[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, FACULTY OF SCIENCE, CAIRO UNIVERSITY]

Dimerization Reactions in Sunlight. V.[1] Photodimerization of Substituted Coumarins

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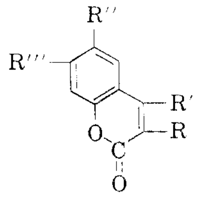
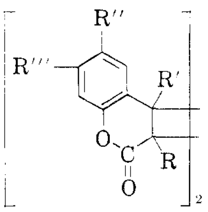
A study of the photodimerization of a large number of substituted coumarins in sunlight now has been undertaken. The colorless photodimers so obtained generally dissociate into their corresponding monomers on heating, a fact which is in favor of the proposed cyclobutane structure for the photodimers.

Coumarin (Ia),[2] and 3-phenylcoumarin (Ib)[3] undergo dimerization when exposed to light. It is now found that the coumarin derivatives Ic–e, Ig–h, and 7,8-benzocoumarin (IIIa) are completely converted by long exposure to sunlight into sparingly soluble crystalline dimers (IIc–e, IIg–h, and IV, respectively).

The photodimers, by analogy, are believed to be cyclobutane derivatives a fact which is favored by regeneration of monomer when a photodimer, e.g. IIc, is heated above its melting point. No molecular weight determination could be carried out as the dimers are difficultly soluble. Numerous photodimers from monomers containing the C═C—C═O group are believed to contain the cyclobutane ring.[4,5]

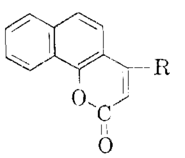


I

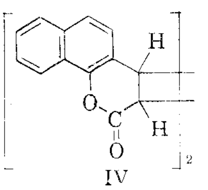


II

(a) $R = R' = R'' = R''' = H$
(b) $R = C_6H_5; R' = R'' = R''' = H$
(c) $R = R' = R''' = H; R'' = CH_3$
(d) $R = R''' = H; R' = R'' = CH_3$
(e) $R = R'' = H; R' = R''' = CH_3$
(f) $R = R''' = H; R' = CH_2COOCH_3; R'' = CH_3$
(g) $R = R'' = H; R' = CH_2COOC_2H_5; R''' = CH_3$
(h) $R = R'' = H; R' = CH_2COOCH_3; R''' = CH_3$
(i) $R = R' = R''' = CH_3; R'' = H$



III



IV

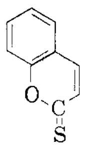
a, $R = H$
b, $R = CH_2COOCH_3$

III IV

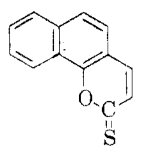
(a) $R = H$
(b) $R = CH_2COOCH_3$

Whereas 3-substituted coumarins, *e.g.* Ib, and 4-substituted coumarins, *e.g.* Id–e, undergo photodimerization in sunlight, 3,4-disubstituted coumarins, *e.g.* 3,4,7-trimethylcoumarin (Ii), are found to be stable or almost stable when their benzene solutions are exposed to sunlight under similar experimental conditions. The stability of Ii toward photodimerization and the ready photodimerization of Id and/or Ie parallel the stability of 2,3-dimethyl-1,4-naphthoquinone and the ready dimerization of 2-methyl-1,4-naphthoquinone in sunlight.[6]

When 6-methyl-(Ic) and 7-methylcoumarin-4-acetic acids (Ie) ($R' = CH_2COOH$) were exposed to sunlight for one month, they were recovered unchanged.[7] The stability of these coumarin derivatives toward photodimerization may be attributed to their insolubility. We were unable to prepare the photodimer of thioncoumarin (V); the crystals were recovered unchanged when exposed to sunlight, and no photoreaction could be detected when a benzene solution of V was irradiated. However, when benzene solution of 7,8-benzothioncoumarin (VI) was exposed to sunlight, the orange-yellow solution turned into dark brown with the separation of brownish crystals which gave the same analytical values for VI. The product is not soluble and for this reason no molecular weight determination could be carried out. The structure of the photoproduct, which may be considered by analogy to IV as a dimer, is under further investigation.



V



VI

4-Styrylcoumarin, which may be considered as the inner lactone of β-(*o*-hydroxyphenyl)cinnamylideneacetic acid, contains two ethylenic linkages,

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(1) Part IV, A. Mustafa and S. A. E. D. Zayed, *J. Am. Chem. Soc.*, 6174 (1956).

(2) A. W. K. de Jong, *Rec. trav. chim.*, **43**, 316 (1924).

(3) A. Schönberg, *et al.*, *J. Chem. Soc.*, 374 (1950).

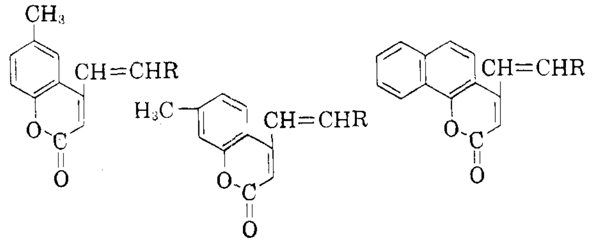
(4) Cf. A. Mustafa, *Chem. Revs.*, **51**, 1 (1952).

(5) W. Davies and F. C. James, *J. Chem. Soc.*, 314 (1955).

(6) A. Schönberg, *et al.*, *J. Chem. Soc.*, 2126 (1948).

(7) Exposure of phenylacetic acid alone in benzene to sunlight for a long period (six months) caused the formation of a little carbon dioxide and a little yellow oil [R. de Fazi, *Atti accad. naz Lincei* [6], **6**, 266 (1925); *Chem. Abstr.*, **20**, 594 (1926); *atti congr. naz. chim. pura ed appl.* **1926** 1287; *Chem. Abstr.*, **22**, 2154 (1928)].

one of which constitutes a part of the heterocyclic ring. In the similarly constituted cinnamylideneacetic acid and its derivatives, photodimerization occurring through the double bond with the formation of a four-membered ring involves the γ,δ —C=C— bond in the case of cinnamylidene malonic acid,[8] and of α-phenylcinnamylideneacetonitrile[9] and the α, β—C=C— double bond together with the γ,δ—C=C— double bond in the case of cinnamylideneacetic acid.[10] When solutions of the colored 4-styrylcoumarins (VIIa–c, VIIIa–c and IXa–c) in benzene are exposed to sunlight, colorless photodimers are separated during irradiation.



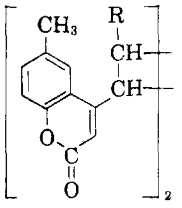
VII VIII IX

(a) R = C_6H_5
(b) R = $C_6H_4OCH_3$-*p*
(c) R = $C_6H_4OCH_3$-*o*

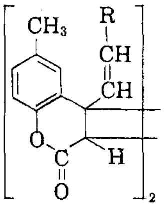
(a) R = C_6H_5
(b) R = $C_6H_4OCH_3$-*p*
(c) R = C_6H_4Cl-*o*

(a) R = $C_6H_4OCH_3$-*p*
(b) R = $C_6H_4OCH_3$-*o*
(c) R = C_6H_4Cl-*o*

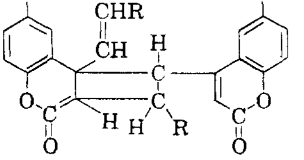
The photodimers are all crystalline substances and were obtained in good yields. The dimer of VIIb is taken as an example of the photodimers, and which are obviously of analogous structure. Whereas VIIb is deep yellow in color, the dimer is colorless. It is insoluble in aqueous sodium hydroxide solution and gives no color with ferric chloride. On heating, the dimer dissociates above its melting point, yielding the monomer almost quantitatively, a fact which favors the cyclobutane structure. By analogy, structures like X and XI are advanced, but we do not wish to exclude a structure like XII.[10]



X



XI



XII (or its stereo-isomers

EXPERIMENTAL

The photochemical reactions were carried out in Pyrex glass Schlenk tubes,[11] from which the air was displaced by dry carbon dioxide prior to sealing by fusion. The benzene was thiophen-free (Kahlbaum), dried over sodium. Control experiments in the dark, but otherwise under identical conditions, showed no reaction.

Preparation of methyl esters of coumarin-4-acetic acids. For the preparation of methyl coumarin-4-acetates (If, Ih, and IIIb), a procedure identical to that described by Bhatt and Shah[12] for the preparation of the methyl esters of 6-alkylcoumarin-4-acetic acids, was followed. The new esters (listed in Table I) are colorless crystalline compounds, readily soluble in ordinary organic solvents. If and Ih remain colorless in concentrated sulfuric acid; while IIIb gives a pale yellow color.

Photodimerization of coumarin derivatives. General procedure. A solution of 0.5 g. of each of the coumarins (Ic–e) in 30 ml. of dry benzene was exposed to sunlight for one month (March–April). In the case of Ig and Ih photodimerization was carried out in the presence of eosin (0.005 g.) as a photosensitizer.[13] The reaction mixtures were worked up either by filtration of the separated photodimer or by concentration of the benzene solution to a small volume (*ca.* 5 ml.), followed by cooling. The photodimers, so obtained, were then crystallized from the proper solvent (cf. Table II).

The photodimers IIc–e, IIg,h, are colorless crystalline compounds. They dissolve in hot benzene, dioxan; and acetic acid, but are sparingly soluble in light petroleum (b.p. 60–80°).

A benzene solution of 0.5 g. of 3,4,7-trimethylcoumarin (Ii) proved to be stable toward the action of sunlight under the above experimental conditions.

Pyrolysis of the photodimers of coumarin derivatives (IIc and IIh). The pyrolysis was carried out at 195–200° (metal bath) for 20 min. in Pyrex glass test tubes, containing 0.1 g. of the dimer in the case of IIc and at 250–258° in the case of IIh. Cooling the reaction mixture, followed by crystallization from a suitable solvent, yielded the corresponding monomers (Ic and Ih), respectively, in an almost quantitative yield.

Photodimerization of 7,8-benzocoumarin (IIIa). A solution of 1 g. of IIIa[14] in 25 ml. of glacial acetic acid was exposed to sunlight for 6 months (January–July). The colorless solution became deep brown and deposited a brown solid (*ca.* 0.5 g.) which gave, upon filtration followed by crystallization from acetone, colorless crystals, m.p. 225° (brown melt).

Anal. Calcd. for $C_{26}H_{16}O_4$: C, 79.59; H, 4.08. Found: C, 79.58; H, 4.36.

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(8) E. P. Kohler, *Am. Chem. J.*, **28**, 233 (1902); C. N. Riiber, *Ber.*, **35**, 2411 (1902); *cf.* ref. 4.

(9) H. Stobbe and Barbaschinow, *Ber.*, **45**, 3396 (1912); H. Stobbe and F. Kuhrmann, *Ber.*, **58**, 85 (1925).

(10) C. N. Riiber, *Ber.*, **46**, 335 (1913); H. Stobbe, A. Hensel, and W. Simon, *J. prakt. Chim.*, **110**, 129 (1925).

(11) W. Schlenk and A. Thal, *Ber.*, **46**, 2840 (1913).

(12) M. R. Bhatt and N. M. Shah, *J. Indian Chem. Soc.*, **32**, 322 (1955).

(13) C. Kögel and A. Steigmann, *Phot. Ind.*, 1169 (1925); *Chem. Abstr.*, **20**, 544 (1926).

(14) K. Bartsch, *Ber.*, **36**, 1966 (1903).

TABLE I

List of New Methylcoumarin-4-acetates

Ester	M.P.[a] °C.	Solvent for Cryst.[b]	Yield, %	Formula	Analysis, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
If	157	A	95	$C_{13}H_{12}O_4$	67.24	67.32	5.17	5.46
Ih	122	B	90	$C_{13}H_{12}O_4$	67.24	67.31	5.17	5.53
IIIb	130	B	93	$C_{16}H_{12}O_4$	71.64	71.74	4.48	4.42

[a] Melting points are uncorrected. [b] A– petroleum ether (b.p. 80–100°). B– a mixture of benzene and light petroleum (b.p. 60–80°).

TABLE II

Photodimers of Coumarin Derivatives

Coumarin Derivative	Photo-dimer	M.P.[a] °C.	Solvent for Cryst.[b]	Color with H_2SO_4	Yield, %	Formula	Analysis, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
Ic[c]	IIc[d]	194	A	Orange	78	$C_{20}H_{16}O_4$	75.00	74.89	5.00	4.77
Id[e]	IId	220	B	Nil	65	$C_{22}H_{20}O_4$	75.85	76.10	5.75	5.71
Ie[f]	IIe	211	C	Nil	70	$C_{22}H_{20}O_4$	75.85	75.99	5.75	5.99
Ig[g]	IIg	259–260	B	Nil	61	$C_{28}H_{28}O_8$	68.29	67.68	5.69	5.54
Ih	IIh	253	B	Pale yellow	42	$C_{26}H_{24}O_8$	67.24	66.95	5.17	5.07

[a] Melting points are uncorrected. [b] A– benzene. B– a mixture of dioxane and light petroleum (b.p. 40–60°). C– benzene and petroleum ether (b.p. 60–80°) mixture. [c] T. J. Thompson and R. H. Edke, *J. Am. Soc.*, **47,** 2557 (1925). [d] This experiment was carried out with A. H. E. Harhash. [e] K. Fries and W. Klostermann, *Ann.*, **362,** 23 (1908). [f] K. Fries and W. Klostermann, *Ber.*, *39*, 871 (1906). [g] B. B. Dey, *J. Chem. Soc.*, 1606 (1915).

TABLE III

Photodimers of 4-Styrylcoumarins

Photo-dimer of	M.P.[a] °C.	Solvent[b] for Cryst.	Color with H_2SO_4	Yield, %	Formula	Analysis, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Chlorine Calcd.	Chlorine Found
VIIa[c]	246	A	Yellow	80	$C_{36}H_{28}O_4$	82.44	82.31	5.35	5.12		
VIIb[c]	328	B	Yellow	92	$C_{38}H_{32}O_6$	78.08	77.78	5.48	5.24		
VIIc[c]	327	C	Yellow	40	$C_{38}H_{32}O_6$	78.08	77.93	5.48	5.13		
VIIIa[d]	251	A	Yellow	70	$C_{35}H_{28}O_4$	82.44	82.29	5.35	4.97		
VIIIb[e]	217	D	Yellow-orange	81	$C_{38}H_{32}O_6$	78.08	77.94	5.48	5.32		
VIIIc[c]	322	E	Yellowish green	60	$C_{38}H_{26}Cl_2O_4$	72.85	72.65	4.38	4.16	11.96	11.52
IXa[e]	290[f]	F	Yellow	53	$C_{44}H_{32}O_6$	80.48	80.27	4.87	4.67		
IXb[c]	above 350	[g]	Yellow[h]	75	$C_{44}H_{32}O_6$	80.48	80.31	4.87	4.77		
IXc[c]	245	H	Yellow	85	$C_{42}H_{26}Cl_2O_4$	75.78	75.46	3.90	3.78	10.67	10.46

[a] Melting points are uncorrected. [b] A– xylene. B– glacial acetic acid. C– a mixture of chloroform and ether. D– toluene. E– a mixture of chloroform and petroleum ether. F– benzene. [c] A. Mustafa, M. Kamel, and M. A. Allam, *J. Am. Chem. Soc.*, **78,** 4692 (1956). [d] A. Mustafa and M. Kamel, *J. Am. Chem. Soc.*, **77,** 1828 (1955). [e] B. B. Dey and K. K. Row, *J. Indian Chem. Soc.*, **1,** 107; 277 (1924). [f] The dimer begins to darken at 290°. [g] The dimer was proved to be pure enough for analytical determination after washing with hot xylene; it is insoluble in most organic solvents. G– phenetole. [h] The solution in sulfuric acid acquires deep green fluorescence.

The photodimer (IVa)[15] is difficultly soluble in benzene, alcohol, acetic acid, and light petroleum, but dissolves in hot acetone. It dissolves in concentrated sulfuric acid with a yellow color.

Photodimerization of 7,8-benzothioncoumarin (VI).[15] A solution of 1 g. of VI in 20 ml. of dry benzene was exposed for 20 days (January). By the end of the exposure period, the benzene solution had turned dark brown and had deposited a brownish black solid (*ca.* 0.3 g.) which was filtered off and crystallized from the minimum of benzene.

Anal. Calcd. for $C_{26}H_{16}O_2S_2$: C, 73.58; H, 3.70. Found: C, 73.39; H, 3.61.

The photoproduct was soluble in benzene, but difficultly soluble in light petroleum.

Exposure of thioncoumarin (V). When V, in the solid state or in dry benzene solution, was exposed to sunlight for 1 month, no reaction took place and V was recovered unchanged.

Photodimerization of 4-styrylcoumarins. General procedure. A solution or a suspension of 0.5 g. of the 4-styrylcoumarin in 30 ml. of benzene was exposed to sunlight for a period varying from 15 to 30 days (January). At the end of the exposure period, the yellow color of the styrylcoumarin had almost disappeared and colorless crystals of the photodimer usually separated out. The separated photodimers were collected by filtration and crystallized from a suitable solvent.

Generally, the dimers are moderately soluble in benzene, alcohol, and acetic acid, but difficultly soluble in ether and light petroleum ether. The properties of the dimers are recorded in Table III.

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(15) This experiment was carried out with Sayed Mohamed Abdel Rahman Omran.

Pyrolysis of the photodimer of VIIIb. The dimer of VIIIb (0.3g.) was heated at 180–185° (metal bath) in a Pyrex test tube for 10 min. The colorless dimer melted with yellow color, and upon cooling the reaction mixture, followed by crystallization, VIIIb was obtained in almost quantitative yield.

GIZA, CAIRO, EGYPT.

[CONTRIBUTION OF THE CENTRAL EXPERIMENT STATION, BUREAU OF MINES, DIVISION OF SOLID FUELS TECHNOLOGY]

Lithium in Ethylenediamine: A New Reducing System for Organic Compounds[1]

LESLIE REGGEL, R. A. FRIEDEL, AND IRVING WENDER

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A new metal-amine reducing system, lithium in ethylenediamine, is described. It reduces aromatic rings to monoölefins and to cycloparaffins; reduces phenols; cleaves ethers; reduces ketones to alcohols; and reduces acetylenes and both terminal and internal olefins to alkanes. It appears to be the most powerful, and perhaps the least selective, of the metal-amine systems.

The present investigation deals with the reduction of organic compounds by the lithium-ethylenediamine system. Most studies with metal-ammonia and metal-amine systems have been carried out using liquid ammonia. Although Kraus[2] predicted in 1953 that methylamine, ethylamine, and ethylenediamine would be valuable solvents for studying the physico-chemical properties of solutions of metals in amines at higher temperatures, ethylenediamine has not hitherto been used in a metal-amine reducing system. The first use of the lower aliphatic amines for metal-amine reductions was recently reported by Benkeser *et al.*,[3] who showed that aromatic rings are reduced to monoölefins by lithium-ethylamine. However, their attempt to replace ethylamine by higher primary amines gave poor yields, perhaps because lithium becomes progressively less soluble in these monofunctional amines as the ratio of nitrogen to carbon decreases. Since ethylenediamine contains one amine group per carbon atom, and since its relatively high boiling point (117°) is a potential advantage, we decided to investigate its use in a metal-amine system. Our results show that the lithium-ethylenediamine system, at 90–100°, is a convenient and effective metal-amine combination for carrying out reductions and cleavage reactions of organic compounds.[4]

EXPERIMENTAL

Materials. Lithium, obtained from the Lithium Corp. of America, was used in the form of one-eighth inch wire.

Anhydrous ethylenediamine (Union Carbide Chemical Co. and Eastman) was purified by heating with sodium for a few days and then distilling; the reaction of sodium with the amine is slow. This once-distilled material was poured directly into the reaction flask without any special precautions to avoid exposure to the atmosphere. (In some experiments, the once-distilled amine was distilled from sodium a second time directly into the dropping funnel on the reaction apparatus; where this material was used, it is referred to as twice-distilled ethylenediamine.)

Diethylenetriamine (Eastman) was purified by distilling it once from a solution of sodium in the amine.

General Procedure. A four-neck flask, or a three-neck flask with a suitable adapter, was fitted with a mercury-sealed double Hershberg stirrer, a thermometer dipping below the surface of the liquid, a spiral reflux condenser with a nitrogen inlet and mercury-sealed outlet, and a straight reflux condenser, 6 to 8 inches long, which was stoppered at the top. (In some experiments, a graduated dropping funnel was so arranged that ethylenediamine could be distilled into the funnel and then added to the flask without exposure to air.) After the apparatus was flushed with nitrogen, the substrate to be reduced and the ethylenediamine were added, the stirrer was started, and the mixture was heated to 90–100°. The lithium was then added in portions through the short reflux condenser; it was added in pieces about 1.5 in. long, about 4 to 8 pieces (0.5–1.0 g.) being added in each portion. The rate of addition of the lithium was controlled by two factors, the hydrogen evolution and the persistence of the dark blue color. Usually the gas evolution was the determining factor, the metal being added during 1.5 to 3 hr., without waiting for discharge of the blue color between portions. The mixture was maintained at 90–100° during addition of the lithium. After all of the metal had been added, the mixture was heated at or just below a gentle reflux for 1 or 2 hr. The mixture was then cooled in ice, and water was added slowly; considerable heat was evolved, and after a little water had been added the mixture usually became almost solid, requiring efficient stirring. After enough water had been added to dissolve most of the solids, the mixture was transferred to a separatory funnel with the aid of water and benzene or ether. The aqueous layer was extracted with the solvent, and the combined organic layers washed with dilute hydrochloric acid, then with saturated sodium chloride solution, dried, and dis-

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[1] I. Wender and L. Reggel, Abstracts of Papers, 127th Meeting, AMERICAN CHEMICAL SOCIETY, Cincinnati, Ohio, April 1955, page 22N. See also *Chem. Eng. News,* **33**, 1525 (1955).

[2] C. A. Kraus, *J. Chem. Ed.*, **30**, 83 (1953).

[3] R. A. Benkeser, R. E. Robinson, D. M. Sauve, and O. H. Thomas, *J. Am. Chem. Soc.*, **76**, 631 (1954); **77**, 3230 (1955). A preliminary investigation of this topic was mentioned in a paper by R. A. Benkeser, R. E. Robinson, and H. Landesman, *J. Am. Chem. Soc.*, **74**, 5699 (1952).

[4] Recent work in these laboratories has shown that coal, which is difficult to hydrogenate at temperatures below 300°, can be reduced by the lithium-ethylenediamine system.