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Phenyl Group Migration during Pyrolytic and Photolytic Deazotizations of 1,2-Bis[2-(phenylated 2,5-dihydrofuranyl)]hydrazines to β , γ -Unsaturated Ketones^{1-3a-c,4a}

C. V. Juelke,^{1,3c} D. W. Boykin, Jr.,*^{2b,c,3b} J. I. Dale,^{2a,3a} and R. E. Lutz*

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901

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Chemistry related to 1,2-bis[2-(phenylated 2,5-dihydrofuranyl)]hydrazines is detailed. Pyrolytic and photolytic deazotizations converted the 2,3,5,5-tetraphenylated derivative into 1,3,4,4-tetraphenyl-3-butenone with migration of a 5-phenyl, but pyrolysis in decalin also gave some isomeric 1,2,4,4-tetraphenyl ketone without phenyl migration. These results were corroborated by ¹⁴C-phenyl tracing. Fusion pyrolysis and photolysis of the 2,4,5,5-tetraphenyl isomer gave mainly the 1,3,4,4-tetraphenyl unsaturated ketone without phenyl migration, but pyrolysis in decalin produced also a small amount of isomeric 1,2,4,4-tetraphenyl ketone with phenyl migration. Pyrolysis of the bis(2,3,4,5,5-pentaphenyl) analog gave 1,2,3,4,4-pentaphenyl-3-buten-1-one, 2,3,4,5,5-pentaphenyl-2,3-dihydrofuran, and tetraphenylfuran. ¹⁴C tracing showed that ketone formation involved some 5- to 2-phenyl migration and that the furan resulted from elimination of a 5-phenyl. Photolysis gave the unsaturated ketone, the dihydrofuran, and 1-benzoyl-1,2,2,3-tetraphenylcyclopropane. Mechanisms are considered. Synthesis, chemistry, and aryl migrations in the 2,3,5,5-tetraphenyl-2,5-dihydrofuranol series, *p*-MeO or *p*-CF₃ labeled in one of the 5,5-diphenyl positions, establish a foundation for further work.

It has been shown^{3a,b,4a} that the product of reaction of 2,3,5,5-tetraphenyl-2,5-dihydrofuranol-2 (4) with hydrazine,^{4b} namely 1,2-bis[2-(2,3,5,5-tetraphenyl-2,5-dihydrofuranyl)]hydrazine^{4a} (1), undergoes pyrolytic deazotization to the 1,3,4,4-tetraphenyl β , γ -unsaturated ketone 14^{4d,5} and empirically involves 5 to 2 transannular migration of a 5phenyl (1,4-cis migration relative to the acyclic tautomeric forms). Related examples of phenyl migrations are known,⁶ but there appears to be no exact precedent for the type described in our previous preliminary report.^{4a} This report contains the details of the study on 1 and extends the investigation to include the 2,4,5,5-tetraphenyl and 2,3,4,5,5pentaphenyl analogs 2 and 3.





The vic-1,2-bis(dihydrofuranyl)hydrazine structures 1-3 (rather than the gem-1,1-bis structures), with intramolecu-



lar hydrogen bonding (32), are supported by ir spectra^{4a,7a} and analogy to 1,2-bis(organosilyl)hydrazines where preference for forming 1,2-bis types increases with increasing steric bulk of the organo groups⁸ and where the two types have been distinguished by the effect of coupling interaction of the N-H stretching modes to give in-phase and outof-phase stretching bands of different frequencies (for H-N-H of the 1,1 isomers the band separations were 76-88 cm⁻¹, but for H-N-N-H of the 1,2 isomers they did not exceed 23 cm⁻¹). The ir spectra of 1-3 obtained in CCl₄^{7b} showed sharp single bands at 3555, 3260, and 3240 cm⁻¹, respectively, with lower frequency shoulders which represent peak separations on the order of 10-20 cm⁻¹, and the latter correspond to the small peak separations for 1,2bishydrazines.⁸

1,2-Bis[2-(2,4,5,5-tetraphenyldihydrofuranyl)]hydrazine (2), the positional isomer of 1, was prepared by reaction of hydrazine in AcOH with 2-ethoxydihydrofuran (10), using the sequence $8^{4g} \rightarrow 9^{3d,g} \rightarrow 10 \rightarrow 2$. Acid-catalyzed ethanolysis of 2 gave cyclic ketal 10 which underwent

Zn-AcOH conjugate reduction to the β , γ -unsaturated ketone 14,^{3g} with proton acquisition at position 3 and without 5- to 4-phenyl migration.



1,2-Bis[2-(2,3,4,5,5-pentaphenyldihydrofuranyl)]hydrazine (3) was obtained by the reaction of hydrazine with dihydrofuranol (12) which had been made by addition of PhLi to *cis*-dibenzoylstilbene (11).^{3a,g} Acid-catalyzed hydrolysis of 3 gave 12, and ethanolysis with or without added H^+ gave ketal 13.



Deazotization of 1,2-Bis[2-(2,3,5,5-tetraphenyldihydrofuranyl)]hydrazine (1). Pyrolysis by fusion (220°), in decalin (160°) or in DMF (153°), and photolysis⁹ in benzene gave N₂ and β , γ -unsaturated ketone 14^{4d} in yields of 68, 58, 40, and 50%, respectively. In 1 the 5,5-diphenyls



were two carbons removed from the one nonterminal 3phenyl, and in product 14 they are adjacent to that phenyl. Therefore, 5 to 2 transannular (or cis-1,4) phenyl migration must have occurred. In only one of these four experiments, pyrolysis in the relatively nonpolar decalin, was the isomeric ketone 15⁴ⁱ also obtained, without phenyl migration (total ketone yield 82%, 14:15 = 58:24%). In no case was there formed either 2,5- or the 4,5-dihydrofuran 16 or 17. That the 2,5 isomer 16 was not an intermediate in the reactions was shown by its preparation from dihydrofuranol (4) by LiAlH₄ reduction to 1,4-glycol 20 and cyclodehydration, and by the distinctive behavior of both isomers 16 and 17 under the deazotizing conditions in giving products, none of which were isolated in the deazotizations of 1.

Although it is certain from the structure of ketone 14 that phenyl migration did occur in the deazotization of 1, this was corroborated by ¹⁴C tracings which also gave pertinent information limiting the mechanistic possibilities. Two samples, 1* and 1#, ¹⁴C-labeled respectively in the gem-diphenyls and at carbon-5, were prepared through dibenzoylstyrenes 21* and 21# and dihydrofuranols 4* and 4#, starting from samples of acetophenone ¹⁴C-labeled respectively in the phenyl and at the carbonyl carbon. To show that in 1* the gem-diphenyls contained all of the orig-



inal ¹⁴C label, and thereby to preclude the possibility of rearrangement during deazotizations or oxidations, a sample was oxidized by CrO_3 to Ph_2CO which within experimental error contained all of the original ¹⁴C (98%).



In the tracing experiments outlined below, oxidations of unsaturated ketone 14* obtained from pyrolysis and photolysis of 22^* (1) gave benzophenone and benzoic acid containing respectively 48 and 52% of the original ¹⁴C activity, thus demonstrating phenyl migration (otherwise ¹⁴C activities would have been 100 and 0%).



The noninvolvement in the above reactions of the 3-phenyl and carbon-3 of 22^* and $22^\#$ (1) was demonstrated by additions of PhLi to the unsaturated ketones 14^* and $14^\#$ and by oxidation of the resulting unsaturated alcohols 23^* and $23^\#$ to benzophenone containing practically all of the original ¹⁴C and benzoic acid containing none. These exper-

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iments show that orderly and extensive *irreversible* 5- to 2-phenyl migration had been involved; they preclude scrambling of 14 C-phenyls between positions 5 and 2; and they preclude total scrambling of the 14 C-phenyls *via* cyclobutenyl intermediates such as 24–26.



To complete proof that phenyl migration or skeletal rearrangement had occurred neither during formation of the minor product 15 nor in the oxidations of 14 and 15, 22* (1) was pyrolyzed and the resulting ketones 14* and 15* were then oxidized; 15* gave benzophenone containing all of the original ¹⁴C and cold benzoic acid, whereas 14* gave benzophenone and benzoic acid each containing half of the original ¹⁴C.

Deazotization of 1,2-Bis[2-(2,4,5,5-tetraphenyl-2,5dihydrofuranyl)]hydrazine (2).^{3c} From fusion pyrolysis (210°), and from photolysis in benzene,⁹ only β , γ -unsaturated ketone 14 was isolated, without phenyl migration. Pyrolysis in refluxing decalin, however, gave a mixture of ketones 14 (32%) and 15 (5.7%), the latter involving 5- to 2-phenyl migration; and the ratio of migration to nonmigration was in the direction opposite that in the comparable pyrolysis of 1, a point of limited significance, however, because of the low total ketone yield (38%).

Deazotization of 1,2-Bis[2-(2,3,4,5,5-pentaphenyldihydrofuranyl)]hydrazine (3).^{3c} Pyrolysis by fusion (280°) or in decalin (190°) gave the expected β , γ -unsaturated ketone 28 and two additional products, 2,3,4,5,5-pentaphenyl-4,5-dihydrofuran (29) and tetraphenylfuran (7). In DMF (153°) no reaction occurred (as did with 1).



It is significant that $KMnO_4$ oxidation of unsaturated ketone 28 to benzophenone and benzoic acid was very slow and that upon interruption it gave a considerable amount

of presumably intermediate dihydrofuranol 12, a type of reaction possible but not observed in oxidations of the tetraphenyl unsaturated ketones 14 and 15. This oxidation is the reverse of conjugate reductions of dihydrofuranol $12 \rightarrow$ 28 (and of $10 \rightarrow 14$); and doubtless steric and resonancestabilized cyclic radical intermediates are involved. Prolonged Zn-AcOH reduction of dihydrofuranol (12) carried the reduction beyond 28 to saturated ketone 30.

It is not known from the foregoing whether ketone 28 produced in the pyrolysis of unlabeled 3 had been formed with or without phenyl migration because in either event the result would be the same. To determine this, 3* ¹⁴Clabeled in the gem-diphenyl was synthesized by additioncyclization of *cis*-dibenzoylstilbene $(11)^{3g}$ by ¹⁴C-labeled *PhLi and treatment of the resulting pentaphenyldihydrofuranol 12* with hydrazine. Two of the products of fusion pyrolysis of 3*, namely 7* and 28*, were oxidized by KMnO₄. Benzoic acid obtained from the furan 7 contained half of the original ¹⁴C, showing that one of the 5,5-diphenyls had been expelled and that little if any prior 5- to 2phenyl migration had occurred (otherwise ¹⁴C activity in the furan would have been higher than 50%). Benzophenone obtained from oxidation of unsaturated ketone 28 contained 78.6% of the original ¹⁴C, proving that phenyl migration actually had occurred to a considerable extent. This result is to be considered in relation to the 50, 67, and 75% expected if competitive mechanisms involved irreversibility of migration at all stages, 5 to 2 scrambling through reversibility at some intermediate stage, and irreversible degeneration from a symmetrical intermediate such as 40.

The photolysis⁹ of 3 in benzene yielded unsaturated ketone 28, the 4,5-dihydrofuran 29 (involving proton transfer to position 2), and 1-benzoyl-1,2,2,3-tetraphenylcyclopropane (31). It had previously been shown^{4b} that under these conditions ketone 28 is relatively stable but that dihydrofuran 29 is converted into 31. Thus, 28 and 29 are the primary photolytic products, and cyclopropyl ketone 31 results from photolysis of 29.



Discussion

2,3,5,5-Tetraphenyldihydrofuranol types 1, 4, and 5 undergo acid-catalyzed furanization easily with facile 5- to 4phenyl migration clearing the way. The isomeric compounds 2 and 10 with the nonterminal phenyl at position 4, however, do not furanize because of obvious mechanistic difficulty in the required phenyl migration. The pentaphenyl compounds 3, 12, and 13 cannot furanize readily because expulsion of a molecule of benzene would be required, but it does happen to a small extent in pyrolysis of 3. The various deazotization products cannot furanize directly because their lower oxidation state constitutes a barrier to be surmounted by some form of oxidation.

The deazotizations of 1 and 2, with or without phenyl migration, involve overall intramolecular oxidation-reduction, in which the hydrazine nitrogens become oxidized to molecular nitrogen (perhaps through diimide or its equivalent) and in which the dihydrofuryl moieties become reduced. The reactions may be concerted with hydrogen bonding playing a role (*e.g.*, 32). Initial cleavage may be heterolytic, 32 (a); giving ketone 15, without phenyl migration, through 32 (b) and dienol 33, or directly by 32 (c); and giving ketone 14 through carbenoid anion¹⁰ 34-35 where

position 2 becomes receptor for the migrating phenyl, through 35 (e,f) and enol 36, or directly by 35 (e,g).



Or the initial cleavage may be homolytic, giving steric and resonance-stabilized intermediate radicals, e.g., 37-40.



Relative yields of ketones 14 and 15 are a measure of phenyl migration aptitudes in 1 and 2 (through 37 and 38), and they show that $1 \gg 2$. In 2 (and 38) steric buttressing stresses on the 5,5-diphenyl group by the 4-phenyl, and minimization of steric interference at the receptor site 2 through absence of phenyl at position 3, call for opposite migrational aptitudes of $1 \ll 2$. Activation energies for intramolecular reaction, however, would be higher for 1 than for 2 because the 1-4 allyloxy system of intermediate 37 with its 3-phenyl lacks the increment of conjugation stabilization which is furnished in 38 (from 2) by terminal conjugation with the 4-phenyl. This would account for the observed migration aptitudes $1 \gg 2$. Although extensive phenyl migration occurs in the deazotization of the pentaphenyl compound 3*, the amount may not be truly measured by the ¹⁴C activity of benzophenone obtained on oxidation of the resulting ketone 28* (as it is in the cases of ketones 14* and 15#). A low activation energy for reaching the symmetrical pentaphenyl intermediate 40 (relative to that for the tetraphenyl analog 39) may permit this as a competitive path involving 5- to 2-phenyl migrational interchange. An important extension of this work would be determination of the true extent of migration here and whether or not any 5- to 2-phenyl migration occurs in related reactions such as reductions of 3, 12, 13, and analogs and in pyrolysis and photolysis of 2-alkoxy, 2-carboxy, and related derivatives.

The pyrolyses and photolyses of 1 and 2 appear to be significantly different because product ratios are quite different, but it is not known whether the migrating phenyl is in different states or in the same as would be the case if the photoexcited state underwent internal conversion to the thermally excited state. Initiating work was undertaken in the migration-prone 2,4,5,5-tetraphenyl series to obtain analogs carrying a p-MeO or p-CF₃ as a label on one of the 5.5-diphenyls toward migrational aptitude and crossover studies which might give pertinent information on the electronic identity of the migrating phenyl and receptor site. Although the few experiments on the reaction of hydrazine with the analogs of 4 and 5 failed to give bis(dihydrofuranyl)hydrazines of type 1, the results on their precursors 41-59 are of interest per se and afford foundation for further study.

Experimental Section¹¹

2,3-Diphenyl-5,5-[¹⁴C-diphenyl]-2,5-dihydrofuranol-2 (4*).^{4b,c} Condensation of benzil with ¹⁴C-phenyl labeled acetophenone [from AcCl¹² + C₆H₆ (30.8 g, 0.1 mCi)] gave *cis*-1,2-diphenyl-4-[¹⁴C-phenyl]-2-butene-1,4-dione (21*, 88%, mp 128-129°^{3a,4g}). Of this, 25 g was added (2 min) to stirred PhLi [from Li wire (4.5 g), PhBr (50 g), Et₂O (300 ml), 0°, 5 min]. Hydrolysis (ice–NH₄Cl), extraction (Et₂O), and crystallization (C₆H₆-hexane) gave 4* [25 g, 80%, mp 140–143° (lit.^{4c} 144–146°)].

1,2-Bis[2-(2,3-diphenyl-5,5-[¹⁴C-diphenyl]-2,5-dihydrofuranyl)]hydrazine (1*). To a solution of 4* [6 g, AcOH (75 ml), 50°] was added dropwise 85% hydrazine hydrate [2 ml in AcOH (15 ml), stirring, 2 min]. Cooling gave 1* (5.0 g, 84%) which was recrystallized (C₆H₆-absolute EtOH): mp 214-218° dec; uv ($\epsilon \times 10^{-3}$) 253.5 nm (28.4); ir (CCl₄)^{3b} 3555 (narrow), shoulder at 3575 (NH), 3440 cm⁻¹ (br, NH, persisting at increased dilution), no absorption in the 1600-cm⁻¹ range assignable to NH₂, C=O, or C=N. Anal. Calcd for C₅₆H₄₄N₂O₂: C, 86.55; H, 5.71; N, 3.61. Found: C, 86.38; H, 5.88; N, 4.04. Furanization [1 (0.2 g), AcOH-concentrated HCl (25:1 ml), heating, 1 hr] gave 7 (94%). Alcoholysis [1 (3 g), absolute EtOH-AcOH (10 ml), reflux, 30 hr] quenching (H₂O), and recrystallization (petroleum ether-hexane) gave 2-ethoxy-2,3-diphenyl-5,5-[¹⁴C-diphenyl]-2,5-dihydrofuran (6*): 1.9 g (60%); mp 112-114° (lit.^{4b.c} 116-118°).

Oxidation of 6* [1.1 g, slurry, AcOH (75 ml), CrO₃ (2 g), 20 min (75°), 20 min (50°), basification (K₂CO₃), steam distillation, and extraction (Et₂O)] gave benzophenone which was chromatographed (Al₂O₃, 1:19–1:9 C₆H₆-petroleum pentane) and converted¹³ into the 2,4-dinitrophenylhydrazone [40%, recrystallized (C₆H₆-EtOH), mp 237–239° (lit.¹³ 239°)]. Attempted KMnO₄ oxidation of 6 failed (6 recovered).

Deazotizations of 1. (A) Pyrolysis [4 g heated slowly to 225° $(\rightarrow N_2)$] and chromatography (Florisil, 30-100% C₆H₆-petroleum ether fractions) gave 1,3,4,4-tetraphenyl-3-buten-1-one [14, 2.6 g (68%), mp 192–193° (lit.^{4d} 194–195°); no 15 was isolated].

(B) Pyrolysis in decalin (1 g, 10 ml), purification by chromatography (Al_2O_3 , 20–40% C_6H_6 -petroleum pentane), and fractional crystallizations gave 14 (0.56 g, 58% total) and 15 (0.23 g, 24%), mp 90–92°.⁴ⁱ

(C) Pyrolysis in DMF (3 g, 600 ml, reflux, 4 hr, 153°), cooling, quenching (H₂O), and recrystallization (EtOH-benzene) gave 14 (1.15 g, 40%), mp 193-195° (no 15 was isolated). Identification of N₂ was by injection of a DMF solution of 1 into the preheated vpc block (225°) and separation on a 5 ft \times $\frac{1}{6}$ in. Cu column (molecular sieve 5A, 30°, carrier gas, He, O₂ for reference peak¹⁴).

(D) Photolysis⁹ [2 g, C₆H₆ (800 ml)] and fractional crystallization (absolute EtOH) gave unchanged 1 (1.35 g, 67%, mp 214–218° dec) and 15 [(0.32 g) 50% from 1 consumed, recrystallized (C₆H₆-EtOH), mp 193–194°]. A similar experiment (chromatographing) gave no 15.

KMnO₄ Oxidations of Unsaturated Ketones 14^{*} and 15^{*}. Typically, a mixture of 14 (0.45 g), 60% pyridine–H₂O (350 ml), and KMnO₄ (1 g) was refluxed until the purple disappeared and then continued with 1-g additions of KMnO₄ to a total of 6 g and persistence of color. Steam distillation gave the pyridine–H₂O azeotrope and then cloudy distillate from which benzophenone was extracted [acidification (HCl), Et₂O] and converted¹³ to the 2,4dinitrophenylhydrazone (0.3 g, 69%). Acidification of the steam distillation residue, reduction (NaHSO₃), extractions (Et₂O), and Deazotizations of Bis(phenylated dihydrofuranyl)hydrazines

Table I

¹⁴C Activities^a of Benzophenone^b and Benzoic Acid from

Oxidative ^{c,d} Degradations of Deazotization Products			
	Reaction ^f	Ph ₂ C=NNHPh-	
Substrate	(of 1* [#] or 1 [#] and 3 [#])	(NO2)2 ^b	PhCOOH
14*	Pyrolysis, neat	48.2	51.8
14*	Pyrolysis, DMF	48.0	52.8
6 * ^{<i>d</i>}	Ethanolysis	98.2	
2 3*	Pyrolysis, DMF; then PhLi	98.9	4.6 ^{<i>e</i>}
15*	Pyrolysis, decalin	95.7	$10.7^{g,h}$
14#	Pyrolysis, DMF	2.2	99
14 [#]	Photolysis, ^m benzene	2.2	99.5
21#	Pyrolysis, decalin	103	19 ^g , ^h
2 3 [#]	Pyrolysis, DMF; then PhLi	102	4.5
$23^{\#d}$	Pyrolysis, DMF; then PhLi	100	14.5 [¢]
23 [#]	Photolysis, ^m DMF; then PhLi	100.6	4.4 ^{<i>g</i>}
2 8*	Photolysis, ^m neat	78.5^{i}	$13.5,^{j}9.3^{k,l}$
7*	Durolucic " nost		52 9

Pyrolysis,^m neat ^a Relative to starting materials taken as 100%; 1*, 4*, 17*, and 3^* randomly ¹⁴C labeled in one of the 5,5-diphenyls and $1^=$ and $25^=$ at ring carbon-5 and chain carbon-1, respectively. Radioactivities were determined by means of a Tracerlab, Inc., Model superscaler, using 100-mg samples in 25-nm stainless steel planchets. Experimental error, 2-3%. ^b Isolated and measured as the 2,4-dinitrophenylhydrazone. ^c KMnO₄ except where ^dCrO₃ is specified. e Formula number of compounds whose 14C content was being determined. / Source of compounds and reactions involved. g These high ¹⁴C activities can be explained in terms of some oxidative attack on phenyl groups prior to carbon chain cleavage, e.g., using the more active CrO_3 or ^ha large excess of $KMnO_4$. This does not vitiate interpretations of results based on ¹⁴C activities of the benzophenone moiety which were consistent within experimental error in a number of comparisons of activities at the several stages of synthesis from ¹⁴C active bromobenzene and acetophenone-1-¹⁴C. The benzoic acid ¹⁴C activities were determined and considered as secondary checks. ⁱ The weight of substrate counted (mg): 75; ^j46; ^k28. ^l During this oxidation there was loss of ca. 18% of the original ¹⁴C activity. This was presumed to result from relatively rapid initial attack at the benzylic C-H group of 28 and 1,2 cleavage followed by partial oxidative destruction of the resulting ¹⁴C labeled benzoic acid during the long drawn out completion of the oxidation of the relatively stable diphenylchalcone which is doubtless the intermediate in formation of benzophenone. The probable correctness of this interpretation was supported by the results of interruption of a typical oxidation of 28 whereby the ¹⁴C activity of the benzoic acid obtained rose to 13.7%, a significantly higher value but one still considerably lower than the stoichiometric 21.4% demanded on the basis of the 14C activity of the benzophenone produced. m Cf. ref 9.

evaporation gave benzoic acid (1.4 g, 48%) which was recrystallized (H₂O): mp 120–122°.

Addition of PhLi to 1,3,4,4-Tetraphenyl-3-buten-1-one (14* and $14^{\#}$). 1,1,3,4,4-Pentaphenyl-3-buten-1-ol (23* and 23[#]). To stirred PhLi [from Li (0.23 g) and PhBr (2.51 g), Et₂O (15 ml), -5°], 14* was added (1.5 g, stirring, 5 min). Hydrolysis (ice-NH₄Cl), extractions (Et₂O), and recrystallization (absolute EtOH) gave 23 (0.95 g, 65%), mp 175–177° (lit^{3a} mp 175.5–178°).

Oxidation of 23* (or 23#) (0.85 g) by CrO_3 (3.6 g) and AcOH (25 ml), reflux, 3 hr), evaporation, basification (5% K₂CO₃), steam distillation, and extraction (Et₂O) gave benzophenone which was converted into the [1⁴C]-2,5-dinitrophenylhydrazone¹³ (75%). Acidification of the steam distillation residue, extraction (Et₂O), and evaporation gave benzoic acid, 0.14 g (61%), which was crystallized (H₂O): mp 120-122° (this had small ¹⁴C activity arising presumably from some oxidative degradation of one of the [1⁴C]-gem-diphenyl groups prior of subsequent to benzophenone formation).

 $\rm KMnO_4$ oxidation of 23* (procedure for 14*) gave benzoic acid with a little $^{14}\rm C$ activity.

1,2,2,4-Tetraphenylbutane-1,4-dione (*pseudo*-Bidesyl, 9^{3d.g}). To PhLi [from Li (0.16 g), PhBr (11.1 g), Et₂O (300 ml), 0°] was added 3,3,5-triphenylcrotolactone [8g^{4g} (16 g), stirring, 2 min]. Quenching (ice-NH₄Cl) gave 9 (16.2 g, 82%) which was recrystallized (C₆H₆-EtOH): mp 156-157° (lit.^{3d} mp 159-160°); uv (EtOH) 244 nm (ϵ 21,950); ir 5.95 μ (aromatic C=O). Anal.^{3d} Calcd for C₂₈H₂₂O₂: C, 86.12; H, 5.68. Found: C, 85.92; H, 5.61.

2-Ethoxy-2,4,5,5-tetraphenyl-2,5-dihydrofuran (10).^{3d,4d} To **9** (5 g) in AcOH (150 ml) was added concentrated H₂SO₄ (2.5 ml). Stirring until solution, standing (4 hr), quenching (H₂O), extraction (Et₂O), washing (H₂O-NaHCO₃), evaporation, and digestion (absolute EtOH) gave **10** (4.6 g, 86%) which was recrystallized (absolute EtOH): mp 148-149° (lit.^{3d} mp 149-153°). Anal.^{3d} Calcd for $C_{30}H_{26}O_2$: C, 86.09; H, 6.26. Found: C, 85.65; H, 6.16. Reduction of **10** [1 g, AcOH (40 ml), Zn dust (2 g), 1 hr] gave **1,3,4,4-tetraphenyl-3-buten-1-one** (14) which was recrystallized (EtOH-AcOH): 39% mp 190-193° (lit.^{4d} 193-195.5°).

Synthesis of Analogs of 2,3,5,5-Tetraphenyl-2,5-dihydrofuranol (4) carrying one p-MeO or p-CF₃ group (44-46) utilized the preference of the appropriate diaroylstyrenes (41¹⁵-43) for additions of PhLi or p-CF₃PhLi to the less hindered carbonyl group and for conjugate additions of PhMgBr and p-CF₃PhMgBr β to the less hindered α,β -unsaturated ketone system. In the PhLi reac-



tion with 41 where the p-MeOPhCO carbonyl activity is somewhat lessened by p-MeO, a significant amount of β addition to the less hindered of the two α,β -unsaturated ketone systems occurs in competition with the 4-carbonyl addition which then follows to give diaddition product 51.^{4d} PhMgBr shows its preference for β addition to the less hindered C=C_C=O of 41, subsequent dehydration giving furan 50. p-CF₃PhMgBr, while reacting β to the less hindered C=C-C=O of 43 to give saturated diketone 52 and furan 49, also to a small extent added β to the more hindered C=C-C=O, giving 53. The structure of 53 was shown by KOH cleavage to 54, by acid-catalyzed rearrangement with 2 to 1 migration of the 2-Ph rather than the 2-p-CF₃Ph, and by methanolysis to 55 whose structure follows by its difference from 46 methyl ether. The 5,5-diaryl-2,5-dihydrofuranols 44-46 were dehydratively rearranged to the expected furans 47 and 48, p-MeOPh consistently migrating in preference to Ph, and Ph migrating in preference to p-CF₃Ph. Oxidations of the furans 47-50 by HNO₃-AcOH, and of saturated diketone 52 by DMSO-KOH-O₂, gave the respective diaroylethylenes 56-59.

4-p-Anisyl-1,2-diphenyl-2-butene-1,4-dione (41):¹⁵ mp 182–184° (lit.¹⁵ mp 177°); uv ($\epsilon \times 10^{-3}$) 239, 320 nm (19.7, 2.31); ir 1665, 1640 cm⁻¹; nmr δ 7.4 (m, 15), 3.77 (s, 3).

2-p-Anisyl-1,4-diphenylbutene-1,4-dione (42).^{15,16} Chromatographing (Florisil, 70–100% benzene-petroleum ether fractions) gave 3.5% which was recrystallized (EtOH): mp 134–136°; uv ($\epsilon \times 10^{-3}$) 247, 344 nm (22.0, 13.7); ir 1645, 1655 cm⁻¹; nmr δ 7.5 (m, 15), 3.77 (s, 3). Anal. Calcd for C₂₃H₁₈O₃; C, 80.68; H, 5.30. Found: C, 80.48; H, 5.11. It had been supposed (erroneously) that this was the isomer expected from condensation of acetophenone with the more active carbonyl of 4-methoxybenzil;¹⁶ structure 42 was proved by the relationships between 41 and 42, 44 and 45, and 47 and 50. The main product, an oil, which had been discarded, doubtless contained large amounts of the expected and presumably predominent isomer of 42.

5-p-Anisyl-2,3,5-triphenyl-2,5-dihydrofuranol (44, prepared like 4): 76%, mp 167–168°; uv ($\epsilon \times 10^{-3}$) 2.52 nm (18.4); ir (KBr) 2475 cm⁻¹; nmr δ 7.1 (m, 20), 3.76 (s, 3), 3.02 (s, 1, D₂O → O). Anal. Calcd for C₂₉H₂₄O₃: C, 82.83; H, 5.75. Found: C, 82.62; H, 5.58.



5-p-Anisyl-2,3,4,5-tetrahydrofuranol-2 (51) was isolated as a minor product in one preparation of 44: 0.35% mp 196–198°; uv ($\epsilon \times 10^{-3}$) 268 nm (4.0); ir 3410 cm⁻¹; nmr δ 7.1 (m, 24), 5.21 (split d, 1, J = 12.5 Hz), 3.73 (split d, 1, J = 12.5, 1.5 Hz, D₂O \rightarrow O), 3.72 (s, 3), 2.58 (split s, 1, J = 1.5 Hz). Anal. Calcd for C₃₅H₃₀O₃: C, 84.31; H, 6.06. Found: C, 84.37; H, 6.08.

44 methyl cyclic ketal (also the ethyl analog) was prepared from 44 (1 g) by a 30:1 milliliter mixture of absolute MeOH (or EtOH)-AcOH (reflux, 5 min, cooled): 74%; recrystallized from MeOH; mp 165–166°; uv ($\epsilon \times 10^{-3}$) 255 nm (22.0); ir 2960, 2935, 2825 cm⁻¹; nmr δ 7.2 (m, 20), 3.70 (s, 3), 3.13 (s, 3). Anal. Calcd for C₃₀H₂₆O₃: C, 82.92; H, 6.03. Found: C, 82.66; H, 6.16. 44 ethyl cyclic ketal: 75%; recrystallized from absolute EtOH; mp 145–146°; uv, ($\epsilon \times 10^{-3}$) 255 nm (22.1); ir 2970, 2925, 2875, 2830 cm⁻¹; nmr δ 7.2 (m, 20), 3.72 (s, 3), 3.27 (q, 2, J = 7 Hz), 1.12 (t, 3, J = 7 Hz). Anal. Calcd for C₃₁H₂₈O₃: C, 83.01; H, 6.29. Found: C, 82.89; H, 6.24.

3-*p*-Anisyl-2,5,5-triphenyl-2,5-dihydrofuranol-2 (45) was prepared (like 44) from 42: 78%; recrystallized from EtOH; mp 134–135°; uv ($\epsilon \times 10^{-3}$) 267 nm (21.2); ir 3420 cm⁻¹; nmr δ 7.2 (m, 20), 3.70 (s, 3), 2.99 (s, 1, D₂O → O). Anal. Calcd for C₂₉H₂₄O₃: C, 82.83; H, 5.75. Found: C, 82.63; H, 5.60. 45 ethyl cyclic ketal (prepared like 44 analog): 41%; mp 151–152°; uv ($\epsilon \times 10^{-3}$) 271 nm (23.8); ir 2935, 2835 cm⁻¹; nmr δ 7.3 (m, 20), 3.70 (s, 3), 3.33 (q, 2, J = 7 Hz), 1.11 (t, 3, J = 7 Hz). Anal. Calcd for C₃₁H₂₈O₃: C, 83.10; H, 6.29. Found: C, 82.75; H, 6.29.

5-p-Trifluoromethyl-2,3,5-triphenyl-2,5-dihydrofuranol-2 (46, Isolated as Methyl or Ethyl Cyclic Ketal). To BuLi from Li wire [1.04 g + n-BuBr (9.8 g), Et₂O, 30 min] was added p-CF₃PhBr [16 g, 0°, dropwise (a test sample + Dry Ice gave p-CF₃PhCOOH] and then cis-dibenzoylstyrene (43) (stirring, 5 min) and quenching (H₂O, ice, NH₄Cl), evaporation of Et₂O extracts, chromatography (Florisil), evaporation of the 70-100% benzene-petroleum ether eluent, and crystallization (EtOH) gave 6.3 g (ca. 70%) of a mixture of 46 and its ethyl cyclic ketal (ir, nmr) which was converted by EtOH (or MeOH)-AcOH (30:1 ml, reflux 2-5 min) into the cyclic ketal. 46 ethyl cyclic ketal: 66%; recrystallized from EtOH; mp 63–64°; uv ($\epsilon \times 10^{-3}$) 253 nm (22.1); nmr δ 7.5 (m, 20), 3.35 (q, 2, J = 7.4 Hz), 1.13 (t, 3, J = 7.5 Hz). Anal. Calcd for $C_{31}H_{25}F_{3}O_{2}$: C, 76.53; H, 5.18. Found: C, 76.32; H, 5.29. 46 methyl cyclic ketal: 47%; recrystallized from MeOH; mp 141–142°; uv ($\epsilon \times 10^{-3}$) 253 nm (21.7); nmr & 7.4 (m, 20), 3.13 (s, 3). Anal. Calcd for C₃₀H₂₃F₃O₂: C, 76.26; H, 4.91; F, 12.06. Found: C, 76.06; H, 4.90; F, 11.89.

Reactions of 44–46 with 85% hydrazine hydrate gave no bishydrazine derivatives (as did 4, 10, and 13). 46 instead underwent dehydrative rearrangement to furan 48, and the products from 44 and 45 on crystallization (EtOH) gave the ethyl cyclic ketals. Doubtless the analogs of 1 could be obtained under more sophisticated conditions.

3- *p*-Anisyl-2,4,5-triphenylfuran (47) was prepared from 44 by AcOH (reflux, 5 min, 98°) and from 45 (AcOH, trace H⁺, 71°) and was recrystallized (AcOH): mp 169–170°; uv ($\epsilon \times 10^{-3}$) 232, 292, 325 nm (28.9, 19.6, 24.1); nmr δ 7.2 (m, 19), 3.74 (s, 3). Anal. Calcd for C₂₉H₂₂O₂: C, 86.54; H, 5.51. Found: C, 86.31; H, 5.64.

2-p-Anisyl-3,4,5-triphenylfuran (50) was prepared by addition of 41 to PhMgBr-Et₂O, treatment with $I_{2,3g}$ and chromatography (Florisil, C₆H₆-petroleum ether): 19%; crystallized from

AcOH; mp 142–143°; uv ($\epsilon \times 10^{-3}$) 232, 250, 327 nm (21.0, 19.9, 22.0); nmr δ 7.2 (m, 19), 3.74 (s, 3). Anal. Calcd for C₂₉H₂₂O₂: C, 86.54; H, 5.51. Found: C, 86.23; H, 5.66.

2-*p***-Trifluoromethylphenyl-3,4,5-triphenylfuran (48).** Portions of the mixture of **46** and its ethyl ketal were treated with (a) AcOH-concentrated HCl (10:1 ml, reflux, 5 min) and (b) Et₂O [100 ml + I₂ (1 g), room temperature, 4 hr]: yields 74 and 10%, respectively; recrystallized from EtOH; mp 187-188°; uv ($\epsilon \times 10^{-3}$) 234, 265, 332 nm (25.8, 16.8, 25.6). Anal. Calcd for C₂₉H₁₉F₃O: C, 79.07; H, 4.35; F, 12.97. Found: C, 79.02, H, 4.39; F, 13.03.

Additions of p-CF₃PhMgBr to cis-Dibenzoylstyrene (43). 3-p-Trifluoromethylphenyl-2,4,5-triphenylfuran (49). To p-CF₃PhMgBr [from Mg (1.16 g + crystal of I₂), p-CF₃PhBr (12.2 g), and Et₂O (200 ml), 0°] was added 43 (10 g, stirring, 10 min). Hydrolysis, extractions (Et₂O), and chromatography (Florisil, benzene-petroleum ether) followed. The 20-40% fractions gave 49 (6.8 g, 48%): recrystallized from absolute EtOH; mp 144-145°; uv ($\epsilon \times$ 10⁻³) 231, 260 nm (shoulder), 320 (26.9, 18.9, 22.4). Anal. Calcd for C₂₉H₁₉F₃O: C, 79.07; H, 4.35. Found: C, 79.14; H, 4.48.

2-*p*-**Trifluorophenyl-1,3,4-triphenylbutane-1,4-dione** (52). The 80–90% benzene fractions (above) gave **52**: 0.58 g (40%); recrystallized from AcOH; mp 216–217°; uv ($\epsilon \times 10^{-3}$) 252 nm (27.3); ir 1665, 1325, 1165, 1130 cm⁻¹; nmr δ 7.5 (m, 19), 6.03 (s, 2). Anal. Calcd for C₂₉H₂₁F₃O₂: C, 75.97; H, 4.62. Found: C, 75.67; H, 4.26. **52** was also made from **59** by Na₂S₂O₄ [88:53 (m)] EtOH-H₂O, reflux, 1 hr]: 93%. It was dehydrated to furan **49** (Ac₂O + trace of concentrated H₂SO₄, reflux, 10 min), hydrolyzed, and chromato-graphed (Florisil, 10%, C₆H₆-petroleum ether fraction): 50%. Autoxidation¹⁷ of **52** (1% KOH-DMSO, stirring, air) gave **59**: 53%.

2-p-Trifluoromethyl-1,2,4-triphenylbutane-1,4-dione (53): from 100% benzene and Et₂O extraction (above); 5 g (34%); recrystallized from AcOH; mp 142–143°; uv ($\epsilon \times 10^{-3}$) 246 nm (24.8); ir 1680 cm⁻¹; nmr δ 7.4 (m, 19), 4.38 (s, 2). Anal. Calcd for C₂₉H₂₁F₃O₂: C, 75.97; H, 4.62. Found: C, 76.13; H, 4.61.

3-p-Triffuoromethylphenyl-1,3-diphenylpropanone (54): from 53 [0.2 g + KOH (0.05 g), warm EtOH (100 ml), 1 hr]; 71%; chromatographed (Florisil, acetone); mp 119–121°; uv ($\epsilon \times 10^{-3}$) 226, 244 nm (17.1, 15.7); ir 1675 cm⁻¹; nmr δ 8.0 (m, 2), 7.4 (m, 12), 4.93 (t, l, J = 7.5 Hz), 3.79 (d, 2, J = 7.5 Hz). Anal. Calcd for C₂₂H₁₇F₃O: C, 74.57; H, 4.84. Found: C, 74.26; H, 4.67.

2-Methoxy-4-*p***-trifluoromethylphenyl-2,5,5-triphenyl-2,5**dihydrofuran (55): from 53 (with 4- to 5-Ph migration^{3g}) by Ac₂O + concentrated H₂SO₄ (trace) [24 hr, hydrolysis solution, MeOH (48 hr, deep freeze)]; 61%, recrystallized from MeOH; mp 138–139°; uv ($\epsilon \times 10^{-3}$) 256, 265 nm (17.1, 14.8); nmr δ 7.3 (m, 19), 6.57 (s, 1), 3.10 (s, 3). Anal. Calcd for C₃₀H₂₃F₃O₂: C, 76.26; H, 4.91. Found: C, 76.40, H, 4.92.

cis-2-p-Anisyl-1,3,4-triphenyl-2-butene-1,4-dione (57): from furan 47 by AcOH-concentrated H₂SO₄ (2 min, 60°, cooled); 58%; recrystallized from AcOH; mp 208-209°; uv ($\epsilon \times 10^{-3}$) 231, 257 nm (26.2, 28.2); ir 1660 cm⁻¹; nmr δ 7.85 (m, 4), 7.2 (m, 15), 3.7 (s, 3). Anal. Calcd for C₂₉H₂₂O₃: C, 83.23; H, 5.30. Found: C, 83.08; H, 5.18.

cis-1-p-Anisyl-2,3,4-triphenyl-2-butene-1,4-dione (56): from 50, (a) like 57, chromatographed (Florisil, C_6H_6 -petroleum ether), 80%; (b) by Br_2 - Et_2O - H_2O^{18} (30 min), 87%; and (c) by CrO_3 (AcOH, 60°, 15 min), 67%. 56 crystallized (MeOH, EtOH, or AcOH) with solvent of crystallization (shown by ir and nmr) and

dried in vacuo: mp 126-127°; uv ($\epsilon \times 10^{-3}$) 260, 291 nm (23.6, 21.9); ir 1655, 1645 cm⁻¹; nmr δ 7.9 (m, 4), 7.2 (m, 15), 2.76 (s. 3). Anal. Calcd for C₂₉H₂₂O₃: C, 83.23; H, 5.30. Found: C, 83.06; H, 5.29

cis-1-p-Trifluoromethylphenyl-2,3,4-triphenyl-2-butene-

1,4-dione (58): prepared like 57; 96%; recrystallized from 50% AcOH; mp 140–141°; uv ($\epsilon \times 10^{-3}$) 251.5 nm (27.5); ir 1665, 1654 cm⁻¹. Anal. Calcd for C₂₉H₁₉F₃O₂: C, 76.30; H, 4.20. Found: C, 76.16: H. 4.41.

2,5-Diethoxy-2-p-trifluoromethylphenyl-3,4,5-triphenyl-2,5-dihydrofuran (58 cyclic diethyl ketal¹⁹): from 58 by absolute EtOH-AcOH (10:1 (ml), reflux, 2 min, cooled); 69%; recrystallized from hexane; mp 160–161°; uv ($\epsilon \times 10^{-3}$) 261 nm (16.5); nmr δ 7.2 (m, 19), 3.75 (q, 4, J = 6.5 Hz), 1.27 (t, 6, J = 6.5 Hz). Anal. Calcd for C₃₃H₂₉F₃O₃: C, 74.73; H, 5.47. Found: C, 74.51; H, 5.52.

cis-2-p-Trifluoromethylphenyl-1,3,4-triphenyl-2-butene-1,4-dione (59): from 49 (like 57); 87%; recrystallized from MeOH; mp 187–188°; uv ($\epsilon \times 10^{-3}$) 259 nm (28.2); ir 1650, 1670 cm⁻¹; nmr δ 7.9 (m, 4), 7.3 (m, 15). Anal. Calcd for C₂₉H₁₉F₃O₂: C, 76.30; H, 4.20. Found: C, 76.42; H, 4.37.

1,2-Bis[2-(2,4,5,5-Tetraphenyl-2,5-dihydrofuranyl)]hydrazine (2). To a solution of cyclic ketal 10 (2 g) in AcOH (10 ml, 100°) was added dropwise 85% hydrazine hydrate in AcOH (1:5 ml), followed by stirring (2 min), cooling (2 crystallizing), and addition of H_2O (second crop): 1.6 g (86%); recrystallized from C_6H_6 -absolute EtOH; mp 194–195° dec; uv ($\epsilon \times 10^{-3}$) 254 nm (2.96); ir (CCl₄) 3250, 3270 (shoulder), 3260, 3270 cm⁻¹ (shoulder); nmr δ 7.1 (m, 40), 5.97 (s, 2), 3.10 (s, 2). Anal. Calcd for C₅₆H₄₄N₂O₂: C, 86.57; H, 5.71; N, 3.61. Found: C, 86.62, H, 5.80, N, 3.54.

Deazotizations of 2. (A) Fusion pyrolysis (6 g, heated slowly, N_2 evolution beginning at 197° and ceasing before 212°) and chromatography (Florisil, 60-100% C₆H₆-petroleum pentane) gave 14^{4d} (3.6 g, 62%): mp 156-159°; recrystallized (C₆H₆-EtOH); mp 193-194°

(B) Pyrolysis in decalin (1 g, 10 ml, reflux, 4 hr), crystallizations (EtOH), and chromatography (Al₂O₃, C₆H₆-petroleum pentane) gave 14 (0.3 g, 32%), mp 176-178°. Crystallization of the residual oil (absolute EtOH) gave 1,2,4,4-tetraphenyl-3-buten-1-one (15): 0.055 g (5.7%); mp 86-87° (lit.4i 91.5-93°).

(C) Photolysis⁹ [3 g, C₆H₆ (500 ml, degassed, N₂), \rightarrow N₂, 4 hr], evaporation (in vacuo), and digestion of the residue hot hexane (200 ml, 30 min, standing overnight)] returned 2 (1.4 g). From the filtrate chromatography (Florisil, 50-60% C₆H₆-petroleum pentane) gave 14 (0.05 g, 7% from 2 consumed), mp 179–180°. The residue (from 90-100% benzene fraction), with EtOH, gave cyclic ketal 12 (0.29 g, 29%), mp 145-146° (that hydrolysis and ethanolysis occur on the column was demonstrated separately).

2,3,4-Triphenyl-5,5-[¹⁴C-diphenyl]-2,5-dihydrofuran-2-ol (12*).^{3e,g} To PhLi [from Li (4.5 g), [¹⁴C]-PhBr (50 g), Et₂O (300 ml), 1.5 hr] was added portionwise 31 g of cis-dibenzovlstilbene (11). Stirring (5 min), quenching (ice-NH4Cl), evaporation of Et2O extracts, and digestion of the residue (absolute EtOH) gave 12 (35.5 g, 95%): recrystallized from C₆H₆-EtOH; mp 163-164° (lit.^{3e,g} 164–165°); uv 250 nm (shoulder, ϵ 12,000); ir 2.8 μ . Anal.^{3e} Calcd for C34H26O2: C, 87.52; H, 5.62. Found: C, 87.31: H, 5.52. 12 was converted into 2-ethoxy ketal 13 by EtOH (trace H⁺): recrystallized from EtOH; mp 157-158° (73%). Anal. Calcd for C₃₆H₃₀O₂: C, 87.42; H, 6.12. Found: C 87.44; H, 6.12. Hydrolysis of 13 [AcOH- H_2O , 10:1 (ml), reflux 15 min] regenerated 12.

1,2-Bis[2-(2,3,4-triphenyl-5,5-[14C-diphenyl]-2,5-dihydrofuranyl)]hydrazine (3*). Hydrazine hydrate [85% (3.5 ml), AcOH (25 ml)] was added dropwise (stirring) to 13 (5 g, AcOH, 125 ml, 70°), crystals soon appearing. Cooling gave 3* (4.3 g, 86%): mp 256-257° dec; recrystallized from C₆H₆-abs EtOH; mp 264-265° dec; uv (CHCl₃) nm ($\epsilon \times 10^{-3}$) 250 nm (20.6); ir 3240, 3220 cm⁻¹ (shoulder); nmr δ 6.9 (m, 50), 4.59 (s, 2, D₂O \rightarrow O). Anal. Calcd for C₆₈H₅₂N₂O₂: C, 87.90; H, 5.64; N, 3.01. Found: C, 88.00; H, 5.64; N, 2.94. Ethanolysis of 3 by absolute EtOH-AcOH [30:1 (ml), reflux 5.5 hr] and cooling returned 3 (0.055 g), and quenching (H₂O) gave 13 (97% from 3 consumed), mp 140-145° (lit.^{3c} 156-157°). Hydrolysis of 3 by AcOH-concentrated HCl [30:1 (ml), reflux, 1 hr], cooling, quenching (H₂O), chromatographing (Florisil, 50-80% C_6H_{6-} petroleum ether), and recrystallization (hexane) gave 12.

Deazotizations of 3. (A) Pyrolysis (4 g), heated slowly to fusion (280°, $\rightarrow N_2$ at 258°), and chromatographing (Florisil, C₆H₆-petroleum pentane) gave tetraphenylfuran (7) [0.2 g (62%); recrystallized from AcOH; mp 174-175°], 2,3,4,5,5-pentaphenyl-4,5-dihydrofuran (29) [0.6 g (15%); recrystallized from absolute EtOH; mp 143-145° (lit.^{3a,e,g} 148-151°)], and 1,2,3,4,4-pentaphenyl-3-buten1-one (28) [2 g (52%); crystallized from C₆H₆-absolute EtOH; mp 185-186° (lit.^{3e} 185°)]. 28 and 29 were subjected to the above conditions and were recovered unchanged.

(B) Pyrolysis in decalin (3 g, 15 ml, reflux 12 hr, cooling) gave 28 (1.3 g). Chromatographing the residue (Florisil, 10-80% C₆H₆-petroleum ether) and crystallization (AcOH) gave 7 (0.186 g, 7.7%). 29 (0.288 g, 9.9%), and 28 (bringing its total to 53%, mp 179–180°).

(C) Pyrolysis in DMF (153°) (4 hr, \rightarrow 30% unchanged) for 14 hr, quenching (H₂O), and chromatographing (Florisil) gave only 12 (50%), mp 153-154° (shown to result from hydrolysis of 3 on the column).

(D) Photolysis⁹ in benzene (degassed N₂, 4 hr), evaporation, digestion of the residue (hexane, 100), and cooling returned 3 (87%). Evaporation of the filtrate and chromatographing (Florisil, 40-100% C_6H_6 -petroleum ether) gave 29 (8%), 31 (10%), and 28 (10%), calculated from 3 consumed. Furan 7 was recovered upon similar irradiation (80%).

1,2,3,4,4-Pentaphenyl-3-buten-1-one (28^{3g}) by Reduction of 2-Ethoxy-2,3,4,5,5-pentaphenyl-2,5-dihydrofuran (13). To 13 (3 g, AcOH, reflux) was added Zn dust (6 g, 15 min, exothermic, color change from red through green to yellow); filtering and cooling gave 28 (1.6 g, 59%) which was recrystallized from absolute EtOH, mp 180-184° (lit.^{3g} 185°).

1,2,3,4,4-Pentaphenylbutan-1-one (30). Reduction of 13 (as above but reflux, 80 min) gave 30 (62%), mp 167-169°, which was recrystallized from absolute EtOH: mp 193-194.5°; ir 1675 cm⁻¹; uv ($\epsilon \times 10^{-3}$) 240 nm (14.6); nmr δ 7.3 (m, 25), 5.12 (d, 1, J = 8.0 Hz), 4.55 (m, 2); nmr (C₆H₆) δ 5.29 (d, 1, J = 8.5 Hz), 4.93 (pair of overlapping doublets, 1, J = 8.5 Hz, J' = 9.0 Hz), 4.67 (dd, 1, J' =9.0 Hz). Anal. Calcd for C34H28O: C, 90.23; H, 6.24. Found: C, 90.15: H. 6.15.

KMnO₄ oxidations of 1,2,3,4,4-pentaphenyl-3-buten-1-one (28 and 28*), carried out as for 14, gave benzophenone 2,4-dinitrophenylhydrazone (15%*), mp 237-238°. The benzoic acid in the ether extract of the acidified steam distillation residue was removed by 10% NaOH and isolated by acidification, Et₂O extraction, sublimation, and recrystallization (H₂O): mp 121-122°. Evaporation of the remaining Et₂O solution containing dihydrofuranol 12*, chromatographing (Florisil), and crystallizing (absolute EtOH) gave cyclic ketal 13* (18%), mp 156-157°. A similar oxidation and work-up, but using only 1 equivalent of KMnO4 (1 hr), gave 13*; 35% from 28 was consumed.

Registry No.-1, 53449-04-0; 2, 53466-62-9; 3, 53466-63-0; 4, 53449-05-1; 6, 53449-06-2; 7, 1056-77-5; 8, 2313-03-3; 9, 53449-07-3; 10, 53449-08-4; 11, 6313-26-4; 12, 53449-09-5; 13, 53449-10-8; 14, 53449-11-9; 15, 2491-41-0; 21, 13249-75-7; 23, 2491-44-3; 28, 53448-80-9; 30, 53448-81-0; 41, 21449-71-8; 42, 53448-82-1; 43, 13249-75-7; 44, 53448-83-2; 44 methyl cyclic ketal, 53448-84-3; 44 ethyl cyclic ketal, 53448-85-4; 45, 53448-86-5; 45 ethyl cyclic ketal, 53448-87-6; 46, 53448-88-7; 46 methyl cyclic ketal, 53448-89-8; 46 ethyl cyclic ketal, 53448-90-1; 47, 53448-91-2; 48, 53448-92-3; 49, 53448-93-4; **50**, 53448-94-5; **52**, 53448-95-6; **53**, 53448-96-7; **54**, 53448-97-8; 55, 53448-98-9; 56, 53448-99-0; 57, 53449-00-6; 58, 53449-01-7; 58 cyclic diethyl ketal, 53449-02-8; 59, 53449-03-9; hydrazine hydrate, 7803-57-8; p-trifluoromethylphenyl bromide, 402-43-7.

References and Notes

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Oxidative Ring Closure of 1-Benzyloxy-3-arylureas to 1-Benzyloxybenzimidazolones¹

James H. Coolev* and Paul T. Jacobs²

Contribution from the Department of Chemistry, University of Idaho, Moscow, Idaho 83843

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Lead tetraacetate oxidation of 1-benzyloxy-3-arylureas (1) results in intramolecular ring closure to form 1-benzyloxybenzimidazolone (2) or in intermolecular nitrogen to nitrogen coupling to form 1,2-dibenzyloxy-1,2-diphenylcarbamylhydrazines (7). Studies of the oxidation of structures related to 1 establish that the requirements for a ring closure are quite specific. Studies of the influence of substituents show that electron-withdrawing substituents on the aryl group inhibit the ring closure particularly when the substituents are ortho to the urea group. The decomposition of the hydrazines 7 occurs rapidly and aryl isocyanates and benzyl alcohol are first formed.

The finding that N-acyl-O-alkylhydroxylamines undergo oxidative coupling to N, N-diacyl-N, N-dialkoxyhydrazines³ prompted us to study the lead tetraacetate oxidation of 1benzyloxy-3-phenylurea⁴ (1). Instead of the expected hydrazine product, oxidation of 1 with excess lead tetraacetate resulted in a single product, 1-benzyloxybenzimidazolone (2a), mp 159-160°, isolated in 85% yield and estimated in 97% yield by spectroscopic measurements. The structure of 2a was established by catalytic hydrogenolysis to 2b with palladium on carbon and to the known compound 2c with Raney nickel. The properties of 2c were identical with those of a sample of benzimidazolone prepared by the method of Kym.⁵



Results and Discussion

The proposed scheme for conversion of 1 to 2 is shown in Scheme I

Substituents on the Aryl Ring. The influence of substituents on the aryl ring of 1-benzyloxy-3-arylureas was studied first. Results are presented in Table I. Strongly electron-withdrawing groups decreased the yield of ring closure, and in these cases a competing reaction, nitrogen to nitrogen coupling, was observed (vide infra).

Groups in the ortho position markedly affect the ring closure. While a *p*- or *m*-chloro substituent appeared not to diminish the ring closure significantly below the unsubstituted case, no ring closure was observed with the o-chloro



substituent. Even when 1-benzyloxy-3-o-chlorophenylurea was slowly added to lead tetraacetate to effect high dilution conditions only a 19% yield of benzimidazolone was realized. Under no conditions, high dilution or otherwise, were we able to affect a ring closure with 1-benzyloxy-3-o-nitrophenylurea.

The inhibition of ring closure with the o-fluoro, o-chloro, and o-nitro compounds is probably a combination of inductive and steric effects. In cases where both electron withdrawal and steric repression are important (e.g., the nitro and chloro compounds), the ring closure reaction is strongly inhibited. In cases where steric repulsion is small and the