Notes

(*E,E*)- and (*E,Z*)-1,4-Dibenzoyl-1,3-butadiene. Synthesis via Wittig Condensation and Solid-State Photochemistry

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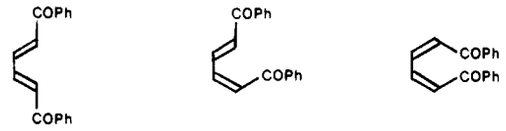
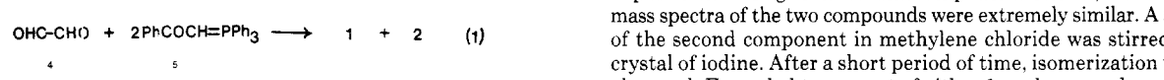
In connection with other studies, we synthesized (*E,E*)-1,4-dibenzoyl-1,3-butadiene (**1**) according to the method of Bailey and Ross,[1] starting with (*E,E*)-1,3-butadiene-1,4-dicarboxylic acid via Friedel–Crafts phenylation of the acid chloride. Compound **1** was found to be extremely photolabile



1 **2** **3**

as a solid or in solution, and it could only be handled using special lighting conditions. Inspired by the elegant work of G. M. J. Schmidt and co-workers[2] on the solid-state photochemistry of other 1,3-butadienes, we decided to investigate the photochemistry of solid **1**. We wish to report formation of a (2 + 2) dimer from solid **1**. In addition, we have succeeded in synthesizing the (*E,Z*) isomer **2** and wish to report preliminary solid-state photochemistry results, the first to be reported on an (*E,Z*)-1,4-disubstituted 1,3-diene.

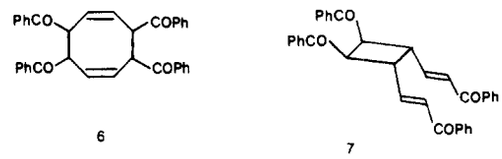
In our hands, attempts to synthesize the stereoisomers of **1**, i.e., **2** and **3**, by organometallic or Friedel–Crafts phenylation of the corresponding 1,3-butadiene-1,4-dicarboxylic acid or acid chloride were unsuccessful, resulting in either Michael additions[3] or in isomerization to **1**. However, we have succeeded in preparing **2** by the Wittig condensation of glyoxal **4** with 2 mol of phenacyltriphenylphosphorane (**5**) (reaction 1).



4 **5**

The reaction product was shown to consist of two compounds, chromatographic separation of which gave **1** and a second component, X. This latter compound was shown to be **2**. Its IR, ^{1}H NMR, and mass spectra were very similar to those of **1**. The IR spectra of **1** and X were extremely similar, both showing strong absorption (KBr) at 1653, 1587, and 1563 cm^{-1}. The ^{1}H NMR spectra of **1** and X were similar, **1** showing multiplets from δ 7.3 to 8.1 and X evincing multiplets from δ 6.0 to 7.0 and from 7.0 to 8.1. The mass spectra of the two compounds both had M$^+$ of 262 plus fragments at *m/e* 197, 157, 128, 105, and 77. A solution of X, when stirred with a crystal of iodine over short periods of time, isomerized to **1**. Extended treatment of X or **1** with either iodine or dilute hydrochloric acid resulted in formation of 2-phenacyl-5-phenylfuran.[3] Finally, the number of lines in the proton-decoupled ^{13}C-NMR spectrum of X (i.e., 11, of a maximum of 14) showed it to be the less symmetrical (**2**). The more symmetrical (*Z,Z*)-**3**, like **1**, could only have shown a maximum of seven lines. Compound **1** indeed gave all seven lines. The number plus the chemical shifts of the resonances support the assignment of structure **2** to compound X, rather than the stereoisomeric **3**.

Compounds **1** and **2** were irradiated in the solid state. Compound **1** gave a single photoproduct, whose IR, ^{1}H-NMR, and mass spectra showed it to be either a (4 + 4) dimer (**6**) or



6 **7**

a (2 + 2) dimer (e.g., **7**). However, the number and chemical shifts of the lines in the proton-decoupled ^{13}C NMR spectrum ruled out the more symmetrical **6** in favor of **7**, whose structure is analogous to the dimer obtained from the solid-state photolysis of the stereoisomeric 1,3-butadiene-1,4-dicarboxylic acids.[4] In addition, the UV spectrum of the dimer was almost identical to that of another α,β-unsaturated ketone, 1-phenyl-2-buten-1-one.

Irradiation of **2** resulted in a mixture of two compounds that have proved difficult to separate. However, the mixture did show a M$^+$ of 524, indicating that at least one of the components is a dimer.

Further work, including X-ray crystallographic studies of both monomers and dimers, is in progress.

Experimental Section

(*E,E*)-1,4-Dibenzoyl-1,3-butadiene (1). This compound was prepared using the method of Bailey and Ross,[1] except that special lighting conditions were used to circumvent the photolability of the compound, i.e., Westinghouse lamp No. F 20T 12/GO "Gold-Bug-A-Way" 20W (0% transmittance <500 nm).

(*E,Z*)-1,4-Dibenzoyl-1,3-butadiene (2). A solution of 1.38 g of freshly prepared glyoxal **4**[5] and 18.1 g of phenacyltriphenylphosphorane (**5**)[6] in 300 mL of absolute ethanol was stirred for 24 h at room temperature. The precipitated solid, 4.5 g, was shown by TLC to consist of two compounds of very similar R_f. A 0.4-g portion of this material was dissolved in a minimum amount of methylene chloride and chromatographed on 140 g of neutral silica gel, eluting with benzene. We were able to partially separate the mixture into 0.21 g of pure **1** and 0.10 g of the second component. The IR, ^{1}H-NMR, and mass spectra of the two compounds were extremely similar. A solution of the second component in methylene chloride was stirred with a crystal of iodine. After a short period of time, isomerization to **1** was observed. Extended treatment of either **1** or the second component with either iodine or dilute HCl resulted in formation of a compound that was shown by spectroscopic analysis to be 2-phenacyl-5-phenylfuran.[3] The ^{13}C-proton-decoupled-NMR spectrum of the second compound was, unlike its ^{1}H-NMR spectrum, markedly different from that of **1**, evincing 11 lines at 129.0, 129.1, 138.0, and 138.3 (aromatic C), 130.6, 133.3, and 133.7 (aromatic and α-olefinic C), 139.8 and 140.0 (β-olefinic C), and 191.6 and 191.7 ppm (carbonyl C). Compound **1** showed only seven lines in its ^{13}C spectrum, at 128.9, 129.1, 132.9, and 137.8 (aromatic C), 128.9 (α-olefinic C), 141.5 (β-olefinic C), and 190.3 ppm (carbonyl C).

Solid-State Photochemistry of (*E,E*)-1,4-dibenzoyl-1,3-butadiene (1). In a typical experiment either 0.3 g of finely divided **1** was placed in an uncovered Petri dish or a solution of 0.3 g of **1** in methylene chloride was placed in an uncovered Petri dish and allowed to evaporate in the dark. The solid was irradiated with a 275 W sunlamp. After 3 h, thin-layer chromatography showed that the conversion to a single photoproduct was quantitative, with no detectible starting material. This material, a slightly off-white solid, mp 206–7 °C (lit.[1] 207–8 °C), could be recrystallized from either benzene or chloroform to give a white solid that showed no change in melting point.

The IR spectrum (KBr) displayed strong absorption at 1661, 1612, 1600, and 1582 cm^{-1}, consistent with an α,β-unsaturated carbonyl. The UV spectrum (95% EtOH) showed $\lambda\lambda_{max}$ at 250 (log ϵ 4.29) and ca. 330 nm (sh, log ϵ 3.23). The UV spectrum (95% EtOH) of 1-phe-

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nyl-2-buten-1-one showed $\lambda\lambda_{max}$ at 254 (log ϵ 4.24) and 330 nm (log ϵ 1.77). Its mass spectrum gave a M^+ at 524 plus fragments at *m/e* 506, 488, 419, 401, 299, 262, 157, 105, and 77. The 100-MHz ^{1}H-NMR spectrum evinced multiplets at δ 7.97 and 7.45 (20 H), a multiplet at δ 6.80 (4 H), and a broad singlet at δ 4.48 (4 H). The proton-decoupled ^{13}C-NMR spectrum showed lines at 40.1 and 48.5 (alicyclic C), 128.9, 129.2, 129.4, 133.1, 136.6, and 137.9 (aromatic C), 134.2 and 145.1 (olefinic C), and 190.9 and 198.1 ppm (carbonyl C).

Solid-State Photochemistry of (*E,Z*)-1,4-Dibenzoyl-1,3-butadiene (2). Irradiation of **2** was carried out in a manner similar to that for **1** (vide supra). The product was shown by TLC to consist of two compounds of nearly identical R_f. Thus far the mixture has resisted all attempts at separation.

Acknowledgments. We wish to thank Drs. Michael Shapiro and Renate Coombs of Sandoz, Inc. for their help in obtaining ^{13}C-NMR and mass spectra and Mr. Robert Casani for obtaining the UV spectra.

Registry No.—**1**, 65682-02-2; **2**, 65682-03-3; **4**, 107-22-2; **5**, 859-65-4; **7**, 65682-04-4; 2-phenacyl-5-phenylfuran, 54980-24-4; 1-phenyl-2-buten-1-one, 495-41-0.

References and Notes

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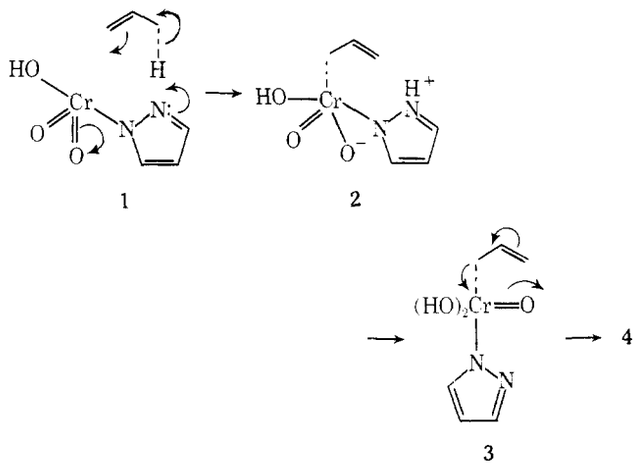
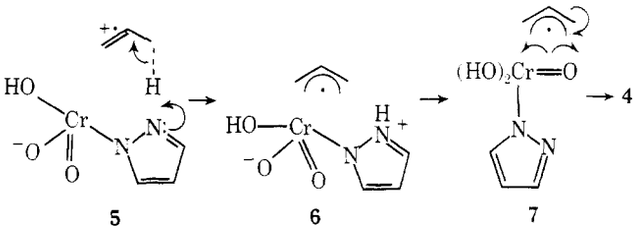
Scheme I



Scheme II



Allylic Oxidation with 3,5-Dimethylpyrazole. Chromium Trioxide Complex. Steroidal Δ^5-7-Ketones

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In our work on syntheses of hydroxylated metabolites of vitamin D[1,2], we have studied various approaches to the introduction of the 5,7-diene system of the provitamins.[3] Bromination at C-7 of a Δ^5-steroid followed by dehydrobromination is a well-known procedure[4] but gives mixtures of $\Delta^{5,7}$- and $\Delta^{4,6}$-dienes, which are often difficult to separate. As an alternative, we recently described the oxidation of a 7β-phenylselenide;[2] this approach does give 5,7-diene uncontaminated by 4,6-diene, but the yield is limited by simultaneous production of a 5β-hydroxy Δ^6-steroid. The thermal decomposition of the lithium salt of a Δ^5-7-tosylhydrazone leads in excellent yield[5] to the corresponding 5,7-diene uncontaminated by 4,6-diene. Accordingly, we set out to study the conversion of Δ^5-steroids to Δ^5-7-ketones.

A number of oxidants based on chromium[6] have been reported to accomplish this transformation. In our work, we chose initially cholesteryl benzoate as a model. The allylic oxidation of cholesteryl benzoate with sodium chromate in acetic acid/acetic anhydride[7] is, in our experience, a poor reaction and our best yield of the Δ^5-7-ketone was 38%. The use of Collins reagent[8,9] produced in situ gave a 68% yield, but the volume of methylene chloride used as solvent and the amount of calcined Celite[11] used to absorb precipitated oily solids is enormous. The time required for complete reaction, in our hands, in the latter case is ca. 50 h and 3–4 days in the former. Pyridinium chlorochromate[12,13] in methylene chloride at room temperature did not bring about any allylic oxidation.

We have found that the allylic oxidation of cholesteryl benzoate with 3,5-dimethylpyrazole chromium trioxide complex[14] (DMP·CrO_3) is remarkably fast.[15] In reactions where the molar ratio of the CrO_3 to steroid is the same (ca. 20:1) as that required for complete reaction with pyridine as ligand, the reaction with DMP as ligand is complete in less than 30 min, representing a rate increase of some 100-fold. The DMP is recoverable in yields ranging from 70–90% and the yield of the Δ^5-7-ketone is routinely 70–75%.

A probable explanation for the rate enhancement of this oxidation lies partly in the much increased solubility of the chromium containing complexes but more importantly in the possibility of intramolecular acceleration due to the pyrazole nucleus. Many of the characteristics of the reaction are consistent with either of the following mechanistic schemes, proposed as reasonable heuristics. They differ only in the details of the manner in which a carbon oxygen bond is first established at C-7. In Scheme I one two-electron transfer is involved; in Scheme II two one-electron transfers take place. The salient feature of both is that the chromium complex attacks first at the double bond and not at the allylic methylene group.[16]

Both schemes assume a one-to-one addition of DMP and CrO_3 to give the complex shown[14,17] (the 3,5-methyl groups are omitted for the sake of clarity), in which one ligand site remains free on the chromium atom allowing facile attack by the π electrons of the double bond. In Scheme I, the complex attacks the 5,6-double bond by means of an "ene" reaction wherein the removal of the axial 7α-hydrogen is hastened by the appositely placed basic nitrogen of the pyrazole ligand. Such an intramolecular course of action is not possible with Py_2·CrO_3 because (a) no ligand sites are available for complexation with π electrons unless pyridine is first displaced and (b) then no basic nitrogen is available to assist in the removal of the 7α-hydrogen except by an intermolecular deprotonation by the displaced pyridine. It is for stereoelectronic reasons[18] that the Cr will attack axially at C-5 and that an axial C-H bond will be severed, since overlap of the interacting orbitals is maximum in this geometrical array.

In passing from **1** to **2**, no reduction of the Cr^{VI} has taken

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