*, **80**, 580 (1958).

driving force for the cleavage step (Scheme II) has been attributed to the electron-withdrawing power of the nitrile group as well as to the formation of the resonance-stabilized anion **4**.[4] In Scheme III, cleavage *via* anion **5** results in the formation of a carboxylic ester accompanied by the elimination of the sulfenate ion, CH_3SO^-.[5] The mechanism also accounts for the formation of benzilic acid, which results from the reaction of benzil with hydroxide ion.

The compatibility of Scheme III to the formation of **2** has been demonstrated by reacting benzil with dimsyl ion under conditions such that one of the intermediates is formed as the predominant product. Thus, acetophenone was obtained in 70% yield by the dropwise addition of a solution of benzil in DMSO to a 20-fold excess of dimsyl ion. From a statistical viewpoint, it is seen that benzil is unlikely to react with acetophenone anion to form **2** in the overwhelming presence of dimsyl ion. This conclusion is based in part on the reasonable assumption that the latter nucleophile possesses nucleophilicity equal to or greater than that of **6**.

The second portion of Scheme III (**6** → **2**) was validated by the reaction of benzil with acetophenone under the influence of sodium phenoxide in DMSO. The reaction was carried out under conditions where, in the absence of acetophenone, no reaction occurs between benzil and sodium phenoxide. As the reaction temperature was increased from 25 to 75°, the yield of **2** showed a noticeable drop. At the same time, **1**, isolated only in trace amounts at the lower temperature, showed an increase in yield with increasing temperature. Benzilic acid and benzoic acid were also isolated in each case, but showed no predictable temperature–yield relationship.

In view of the temperature effect in the above reaction, thought was given to the possibility that **2** is a precursor to **1** in the benzil–dimsyl ion reaction. That this hypothesis is correct was suggested by the fact that **2** reacts with benzil in DMSO under the influence of sodium phenoxide to produce **1** along with an equivalent of benzoic acid.[6] Sodium phenoxide fails to react with either reagent alone under the conditions employed.

Further investigation led to the discovery that several aprotic solvents as well as a variety of bases are applicable in the transformation of **2** and benzil to **1** and benzoic acid. The results are summarized in Table I.

One obvious conclusion is that the stronger bases are more effective in promoting the reaction. For example, whereas long periods of heating are required using sodium phenoxide, relatively shorter reaction times are possible, and in general better yields are obtainable with the stronger bases. The poor results utilizing sodium phenoxide in the etheral solvents probably reflect the lessened basicity of this material in the low dielectric solvents as compared with the dipolar aprotic solvent, DMSO, where dissociation of the ions is expected to be more complete.[7]

TABLE I

REACTION OF BENZIL WITH *cis*-α,β-DIBENZOYLSTYRENE UNDER THE INFLUENCE OF BASE

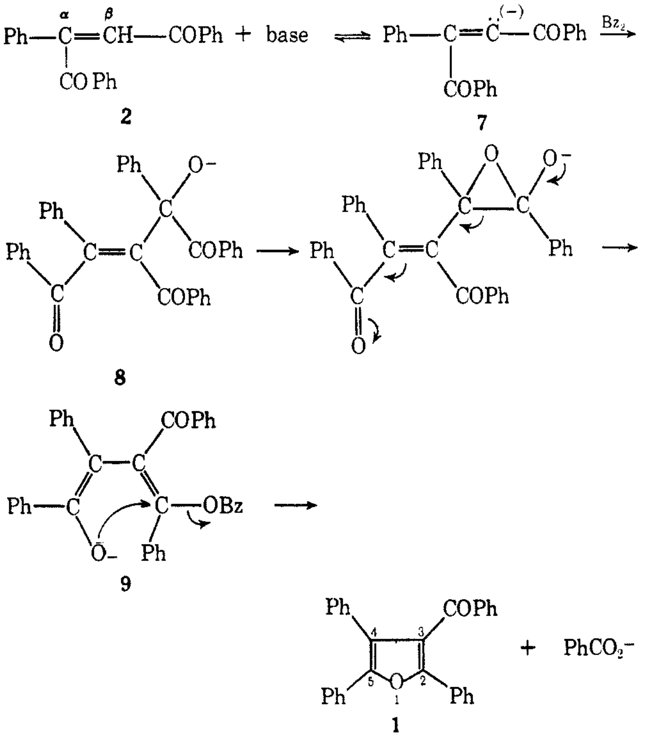
Solvent	Base	Temp, °C	Reaction time, hr	Yield of 1, %[a]	Yield of $PhCO_2H$, %[a]
DMSO	NaOPh	75	12	53	54
DME	NaOPh	83	48	12	10
Diglyme	NaOPh	85	48	17	20
DMSO	NaH	25	3.5	52	49
DMF	$NaOCPh_3$	25	1.7	71	66
DMSO	Na_2CO_3	100	48	0	0

[a] Percentage yields are based on starting materials, which were employed in a 1:1:1 mole ratio.

The data in Table I lend support to the previous inference that the role of DMSO in the benzil–sodium phenoxide reaction[2] is played prior to the formation of **2**. The second phase of the reaction (**2** → **1**) has only the general requirement of aprotic solvent and base.

A mechanism consistent with the data gathered for the base-induced transformation of **2** to **1** and benzoic acid is outlined in Scheme IV.

SCHEME IV



An initial feature of the scheme is formation of the vinyl anion **7**.[8] First attempts to trap **7** involved reacting **2** with base, usually sodium hydride, followed by addition of the trapping agent, carbon dioxide, methyl iodide, or benzoyl chloride. Success was not realized, since in each instance only **2** was recovered. The

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(5) Examples of other elimination reactions involving the leaving group, methane sulfenate ion, have been reported. *Cf.* C. Walling and L. Bollyky, *J. Org. Chem.*, **29**, 2699 (1964); T. J. Wallace, J. E. Hofmann, and A. Schriesheim, *J. Amer. Chem. Soc.*, **85**, 2739 (1963); C. A. Kingsbury and D. J. Cram, *ibid.*, **82**, 1810 (1960).

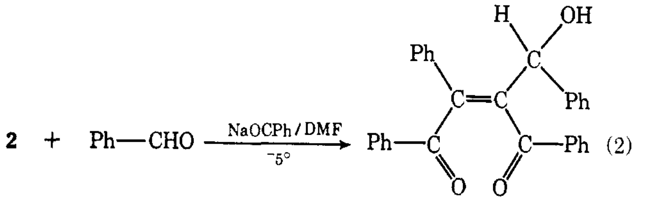
(6) Other possible nucleophiles in the system, *i.e.*, dimsyl ion and acetophenone anion, have also been treated with **2**. In each case, products were obtained that are apparently unrelated to **1** and benzoic acid. This investigation is to be the subject of a future report.

(7) For a discussion of enhanced anion basicity in dipolar aprotic solvents, see D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, Inc., New York, N. Y., 1965, pp 32–45; A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962).

(8) Factors relating to vinyl anion stability have been discussed by D. H. Hunter and D. J. Cram, *J. Amer. Chem. Soc.*, **86**, 5478 (1964).

second approach was to react 2 with base in the presence of a trapping agent (a compound showing little reactivity to the base employed). In view of the success in reacting benzil with 2 and base, it was decided that a carbonyl compound presented the greatest opportunity for success in demonstrating the existence of 7. Owing to obvious complications in a strongly basic medium, carbonyl compounds containing α-hydrogens were avoided.

The base-induced reaction of 2 with benzaldehyde, carried out in DMF at low temperature, resulted in the predicted adduct, 2-(α-hydroxybenzyl)-1,3,4-triphenyl-2-butene-1,4-dione (**10**), in 86% yield (eq 2). Thus, the involvement of 7 in the reaction of 2 with carbonyl compounds under the influence of base is established.



10

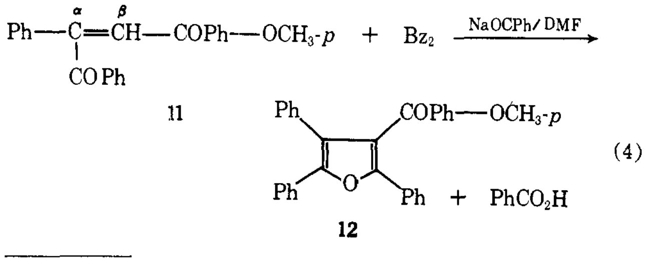
Structure assignment of **10** was based on its facile conversion to **1** as well as on spectral data. Owing to the insolubility of the compound in most organic solvents, its methyl ether was prepared in order to obtain a suitable nmr spectrum. Attempts to react **10** or its methyl ether with hydrazine to establish *cis* or *trans* character of the C=C bond were unsuccessful, presumably owing to the bulkiness of the molecule in each case. However, the geometry of **10** is irrelevant to the successful trapping of **7**.

Compound 2 was treated with *p*-methoxybenzil to yield 1 and 1 equiv of *p*-methoxybenzoic acid (eq 3).

$$2 + p\text{-CH}_3\text{O—PhCO—COPh} \xrightarrow{\text{NaH/DMSO}} 1 + p\text{-CH}_3\text{O—PhCO}_2\text{H} \quad (3)$$

The transformation is significant for two reasons. First, the requirement in the proposed mechanism that 1 be made up of one molecule of 2 and one of the two Ph–C units of benzil is confirmed. Benzoic acid then arises from the remaining Ph–C unit. Once again, the Kwart and Baevsky[4] type cleavage is utilized to explain scission of the central C–C bond of benzil. Secondly, the ability of a *para*-methoxyl substituent on benzil to direct attack to the opposite carbonyl group verifies the nucleophilic nature of the attack on benzil.[9,10]

From Scheme IV it is seen that the β-benzoyl group of 2 ultimately becomes the 3-benzoyl group of 1.



11

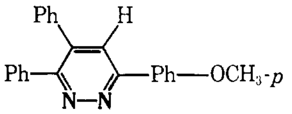
12

This facet of the mechanism has been confirmed from the reaction of benzil with *cis*-α-benzoyl-β-(*p*-methoxybenzoyl)styrene (**11**) to produce 3-(*p*-methoxybenzoyl)-2,4,5-triphenylfuran (**12**) and benzoic acid (eq 4).

The methoxyl substituent is expected to inhibit the acidity of the β-hydrogen atom in **11** compared to 2, owing to resonance interaction of the substituent with the β-carbonyl group, which results in an increased electron density near the reaction site. That this effect is obtaining is suggested by the fact that the weak base, sodium phenoxide, is unable to effect the reaction under conditions where 2 is readily converted to products.

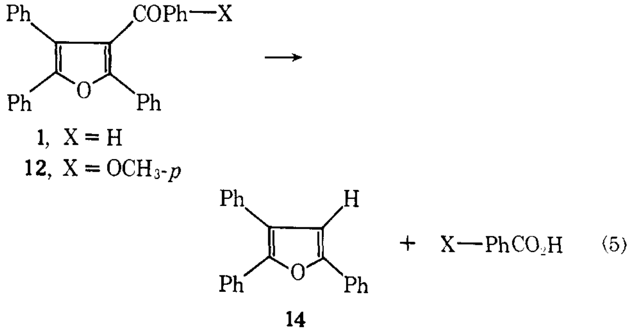
In view of the importance placed on the fact that the β-benzoyl group of 2 becomes the 3-benzoyl group of **1**, it was necessary to establish the structure of **12** relative to other possible methoxyl-substituted 3-benzoyl-2,4,5-triphenylfurans with a great degree of certainty. Infrared spectroscopy is of little benefit, since the shift in carbonyl absorption of this product relative to **1** is too small to be of any value. The use of nmr spectroscopy is suggestive of correct structure assignment. As predicted, the pair of equivalent protons *ortho* to the carbonyl group is deshielded to a greater extent than other phenyl protons and appears as the downfield doublet of an AB system. The two equivalent protons *ortho* to the methoxyl group are shielded upfield from the phenyl multiplet and show up as the other doublet of the AB system.

During the course of the investigation, the pyridazine **13** was prepared from **11** to establish the *cis* character of the latter compound.[11] It was found, however, that the nmr spectrum of **13** exhibits shielding and deshielding effects very similar to those observed for **12**. Consequently, it was concluded that differentation between isomers of **12**, based solely on spectroscopic evidence, involved a certain degree of uncertainty.



13

The procedure described by Gassmann and coworkers[12] for the cleavage of non-enolizable ketones was employed with great success to the degradation of **12** and **1** to known compounds (eq 5), thereby estab-



1, X = H
12, X = OCH3-p

14

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[9] Kwart and Baevsky[4] have reported that methoxybenzil reacts with cyanide ion in alcoholic solvent to yield benzaldehyde and the corresponding anisate ester.

[10] For a review of substituent effects in the benzilic acid rearrangement, see S. Selman and J. F. Eastham, *Quart. Rev.* (London), **14**, 221 (1960).

[11] The *cis* isomer of **2** reacts with hydrazine to form the pyridazine, whereas the *trans* isomer forms the monohydrazone [E. Oliveri-Mandala, *Gazz. Chim. Ital.*, **44**, 85 (1914)].

[12] P. G. Gassmann, J. T. Lumb, and F. V. Zalar, *J. Amer. Chem. Soc.*, **89**, 946 (1967).

lishing unequivocally the structure of these compounds. The procedure involves heating the compound with an excess of the reagent, potassium *t*-butoxide–water (10:3 mole ratio), in an aprotic solvent for several hours. In each case, triphenylfuran (**14**) and the corresponding benzoic acid were obtained in near-quantitative yield.

Experimental Section[13]

Starting Materials.—Benzil was recrystallized from ethanol: mp 94–95°. Benzaldehyde was freshly distilled and stored under a nitrogen atmosphere prior to use. Potassium *t*-butoxide,[14] sodium phenoxide,[15] *cis*-α,β-dibenzoylstyrene (**2**),[16] and 4-methoxybenzil[17] were prepared by reported methods. Dimethyl sulfoxide (DMSO) and N,N-dimethylformamide (DMF) were distilled from calcium hydride at reduced pressure (*ca.* 20 mm). 1,2-Dimethoxyethane (DME) and diglyme were distilled from lithium aluminum hydride. Other materials, commercially obtained, were of reagent grade and were used without further purification.

Methylsulfinyl Carbanion and Benzil (20:1).—DMSO (110 ml) was stirred with sodium hydride (4.30 g, 0.10 mol)[18] at 65° for 1.5 hr under nitrogen. Benzil (1.05 g, 5.0 mmol) in 45 ml of DMSO was added dropwise over a period of 15 min to the resulting solution. The temperature during addition was maintained at 18°. After being stirred for an additional 10 min, the reaction mixture was poured into ice–water, acidified, and extracted with ether. The ether solution was washed with water, extracted with 5% sodium hydroxide solution, washed with water, dried over calcium chloride, and evaporated. The residue was dissolved in 10 ml of dry benzene and placed on a column containing 50 g of alumina (Alcoa, F-20). Elution with petroleum ether (bp 30–60°)-ethyl ether (95:5) resulted in an oil which, when reacted with Shine's reagent,[19] afforded 1.0 g (67%) of acetophenone 2,4-dinitrophenylhydrazone, mp 247.5–249.5°. A mixture melting point with authentic material showed no depression.

Benzil, Acetophenone, and Sodium Phenoxide in DMSO.—Benzil (2.10 g, 10.0 mmol), sodium phenoxide (1.77 g, 15.0 mmol), and acetophenone (0.62 g, 5.0 mmol) were dissolved in 50 ml of DMSO and heated under nitrogen to 50° for a period of 12 hr. The reaction mixture was poured into ice–water, acidified, and extracted with ether. The ether solution was washed with water, extracted with bicarbonate solution followed by 5% sodium hydroxide solution, washed with water, dried with calcium chloride, and evaporated. The residue was dissolved in a small quantity of dry benzene and placed on a column containing 50 g of alumina (Alcoa, F-20). Unreacted benzil, 0.25 g, and 3-benzoyl-2,4,5-triphenylfuran (**1**), 0.17 g, were eluted with petroleum ether–ethyl ether (90:10) while *cis*-α,β-dibenzoylstyrene (**2**), 1.35 g, was eluted with petroleum ether–ethyl ether (70:30).

The bicarbonate extract was acidified and extracted with ether. The ether layer was washed with water, dried over calcium chloride, and evaporated. Sublimation of the residue resulted in 0.15 g of benzoic acid, mp 118–120°, and 0.39 g of benzilic acid, mp 146–148° (from water).

Using the same quantities of starting materials at 25° for 12 hr, only a trace of **1** was obtained while the yield of **2** was increased to 1.72 g. The yields of benzoic acid and benzilic acid were 0.10 and 0.19 g, respectively.

At 75°, the yields of **1** and **2** were 0.29 and 0.74 g, respectively, while the corresponding yields of benzoic acid and benzilic acid were 0.18 and 0.46 g.

In the absence of acetophenone, no reaction was observed between benzil and sodium phenoxide under the conditions employed.

Benzil, *cis*-α,β-Dibenzoylstyrene (2), and Base in Aprotic Solvents.—Benzil and **2** were treated with a variety of bases in a number of solvents as listed in Table I, of which the following procedure is typical.

Sodium hydride (0.24 g, 5.6 mmol)[18] was treated with triphenylcarbinol (1.30 g, 5.0 mmol) in 25 ml of DMF and stirred until the evolution of hydrogen gas had subsided (*ca.* 20 min). A solution of **2** (1.56 g, 5.0 mmol) and benzil (1.05 g, 5.0 mmol) in 20 ml of DMF was added. After being stirred for 1.7 hr, the mixture was poured into ice–water, acidified, and extracted with ether. The ether layer was washed with water, extracted with bicarbonate solution, washed again with water, dried over calcium chloride, and evaporated. The residue was triturated with ethanol to afford 1.13 g (56%) of **1**, mp 175.5–176.5°. The mother liquor was evaporated, and the residue was dissolved in 10 ml of benzene and chromatographed on 50 g of alumina [eluted with petroleum ether–ethyl ether (90:10)] to yield an additional 0.29 g (15%) of **1**, mp 176–177° (from ethanol).

The bicarbonate solution was acidified and extracted with ether. The ether solution was washed with water, dried over calcium chloride, and evaporated. The residue was sublimed to yield 0.40 g (66%) of benzoic acid, mp 121–122°. The sublimation residue was recrystallized from hexane–acetone to give 0.16 g of benzilic acid, mp 146–149°.

2-(α-Hydroxybenzyl)-1,2,4-triphenyl-2-butene-1,4-dione (10).—Sodium hydride (0.25 g, 5.8 mmol)[18] was reacted with triphenylcarbinol (1.30 g, 5.0 mmol) in 30 ml of DMF for 1 hr at room temperature. A solution of **2** (1.56 g, 5.0 mmol) and benzaldehyde (0.53 g, 5.0 mmol) in 40 ml of DMF was added dropwise over a period of 30 min while maintaining a temperature of −5°. The solution was allowed to warm to 0° and stirred for an additional 1.5 hr. The reaction mixture was poured into a crushed ice–water slurry and neutralized with hydrochloric acid. A small quantity of ether was added and the white precipitate concentrated between the organic and aqueous phases was filtered, washed with water, washed with ether, and triturated with benzene to give 1.7 g (81%) of **10**, mp 201–204° dec. Recrystallization from benzene resulted in white crystals (light and fluffy), mp 205° dec (attempts to recrystallize from ethanol caused furanization to **1**). The ether phase was separated, washed with water, dried over calcium chloride, and evaporated. Trituration of the residue with benzene afforded an additional 0.10 g (5%) of **10**, mp 202–203.5° dec. The infrared spectrum showed a sharp absorption at 2.95 μ (hydroxyl) and absorptions at 6.10 and 6.15 μ (carbonyl).

Anal. Calcd for $C_{29}H_{22}O_3$: C, 83.23; H, 5.29. Found: C, 83.31; H, 5.38.

It was necessary to convert **10** to its methyl ether for nmr analysis due to its insolubility in most organic solvents. Sodium hydride (0.12 g, 2.5 mmol)[18] was added to 30 ml of DMF and cooled to −5° to which a solution of **10** (1.04 g, 2.5 mmol) in 40 ml of DMF was added dropwise over a period of 2 hr. The system was stirred for 1 hr, methyl iodide (0.43 g, 3.0 mmol) in 10 ml of DMF was added, and stirring was continued for 1 hr. The reaction mixture was poured into ice–water, acidified, and extracted with ether. The ether layer was washed with water, dried over calcium chloride, and evaporated. The residue was triturated with ethanol to afford 0.78 g (72%) of the methyl ether of **10**, mp 131–132° (from ethanol). The infrared spectrum contained carbonyl absorption at 5.97 μ. The nmr spectrum showed a 3 H absorption at δ 3.53 (CH_3O), a 1 H singlet at δ 6.51 (methinyl), and a 20 H multiplet at δ 6.8–7.8 (aromatic).

Both **10** and its methyl ether were refluxed with hydrazine hydrate (85%) in ethanol. In each case, starting material was recovered.

***p*-Methoxybenzil, *cis*-α,β-Dibenzoylstyrene (2), and Sodium Hydride in DMSO.**—Sodium hydride (0.25 g, 5.8 mmol),[18] *p*-methoxybenzil (1.20 g, 5.0 mmol), and **2** (1.56 g, 5.0 mmol) were stirred in 35 ml of DMSO for 4 hr under a nitrogen atmosphere. The reaction mixture was poured into ice–water, acidified, and extracted with ether. The ether layer was extracted with bicarbonate solution followed by sodium hydroxide

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[13] Melting points are uncorrected. Elemental analyses were carried out by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were obtained using the Nujol mull technique. The nmr spectra were determined in deuterated chloroform at 60 Mc using tetramethylsilane as an internal standard.

[14] W. S. Johnson and W. P. Schneider, "Organic Syntheses," Coll. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1963, p. 132; G. A. Swan, *J. Chem. Soc.*, 1408 (1948).

[15] N. Kornblum and A. P. Lurie, *J. Amer. Chem. Soc.*, **81**, 2705 (1959).

[16] F. R. Japp and F. Klingemann, *J. Chem. Soc.*, **57**, 673 (1890).

[17] N. J. Leonard, R. T. Rapala, H. L. Herzog, and E. R. Blout, *J. Amer. Chem. Soc.*, **71**, 2997 (1949). We have found it advisable to chromatograph *p*-methoxybenzil from a column of alumina (Alcoa F-20), using petroleum ether–ethyl ether (90:10) as eluent, to remove the contaminant, anisil. The melting point of the purified material is 63–64°.

[18] Quantity of sodium hydride refers to a 56% by weight suspension in mineral oil. In each instance, mineral oil was removed by washing with petroleum ether.

[19] H. J. Shine, *J. Org. Chem.*, **24**, 252 (1959); *J. Chem. Educ.*, **36**, 575 (1959).

(5%) solution, washed with water, dried over calcium chloride, and evaporated. Trituration of the residue with ethanol afforded 0.79 g (40%) of **1**, mp 173–175° (from ethanol). The mother liquor was evaporated, and the residue was dissolved in 10 ml of benzene and placed on 50 g of alumina. Elution with petroleum ether–ethyl ether (90:10) yielded an additional 0.19 g (9%) of **1**, mp 176–176.5° (from ethanol).

The bicarbonate solution was acidified, extracted with ether, dried over calcium chloride, and evaporated. The residue was triturated with ether to yield 0.17 g (22%) of *p*-methoxybenzoic acid, mp 180–182°. The mother liquor was evaporated, recrystallized from dilute aqueous ethanol, and sublimed to give an additional 0.18 g (24%) of *p*-methoxybenzoic acid, mp 176–179°. A mixture melting point with an authentic sample showed no depression.

***cis*-α-Benzoyl-β-(*p*-methoxybenzoyl)styrene (11).**—Benzil (21.0 g, 0.10 mol), *p*-methoxyacetophenone (16.0 g, 0.10 mol), and potassium hydroxide (5.6 g, 0.10 mol) were dissolved in 100 ml of ethanol and allowed to stand for 2 hr. Solid material precipitated, which was filtered and triturated with ethanol. Recrystallization from ethanol–benzene afforded 18.5 g (54%) of **11**, mp 181–182° (lit.[20] mp 177°). The infrared spectrum showed carbonyl absorption at 6.0 and 6.1 μ. The nmr spectrum exhibited a 4 H doublet at δ 7.98 (*ortho* protons on benzoyl and *p*-methoxybenzoyl) and a 2 H doublet at δ 6.92 (*meta* protons on *p*-methoxybenzoyl) ($J \cong 9.0$ cps), a 9 H multiplet (aromatic and vinyl) at δ 7.2–7.7, and a 3 H singlet (CH_3O) at δ 3.82.

Anal. Calcd for $C_{23}H_{18}O_3$: C, 80.68; H, 5.29. Found: C, 80.55; H, 5.40.

Compound **11** (0.34 g, 1.0 mmol) and 1 ml of hydrazine hydrate (85%) were refluxed in 20 ml of ethanol for 30 min. On cooling, 0.25 g (74%) of 3-(*p*-methoxyphenyl)-5,6-diphenylpyridazine (**13**), mp 178–180°, was deposited as a white solid. The infrared spectrum did not show NH or carbonyl absorption (as required for a monohydrazone derivative). The nmr spectrum contained a pair of 2 H doublets at δ 8.14 and 7.01 ($J \cong 9.0$ cps) corresponding to the *p*-methoxyphenyl group, a 10 H multiplet (aromatic) at δ 7.2–7.6, a 1 H singlet (proton on pyridazine ring) at δ 7.72, and a 3 H singlet (CH_3O) at δ 3.82. The formation of **13** establishes the *cis* character of **11**.[11]

3-(*p*-Methoxybenzoyl)-2,4,5-triphenylfuran (12).—Sodium hydride (0.25 g, 5.8 mmol)[18] and triphenylcarbinol (1.30 g, 5.0 mmol) were treated in 25 ml of DMF and stirred until the evolution of hydrogen gas had subsided. Benzil (1.05 g, 5.0 mmol) and **11** (1.72 g, 5.0 mmol) in 20 ml of DMF were added and the solution was stirred for a period of 2 hr. The reaction mixture was poured into ice–water, acidified, and extracted with ether. The ether solution was washed with water, dried over calcium chloride, and evaporated. The residue was recrystallized from ethanol to yield 0.68 g (32%) of **12**, mp 158–160° (from ethanol). The infrared spectrum contained carbonyl absorption at 6.08 μ and the characteristic absorption at 11.07 μ reported earlier for **1**.[2] The nmr spectrum showed a pair of doublets (*p*-methoxybenzoyl) at δ 5.83 and 7.74 ($J \cong 9.0$ cps), a 15 H multiplet (aromatic) at δ 7.1–7.7, and a 3 H singlet (CH_3O) at δ 3.75.

Anal. Calcd for $C_{30}H_{22}O_3$: C, 83.70; H, 5.15. Found: C, 83.53; H, 5.29.

The mother liquor was evaporated, and the residue was dissolved in 10 ml of benzene and placed on 50 g of alumina. Elution with petroleum ether–ethyl ether (90:10) afforded 0.23 g of unreacted benzil, mp 93–94° (from ethanol). Elution with petroleum ether–ethyl ether (80:20) resulted in an additional 0.53 g (25%) of **12**. Further elution with petroleum ether–ethyl ether (70:30) yielded 0.72 g of crude unreacted **11**, mp 180–181° (from ethanol).

The bicarbonate extract was acidified and extracted with ether. The ether layer was washed with water, dried over calcium chloride, and evaporated. The residue, on sublimation, produced 0.38 g (62%) of benzoic acid, mp 120–122°.

In a reaction where sodium phenoxide was employed as base, only starting material was recovered.

Cleavage of 12.—A cleavage mixture[12] was prepared with potassium *t*-butoxide (1.50 g, 13.4 mmol), water (0.08 ml, 4.5 mmol), and DMSO (12 ml) under a nitrogen atmosphere. A solution of **12** (0.32 g, 0.75 mmol) in 10 ml of warm DMSO was added and stirred at room temperature for 9 hr. The reaction mixture was poured into water, acidified, and extracted with ether. The ether solution was extracted with bicarbonate solution, washed with water, dried over calcium chloride, and evaporated. The residue was chromatographed from 40 g of alumina with petroleum ether to yield 0.22 g (100%) of 2,3,5-triphenylfuran (**14**), mp 89–90.5° (from petroleum ether) (lit.[21] mp 90.5–92°). A mixture melting point with authentic material showed no depression.

The bicarbonate solution was acidified and extracted with ether. The ether layer was washed with water, dried over calcium chloride, and evaporated to yield 0.11 g (97%) of *p*-methoxybenzoic acid, mp 175–180°. The crude material, on trituration with petroleum ether–ethyl ether, gave a product, mp 179.5–181.5°. A mixture melting point with an authentic sample showed no depression.

Compound **1** was cleaved in diglyme at 50° for 4 hr to yield **14** (77%) and benzoic acid (95%).

Registry No.—**1**, 15440-99-0; **2**, 13249-75-7; **10**, 21363-64-4; **11**, 21449-71-8; **12**, 21363-65-5; **13**, 21367-74-8; benzil, 134-81-6; methylsulfinyl carbanion, 13810-16-7; methyl ether of **10**, 21367-76-0.

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[20] C. F. H. Allen and B. Rosener, *J. Amer. Chem. Soc.*, **49**, 2110 (1927).

[21] H. M. Taylor and C. R. Hauser, *ibid.*, **82**, 1790 (1960).