Table IX

R	ΔH_{exptl} ($CH_2R^+ \rightarrow CH_3R$)[1,20]	ΔH_{stab} (exptl)[1,20]	ΔE_{stab} (calcd)	ΔE_{stab} (res)	ΔE_{stab} (ind)
H	280				
CH_3	238–249	31–42	27	11	16
NH_2	183.5	96.5	89	66	23
OH	223–248	32–57	45	48	−3
F	276	4	−5	31	−36

compensate for the electronegativity of the heteroatom and help to disperse the positive charge of the carbonium ion.

Conclusions and Future Issues

Let us compare the calculated results with CNDO/2 with those found in the *ab initio* calculations. The rotational barrier results are encouraging; the proton affinity results discouraging. Most of the trends in the population analysis are qualitatively similar in the three results although in the methylenimmonium ion CNDO/2 predicts a much less negative nitrogen (-0.01) than STO-3G (-0.28) or double ζ (-0.56).

We can predict from these results that the proton affinity of methylenimine should be ~200 kcal/mol and the rotational barrier of $CH_2NH_2^+$ 72 kcal/mol. $CH_2NH_2^+$ is significantly resonance stabilized and might be observable in solutions without strong nucleophiles.

There are three subjects of future interest: first, one would like to study substituent effects on the electronic structure of immonium ions by CNDO/2 or with small *ab initio* basis sets; secondly, a potential surface for nucleophilic attack on immonium ions will be of interest; finally, and most importantly, the development of an appropriate solvation model to estimate solvent stabilization of the various immonium ions and other possible intermediates in N-dealkylation reactions[3] would be very useful.

Acknowledgments. One of us (P. A. K.) appreciates useful discussions with Dr. Joel Liebman. P. A. K. is grateful for support from the Academic Senate of UCSF.

Photoisomerization of 4*H*-Pyran-4-ones to 2*H*-Pyran-2-ones

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Contribution from the Department of Chemistry, Kyoto Institute of Technology, Matsugasaki, Kyoto 606, Japan. *Received May 13, 1972*

Abstract: Ultraviolet irradiation of 2,6-dimethyl-3,5-diphenyl-4*H*-pyran-4-one with a medium-pressure mercury lamp yielded 3,6-diphenyl-4,5-dimethyl-2*H*-pyran-2-one. Photolysis of 2,3,5,6-tetraphenyl-4*H*-pyran-4-one afforded 3,4,5,6-tetraphenyl-2*H*-pyran-2-one and 5,6,7,8-dibenzo-2,3-diphenyl-4-chromen-4-one. The photorearrangement of the hindered 4*H*-pyran-4-ones appears to proceed through two consecutive photoreactions; the first step is the light-induced rearrangement of the hindered 4*H*-pyran-4-ones to the 4,5-epoxycyclopent-2-en-1-one derivatives and the second is the photoisomerization of the latter to 2*H*-pyran-2-ones.

Under the influence of ultraviolet light, 2,6-disubstituted 4*H*-pyran-4-ones (Ia, Ib, and Ic) undergo dimerization to "head-to-tail" dimers (II).[1,2] When the photolysis of Ia was carried out under conditions chosen to retard dimerization, 4,5-dimethyl-2-furaldehyde (IIIa) was isolated in very low yield.[3] Yates and Still[3] suggested that this photoreaction proceeds by rearrangement to 3,4-dimethyl-4,5-epoxycyclopent-2-en-1-one (IVa), which is analogous to the photochemical transformation of cyclohexa-2,5-dienone derivatives.[4]

Studies on the photochemistry of 4,5-epoxycyclopent-2-en-1-one derivatives (IVb and IVc) have revealed that IV undergoes photoisomerization to the corresponding 2*H*-pyran-2-ones (Vb and Vc),[5–8] while furaldehyde derivatives (III) were actually formed *via* the acid-catalyzed rearrangement of IV.[5] Padwa and Hartman[5] have examined the photolysis of 2,6-diphenyl-4*H*-pyran-4-one (Ic) and could not detect the formation of either 3,4-diphenyl-4,5-epoxycyclopent-2-en-1-one (IVb) or 4,5-diphenyl-2*H*-pyran-2-one (Vb), but obtained only a "head-to-tail" cage dimer, IIc.[2,9]

It was anticipated that introduction of the phenyl group into the C-3 and C-5 positions of 4*H*-pyran-4-one

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(1) P. Yates and M. J. Jorgenson, *J. Amer. Chem. Soc.*, **85**, 2956 (1963); P. Yates, E. S. Hand, P. Singh, S. K. Roy, and I. W. J. Still, *J. Org. Chem.*, **34**, 4046 (1969).

(2) N. Sugiyama, Y. Sato, and C. Kashima, *Bull. Chem. Soc. Jap.*, 43, 3205 (1970).

(3) P. Yates and I. W. J. Still, *J. Amer. Chem. Soc.*, **85**, 1208 (1963).

(4) For reviews, see P. J. Kropp, "Organic Photochemistry," Vol. 1, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967, p 1; H. E. Zimmerman, *Angew. Chem., Int. Ed. Engl.*, **8**, 1 (1969).

(5) A. Padwa and R. Hartman, *J. Amer. Chem. Soc.*, **88**, 1518 (1966).

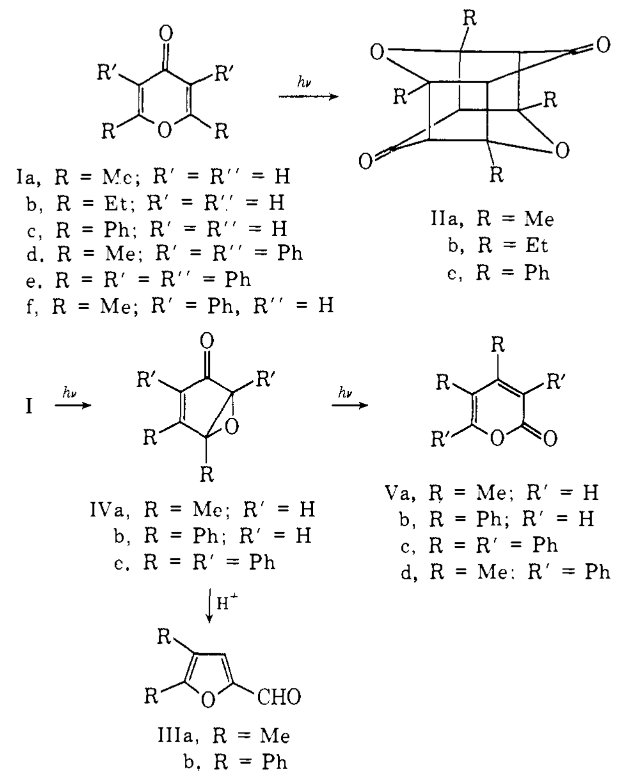
(6) J. M. Duston and P. Yates, *Tetrahedron Lett.*, 505 (1964).

(7) For reviews of the photochemistry of small-ring carbonyl compounds, see A. Padwa, "Organic Photochemistry," Vol. 1, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967, p 92; A. Padwa, *Accounts Chem. Res.*, **4**, 48 (1971).

(8) In the case of IVc,[6] a pyrylium-3-oxide was formed by a photochemical valence isomerization. For a review, see E. F. Ullman, *ibid.*, **1**, 353 (1968).

(9) The structure of IIc was deduced from the spectral data of the photoproduct only,[2] while the structures of IIa and IIb were confirmed not only by their spectral data but also some chemical reactions[1] (Scheme I).

Scheme I



Ia, R = Me; R′ = R″ = H
b, R = Et; R′ = R″ = H
c, R = Ph; R′ = R″ = H
d, R = Me; R′ = R″ = Ph
e, R = R′ = R″ = Ph
f, R = Me; R′ = Ph, R″ = H

IIa, R = Me
b, R = Et
c, R = Ph

IVa, R = Me; R′ = H
b, R = Ph; R′ = H
c, R = R′ = Ph

Va, R = Me; R′ = H
b, R = Ph; R′ = H
c, R = R′ = Ph
d, R = Me; R′ = Ph

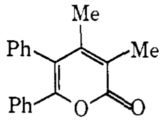
IIIa, R = Me
b, R = Ph

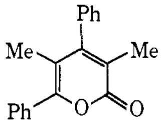
would prevent the formation of the photodimer due to their steric effect and indeed this was the case in the photolysis of 2,6-bis(alkylthio)-3,5-diphenyl-4*H*-thiopyran-4-ones which afforded 3,4-bis(alkylthio)-2,5-diphenylcyclopentadienone derivatives.[10] These results lead us to choose 2,6-dimethyl-3,5-diphenyl-4*H*-pyran-4-one (Id), 2,3,5,6-tetraphenyl-4*H*-pyran-4-one (Ie), and 2,6-dimethyl-3-phenyl-4*H*-pyran-4-one (If) as the hindered 4*H*-pyran-4-ones to start with. The present paper[11] deals with the photochemistry of these hindered 4*H*-pyran-4-ones and the possible connection between the photorearrangement of 4,5-epoxycyclopent-2-en-1-ones to 2*H*-pyran-2-ones and the photoisomerization of hindered 4*H*-pyran-4-ones to 2*H*-pyran-2-ones.

Results

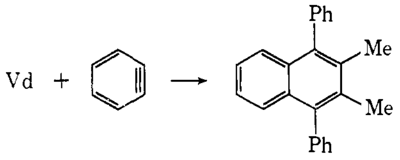
The Products. Photolysis of Id in acetonitrile using a 500-W medium-pressure mercury lamp with a Vycor filter gave a single colorless solid, mp 156–157° in 67% yield. The elemental analysis and the mass spectrum of the photoproduct (M^+ 276) clearly indicate that it is an isomer of Id. As mentioned earlier, 2-furaldehyde (III), 4,5-epoxycyclopent-2-en-1-one (IV), and 2*H*-pyran-2-one (V) can be formulated as the possible structures of the photoproduct. The spectral properties of the photoproduct, in particular the infrared and mass spectra, ruled out III and IV. The infrared spectrum of the photoproduct did not exhibit any characteristic ring vibration of the epoxy ring compound at 1230–1280 cm^{-1} [12] and the stretching vibration of the aldehyde group,[13] but showed strong bands at 1700 ($\nu_{C=O}$), 1630, and 1550 cm^{-1} ($\nu_{C=C}$), in agreement with its formulation as 2*H*-pyran-2-one. The mass spectrum of the photoproduct showed the base peak at *m*/*e* 248 ($[M - CO]^+$) and an intense peak at *m*/*e* 143. A loss of CO from the molecular ion is characteristic with 2*H*-pyran-2-one,[14-16] although IVb and Vb showed almost identical fragmentation patterns in their mass spectra.[17] When the photoproduct was heated with P_2S_5 in benzene, the corresponding 2*H*-pyran-2-thione derivative was formed. Its infrared spectrum contained no carbonyl absorption, but exhibited the strong band at 1270 cm^{-1} due to the stretching vibration of the thioketone group. This transformation of the carbonyl moiety to the thiocarbonyl group is typical of pyrone derivatives.[18]

Our next problem is to determine the position of the substituents in 2*H*-pyran-2-one. The nmr spectrum of the photoproduct showed two singlets at δ 2.07 (3 H) and 2.13 (3 H) due to the methyl protons, while all the six methyl protons of Id appeared as a singlet at δ 2.24. The mass spectrum of the photoproduct, however, exhibited an intense peak at *m*/*e* 143, formed by the elimination of the benzoyl radical from the fragment, $[M - CO]^+$, at *m*/*e* 248. This strongly indicates the presence of the phenyl group at C-6 of 2*H*-pyran-2-one, since the elimination of the substituent at C-6 of 2*H*-pyran-2-ones as the acyl radical is typical of 2*H*-pyran-2-ones.[14,15,17] These spectral properties of the photoproduct left structures Vd, VI, and VII as the possible alternatives for consideration. Confirmation was obtained from the Diels–Alder reaction of the photoproduct[19] with benzyne, generated from diphenyliodonium-2-carboxylate,[21] which gave 1,4-diphenyl-2,3-dimethylnaphthalene (VIII) (Scheme II). The nmr spectrum of the adduct exhibited a singlet at δ 2.15 due to the methyl protons in addition to the multiplet for the aromatic protons at


VI


VII

Scheme II


VIII

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(10) N. Ishibe and M. Odani, *Chem. Commun.*, 702 (1971); N. Ishibe, M. Odani, and R. Tanuma, *J. Chem. Soc., Perkin Trans. 1*, 1203 (1972).

(11) A preliminary report of this work has appeared; N. Ishibe, M. Odani, and M. Sunami, *Chem. Commun.*, 1034 (1971).

(12) N. M. Colthup, L. H. Daly, and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, N. Y., 1964, p 273.

(13) Reference 12, p 240.

(14) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, p 208.

(15) Q. N. Porter and J. Baldas, "Mass Spectrometry of Heterocyclic Compounds," Wiley-Interscience, New York, N. Y., 1971, p 139.

(16) M. M. Bursey and L. R. Dusold, *Chem. Commun.*, 712 (1967); P. Brown and M. M. Green, *J. Org. Chem.*, **32**, 1681 (1967).

(17) M. M. Bursey, L. Dusold, and A. Padwa, *Tetrahedron Lett.*, 2649 (1967).

(18) E. Mayer, W. Broy, and R. Zahradnik, *Advan. Heterocycl. Chem.*, **8**, 238 (1967).

(19) The Diels–Alder reaction of Vd with maleic anhydride or dimethyl acetylenedicarboxylate in mesitylene or bromobenzene was unsuccessful due to steric hindrance, though it is well known that the Diels–Alder reaction of unhindered 2*H*-pyran-2-one derivatives with dienophiles gave the 1,4-addition products.[20]

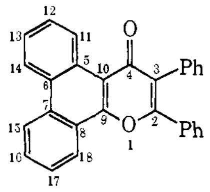
(20) H. Behringer and P. Heckmaier, *Chem. Ber.*, **102**, 2835 (1969); J. A. Reed, C. L. Schilling, Jr., R. F. Rarvin, T. A. Retting, and J. K. Stille, *J. Org. Chem.*, **34**, 2188 (1969), and references cited therein.

(21) L. F. Fieser and M. J. Haddadin, *Org. Syn.*, **46**, 107 (1966).

δ 7.1–7.5. This equivalence of the methyl protons excludes VI and VII as the structure of the photoproduct.[22]

A solution of Ie in methylene chloride was irradiated under nitrogen by a 500-W medium-pressure mercury lamp, the light filtered through Pyrex glass. The products were separated by column chromatography and identified as 3,4,5,6-tetraphenyl-2*H*-pyran-2-one (Vc) (42%) and 5,6,7,8-dibenzo-2,3-diphenyl-4-chromen-4-one (IX) (7%). The mass spectrum of Vc showed a base peak at *m*/*e* 372, by loss of CO from the original compound, which is typical of 2*H*-pyran-2-ones.[14–16] Its infrared spectrum exhibited a strong carbonyl band at 1700 cm^{-1}. When Vc is heated with P_2S_5 in benzene, the corresponding 2*H*-pyran-2-thione was formed. The photoproduct Vc was identified (mixture melting point, infrared and nmr spectra) with an authentic sample prepared independently by the reaction of dimethylsulfonium α-phenylphenacylide with diphenylcyclopropenone.[24]

The structure of IX was deduced from its elemental analysis and spectral data. The mass spectrum of IX displayed the parent peak at *m*/*e* 398, whereas the parent peak of Ie was at *m*/*e* 400. The ultraviolet spectrum of IX in chloroform showed bands at 264 (log ϵ 3.48), 293 (3.28), 337 (2.70), and 352 nm (2.48), a pattern similar to that of phenanthrene.[25] Its infrared spectrum exhibited a strong carbonyl band at 1625 cm^{-1}, in agreement with the structure of 4*H*-pyran-4-ones. In addition to the ultraviolet similarity noted above, the nmr spectrum of IX showed a singlet at δ 7.40 (10 H), and multiplets at δ 7.5–7.9 (5 H), 8.6–8.8 (2 H), and 10.3 (1 H). The multiplet at δ 8.6–8.8 can be assigned to the resonating protons at C-14 and C-15, since it is well known that the protons at C-4 and C-5 in phenanthrene experience marked deshielding by all three benzene rings.[26] A molecular model of IX indicates that the proton at C-11 lies in a region deshielded by the carbonyl group,[27] which leads to an abnormally high δ value (10.3).



IX

Irradiation of Ie for shorter periods of time gave both Vc and IX, separated by silica gel chromatography. Consideration of the product distribution as a function of time in a number of photolyses showed that neither Vc nor IX is a precursor for each other for formation of IX and Vc (Table I). The formation of IX might be rationalized by the photocyclization of Ie to give the dihydro intermediate, followed by oxidation to IX, since oxidative photocyclization of *cis*-stilbene and related systems to phenanthrene derivatives is well known.[28,29] Irradiation of Ie in the presence of iodine gave IX as the sole product. The photolysis of Ie in methylene chloride exposed to air did not furnish Vc, but IX and another unidentified product. Both iodine and oxygen serve as good oxidizing reagents for dihydrophenanthrene.[28] These results suggest that the dihydro derivative is the intermediate in the formation of IX.

Table I. Product Distribution *vs.* Extent of Conversion from the Photolysis of Ie

Run	Time, hr	Product yield,[a] % Vc	IX
1	0.75	15	4
2	2	34	9
3	5	45	9
4	7.5	42	7
5	10	42	8

[a] Material balance added up to 95% in the longer photolysis experiments.

Table II. Product Distribution from the Photolysis of Ie under Various Reaction Conditions

Reaction condition[a]	Product yield, % Vc	IX
Vacuum	43	7
Nitrogen	45	10
Nitrogen with Iodine	nil	50
Air[b]	nil	35

[a] For details of the experimental conditions, see the Experimental Section. [b] In addition to IX, there was another product which was not identified.

Direct photolysis of If through a Vycor filter resulted in the recovery of starting material. When photolysis was sensitized by acetophenone, If was also recovered unchanged. These results indicate that in 4*H*-pyran-4-one the presence of phenyl substituents at C-3 and C-5 is essential in order to undergo photorearrangement to 2*H*-pyran-2-ones.

Quantum Yield Determinations. The quantum yields for appearance of Vd in acetonitrile or dioxane were determined using potassium ferrioxalate actinometry.[30] The deaerated samples were irradiated with the 253.7-nm light. Reactions were carried out to 1–2% conversion and the yield of products was determined by the ultraviolet spectrophotometric method. The results of these runs showed the average quantum yield to be

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(22) A referee pointed out the possibility of 3,6-dimethyl-4,5-diphenyl-2*H*-pyran-2-one as a structure for the photoproduct. If this were the case, the Diels–Alder reaction of the photoproduct with benzyne would give 1,4-dimethyl-2,3-diphenylnaphthalene. The observed high-field signal of the methyl protons of the Diels–Alder adduct, however, is consistent with that of the β-methyl ones.[23] Moreover, the mass spectral data of the photoproduct, particularly the presence of intense peaks at *m*/*e* 143 and 105 ($[PhC{\equiv}O]^+$) and the absence of a peak at *m*/*e* 43 ($[CH_3C{\equiv}O]^+$), clearly eliminate 3,6-dimethyl-4,5-diphenyl-2*H*-pyran-2-one as a structure for the photoproduct.

(23) B. A. Nagasampagi, R. C. Pandey, V. S. Pansare, J. R. Praklad, and S. Dev, *Tetrahedron Lett.*, 411 (1964); F. F. Yew, R. J. Kurland, and B. J. Mair, *Anal. Chem.*, **36**, 843 (1964).

(24) Y. Hayashi and H. Nozaki, *Tetrahedron*, **27**, 3085 (1971).

(25) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," Wiley, New York, N. Y., 1951.

(26) R. H. Martin, N. Defay, F. Greets-Evrand, and H. Fiyes, *Bull. Soc. Chim. Belg.*, **73**, 199 (1964); R. H. Martin, N. Defay, F. Greets-Evrand, and S. Delavarenne, *Tetrahedron*, **20**, 1073 (1964).

(27) J. A. Pople, *J. Chem. Phys.*, **37**, 602 (1962); R. H. Martin, N. Defay, and F. Greets-Evrand, *Tetrahedron*, **20**, 1505 (1964).

(28) For a review, see E. V. Blackburn and C. J. Timmons, *Quart. Rev., Chem. Soc.*, **23**, 482 (1969).

(29) For nonoxidative photocyclization, see O. L. Chapman, G. I. Eian, A. Bloom, and J. Clardy, *J. Amer. Chem. Soc.*, **93**, 2918 (1971).

(30) C. H. Hatchard and C. A. Parker, *Proc. Roy. Soc.*, *Ser. A*, **235**, 518 (1956).

moderate (0.40). The photolysis of Id in dioxane does not appear to be sensitized by acetophenone (1.0 *M*, E_T = 73.6 kcal/mol[31]) absorbing over 98% of the incident light. When a deaerated solution of Id in acetone (E_T = 78 kcal/mol[32]) was irradiated with the light absorbed mostly by acetone, Vd was not formed but Id was recovered.[33] As shown in Table III both *trans*-penta-1,3-diene and cyclohexa-1,3-diene quenched the photorearrangement of Id to Vd, even though the concentration of quencher used was kept to serve as a good triplet quencher.[34–36] The preparative photolysis of Id in the presence of *trans*-penta-1,3-diene in dioxane did not give the addition product but only Vd, while the photolysis of Ia in the presence of acetylene derivatives produced the 1:1 adducts involving the cyclobutene moiety.[37] Addition of the same amount of hydrocarbons (cyclohexene, cyclohexane, or *n*-hexane) instead of dienes to the dioxane solution[38] showed no effect on the quantum yield of the formation of Vd (Table III). Because of these contradictory facts, the discussion has avoided the problem of identifying the nature of the excited state involved in the photorearrangement of Id to Vd. Since in particular this photorearrangement seems to involve two consecutive photoreactions (see Discussion), conclusions concerning the multiplicity of the excited states should be obtained from a study of the emission spectroscopic properties of I.

Table III. Quantum Yields for Formation of Vd

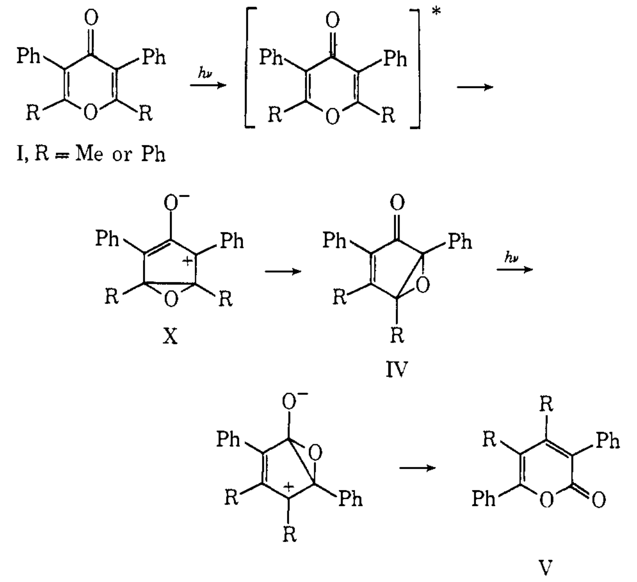
Solvent	Additive, 0.1 *M*	Quantum yield[a]
Dioxane	None	0.40
Acetonitrile	None	0.38
Dioxane	*trans*-Penta-1,3-diene	0.28
Dioxane	Cyclohexa-1,3-diene	0.18
Dioxane	Cyclohexene	0.39
Dioxane	Cyclohexane	0.41
Dioxane	*n*-Hexane	0.40

[a] Average of two or more determinations at 253.7 nm.

Discussion

A mechanism consistent with the observed rearrangement of the hindered 4*H*-pyran-4-ones (Id and Ie) is the one outlined in Scheme III. The photolysis of hindered 4*H*-pyran-4-ones leads initially to the polar species, X, which then rearranges to IV. Photoisomerization of I to IV is analogous to that of cyclohexa-2,5-dienones to bicyclo[3.1.0]hex-3-en-2-ones.[4] This intermediate IV is excited again by light and rearranges to V.

Scheme III



Padwa and Hartman[5] found that the photolysis of IVb leads to Vb and proposed that this photorearrangement proceeds *via* the excited singlet state of IVb. Matsuura, *et al.*,[39] have reported the photochemical rearrangement of flavonoid derivatives to indandione derivatives and suggested the mechanism involving 2,3-epoxy-1-indanone as an intermediate. An attempt to trap the hypothetical intermediate IV in the photolysis of Id in the presence of triphenylphosphine at −40° was unsuccessful. Since ultraviolet irradiation of IVb and IVc leads to a rapid rearrangement to Vb and Vc,[5,6] this intermediate, IV, should also be very photoreactive. Dunston and Yates[6] found the existence of photochemical valence tautomerization between IVc and tetraphenyl pyrylium-3-oxide, in addition to the formation of Vc. Ullman also found similar valence tautomerization between related cyclopentenone oxides and the dipolar pyrylium-3-oxides.[8] An attempt to trap a transient pyrylium 3-oxide with dimethyl acetylenedicarboxylate in the photolysis of Ie was unsuccessful. Examination of the visible spectrum of the reaction mixture during the course of the photoreaction of Ie in methylene chloride, however, showed a weak absorption band at 490 nm, the intensity of which slowly decreased on cessation of the irradiation.[40] The similarity of this visible spectrum to that observed in the photolysis of IVc, in respect to both band position and behavior on irradiation, suggests that this peculiarity should be attributed to the presence of tetraphenyl pyrylium-3-oxide. These results support the mechanism outlined in Scheme III.

Padwa and Hartman[5] also found that the prolonged irradiation of IVb led to the formation of 1,2,4,7-tetraphenylcyclooctatetraene and suggested the mechanism which involved internal photoaddition of Vb to a bicyclic β-lactone,[41] followed by thermochemical 1,4 addition to Vb with the elimination of carbon dioxide.

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(31) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 4537 (1964).

(32) N. J. Turro, "Energy Transfer and Organic Photochemistry," A. A. Lamola and N. J. Turro, Ed., Interscience, New York, N. Y., 1969, p 194.

(33) While the triplet excitation energies of 4*H*-pyran-4-one derivatives are not known, those of chromone[36] and xanthone[32] are 75 and 74 kcal/mol, respectively.

(34) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. A. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).

(35) In the concentration range of 0–1 *M* a plot of ϕ_0/ϕ for Id (0.002 *M*) against *trans*-penta-1,3-diene is cleanly linear with a slope of 2.3 M^{-1}.

(36) J. B. Gallivan, *Can. J. Chem.*, **48**, 3928 (1970).

(37) J. W. Hanifin and E. Cohen, *J. Org. Chem.*, **36**, 910 (1971).

(38) The poor solubility of Id in saturated hydrocarbons prevents us from determining the quantum yield of formation of Vd in these solvents.

(39) T. Matsuura, T. Takemoto, and R. Nakashima, *Tetrahedron Lett.*, 1539 (1971).

(40) We thank a referee for suggesting the possibility of detecting the formation of pyrylium-3-oxide by a spectrophotometer. A failure to trap this intermediate with dimethyl acetylenedicarboxylate would be due to low concentration of IVc, resulting in a concentration of the pyrylium-3-oxide too low to permit trapping.

(41) E. J. Corey and J. Streich, *J. Amer. Chem. Soc.*, **86**, 950 (1964).

We have, however, found that both the prolonged irradiation of Id or Ie (48 hr) with a Vycor filter and the independent irradiation of Vd or Vc using a Pyrex filter resulted in the recovery of the starting materials.

As mentioned earlier, the ultraviolet irradiation of unhindered 4*H*-pyran-4-ones (Ia, Ib, and Ic) affords "head-to-tail" dimers.[1,2,5] On the other hand, the photolysis of hindered 4*H*-pyran-4-ones (Id and Ie) did not give the dimer, and only the isomeric 2*H*-pyran-2-ones were the final products. The steric effect of substituents in Id and Ie prevents formation of the photodimers. A Dreiding molecular model indicates that in the structure of Id and Ie, the coplanarity of the phenyl ring with the heterocyclic ring is prevented by the steric repulsion between a phenyl proton and a methyl or phenyl proton. These steric effects are reflected in the hypsochromic shifts of their ultraviolet spectra[42] relative to the spectra of unhindered 4*H*-pyran-4-ones. The ultraviolet spectra of Id, Ie, and If in acetonitrile showed their maxima at 255 (log ϵ 4.19), 275 (4.54), and 257 nm (4.22), respectively, those of the unhindered 4*H*-pyran-4-ones substituted for the C-2 and/or C-6 positions with the phenyl group being at 274–283 nm (log ϵ 4.3–4.4).[43] This steric crowding seems very important for the photorearrangement of 4*H*-pyran-4-ones to 2*H*-pyran-2-ones.[44] Another important factor for this photoisomerization would be stabilization of intermediate, X, by the phenyl group.[45] This was the case in the photorearrangement of hindered 4*H*-thiopyran-4-ones[10] and *N*-alkyl-4-pyridones.[46] Irradiation did not affect 2,6-bis(methylthio)-3,5-dimethyl-4*H*-thiopyran-4-one and 3,5-diphenyl-4*H*-thiopyran-4-one, whereas photolysis of 2,6-bis(alkylthio)-3,5-diphenyl-4*H*-thiopyran-4-ones gave 3,4-bis(alkylthio)-2,5-diphenylcyclopentadienones. Ultraviolet irradiation of hindered *N*-alkyl-4-pyridones afforded *N*-alkyl-2-pyridones, whereas unhindered *N*-alkyl-4-pyridones were not affected by irradiation. The nature of the steric effect on the excited states and the photochemical reactivity of 4*H*-pyran-4-ones and the related compounds remains sufficiently attractive to warrant further investigation.

Experimental Section

The melting points are not corrected. Elemental analyses were performed by the Microanalytical Laboratory of Kyoto University, Kyoto, Japan. The infrared spectra were determined with a JASCO-402G spectrophotometer in a KBr disk. The ultraviolet spectra were recorded on a Hitachi 125 spectrophotometer. The nuclear magnetic resonance spectra were taken with a JEOL PS-100 spectrometer in deuteriochloroform solution using tetramethylsilane as an internal standard. The mass spectra were taken with a Hitachi RMU-6L.

2,6-Dimethyl-3,5-diphenyl-4*H*-pyran-4-one[47] and 2,6-dimethyl-3-phenyl-4*H*-pyran-4-one[48] were prepared by condensation of acetic acid in polyphosphoric acid with dibenzyl ketone and benzylmethyl ketone, respectively. 2,3,5,6-Tetraphenyl-4*H*-pyran-4-one[49] was synthesized by the action of phosgene on the sodium salt of deoxybenzoin. Solvents were spectrograde for photolysis and reagent grade for column and thin layer chromatography.

Irradiation of 2,6-Dimethyl-3,5-diphenyl-4*H*-pyran-4-one (Id). A solution of 0.5 g of **Id** in 350 ml of acetonitrile was irradiated under nitrogen with a Ushio 500-W medium-pressure mercury lamp using a Vycor filter to eliminate wavelengths below 220 nm.[50] After 5 hr, the solvent was removed *in vacuo* and the resulting residue was chromatographed on silica gel using chloroform–ether (95:5). 3,6-Diphenyl-4,5-dimethyl-2*H*-pyran-2-one (0.335 g, 67%) was isolated as a colorless solid which after recrystallization from methanol had mp 156–157°. The infrared spectrum was characterized by bands at 1700, 1630, 1550, 1095, 1020, and 955 cm^{-1}. The ultraviolet spectrum in dioxane showed a maximum at 325 nm (log ϵ 4.27). The nmr spectrum exhibited two singlets at δ 2.07 (3 H) and 2.13 (3 H) and a multiplet centered at δ 7.43 (10 H). The mass spectrum displayed important fragments at *m/e* (relative intensity, %): 277 (9.4), 276 (M$^+$ 41), 249 (25), 248 (100), 205 (7.1), 144 (7.5), 143 (59), 141 (6.1), 128 (20), 124 (11), 115 (14), 105 (42), 103 (6.1), 91 (7), 51 (48). *Anal.* Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.83, O, 11.59. Found: C, 82.32; H, 6.01; O, 11.34.

Irradiation of 2,3,5,6-Tetraphenyl-4*H*-pyran-4-one (Ie). Photolysis of 0.5 g of Ie in 350 ml of methylene chloride was carried out for 7.5 hr using a 500-W medium-pressure mercury arc lamp with a Pyrex filter. The solvent was removed under reduced pressure and the resulting residue chromatographed on silica gel with chloroform as the eluant. The 300-ml collection afforded a colorless solid, which after recrystallization from benzene gave 0.03 g (7%) of 5,6,7,8-dibenzo-2,3-diphenyl-4-chromen-4-one (IX), mp 240–241°. The infrared spectrum of this compound was characterized by bands at 1625, 1490, 1445, 1410, 1230, and 975 cm^{-1}. The ultraviolet spectrum in chloroform showed maxima at 264 (log ϵ 3.48), 293 (3.28), 337 (2.70), and 352 nm (2.48). The nmr spectrum showed a singlet at δ 7.40 (10 H), and multiplets at δ 7.5–7.9 (5 H), 8.6–8.8 (2 H), and 10.3 (1 H). The mass spectrum displayed important peaks at *m/e* (relative intensity, %): 399 (13), 398 (M$^+$ 61), 397 (100), 178 (42), 164 (34), 163 (16). *Anal.* Calcd for $C_{29}H_{18}O_2$: C, 87.14; H, 4.55; O, 8.04. Found: C, 87.29; H, 4.78; O, 7.93.

The next 150-ml fraction furnished a crude solid, which, after recrystallization from *n*-hexane, gave 0.21 g (42%) of 3,4,5,6-tetraphenyl-2*H*-pyran-2-one, mp 160–161° (lit.[24] 154–156°). The infrared spectrum showed intense bands at 1700, 1605, 1515, 1020, and 925 cm^{-1} and the ultraviolet (in dioxane) maximum at 346 nm (log ϵ 4.28). The nmr spectrum exhibited a multiplet at δ 6.5–7.3. The mass spectrum had significant peaks at *m/e* (relative intensity, %): 401 (12.5), 400 (M$^+$ 43), 373 (28), 372 (100), 268 (18), 267 (86), 265 (18), 165 (15), 105 (48), 77 (43). *Anal.* Calcd for $C_{29}H_{20}O_2$: C, 86.97; H, 5.03; O, 8.00. Found: C, 86.70; H, 4.85; O, 7.95.

Irradiation of 2,6-Dimethyl-3-phenyl-4*H*-pyran-4-one (If). A solution of 0.5 g of If in 350 ml of acetonitrile was irradiated with a Ushio 500-W medium-pressure mercury lamp using a Vycor filter. The photolysis was followed by withdrawing small samples at definite intervals without disturbing the system and the samples were analyzed by thin layer chromatography. No new spots on tlc appeared. After 12 hr the solution was concentrated to 5 ml, which showed only one spot in tlc; the R_f value was the same as If. The recovery of If was nearly 100%.

The solution containing 0.3 g of If and 10 g of acetophenone in 200 ml of acetonitrile was irradiated with a Ushio 500-W medium-pressure mercury lamp using a Pyrex filter. After 12 hr of irradiation, chromatography on silica gel afforded only acetophenone and If, and the recovery of If was nearly 100%.

3,6-Diphenyl-4,5-dimethyl-2*H*-pyran-2-thione and 3,4,5,6-Tetraphenyl-2*H*-pyran-2-thione. A mixture of 0.1 g of Vd and 0.1 g of P_2S_5 in 10 ml of benzene was refluxed for 2.5 hr. After addition of aqueous ammonium sulfide to the reaction mixture at room temperature, the benzene layer was separated and dried over anhydrous sodium sulfate. Removal of the solvent gave a solid, which, upon recrystallization from methanol, afforded 0.75 g (71%) of an orange compound identified as 3,6-diphenyl-4,5-dimethyl-2*H*-pyran-2-thione, mp 249–250°. The infrared spectrum showed major peaks at 1625, 1520, 1280, and 1270 cm^{-1} and the nmr spectrum had two singlets at δ 1.97 (3 H) and 2.20 (3 H), and a multiplet at δ 7.1–7.7

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(42) H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962, p 384.

(43) P. Franzosini, G. Traverso, and M. Sanesi, *Ann. Chim.* (*Rome*), **43**, 128 (1955); R. J. Light and C. R. Hauser, *J. Org. Chem.*, **25**, 538 (1960).

(44) Even though the ultraviolet spectrum of If is similar to that of Id, we have no explanation on its lack of photoreactivity.

(45) The study of substituent effect upon this photorearrangement would clarify the stability of intermediate X, which is in progress.

(46) N. Ishibe and J. Masui, manuscript in preparation.

(47) T. L. Emmick and R. L. Letsinger, *Org. Syn.*, **47**, 54 (1967).

(48) R. L. Letsinger and J. D. Jamison, *J. Amer. Chem. Soc.*, **83**, 193 (1961).

(49) P. Yates and J. A. Weisbach, *ibid.*, **85**, 2943 (1963).

(50) Photolysis of Id filtered by a Pyrex glass in place of Vycor filter resulted in recovery of Id.

(10 H). *Anal.* Calcd for $C_{19}H_{16}OS$: C, 78.05; H, 5.52; O, 5.47; S, 10.96. Found: C, 77.97; H, 5.69; S, 11.07.

A mixture of 0.1 g of Vc and 0.1 g of P_2S_5 in 10 ml of benzene was refluxed for 24 hr and worked up as before. An orange solid, 0.065 g (63%), was obtained and identified as 3,4,5,6-tetraphenyl-2*H*-pyran-2-thione, mp 195–197°. The infrared spectrum was characterized by bands at 1605, 1590, 1440, 1290, and 1270 cm^{-1} and the nmr spectrum showed a multiplet at δ 6.6–7.3. *Anal.* Calcd for $C_{29}H_{20}OS$: C, 83.62; H, 4.84; O, 3.84; S, 7.70. Found: C, 83.44; H, 4.69; S, 7.57.

Diels–Alder Reaction of 3,6-Diphenyl-4,5-dimethyl-2*H*-pyran-2-one (Vd) with Benzyne. A mixture of 0.138 g of Vd and 0.225 g of diphenyliodonium-2-carboxylate[20] in 3 ml of diethylbenzene was heated with a microburner until the reaction turned to an amber solution. After diethylbenzene was carefully distilled off, 10 ml of 95% ethanol was added to the residual oil and refluxed for 1 hr. Upon standing the solution at 0°, a colorless solid was separated, which on recrystallization from ethanol afforded 0.1 g (65%) of pure 1,4-diphenyl-2,3-dimethylnaphthalene (VIII), mp 160–161°. The ultraviolet spectrum in cyclohexane exhibited maxima at 234 (log ϵ 4.78) and 292 nm (4.06). The nmr spectrum in carbon tetrachloride showed a singlet at δ 2.14 (6 H) and a multiplet at δ 7.1–7.5 (14 H). *Anal.* Calcd for $C_{24}H_{22}$: C, 93.48; H, 6.52. Found: C, 93.48; H, 6.77.

Oxidative Photocyclization of 2,3,5,6-Tetraphenyl-4*H*-pyran-4-one to 5,6,7,8-Dibenzo-2,3-diphenyl-4-chromen-4-one (IX). The olution containing 0.4 g of Ie and 0.126 g of iodine in 350 ml of methylene chloride was irradiated under nitrogen with a Ushio 500-W medium-pressure mercury lamp with a Pyrex filter for 5 hr. After removal of the solvent under vacuum, the residue was chromatographed over silica gel using chloroform as the eluant. The first fraction gave 0.2 g (50%) of IX and the second 0.19 g of the starting material.

Photolysis of 0.4 g of Ie in 350 ml of methylene chloride was carried out in the presence of air for 5 hr using a Ushio 500-W medium-pressure mercury lamp with a Pyrex filter. By removal of the solvent *in vacuo* and working up in the usual way, 0.14 g (35%) of IX, 0.05 g of an unidentified product, and 0.16 g of the starting material were obtained.

Measurement of Quantum Yields. The quantum yields for the formation of Vd were measured by irradiating 10 ml of 1–3 × 10^{-3} *M* Id in appropriate solvents in quartz test tubes using four RPR 253.7 nm lamps (New England Ultraviolet Co.) in a merry-go-round apparatus. The samples in the photolysis tubes were degassed using three freeze–thaw cycles using a pump, 10^{-2} mm, before being sealed off. Potassium ferrioxalate actinometry[30] provided light intensities in the order of 6.0 × 10^{-3} mEinstein/min (10 cm^3). After irradiation, the concentration of the photoproduct was determined by quantitative ultraviolet spectroscopy at 325 nm for Vd. The absorption due to the starting material was corrected to determine the degree of reaction.

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Photoisomerization of Bicyclo[3.1.0]hexan-2-ones[1,2]

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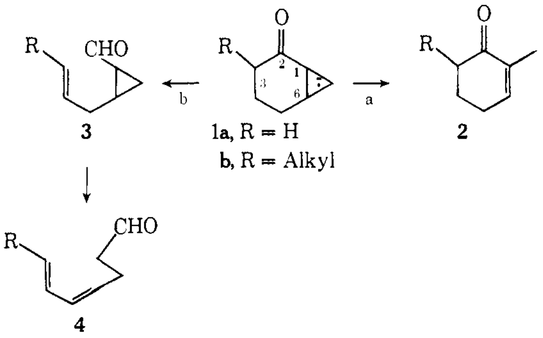
Abstract: The photoisomerization of alkyl-substituted bicyclo[3.1.0]hexan-2-ones has been studied. Using the n → π^* excitation, two different isomerizations have been found: one route involves opening of the cyclopropane ring with hydrogen migration to give an unsaturated ketone, the other route a type I α cleavage independent of the cyclopropane ring. Opening of the cyclopropane ring as a primary photochemical reaction only occurred when the 3 position was unsubstituted. The product resulted from the opening of the internal C-1:C-5 bond to yield a cyclohexenone in all but one case, compound **5**. The opening of this bond was in contrast with the previous findings in the photoisomerization of bicyclo[4.1.0]heptan-2-ones. Type I α cleavage to yield unsaturated aldehydes was favored by increased substitution on C-3. The aldehydes, in turn, were found to undergo further photoisomerization to yield acyclic ketenes. The mechanisms for all photoisomerizations reported are discussed.

The photoisomerization of conjugated cyclopropyl ketones to unsaturated carbonyl compounds (aldehydes, ketones, or ketenes) has been shown to proceed *via* a direct rearrangement of the chromophore, itself (see path a),[5] or to proceed stepwise such that the opening occurred *via* a Norrish type I cleavage reaction (see path b).[5,6] When this chromophoric grouping is part of a bicyclo[4.1.0]heptan-2-one ring system, the reaction pathway followed is controlled by the substitution pattern of the ring system. If there is no substituent on C-3 (**1a**), the primary photoreaction is the opening of the cyclopropane ring involving that cyclopropane bond which has the optimum overlap with the carbonyl group with the least movement of atoms during the reaction of **1a** to **2** (path a). The efficiency of the rearrangement process has been found to be dependent upon the substitution pattern at C-6 and C-7.[2] If there is a substituent on C-3 (**1b**), the preferred, but not necessarily exclusive, primary photoreaction is a type I α cleavage to yield first the cyclopropane alde-



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[2] For the previous paper in this series, see W. G. Dauben and W. M. Welch, *Tetrahedron Lett.*, 4531 (1971).

[3] National Institutes of Health Predoctoral Fellow.

[4] National Institutes of Health Postdoctoral Fellow.

[5] For a general discussion, see W. G. Dauben, G. W. Shaffer, and E. J. Deviny, *J. Amer. Chem. Soc.*, **92**, 6273 (1970).

[6] W. G. Dauben, L. Schutte, and R. E. Wolf, *J. Org. Chem.*, **34**, 1849 (1969).