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Photolysis of Desyl Compounds.   A New Photolytic Cyclization

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Benzoin acetate has been observed to undergo photolytic cyclization to 2-phenylbenzofuran (2). Desyl chloride, benzoin tosylate, 4,4'-dimethoxybenzoin acetate, 3,3'-dimethoxybenzoin acetate, and desyldimethylamine hydrochloride also cyclize to the corresponding furans. This reaction appears to result from an n $\rightarrow$ π^* excitation of the benzoyl carbonyl. Spectroscopic data indicate that the cyclization and excitation are intimately associated through interaction of the nonbonding electrons on oxygen with the π-system in the isolated phenyl group.

A substantial effort has been expended elucidating the various photochemical reactions of the desyl moiety.[1] The results of these studies are summarized in Fig. 1. Course a is favored if the α-substituent is easily eliminated as a radical, thus, desyl thiobenzoate (X = −SCOPh) yields bidesyl and bithiobenzoate when exposed to sunlight filtered through Pyrex.[1a] When this type of radical fission is not possible, the distribution of photolysis products depends on the solvent. Desoxybenzoin (X = H) photolysis, if conducted in sunlight with a Pyrex vessel and in an inert solvent such as benzene, gives rise to bibenzyl, benzaldehyde, and bidesyl through route b, whereas, if the solvent possesses labile hydrogens, reductive dimerization occurs via path c.[1b−d] In other cases simple reduction is favored.[1e]

Fig. 1.—Various decomposition schemes observed in desyl photolyses.

Considering the breadth of previous studies we were surprised to observe an additional mode of desyl decomposition. Photolysis of benzoin acetate (1), under an atmosphere of nitrogen using a Pyrex filter and a high-pressure mercury-vapor lamp, produces as the major isolable product 2-phenylbenzofuran (2). This benzofuran (2) is accompanied by over-irradiation products[2] and the dihydrobenzoin acetates (path b, Fig. 1).

(1) (a) A. Schönberg, A. K. Fateen, and S. Omran, J. Am. Chem. Soc., 78, 1224 (1956); (b) J. Kenyon, A. Rassoul, and G. Soliman, J. Chem. Soc., 1774 (1956); (c) W. D. Cohen, Chem. Weekblad, 13, 902 (1916); (d) E. Paterno, G. Chieffi, and G. Perret, Gazz. Chim. Ital., 44, I, 151 (1914); (e) G. Ciamician and P. Silber, Ber., 34, 1530 (1901).

(2) In a control experiment there were at least six and possibly seven components that resulted when 2 was irradiated in isopropyl alcohol. These materials frequently appeared as companion products to the benzofuran 2. Only one of them can be purified readily; m.p. 282–285°. The analysis of this material is consistent with $C_{28}H_{22}O_2$, which corresponds to a reductive dimerization between two molecules of 2 and two atoms of hydrogen. The ultraviolet curve, $\lambda_{max}^{CH_2Cl_2}$ 283 mμ, shoulder 292 mμ, is rather similar to that of a 2,3-dihydrobenzofuran, 280 and 288 mμ (J. I. DeGraw, Jr., D. M. Bowen, and W. H. Bonner, Tetrahedron, 19, 19 (1963)). The infrared has strong carbon–oxygen stretching bands, ν_{max}^{KBr} 1245 and 1010 cm.$^{-1}$ and the heaviest fragment in the mass spectrum is half of the expected molecular weight, m/e = 195. This would indicate that the dimeric halves are linked by a single weak bond. The only other major peak falls at m/e = 195 − CH_2O = 165 which tends to confuse the interpretation, since any structure with a

We have embarked on a study of the factors influencing this cyclization reaction. The yields of 2 are to a small extent solvent dependent amounting to 15% in an inert solvent such as benzene and 8 to 10% in dioxane and isopropyl alcohol, both solvents possessing labile hydrogens. Possibly the diminished yield is the result of a side reaction such as process c in Fig. 1, although no reduction products were isolated.[3] Table I contains the products and the corresponding yields for these and subsequent reactions.

1, R_1–R_4 = H; X = OAc
3, R_1–R_4 = H; X = Cl
4, R_1–R_4 = H; X = OTs
5, R_1–R_4 = H;
      X = NH(CH_3)$_2$Cl
6, R_1, R_3 = H; R_2, R_4 = OCH$_3$;
      X = OAc
7, R_2, R_4 = H; R_1, R_3 = OCH$_3$;
      X = OAc

2, R_5–R_9 = H
8, R_5, R_7, R_8 = H;
      R_6, R_9 = OCH$_3$
9, R_5, R_6, R_9 = H;
      R_7, R_8 = OCH$_3$
10, R_6, R_7, R_9 = H;
      R_5, R_8 = OCH$_3$

The choice of the leaving group is crucial to the success of the reaction. If desyl chloride (3) is photolyzed in benzene under the same conditions as 1 the benzofuran 2 is formed, but the yield is reduced drastically to about 1%. Unlike the acetate 1, the chloride gives rise to bidesyl as the major product (path a, Fig. 1). Similarly, irradiation of benzoin tosylate (4) leads to the furan 2 in only 3% yield. Tetraphenylfuran also is found (4%). The precursor of this substance could well be bidesyl which can be cyclized quite easily in benzene with toluenesulfonic acid as a catalyst.

Conversely, desyldimethylamine hydrochloride (5), when photolyzed in aqueous solution, is converted to 2 in 67%. Of this 67%, 54% is isolated as the furan itself and the remaining 13% as the dimeric over-irradiation products. No other discrete products were found. There are numerous examples of photochemical elimination of halogen and ester substituents α to a carbonyl, but, to our knowledge, this is the first case of an α-aminoketone hydrochloride participating in this type of reaction.

phenyl group in the 2-position would not seem capable of producing such a fragment. One further compound of the set could be obtained by preparative thin-layer chromatography and occasionally a minute amount of one of the other compounds could be separated by recrystallization. Several of these materials had infrared spectra that were very similar to the compound described above. We have not pursued this aspect of the problem further, but it seems likely that these compounds arise from furan dimerizations.

(3) Even though these reaction mixtures are disturbingly complex, in most instances the furans are separated easily from the other, more polar materials by a single pass through an alumina column.

TABLE I

PHOTOLYSES OF DESYL COMPOUNDS[a]: REACTION CONDITIONS, PRODUCTS, AND YIELDS

Reactants	Solvent	Irradiation time, hr.	Products	Yield, %
Benzoin acetate (1)	i-C_3H_7OH	16	2-Phenylbenzofuran (2)	10
	CH_2Cl_2	1.5	2-Phenylbenzofuran (2)	12
	Dioxane	6	2-Phenylbenzofuran (2)	8
	Benzene	17	2-Phenylbenzofuran (2)	15
			Dihydrobenzoin diacetate	5
			Dimeric furans	5
Desyl chloride (3)	Benzene	18	2-Phenylbenzofuran (2)	1
			Bidesyl[b]	13
Benzoin tosylate (4)	Benzene	17	2-Phenylbenzofuran (2)	3
			Tetraphenylfuran	4
Desyldimethylamine hydrochloride (5)	Water	146[c]	2-Phenylbenzofuran (2)	54
			Dimeric furan	13
4,4'-Dimethoxybenzoin acetate (6)	Benzene	17	p-Anisil	12
			Benzofuran (8)	1
3,3'-Dimethoxybenzoin acetate (7)	Benzene	17	Benzofuran (9)	46
			Benzofuran (10)	2

[a] All of these reactions were conducted in a nitrogen atmosphere using a Hanovia high-pressure quartz mercury vapor lamp in conjunction with a Pyrex filter. [b] Only the higher melting pair of stereoisomers was isolated. [c] The immersion well becomes coated with an opaque solid which reduces the efficiency of the light even when the well is cleaned frequently.

The cyclization is also affected by substituents on the phenyl groups. The irradiation of 4,4'-dimethoxybenzoin acetate (6) in benzene with a Pyrex filter produces only a trace of the expected furan 8. The
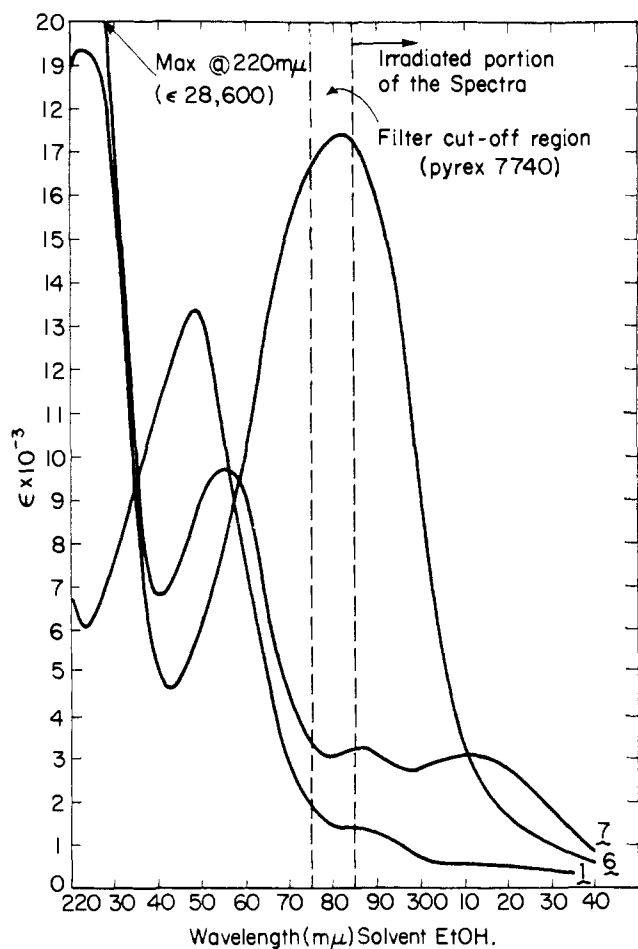
Fig. 2.—Ultraviolet spectra of benzoin acetate (1), 4,4'-dimethoxybenzoin acetate (6), and 3,3'-dimethoxybenzoin acetate (7).

chief product is p-anisil. In contrast, no benzil could be detected in the photolysis mixture of benzoin acetate. If 3,3'-dimethoxybenzoin acetate (7) is photo-

lyzed in the same manner as the preceding acetates, a 48% yield of a mixture of two isomeric furans 9 and 10 is obtained.[4] Independent synthesis established the structures of 9 and 10, and vapor phase chromatography fixed their ratio at 9:10 = 96:4.[5] The structure of furan 8 was assigned on the basis of the mode of formation, analysis, infrared spectrum which possesses ν_{max}^{KBr} 1620 cm.$^{-1}$ (2,3->C=C<), 1262, 1163, and 1118 cm.$^{-1}$ (>C-O-), and ultraviolet spectrum which is very similar in shape to that of 2 except shifted to longer wave length by about 15–16 mμ.

We would like to present now an attractive mechanistic interpretation of this new photolytic cyclization, although we recognize that other explanations may account for this phenomenon. A comparison of the ultraviolet absorption curves of acetates 1, 6, and 7 is most informative (see Fig. 2). In the irradiated portion of these spectra 1 and 7 exhibit only two absorptions, one at 285–290 mμ, which can probably be attributed to the $\pi \to \pi^*$ transition of an isolated phenyl group, and the other at 305–315 mμ, which corresponds to the n $\to \pi^*$ carbonyl excitation. The intensity of this n $\to \pi^*$ band seems to parallel the furan yield (i.e., n $\to \pi^*\epsilon$ of 7 > 1, with 6 being uncertain owing to the end absorption from the 282 mμ peak.)[6] Furthermore, the n $\to \pi^*$ band of 7 is extremely intense (ϵ 3000). This same band in the spectrum of 1 also possesses an enhanced intensity, but since it is so broad and merges with the $\pi \to \pi^*$ absorption of the aromatic systems, only an approximate value for ϵ can be determined (ϵ 500). β,γ-Unsaturated ketones frequently display this type of accentuated n $\to \pi^*$ absorption. In contrast, saturated and α,β-unsaturated ketones generally possess an ϵ <70.

The source of this effect has been traced to the interaction of the carbonyl nonbonding electrons with the π-orbitals of a β,γ-double bond.[7]

(4) These furans do not seem to be as sensitive to further irradiation as the unsubstituted system.

(5) S. Kawai, T. Nakamura, and N. Sugiyama, Ber., 72, 1146 (1939).

(6) The possibility that cyclization was caused by a $\pi \to \pi^*$ excitation of the isolated phenyl group had to be tested in view of Zimmerman's recent work dealing with the photolytic solvolysis of benzyl esters (H. E. Zimmerman and V. R. Sandel, J. Am. Chem. Soc., 85, 915 (1963)). The failure to observe a reaction when the sodium salt, the free acid, and the methyl esters of acetylmandelic acid were photolyzed under various conditions seems to negate any aromatic $\pi \to \pi^*$ mechanism.

A theoretical analysis of the ultraviolet spectrum of 11 demonstrates that such an interaction would indeed account for this enhanced n → π* absorption.[8] In this
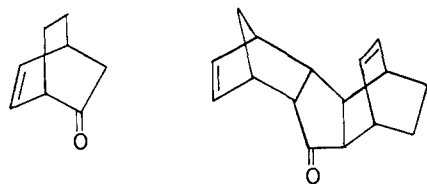
11, 293 mμ (ε 101).   12, 314 mμ
cyclohexane   (ε 126), cyclohexane

particular example the nonbonding electrons are involved chiefly with the π-orbital β to the carbonyl; however, in 12 the overlap must be principally with the π-orbital in the γ-position.[9] The rigid stereochemistry of 11 and 12 apparently is not necessary to bring about this interaction, since open chain β,γ-unsaturated ketones also possess an enhanced n → π* band. Thus the nonbonding orbitals of an unrestricted, β,γ-unsaturated ketone should be capable of interacting with the carbon-carbon double bond at both the β- and γ-sites.

Furthermore, if the β,γ-unsaturation is derived from an aromatic nucleus, an additional n → π* intensification results if that nucleus is substituted with electron-donating substituents (see Fig. 3).[10]

R = H   λ_max = 292 (ε 470), H₂O
R = CH₃   289 (790), H₂O
R = OCH₃   291 (1350), H₂O
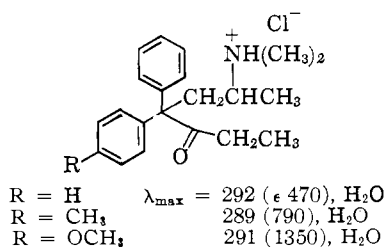
Fig. 3.—The dependence of ε on ring substitution.

The unusually intense n → π* bands in the ultraviolet curves of 1 and 7 probably originate from an interaction similar to that described above. Indeed, the fact that this overlap plays such an important role in the excitation process is the best rationale for the occurrence of the cyclization reaction. When this mixing is encouraged, as evidenced by the enhanced n → π* absorption of 7, in contrast to that of 1, the cyclization yield is increased. One can now write a crude mechanism for this reaction, where 13 depicts the excited state of a species that possesses a strong interaction between the

1   13

2
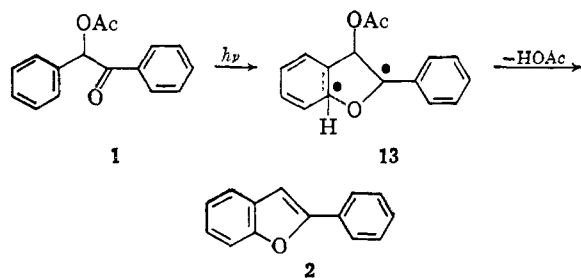
nonbonding oxygen orbital and the π-electrons of the isolated aromatic nucleus.

The case of 6 can now be considered. The ultra-

violet curve of this compound (see Fig. 2) does not resemble those of the other two benzoin acetates 1 and 7. The disappearance of the usual 250 mμ band and the appearance of a strong absorption at 282 mμ seems to indicate that the 250 mμ band has shifted to longer wave length and coalesced with the phenyl π → π* and ketone n → π* band.

Nagakura and Tanaka have found that absorptions of the 250 mμ type are predicted by MO theory if one allows the highest occupied orbital of the phenyl group to interact with the lowest unoccupied orbital of the carbonyl, thus, forming two new states. Electronic excitation from the lower of these new states to the higher would give rise to a charge-transfer band of about the same energy and intensity as that observed experimentally.[11] If complementary substituents are situated at opposite ends of the π-system, then excitation is accompanied by a migration of charge density from the donor to the acceptor group by a process similar to that described above.[12] In this type of system the 250 mμ band is replaced by an absorption at longer wave length.

The 282 mμ absorption in the spectrum of 6 is probably one of these charge-transfer transitions. The low yield of furan 8 from 6 is rationalized, at least in

6
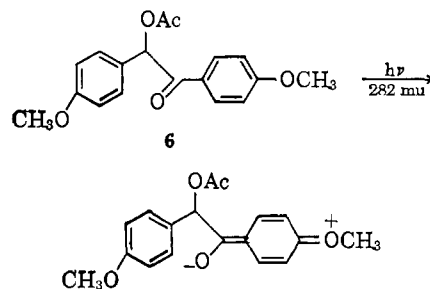
part, by this massive absorption which reduces the amount of light available for n → π* excitation. Also the p-methoxy substituent of the benzoyl moiety may delocalize the electronic disturbance on the carbonyl carbon of the n → π* state to the extent that the acetate functionality is not expelled readily.[13]

The rationale for the high ratio of furans obtained from the photolysis of 7 (9:10 = 96:4) and for the ease of desyl cyclization when the leaving group is dimethylamine hydrochloride is not readily extracted from the data at hand.

In addition to the novelty of this cyclization, we should like to emphasize the role of the nonbonding π-orbital interaction from which this reaction seems to stem. At least for intramolecular photoreactions an awareness of this overlap and the factors which influence it should be of considerable mechanistic and practical value. Studies designed to define these factors more precisely are in progress.

Experimental[14]

3,3′-Dimethoxybenzoin Acetate (7).—To a solution of 9.29 g. (0.0342 mole) of 3,3′-dimethoxybenzoin[15] and 6.87 g. (0.087

(7) For background material and references on this subject see K. Mislow, et al., J. Am. Chem. Soc., 84, 1455 (1962).

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(11) S. Nagakura and J. Tanaka, J. Chem. Phys., 22, 236 (1954).

(12) S. Nagakura, ibid., 23, 1441 (1955).

(13) H. E. Zimmerman, B. R. Cowley, C. Y. Tseng, and J. W. Wilson, J. Am. Chem. Soc., 86, 947 (1964).

(14) Melting points are uncorrected. The authors are indebted to Dr. S. M. Nagy and his associates for microanalyses, Chemistry Department, M.I.T., Cambridge 39, Mass., and to Professor K. Biemann for his kind assistance in the measurement and interpretation of mass spectral data.

mole) of pyridine in 25 ml. of methylene chloride at ice bath temperature 4.3 g. (0.055 mole) of acetyl chloride in 40 ml. of methylene chloride was added dropwise with stirring. After standing at room temperature overnight, the solution was washed with dilute hydrochloric acid, dilute sodium hydroxide, and twice with water, dried by filtering through $MgSO_4$, and evaporated to dryness under reduced pressure. A red oil resulted that would not crystallize even after extended refrigeration. This oil was chromatographed on 100 g. of activity III alumina to obtain 9.97 g. (93%) of a pale yellow, viscous oil that gave only one spot upon thin-layer chromatography. The oil distilled at 179° at about 0.005 mm. yielding a distillate having $\nu_{max}^{CHCl_3}$ 1740 and 1697 cm.$^{-1}$; λ_{max}^{EtOH} 220 mμ (log ϵ 4.46), 256 (3.99), 287 (3.51), and 312 (3.48); n.m.r. (CDCl$_3$): singlet 2.21 p.p.m. (3H), singlet 3.78 (6), singlet 6.88 (1), and complex 6.90-7.80 (8).

Anal. Calcd. for $C_{18}H_{18}O_5$: C, 68.78; H, 5.77. Found: C, 69.40; H, 5.73.

This oil was used in subsequent experiments as it could not be induced to crystallize.

Desyldimethylamine Hydrochloride (5).—A modification of the procedure of Lespagnol, *et al.*,[16] was followed, without isolating intermediates from desoxybenzoin to the hydrochloride 5, in 54% yield. After crystallization from ethanol–ether the hydrochloride had m.p. 240-243° (lit.[16] 226-230°), ν_{max}^{KBr} 2575 (broad) and 1685 cm.$^{-1}$; n.m.r. (D$_2$O): singlet 3.37 p.p.m. (6H), singlet 5.23 (1H exchanged with D$_2$O), singlet 6.83 (1), complex 7.4-8.4 (10).

Photolysis Apparatus and Procedures.—The apparatus was constructed from a Kjeldahl flask fitted with condenser and nitrogen sparger connections. The light well, a simple glass tube of the desired optical properties (only Pyrex 7740 is used in the irradiations described in this paper), was fitted firmly into the neck of the flask with a gooch rubber seal. The sparger, a gas dispersion tube extended with an inner joint, was sealed into the flask with glyptal and wrapped with Parafilm. Prior to irradiation the solutions were flushed for 0.5 hr. with prepurified nitrogen and circulated by means of a magnetic stirrer. The light source was a Hanovia, 200 watt, Type S, mercury immersion lamp emitting the complete ultraviolet spectrum (1849–4000 Å.). During the reaction the solution was cooled in a water bath, the stirring continued, and a light spray of nitrogen maintained. The progress of the reaction was followed by thin-layer chromatography.

Photolysis of Benzoin Acetate (1). (A) The High Melting Overirradiation Product of 2.—A solution of 5.1 g. (0.0201 mole) of 1[17] in 800 ml. of benzene was irradiated for 17 hr. using a Pyrex well. After removal of the benzene under reduced pressure and refrigeration of the resulting oil overnight, crystals developed in the oily residue. Recrystallization from hot dimethylformamide afforded 0.095 g. of needles, m.p. 282-282.5°, $\lambda_{max}^{CH_2Cl_2}$ 283 mμ (log ϵ 3.88) and shoulder 292 mμ (log ϵ 3.79); ν_{max}^{KBr} 1480, 1245, 1010, 760, 749, and 698 cm.$^{-1}$; *m/e* 195 and 165.

Anal. Calcd. for $C_{28}H_{22}O_2$: C, 86.12; H, 5.68. Found: C, 86.14; H, 5.46.

(B) 2-Phenylbenzofuran (2).—The aforementioned filtrate was chromatographed on 150 g. of activity I Woelm alumina. The furan was eluted first. After recrystallization from hot methanol-water 0.589 g. (15%) of thin plates was obtained, m.p. 120-121°; mixture m.p. was undepressed and the infrared spectrum was identical with that of an authentic sample.[18]

(C) Dihydrobenzoin Diacetate and Overirradiation Products of 2.—Further chromatography yielded 0.098 g. of a complex mixture of 2-phenylbenzofuran photolysis products. This was followed by a yellow band that formed an oily crystalline residue. After two recrystallizations from methanol, 0.072 g. of hydrobenzoin diacetate, m.p. 134-135° (lit.[19] 133-134°), was obtained. The mother liquors were rechromatographed on 45 g. of activity I alumina. Recrystallization from methanol yielded 0.066 g. of a mixture of hydro- and isohydrobenzoin diacetate; approximate yield 0.137 g. (5%).

Photolysis of 2-Phenylbenzofuran (2).—A solution of 0.506 g. (0.00261 mole) of 2 in 66 ml. of isopropyl alcohol was irradiated for 3 hr. using a Pyrex well. The solid which precipitated during the reaction was collected by filtration and recrystallized from

hot dimethylformamide to give 0.148 g. of colorless needles, m.p. 284°, possessing the same infrared spectrum as the 282-282.5° material from the photolysis of 1. The filtrate contained a complex mixture of about six compounds identical by thin-layer comparison with the materials isolated from the reaction mixture of 1. Even with preparative thin-layer chromatography only one of the six was isolated in the pure state. No further attempt was made to effect separation.

Photolysis of 4,4'-Dimethoxybenzoin Acetate (6). (A) 2-(4'-Methoxyphenyl)-6-methoxybenzofuran (8).—A solution of 5.02 g. (0.016 mole) of 6[20] in 800 ml. of benzene was irradiated for 17 hr. using a Pyrex well. The benzene was removed under reduced pressure and the residue chromatographed on 70 g. of activity III alumina. The first band eluted was 8 which after recrystallization from hot methanol yielded 0.028 g. (1% based on 71% conversion) of thin plates, m.p. 159-161°; λ_{max}^{EtOH} 317 mμ (log ϵ 4.65), 332 (4.55), and shoulder 286 (4.31); ν_{max}^{KBr} 1620, 1496, 1262, 1163, 1118, and 826 cm.$^{-1}$.

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.29; H, 5.80.

(B) *p*-Anisil.—By further chromatography both *p*-anisil and starting material were collected together. Separation by fractional recrystallization from ethanol gave 0.399 g. (13% based on 71% conversion), m.p. 132-134° (lit.[21] 133°, undepressed mixture m.p. with authentic sample), of *p*-anisil and 1.465 g. (71% conversion), m.p. 94-96°, of the acetate 6.

Photolysis of 3,3'-Dimethoxybenzoin Acetate (7). (A) 2-(3'-Methoxyphenyl)-5-methoxybenzofuran (9).—A solution of 5.01 g. (0.016 mole) of 7 in 800 ml. of benzene was irradiated for 17 hr. using a Pyrex well. Upon removal of the benzene under reduced pressure, the resulting red oil deposited crystals after standing several days. These were recrystallized from hot methanol to give 1.062 g. of colorless crystals of 9 which had m.p. 96-97°; λ_{max}^{EtOH} 214 mμ (log ϵ 4.59), 290 (4.32), 316 (4.41), and shoulder 303 (4.35); ν_{max}^{KBr} 1612, 1475, 1207, 1168, 1027, 841, and 780 cm.$^{-1}$.

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.51; H, 5.52.

(B) 2-(3'-Methoxyphenyl)-7-methoxybenzofuran (10).—The above filtrate was chromatographed on 120 g. of activity III alumina to obtain 0.665 g. of a furan mixture and 0.530 g. (89% conversion) of starting material. Careful fractional recrystallization of the furan fraction from hot methanol followed by sublimation yielded an analytic sample of 10 which had m.p. 74.5-76°; λ_{max}^{EtOH} 211 mμ (log ϵ 4.52), 241 (4.19), 296 (4.43), 318 (4.26), and shoulder 304 (4.39); λ_{max}^{KBr} 1487, 1283, 1209, 1095, 774, and 727 cm.$^{-1}$.

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.70; H, 5.49.

The ratio of the furans 9 and 10 in the chromatography fraction was determined by vapor phase chromatography at 270° on a 8 ft. × 0.25 in. 20% Se-30 silicone rubber on 60-80 mesh Chromosorb W column using benzoin acetate as the standard (9:10 = 89:11; thus, the over-all percentage yield, based on 89% conversion, is 46% for 9 and 2% for 10).

Syntheses of Isomeric Furans 9 and 10.—Condensation of 2-hydroxy-5-methoxybenzaldehyde[22] with methyl α-chloro-3-methoxyphenylacetate[23] followed by saponification and decarboxylation gave 9.[5] The same sequence using 2-hydroxy-3-methoxybenzaldehyde in place of the 5-methoxy isomer led to 10. Comparison of infrared spectra and undepressed mixture m.p. demonstrated that the synthetic materials were identical with the materials obtained photolytically.

Photolysis of Desyl Chloride (3).—A solution of 5.00 g. (0.0216 mole) of 3 in 800 ml. of benzene was irradiated for 18 hr. using a Pyrex well. After removal of the benzene under reduced pressure bidesyl precipitated (0.533 g., 13%) which after filtration and recrystallization from hot dimethylformamide had m.p. 255-259° (lit.[1a] 255°). Chromatography of the oily filtrate through 15 g. of activity I alumina gave crude 2 (0.058 g., m.p. 105-120°) which when recrystallized twice from hot methanol had m.p. 120-122° (undepressed mixture m.p. and identical infrared spectra).

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Photolysis of Desyldimethylamine Hydrochloride (5).—A solution of 5.00 g. (0.0191 mole) of 5 in 800 ml. of distilled water was photolyzed using a Pyrex well. After about 48 hr. the solution, now opaque with particles and a solid suspension, was diluted with about 600 ml. of methanol and condensed under reduced pressure to about 500 ml. This operation coagulated the suspension leaving a transparent solution. The solid was collected by filtration and the filtrate returned to the photolysis apparatus, the volume adjusted to 800 ml., and irradiation continued. These manipulations had to be repeated every 48 hr. until precipitation ceased (146 hr.). The accumulated solid was dissolved in a minimum amount of methylene chloride and filtered to remove insoluble dimeric material (0.160 g., m.p. 284–285° after one recrystallization from boiling dimethylformamide). The filtrate was chromatographed on 80 g. of activity I alumina. Only two substantial fractions were obtained: 2.02 g. of 2 (54%, m.p. 119–120°, undepressed mixture m.p. and identical infrared spectra) and 0.316 g. of the dimeric furans (mixture spot test by thin layer chromatography with the photolysis products of 2).

Suspension problems may be eliminated by photolysis in methanol, but the yield of 2 is reduced to 35%.

Photolysis of Benzoin Tosylate (4).—A solution of 5.00 g. of 4[24] was dissolved in 800 ml. of benzene and irradiated 17 hr. using a Pyrex well. The solid which formed during photolysis was removed by filtration from the concentrated reaction mixture. This solid is very hygroscopic, soluble in water, acidic, and after one recrystallization from boiling benzene has m.p. 92–100°. It was not purified further. The aforementioned filtrate was next filtered through 20 g. of activity III alumina and chromatographed on 100 g. of activity I alumina. The first substance eluted (0.080 g.) had, after one recrystallization from hot methanol, m.p. 119–121° (mixture m.p. undepressed and identical infrared spectra with 2). The second material eluted (it fluoresces brightly in ultraviolet light when on the column) had, after one recrystallization from methanol–methylene chloride by heating until crystallization begins, m.p. 170–173° (0.100 g.). An authentic sample of tetraphenylfuran had an undepressed mixture m.p. and identical infrared spectrum with this substance. No other discrete materials were isolated.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KANSAS, LAWRENCE, KANSAS]

# Chemistry of o-Di-t-butylbenzene[1]

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Various chemical and photochemical reactions of the highly hindered hydrocarbon o-di-t-butylbenzene (I) have been investigated. Depending on the reagents used, nitration of I gave either 1,2-di-t-butyl-4-nitrobenzene (VIIa) or 1,2-di-t-butyl-4,5-dinitrobenzene (VIIIa). By reduction, diazotization, and acetolysis of the diazonium fluoroborate, VIIa was converted into 3,4-di-t-butylphenol acetate (VIId). The corresponding phenol VIIc did not show any tendency to exist in the tautomeric dienone structure Xa, whose stabilization by relief of strain in the o-di-t-butyl system might have been expected. Bromination of VIIc afforded 2,4-dibromo-5-t-butylphenol (XII). The aluminum chloride catalyzed acetylation of I yielded 2,4-, 3,5-, and 3,4-di-t-butylacetophenone, plus p-t-butylacetophenone, together with minor amounts of m- and p-di-t-butylbenzene and 1,3,5-tri-t-butylbenzene. With the exception of 3,4-di-t-butylacetophenone, these same products were also formed in the similar acetylation of m- and p-di-t-butylbenzene. Controlled reduction of I by lithium in liquid ammonia in the presence of isopropyl alcohol gave mainly 2,3-di-t-butyl-1,4-cyclohexadiene (XIX), which was isomerized by lithium ethylamide into 1,6-di-t-butyl-1,3-cyclohexadiene (XXII). On irradiation with a mercury arc lamp in an all-quartz apparatus I underwent slow isomerization to a 1:4 photostationary mixture of m- and p-di-t-butylbenzene, along with the formation of polymeric by-products. The same photostationary condition was also reached from m- and p-di-t-butylbenzene.

Because of the high degree of strain present in o-di-t-butylbenzene (I), the chemical and physical properties of this hydrocarbon and related compounds have been of interest for some time.[3] Only recently, however, have successful synthetic routes to I been developed. In the first of these the synthesis of I was achieved by the reaction of acetylene with a dicobalt carbonyl complex of di-t-butylacetylene.[4,5] In the second, two variations of a multistep sequence starting from 1,1,4,4-tetramethyltetralone were employed.[6,7] With a slight modification in the last step, one[7] of the latter routes has been utilized in the present study.

The strain energy in I arising from the steric repulsion of two o-t-butyl groups was first predicted by

I   II   III
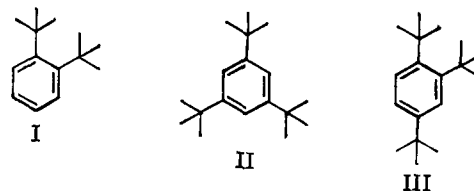
Brown and co-workers to be about 25 kcal./mole.[8] By means of a comparison of the heat of combustion of 1,3,5-tri-t-butylbenzene (II) with that of 1,2,4-tri-t-butylbenzene (III), Hübel, et al.,[9] have determined the strain energy of the latter to be 16.8 ± 1.7 kcal./mole. On this basis, the strain energy of I may be estimated at about 17 kcal./mole.

This degree of aromatic destabilization in I is reflected in its ultraviolet and nuclear magnetic resonance (n.m.r.) spectral properties. Thus, in the 240–280 mμ region of the ultraviolet spectrum, the usual benzene ring fine structure is almost entirely absent. Instead, only a single broad maximum at 261.5 mμ is present. In the

(1) Taken in part from the Ph.D. Theses of P. L. C. (1964) and M. O. A-R. (1963). An account of this work was presented before the Division of Organic Chemistry at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1, 1964.

(2) Alfred P. Sloan Research Fellow, 1961–1964.

(3) For a discussion and leading references, see H. C. Brown, *J. Chem. Educ.*, **36**, 424 (1959); see also other papers cited below.

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(8) H. C. Brown, D. Gintis, and L. Domash, *ibid.*, **78**, 5387 (1956); cf. ref. 3.

(9) U. Kruerke, C. Hoogzand, and W. Hübel, *Chem. Ber.*, **94**, 2817 (1961); cf. C. Hoogzand and W. Hübel, *Tetrahedron Letters*, 637 (1961).