in ether, *cis*-1,3-pentadiene in benzene, styrene in benzene, and 1,1-diethoxyethylene in ether. No adduct was detected in all these systems.

The quenchings of photorearrangements of *o*-phenoxybenzoic acid (**1a**) and methyl *p*-phenoxybenzoate (**13**) in benzene by *cis*-1,3-pentadiene were also investigated. Because of their low quantum efficiencies, only qualitative investigations were carried out. Parallel irradiations through a Corex D filter were performed with solutions containing 0.015 *M* of the substrate in benzene with or without 0.5 *M* of the diene. In the case of **1a**, we found that the formation of phenyl salicylate was reduced approximately 43% and about 20% of the diene had been isomerized to the trans isomer as indicated by vpc analysis. In the case of **3**, we found that the formation of products was reduced by approximately 85% but the consumption of the substrate was increased by about threefold as indicated by both tlc and vpc analyses. In the meantime, about 15% of the diene had isomerized.

Registry No.—**1a**, 2243-42-7; phenyl salicylate, 118-55-8; *o*-(*o*′-chlorophenoxy)benzoic acid, 36809-08-2; *o*-chlorophenyl [*o*-(*o*′-chlorophenoxy)benzoyl]salicylate, 36809-09-3; phenyl *o*-phenoxybenzoylsalicylate, 36809-10-6.

Acknowledgment.—The authors wish to thank the Institute of Arthritis and Metabolic Diseases, U. S. Public Health Service, for the support of this work (Grant AM-11,676), and Mr. Robert H-K. Chen for his assistance in the laboratory.

Photochemical Reductions of Unsymmetrical Benzils[1]

YOSHIRO OGATA,* KATSUHIKO TAKAGI, AND YUICHI FUJII

Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan

Received May 21, 1972

Eight 4-substituted benzils have been subjected to photoreduction by 2-propanol, where one of two carbonyl groups is selectively reduced; *i.e.*, on irradiation, the corresponding benzoins and/or benzilpinacols together with 4-substituted benzoic acid derivatives were obtained. The benzoyl group substituted by a more electron-withdrawing group is preferentially reduced in the order 4-CN > 4-Cl > H > 4-Me > 4-MeO ~ 4-NMe$_2$. The configuration of unsymmetrical benzils in the lowest excited triplet state was also discussed by comparing their absorption and emission spectra with their photochemical reactivities.

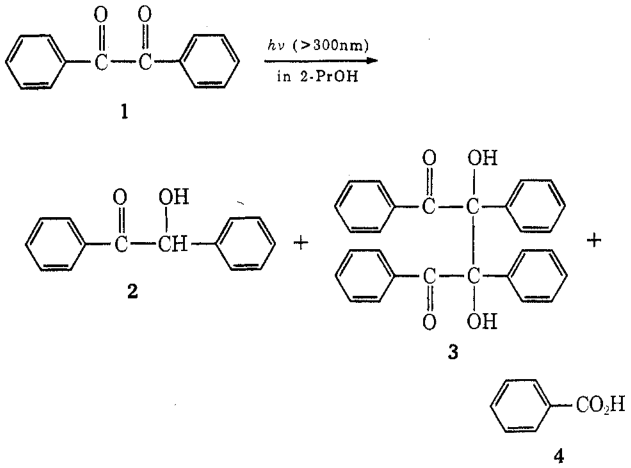
The photochemical reduction of α-dicarbonyl compounds has been an intriguing subject to a number of photochemists.[2] Some knowledge of the excited state is required to understand the photoreduction of α diketones. Reactivity might be influenced by their excited state geometries, which have been suggested to be coplanar based on absorption and emission spectra.[3] Although biacetyl is photoreduced to acetylpinacol,[4] aliphatic α diketones capable of intramolecular hydrogen abstraction through a six-membered transition state are transformed to 2-hydroxybutanones on irradiation.[5] An unsymmetrical α diketone, bornanedione, in which the carbonyl groups are essentially held in the s-cis configuration, equally yields two isomeric reduction products through a common transition state.[6]

An aromatic α diketone, benzil, is known to be twisted *ca.* 90° around its central bond at the ground state; the conjugation between two carbonyls is reduced by cross conjugation between a CO group and a phenyl group attached to the CO.[7] However, the phenyl–carbon interaction is again decreased with increasing steric hindrance at the ortho carbon of benzil. As reported by Bunbury,[8] the photoreduction of benzil by 2-propanol gives benzoin and benzilpinacol together with a small amount of decomposition products, *i. e.*, benzoic acid and benzaldehyde. Maruyama, *et al.*,[9] reported in their study on the photolyses of polymethylbenzils that ortho-substituted benzils are very photounreactive and afford low quantum yield for intersystem crossing.

The authors wish to report the photoreduction of unsymmetrical 4-substituted benzils and to correlate excited nπ* triplet-state geometries with reductive behaviors and emission and absorption spectra.

Results and Discussion

Irradiation of benzil (**1**) in 2-propanol (~10^{-2} *M*) through a Pyrex filter under nitrogen for 12 hr results in the disappearance of benzil and the formation of a precipitate of benzilpinacol (**3**, 22.5%). The product was identified by melting point, molecular weight (420), and ir spectrum (COH). The mother liquior gave benzoin (**2**, 13.5%) and benzoic acid (**4**, 9.4%).



---

[1] Contribution No. 186.

[2] For a comprehensive review, see B. M. Monroe, "Advances in Photochemistry," Vol. 8, Interscience, New York, N. Y., 1971, p 77, and references cited therein.

[3] (a) T. R. Evans and P. A. Leermakers, *J. Amer. Chem. Soc.*, **89**, 4380 (1967); (b) W. G. Herkstroeter, J. Saltiel, and G. S. Hammond, *ibid.*, **85**, 482 (1963).

[4] (a) W. G. Bentrude and K. R. Darnall, *Chem. Commun.*, 810 (1968); (b) W. H. Urry and D. J. Trecker, *J. Amer. Chem. Soc.*, **84**, 118 (1962).

[5] W. H. Urry, D. J. Trecker, and D. A. Winey, *Tetrahedron Lett.*, 609 (1962).

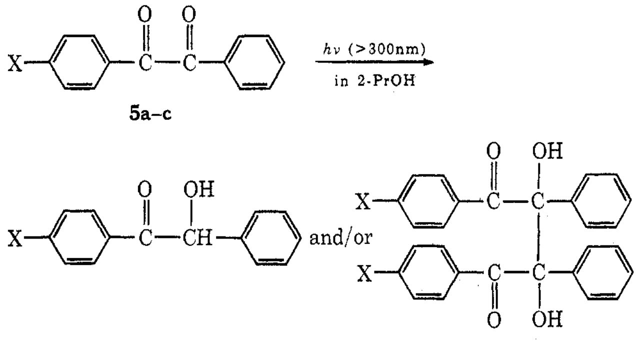
[6] B. M. Monroe, S. A. Weiner, and G. S. Hammond, *J. Amer. Chem. Soc.*, **90**, 1913 (1968).

[7] N. J. Leonard and E. R. Blout, *ibid.*, **72**, 484 (1950).

[8] D. L. Bunbury and C. T. Wang, *Can. J. Chem.*, **46**, 1473 (1968).

[9] K. Maruyama, K. Ono, and J. Osugi, *Bull. Chem. Soc. Jap.*, **45**, 847 (1972).

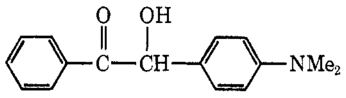
Photoreduction of Benzils with an Electron-Releasing Group.—Benzils with a para electron-releasing group (**5**) yield in 2-propanol on irradiation 4-substituted benzoins (**6**) and/or 4-substituted benzilpinacols (**7**) which are formed by the selective reduction at unsubstituted benzoyl.



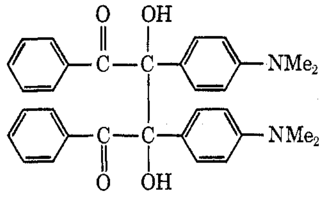
5a–c **6a–c** **7a–c**

a, X = NMe$_2$
b, X = OMe
c, X = Me

4-Dimethylaminobenzil (5a).—Diketone **5a** was photoreduced in 2-propanol until the carbonyl group disappeared. The condensed reaction mixture was separated into three components; one was 4-dimethylaminobenzoin (**6a**, 11.7%). Although the structures of the other two products are still unknown, they are not benzoin and/or benzilpinacol, which was reduced at the dimethylaminobenzoyl group in comparison with the authentic samples of **6′a** and **7′a**, respectively.

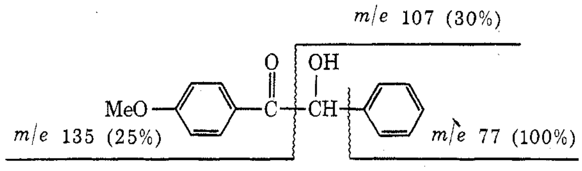


6′a



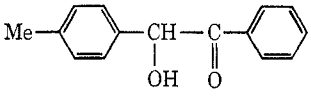
7′a

4-Methoxybenzil (5b).—Irradiation of a 2-propanol solution of **5b** for 12 hr yields 4-methoxybenzoin (**6b**, 5.5%). The ir spectrum of the product shows carbonyl stretching vibration at 1650 cm^{-1}, whereas the starting benzil exhibits two carbonyl stretching vibrations at 1670 and 1650 cm^{-1}, corresponding to benzoyl and anisoyl carbonyl stretching vibrations, respectively. Moreover, fragment ion peaks are observed at *m/e* 242 as M$^+$ and mainly at *m/e* 107 and 135, which are expected from the structure **6b**.



6b

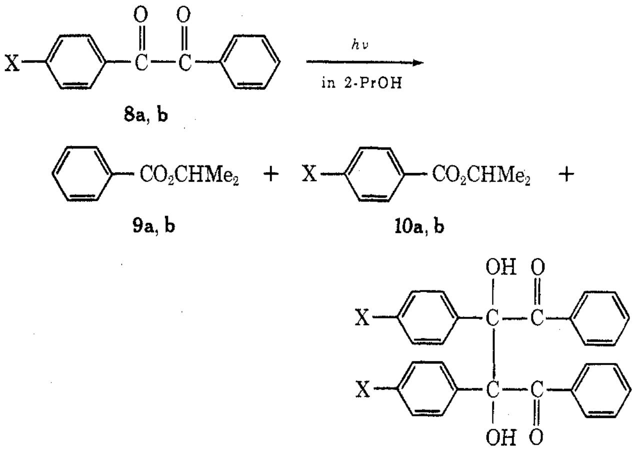
4-Methylbenzil (5c).—Photoreduction of **5c** affords two products; one was 4-methylbenzoin (**6c**, 8.8%) based on its ir and uv spectra (λ_{max} 256 nm), but not **6′c** (λ_{max} 245 nm). In the mass spectral fragmentation, the relative peak intensity of benzoyl ion to benzhydryl ions caused by the central C–C bond scission of **6c** was P_{105}/P_{107} = 2.8 in contrast to that in **6′c** of P_{119}/P_{121} = 4.



6′c

Another reduction product was **7c** (34.8%), which was confirmed by cryoscopic molecular weight, a mass spectrum similar to that of **6c**, and characteristic ir spectrum.

Photoreduction of Benzils with an Electron-Withdrawing Group. 4-Chlorobenzil (8a).—Diketone **8a** was almost completely photodecomposed within 6 hr. The separation of product by silica gel column gave a reduction dimer (**11a**, 51.6%) together with a little starting material (16%), a mixture of isopropyl benzoate and 4-chlorobenzoate (**9a** + **10a**, 4.9%), and a trace of unidentified viscous oil.



8a, b **9a, b** **10a, b** **11a, b**

a, X = Cl
b, X = CN

Fission products **9a** and **10a** were identified by ir and nmr spectra. The structure of **11a** was determined by elemental analysis and ir and nmr spectra. Carbonyl stretching vibration of the product (**11a**) at 1670 cm^{-1} corresponds to that at 1660 cm^{-1} in the benzoyl carbonyl of **8a**, but absorption at 1650 cm^{-1} for *p*-chlorobenzoyl carbonyl disappears in **11a**. A molecular ion peak for **11a** could be detected but a trace of half value for the molecular ion peak at *m/e* 245 was observed in the mass spectrum of **11a**. Furthermore, a large difference between the relative intensity of $P_{105}(C_6H_5CO^+)/P_{106}(C_6H_5COH^+)$ = 11 and that of $P_{139+140}$(Cl-

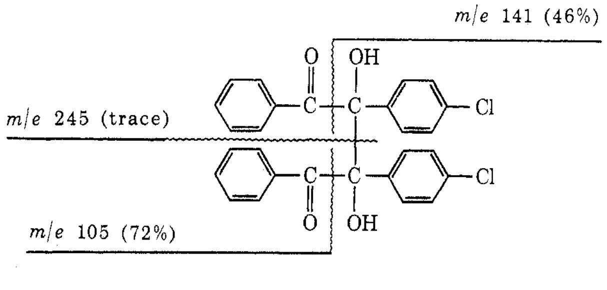


TABLE I

YIELDS FOR THE PHOTOREDUCTION OF BENZILS IN 2-PROPANOL[a]

X in 4-X-$C_6H_4C(=O)C(=O)C_6H_5$		Irradn time,	X and Y in 4-X-$C_6H_4C(=O)CH(OH)C_6H_4Y$-4′				X and Y in [4-X-$C_6H_4C(=O)C(OH)C_6H_4Y$-4′]$_2$				4-X-$C_6H_4CO_2R'$	
Registry no.		hr	Registry no.	X	Y	Yield, %	Registry no.	X	Y	Yield, %	R′ (H or 2-Pr)	Yield, %
22711-20-2	NMe_2	32	6317-85-7	NMe_2	H	11.7					. . .[b]	
22711-21-3	OMe	12	4254-17-5	OMe	H	5.5					. . .[b]	
2431-00-7	Me	28	2431-23-4	Me	H	8.8	36803-60-8	Me	H	34.8	. . .[b]	
134-81-6	H	12	119-53-9	H	H	13.5	36803-61-9	H	H	22.5	H	9.4
36803-53-9	Ph	98									2-Pr	[c]
22711-23-5	Cl	6					36803-62-0	H	Cl	51.6	2-Pr	4.9[c]
22711-24-6	NO_2	28										
36803-56-2	CN	4					36803-63-1	H	CN	57.0	2-Pr	4.8[c]

[a] Isolated yield was based on starting benzil used. [b] Yield was not determined. [c] A mixture of substituted and unsubstituted benzoates.

$C_6H_4CO^+$)/$P_{140+141}$($ClC_6H_4COH^+$) = 1.8 seems to justify the structure **11a**. Thus, the reduction occurs at the carbonyl attached to 4-chlorophenyl, giving solely dimer **11a** alone among two possible isomers.

4-Cyanobenzil (8b).—The product from irradiated **8b** in 2-propanol is a reduction dimer, 4′-cyanobenzilpinacol (**11b**, 57.0%), together with fission products, *i.e.*, a mixture of isopropyl benzoate and 4-cyanobenzoate (**9b** + **10b**, 4.8%). The dimer (mp 170–171°) was 4′-cyanobenzilpinacol (**11b**) on the basis of elemental analysis and nmr and ir spectra in which the product has one carbonyl absorption of unsubstituted benzoyl at 1680 cm^{-1} although **8b** has two carbonyl stretching vibrations at 1680 cm^{-1} for benzoyl carbonyl and 1650 cm^{-1} for 4-cyanobenzoyl. A trace of half value for the molecular ion peak was detected in the mass spectrum of **11b**, and a remarkable difference between the relative intensity of $P_{105}(PhCO^+)/P_{106}(PhCOH^+) = 8$ and that of $P_{135}(CNC_6H_4CO^+)/[P_{131}(CNC_6H_4COH^+) + P_{104}(P_{131} - CN)] = 1.2$ supports the structure **11b**.

4-Phenylbenzil (12).—Irradiation of **12** in 2-propanol for 98 hr afforded a solid product (mp over 300°), as well as isopropyl 4-phenylbenzoate. The former product has not yet been identified, although it has a hydroxyl group in view of its ir spectra.

The results are summarized in Table I.

Quantum Yields.—Table II lists the quantum yields for the disappearance of starting benzils. It can be seen from Tables I and II that the yield of photoproduct increases with an increase in electron-withdrawing ability of the substituent, and that the carbonyl reduction is selective, a CO group with a greater electron-withdrawing substituent being reduced exclusively, although some benzils mainly photodecompose through carbonyl–carbonyl fission.

TABLE II

QUANTUM YIELDS FOR DISAPPEARANCE OF BENZILS[a]

X in 4-X-$C_6H_4C(=O)C(=O)C_6H_5$	Solvent	
	2-PrOH	Et_2O
NMe_2	. . .[b]	. . .[b]
OMe	0.14	0.015
Me	0.076	. . .[b]
H	0.11	0.012[c]
Ph	0.076	0.087[c]
Cl	. . .[b]	0.11
NO_2	. . .[b]	. . .[b]
CN	. . .[b]	0.14

[a] A ferrioxalate solution was used as an actinometer. [b] Not determined. [c] Cyclohexane was used as solvent.

Absorption and Emission Spectra of Benzils.—Observed absorption and emission spectral data of these benzils are summarized in Table III. They show an $n\pi^*$ absorption maximum around 370 nm in methanol, which shifts bathochromically on lowering the solvent polarity. The absorption maximum is a broad and single one, which is expected to be due to overlapping of two possible $n\pi^*$ transitions on unsubstituted and substituted benzoyl carbonyls in a molecule. Hence, excitation energies by $n\pi^*$ transition remain at an almost equal level.

Phosphorescence spectra were also determined at 77°K in ether–isopentane–ethanol (EPA) and isopentane, but the emission spectra have little fine structure. In general, the emission is derived from the lowest excited $n\pi^*$ triplet state on the basis of solvent effect; *i.e.*, the red shift of emission was observed on changing solvent from EPA to isopentane. Observation of one emission maximum implies only one emissive triplet unsymmetrical benzil; *i.e.*, one lowest triplet $n\pi^*$ state in an unsymmetrical benzil can radiate and another higher triplet state falls to the former level only by radiationless decay.

Evans and Leermakers[3a] postulated in their phosphorescence study on benzil the coplanarity of carbonyl groups in the lowest excited triplet in spite of their twist in the ground state. The twist angle of 90° in 4-substituted benzils may also be conceivable, since the steric effect between acyl ortho hydrogen and carbonyl oxygen is not changed with para substitution.

Table III also gives energy differences ($A - P$) between the absorption maximum and phosphorescence maximum (P) (*ca.* 6000–10,000 cm^{-1}), which evaluated the energy difference between the excited singlet, formed *via* Franck–Condon transition from the ground state conformation and the emitting triplet;[3a] the value is significantly larger than the 3200-cm^{-1} splitting found for biacetyl (trans-coplanar emitting state). Accounding to Evans and Leermakers, unsymmetrical benzil as well as unsubstituted benzil may be considered to be coplanar in their excited triplet state, since the large splitting value ($A - P$) demands that there be a significant configurational change between the ground state (90° twisted) and the emitting triplet state.

Excited triplet energies were also estimated by the phosphorescence 0–0 band, and are summarized in Table III. The triplet energy tends to increase with

TABLE III

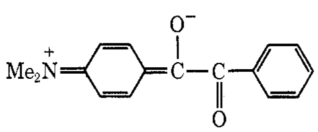
ABSORPTION AND EMISSION SPECTRA OF BENZILS[a]

X in 4-X-$C_6H_4C(=O)C(=O)C_6H_5$	Absorption λ_{max}^{MeOH}, nm (*A*)	Phosphorescence λ_{max}^{EPA},[b] nm (*P*)	Phosphorescence λ_{max}^{IP},[c] nm	*A* − *P*, cm^{-1}	E_T, kcal/mol in EPA	E_T, kcal/mol in IP
NMe_2	380	538	559	7700	57.4	54.6
OMe	380	498	508	6200	62.6	58.8
Me	385	498	508	5800	61.9	60.6
H	378	495	521	6300	61.6	58.0
Ph	386	508	538	6300	60.6	55.8
Cl	387	505	530	6000		56
NO_2	380	518	535	7600	57.4	55.9
CN	340	510	545	9800		54.5
Cf. bornanedione[d]	483			2300		51.6

[a] Phosphorescence spectra were measured at 77°K. [b] EPA: ether–isopentane–ethanol (5:5:2, v/v). [c] IP: isopentane. [d] Reference 3a.

an increase in electron-releasing ability of substituent. In general, the substituent effect on $n\pi^*$ triplet energy may be rather small within the difference of 6 kcal/mol.

In view of the large uv absorption intensity around 380 nm (log ε 4.35), dimethylaminobenzil (**5a**) has exceptionally a charge-transfer level as the lowest triplet state in the following form (**13**).

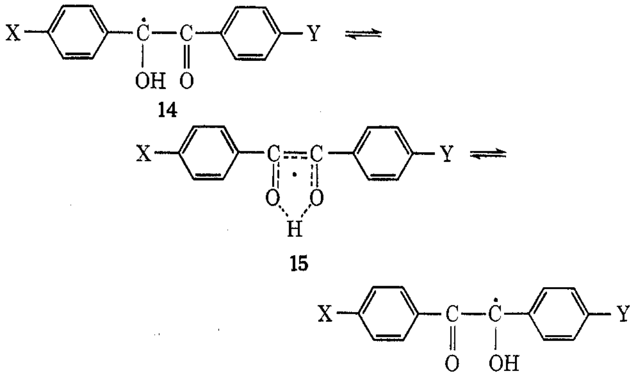


13

On addition of hydrochloric acid to **5a**, the C-T band at 358 nm disappears, and at the same time a $n\pi^*$ absorption at 370 nm appears, which is perhaps due to unsubstituted benzoyl $n\pi^*$. On the other hand, no photoreduction of 4-dimethylaminobenzophenone occurs at all, which possesses the C-T level as the lowest triplet but not the $n\pi^*$ level.[10]

Reaction Pathways.—Either of the two carbonyl group of benzils can be excited to their own $n\pi^*$ singlet state by uv light of over 300 nm. The $n\pi^*$ singlet readily cascades to the triplet. The selective photoreduction of one of two carbonyls may occur at the carbonyl of lower E_T. Though the hydrogen abstraction of the upper carbonyl triplet state competes with the decay to the lowest triplet state, the more than 100-fold difference of rate for these processes makes the latter predominate, assuming the rate for the former process[11] to be *ca.* 10^8 M^{-1} sec^{-1} and the latter one[12a,b] to be over 10^{10} sec^{-1}. The selectivity may be explained if the upper excited triplet $n\pi^*$ level is exclusively transformed to the lowest triplet $n\pi^*$ level of two carbonyls through intramolecular T–T transition followed by reduction of the two carbonyls bearing the lowest $n\pi^*$ triplet.

In order to justify the above scheme, it is necessary to assume that the carbonyl group which abstracts a hydrogen atom is the carbonyl which becomes the hydroxyl in the final product. However, biacetyl radical tautomerizes by a shift of a hydrogen atom from one oxygen to the other with a rate of *ca.* 8 × 10^7 sec^{-1} at very low [H^+],[13] although no data for benzil ketyl radical are available. In contrast, the resulting benzil ketyl radicals, *e.g.*, **14** and **16**, have been reported to couple with a second-order rate constant of 2–4 × 10^8 M^{-1} sec^{-1}.[11] If this estimation can be applied also to our unsymmetrical benzils, benzil ketyl radicals tautomerize faster than coupling to yield dimer when the concentration of a radical is less than 10^{-1} *M*. The concentrations of radicals **14** and **16** in an equilibrium vary with their substituents. The orientations for the formation of the reduction dimer are determined by the following two factors: (i) the stabilities (*i.e.*, concentrations) of radicals **14** and **16**, and (ii) their reactivities for coupling.[12c] The observed substituent effect suggests that the effect depends much more on the reactivities than on the stabilities, since an electron-withdrawing group tends to increase the former but affects the latter in a complex way. Therefore, it is also probable that the resulting benzoins and/or benzilpinacols are derived from a more reactive ketyl radical substituted by an electron-withdrawing group on the basis of our observation.



14 **15** **16**

However, we could not preclude that the product-determining step may be hydrogen abstraction step by the lowest $n\pi^*$ carbonyl, since kinetic data for unsymmetrical benzil ketyl radicals are unavailable at present.

Finally, it is noteworthy that no photoisomerization between 4-methylbenzoin (**6c**) and 4′-methylbenzoin (**6′c**) was observed.

The mechanism for the formation of fission products such as benzaldehydes, benzoic acid, and benzoates is

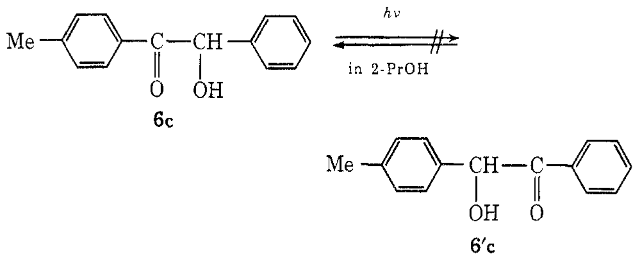
---

[10] (a) G. Porter and P. Suppan, *Proc. Chem. Soc.*, 191 (1964); (b) S. G. Cohen and M. W. Siddiqui, *J. Amer. Chem. Soc.*, **86**, 5047 (1964).

[11] (a) S. A. Weiner, E. J. Hamilton, Jr., and B. M. Monroe, *ibid.*, **91**, 6350 (1969); (b) T. Fujisawa and G. S. Hammond, *ibid.*, **94**, 4175 (1972).

[12] (a) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965, p 119; (b) D. O. Cowan and A. A. Baum, *J. Amer. Chem. Soc.*, **93**, 1153 (1971); (c) C. G. Swain, W. H. Stockmayer, and J. T. Clarke, *ibid.*, **72**, 5426 (1950).

[13] H. Staudinger, *Ber.*, **46**, 3530 (1913).



obscure. Perhaps they are derived from benzoyl radicals *via* carbonyl–carbonyl fission in the reactive triplet.

Experimental Section

Materials.—Benzil was prepared by the oxidation of benzoin with nitric acid and recrystallized from ethanol (mp 95°): $\lambda_{\max}^{\mathrm{MeOH}}$ 257 nm (log ϵ 4.33) and 378 (1.86). Dimethylaminobenzil (**5a**)[13] was prepared by the oxidation of 4-dimethylaminobenzoin with Fehling's solution (mp 115–116°): $\lambda_{\max}^{\mathrm{MeOH}}$ 258 nm (log ϵ 4.15) and 358 (4.35). 4-Nitrobenzil[14] was prepared by the nitration of benzoin acetate with potassium nitrate in acetic acid and recrystallized from CCl_4 (mp 142°): $\lambda_{\max}^{\mathrm{MeOH}}$ 265 nm (log ϵ 4.17). 4-Methylbenzil[15] (**5c**) was prepared by the oxidation of 4-methyldeoxybenzoin with selenium oxide and recrystallized from ethanol (mp 31°): $\lambda_{\max}^{\mathrm{MeOH}}$ 264 nm (log ϵ 4.26) and 386 (1.75). 4-Phenylbenzil (**12**) was prepared by the oxidation of 4-phenyldeoxybenzoin[16] with selenium oxide and recrystallized from ethanol (mp 105°): $\lambda_{\max}^{\mathrm{MeOH}}$ 255 nm (log ϵ 4.15), 300 (4.28), and 386 (1.26). 4-Methoxybenzil (**5b**)[17] was prepared by the oxidation of 4-methoxybenzoin with Fehling's solution and purified by silica gel column chromatography using petroleum ether (bp 30–60°)–ethyl acetate (7:3, v/v) as an eluent (mp 61°): $\lambda_{\max}^{\mathrm{MeOH}}$ 255 nm (log ϵ 4.18), 291 (4.26), and 380 (2.08). 4-Chlorobenzil (**8a**)[18] and 4-cyanobenzil (**8b**)[18] were prepared by the decomposition of 5 *p*-chloro- and 5-*p*-cyanophenyl-2-methyl-4-phenyloxazoles with bromine in acetic acid solution, respectively, and recrystallized from aqueous EtOH: 4-chlorobenzil, mp 74–75°; $\lambda_{\max}^{\mathrm{EtOH}}$ 265 nm (ϵ 22,900) and 387 (927); $\lambda_{\max}^{\mathrm{cyclohexane}}$ 266 nm (ϵ 21,600) and 405 (711); 4-cyanobenzil, mp 109–110°; $\lambda_{\max}^{\mathrm{EtOH}}$ 260 nm (ϵ 21,150) and 340 (1175). Commercial cyclohexane was purified successively by washing with H_2SO_4, aqueous NaOH, and water, and then through a silica gel column followed by distillation. Ethyl ether (first grade) was purified by rectification after treatment with H_2SO_4, NaOH, and Na, bp 34.0–34.5°. Ethyl alcohol was rectified after treatment with H_2SO_4 and KOH and then through a silica gel column. Extra pure grade 2-propanol and isopentane were used without further purification. The silica gel used in the column chromatography was 100 mesh Mallinckrodt guaranteed reagent and baked at 100° for 1–2 hr before use.

Apparatus.—Melting points, measured by a Yanagimoto micro melting point apparatus, are uncorrected. Infrared spectra were measured on a Perkin-Elmer Model 337 grating infrared spectrophotometer. Ultraviolet spectra were determined on a Hitachi double-beam instrument, Model 124. Nmr spectra were determined by a Japan Electron Optic Laboratory Co., C60 HL nmr instrument. Electron impact fragmentations were carried out on a Mattauchi-Herzog type (JMS-OSG) mass spectrometer. The irradiation was carried out using a Halos 300-W high-pressure Hg lamp, which emits exclusively uv light of over 300 nm through a Pyrex filter.

Irradiation of Benzils.—The reaction vessel was a Pyrex cylindrical tube of 120 ml in which a 2-propanol solution of benzils ($\sim 10^{-2}$ *M*) was placed. The solution was flushed with nitrogen for 30 min prior to irradiation and then nitrogen flow was continued throughout the irradiation. The reaction vessel and the mercury lamp were dipped in a bath of running water at 20–30°.

Benzoin (2).—Benzil (1.94 g) dissolved in 2-propanol (1.85×10^{-2} *M*) was irradiated in the absence of oxygen. After the characteristic yellow color of benzil faded out (*ca.* 2 hr), 2-propanol was evaporated under reduced pressure. The resulting brown liquid was separated by column chromatography to yield a substance (264 mg, 13.5%), mp 137°. A mixture melting point with authentic benzoin showed no depression and its ir and uv spectra and tlc were identical with those of the authentic sample.

Benzilpinacol (3).—After removal of 2-propanol from the irradiated reaction mixture, crystals were filtered off and washed by acetone; there was obtained benzilpinacol (**3**), 439 mg (22.5%), mp 136° (lit.[8] mp 136°). The molecular weight measured by the cryoscopic method was 420 (calcd for $C_{28}H_{22}O_4$, 422); the ir peak (3400 cm^{-1}, OH) and mass spectrum, resembling that of benzoin, confirm its structure.

4-Dimethylaminobenzoin (6a).—4-Dimethylaminobenzil (1.2 g) in 2-propanol was irradiated for 32 hr until it was consumed; separation of the condensed mixture by column chromatography yielded crystals of 4-dimethylaminobenzoin (**6a**), 142 mg (12.4%), mp 157–158°. This was identified by tlc and uv and ir spectra.

Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49. Found: C, 72.82; H, 6.31; N, 5.89.

4-Methoxybenzoin (6b).—4-Methoxybenzil (234 mg) in 2-propanol (80 ml) was irradiated for 12 hr. The first fraction eluted from a column gave the starting material (98 mg, 42%) identified by comparison of tlc, ir, and uv spectra with those of **6b**. The second fraction was 4-methoxybenzoin (13 mg, 5.5%) by tlc, ir, and uv spectra in comparison with those of the authentic 4-methoxy-[20] and 4′-methoxybenzoins.[22] Its mass spectrum exhibits a molecular ion peak at *m/e* 242, a base ion peak at *m/e* 77 (100%), and other peaks at *m/e* 107 ($PhCHOH^+$), and 135 ($CH_3C_6H_4C{=}O^+$).

4-Methylbenzoin (6c).—After the solution (1.25×10^{-2} *M*) of 4-methylbenzil (**5c**) (1.12 g) in 2-propanol was irradiated for 28 hr, the solution was concentrated to yield a brown liquid containing precipitate. The filtrate was chromatographed by silica column to afford 4-methylbenzoin (100 mg, 8.8%); its characterization was performed by the mass spectrum (molecular ion peak at *m/e* 226, 4-methylbenzoyl ion at *m/e* 119, benzhydryl ion at *m/e* 107) and by the comparison of ir and uv ($\lambda_{\max}^{\mathrm{MeOH}}$ 255 nm) spectra with those of authentic 4-methyl- and 4′-methylbenzoins.[19]

4-Methylbenzilpinacol (7b).—A solid (393 mg, 34.8%) precipitated from the above irradiated mixture was 4-methylbenzilpinacol (**7b**), mp 140° dec and cryoscopic molecular weight 450 (calcd for $C_{30}H_{26}O_4$, 450). Moreover, its ir spectrum exhibits a characteristic OH absorption (3400 cm^{-1}) and the mass spectrum resembles that of 4-methylbenzoin.

4′-Chlorobenzilpinacol (11a).—4-Chlorobenzil (**8a**, 511 mg) in propanol was irradiated for 6 hr. Removal of solvent and column chromatography yielded a solid which was purified by sublimation to crystalline 4′-chlorobenzilpinacol (**11a**) (mp 119–120°), 265 mg (51.6%), nmr (DMSO-d_6) τ 2–3 (m), and $\nu_{\mathrm{C=O}}$ 1670 and ν_{OH} 3400 cm^{-1}.

Anal. Calcd for $C_{28}H_{20}O_4Cl_2$: Cl, 14.5. Found: Cl, 15.5.

4′-Cyanobenzilpinacol (11b).—4-Cyanobenzil (473 mg) in 2-propanol (120 ml) was irradiated for 4 hr. The solvent was removed and separated by column chromatography to yield 4′-cyanobenzilpinacol (**11b**) (271 mg, 57.0%), which on sublimation had mp 170–171°; $\nu_{\mathrm{C=O}}$ 1680, ν_{OH} 3400 cm^{-1}; nmr (DMSO-d_6) τ 2–3 (m) and nmr ($CDCl_3$) τ 2–3 (m, 9 H), 4.2 (s, 1 H).

Anal. Calcd for $C_{30}H_{20}O_4N_2$: N, 5.93. Found: N, 5.8.

Determination of Quantum Yields.—A solution (*ca.* 10^{-5} *M*) of benzils (5 ml total volume) was degassed by several freeze–thaw cycles and sealed *in vacuo* in a quartz uv cell. The cell was then irradiated through a Pyrex filter (over 300-nm light) using a Halos HIP 300-W high-pressure lamp. The disappearance of starting benzils was monitored at its $n\pi^*$ absorption maxima on the above spectrometer. Actinometries were carried out simultaneously using a ferrioxlate actinometer.

Measurement of Phosphorescence Spectra.—The phosphorescence spectra were measured by a Hitachi MPF-2A fluorescence spectrometer. All phosphorescence spectra were recorded

---

[14] E. B. Womack, N. Campbell, and G. B. Dodds, *J. Chem. Soc.*, 1402 (1938).

[15] M. T. Clark, E. C. Hendley, and O. K. Neville, *J. Amer. Chem. Soc.*, **77**, 3280 (1955).

[16] C. V. Ferriss and E. E. Turner, *J. Chem. Soc.*, 1148 (1920).

[17] C. R. Kinney, *J. Amer. Chem. Soc.*, **51**, 1952 (1929).

[18] T. van Es and O. G. Backberg, *J. Chem. Soc.*, 1371 (1963).

[19] R. T. Arnold and R. C. Fuson, *J. Amer. Chem. Soc.*, **58**, 1295 (1936).

as a solution of EPA (ether–isopentane–ethanol, 5:5:2 v/v) or isopentane. The solvent was checked for emission at each time. No interference due to emission of solvent was observed. The solution contains *ca.* 10^{-5} *M* solute and they formed clear glasses without micro crystals at 77°K.

Acknowledgments.—The authors wish to thank Dr. Y. Izawa for his advice, Miss M. Ogimura for nmr measurements, and Dr. K. Aoki for emission spectra measurements.

Photochemical and Thermal Reactions of Naphthoquinones and Ynamines. Formation of Intermediate Cyclobutadienes

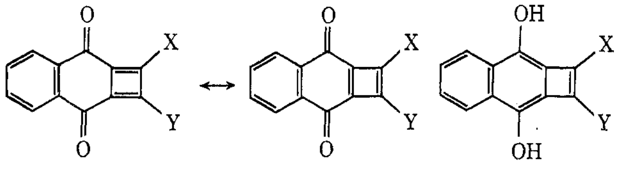
MARTIN E. KUEHNE* AND HAROLD LINDE

Department of Chemistry, University of Vermont, Burlington, Vermont 05401

Received June 20, 1972

Photochemical and thermal reactions of naphthoquinones with ynamines were found to give cyclobutene, quinone methine, and naphthothiophene products. The reaction course was governed by naphthoquinone and ynamine substituents and reaction conditions. Conversions of the cyclobutenes to naphthocyclobutadienes, the corresponding naphthoquinones, and their dimerizations were studied.

The acid-promoted dimerization of ynamines to four-membered ring imonium salts and their subsequent treatment with base gave stable, tetrasubstituted cyclobutadiene compounds.[1,2] In order to study the limits of stability of these long elusive smallest cyclic polyenes, we undertook studies which should lead to the cyclobutadiene–naphthoquinone and cyclobutadiene–dihydroxynaphthalene systems A and B, in which one might expect some measurable π bond localization, depending on the substituents X and Y.

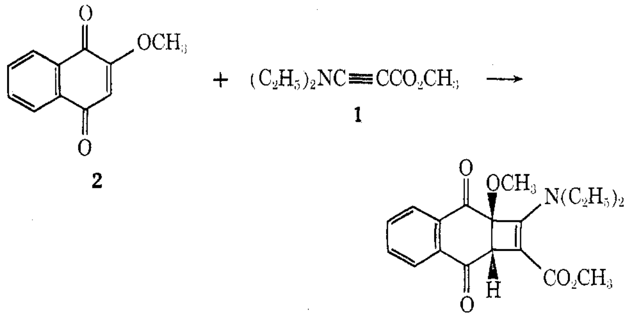


A A′ B

While enamines react with quinones, quinone imines, and naphthoquinones to form substituted hydroquinones or their corresponding derivatives,[3–8] ynamines were found to give products derived from addition to the quinone carbonyl group.[9] The formation of intermediate oxirans was again observed in the photochemical reactions of other acetylenes with naphthoquinones, but these reactions also gave fused cyclobutene products.[10–13] This paper describes studies of the photochemical and nonphotochemical reactions of naphthoquinones with ynamines and subsequent conversions designed to give A and B.

Irradiation of a solution of carbomethoxydiethylaminoacetylene (1) and 2-methoxynaphthoquinone (2) in acetonitrile through a Pyrex filter (λ >280 mμ) produced a 58% yield of the adduct **3**. Since ir, uv, and nmr spectra did not allow a rigorous exclusion of the isomeric cyclobutene product with adjacent carbomethoxy and methoxy groups (though there was no double-bond isomerization evident in our product), a single-crystal X-ray analysis was enlisted.[14] This firmly established the structure of **3**.

A uv spectrum of the reaction mixture prior to irradiation did not reveal formation of an initial complex of the reactants, and the isolated product **3** proved to be stable to further irradiation. The 1,3-photorearrangement[15] through Norrish type I cleavage, which has been observed for other naphthoquinone–acetylene adducts, would not be expected in this case, since it would lead to the cyclobutene where amine and ester group conjugation is lost. No adduct **3** was formed in acetonitrile without irradiation.



2 **1** **3**

Similarly, the cyanoynamine **4** was found to react with 2-methoxynaphthoquinone (**2**) to form the cyclobutene **5** in 70% yield. The structure of this product was suggested by a close spectroscopic correlation with **3**. (Profound differences were found in the isomeric cyclobutenes obtained in the acetoxy series, below.)

Together with the cyclobutene **5**, a quinone methine **6** was obtained in 2–5% yield. This product arises on opening of the oxirane obtained by addition of the ynamine to one of the naphthoquinone carbonyl groups.

A cyclobutene product was also formed from diethylaminophenylacetylene (**7**) and 2-methoxynaphtho-

---

(1) R. Gommper and G. Seybold, *Angew. Chem., Int. Ed. Engl.*, **7**, 824 (1968).

(2) N. Neuenschwander and A. Niederhauser, *Helv. Chim. Acta*, **53**, 519 (1970).

(3) K. C. Brannock, R. D. Burpitt, H. E. Davis, H. S. Pridgen, and J. G. Thweatt, *J. Org. Chem.*, **29**, 2579 (1964).

(4) H. B. Henbest and P. Slade, *J. Chem. Soc.*, 1555 (1960).

(5) G. Domschke, *Z. Chem.*, **4**, 29 (1964).

(6) G. Domschke, *Ber.*, **98**, 930, 2920 (1965); **99**, 934, 939 (1966).

(7) V. I. Shvedov and A. N. Grinev, *Zh. Org. Khim.*, **1**, 1125 (1965).

(8) M. E. Kuehne, *J. Amer. Chem. Soc.*, **84**, 837 (1962).

(9) J. Ficini and A. Krief, *Tetrahedron Lett.*, 2497 (1967).

(10) S. P. Pappas and N. A. Portnoy, *J. Org. Chem.*, **33**, 2200 (1968).

(11) S. P. Pappas, B. C. Pappas, and N. A. Portnoy, *ibid.*, **34**, 520 (1969).

(12) S. Farid, W. Kothe, and G. Pfundt, *Tetrahedron Lett.*, 4147 (1968).

(13) (a) R. H. Grubbs, Ph.D. Dissertation, Columbia University, 1968; (b) R. Breslow, R. Grubbs, and S. Murahashi, *J. Amer. Chem. Soc.*, **92**, 4139 (1970).

(14) J. A. Lerbscher and J. Trotter, *J. Cryst. Mol. Struct.*, **1**, 355 (1971). We thank these investigators for their cooperative interest.

(15) W. Kothe, *Tetrahedron Lett.*, 5201 (1969).