bimolecular radical-radical combination and unimolecular degradative chain transfer. (4) The triangles in Fig. 2 represent the results obtained by employing 3650Å under comparable experimental conditions (row 1, Table I). It is seen that the points lie close to the respective lines extrapolated from the results for 3341 Å. This observation leads one to assume that there is no appreciable difference in efficiency between the two wave lengths.

Experimental

Materials Used.—Butadiene was the research grade of Phillip's Petroleum Company. Ethyl tribromoacetate (ETBA) was prepared by esterification of tribromoacetic acid following the procedure of Broche.[3] Tribromoacetic acid was prepared by the method described by Schaeffer.[4]

Ethyl 2,2′,6-Tribromohexene-4-oate-1.—When butadiene was mixed with excess ETBA (1 mole of butadiene to 2 moles or greater of ETBA) at room temperature under the influence of daylight, quantitative conversion of butadiene to ethyl 2,2′,6-tribromohexene-4-oate-1 was obtained in several hours. The product was separated from ETBA by distillation using a 1-in. Vigreux column. After removal of ETBA, ethyl 2,2′,6-tribromohexene-4-oate-1 was obtained as a pale yellow liquid; b.p. 90–93°/0.04 mm; $n^{25}\text{D}$ 1.5472.

Anal. Calcd. for $C_8H_{11}O_2Br_3$: C, 23.56; H, 2.93; Br, 63.27; O, 8.44. Found: C, 24.91; H, 2.90; Br, 62.48.

Kinetic Runs.—The source for both monochromatic light at 3650 Å. and 3341 Å. was an 85-watt AH-3 mercury lamp. A simple shutter permitted light to enter the box containing sample and filters, as desired. A black cloth was placed over the entire set up (except source) to exclude any outside light. The filter system to isolate the 3650 Å. group of emission lines consisted of Corning filters numbers 7380 (2 mm.) and 5860 (5 mm.) The filter system to isolate the 3341 Å. emission line, taken from Kasha,[5] consisted of Corning filter number 5970 (5 mm.), a solution of 12.8 g. of naphthalene/l. of iso-octane in a 10-mm. quartz cell, and a solution of 100 g. of nickel sulfate hexahydrate/l. water in a 50-mm. quartz cell.

The reactions were carried out in a 20-mm. quartz cell with a silicon rubber stopper which prevented the escape of butadiene. A typical run was begun by weighing the desired amount of ETBA into the tared cell. Uuder a black cloth, butadiene, twice distilled, was bubbled into the cell *via* a glass capillary tube until the cell was filled (3-ml. capacity). The cell was then reweighed on an analytical balance protected completely from light by a black cloth except the door which was covered by an orange sheet of plastic to permit visibility. Initial absorption data for the known concentration of butadiene in ETBA were obtained at 1.63 μ on the Cary 14 spectrophotometer by scanning the region from 1.66–1.59 μ *vs.* ETBA in a 20-mm. cell in the reference beam, with yellow filters in both beams to exclude ultraviolet light. The sample cell, protected from extraneous light during all manipulations, was then placed in the sample holder of the apparatus and exposed to the monochromatic light for time intervals. After each interval the absorption of butadiene at 1.63 μ was determined. The reactions were carried out in a constant temperature room maintained at 25.0 ± 0.5°. The reactions were followed until 10–20% of the butadiene had disappeared.

The optical densities (absorbances) at 1.63 μ were corrected for background, and the concentration of butadiene was calculated from the linear relationship between absorbance and concentration (determined by least squares analysis of the straight line plot of concentration of butadiene in standard solution *vs.* $A_{1.63\,\mu}$).

The ferrioxalate actinometer solution was used for determining the incident energy of the two wave lengths after each run, following the standard procedure.[6] Different intensities were obtained by inserting wire screens of varying absorbancy between the light source and the sample. The number of quanta absorbed was determined by utilizing absorption coefficients at appropriate wave lengths obtained from the ultraviolet absorption spectrum of the ETBA after ascertaining that the presence of the butadiene and the product did not alter the absorption coefficients.

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Substituted γ-Lactones. IX.[1] Synthesis of Some Substituted 3-Arylidenephthalides[2]

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In a previous paper[1] the alkali-catalyzed aldol-type condensation between phthalide and aromatic aldehydes was described. Contrary to the literature[3] it was found that condensation occurred, and even more interestingly, under certain conditions the corresponding aldols were formed in high yields and could be isolated and characterized. It has been known for some time[4] that 6-nitrophthalide condenses with aromatic aldehydes to yield 3-arylidene-6-nitrophthalides. In the light of our findings and the fact that only a few aldehydes with electron-donating substituents were employed for the condensation with 6-nitrophthalide, it was decided to investigate further this reaction. Consequently, a number of benzaldehydes substituted with activating as well as deactivating groups were subjected to condensation with 6-nitrophthalide.

All of the aldehydes which were employed, condensed with 6-nitrophthalide; however, no aldols were found. The results given in Table I

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[1] Paper VIII, H. Zimmer and R. D. Barry, *J. Org. Chem.*, **27**, 1602 (1962).

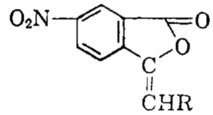
[2] Taken in part from the Ph.D. thesis of R. D. Barry, University of Cincinnati, 1960; Chattanooga Medicine Co. Fellow, 1957–1959; Ethyl Corp. Fellow 1959–1960. Present address: Organic Research Laboratories, Department of Obstetrics and Gynecology, University Hospital, The Ohio State University, Columbus, Ohio.

[3] See ref. 1 for pertinent references.

[4] W. Borsche, K. Diacont, and H. Hanau, *Ber.*, **67**, 675 (1934).

TABLE I

CONDENSATION PRODUCTS OF 6-NITROPHTHALIDE WITH VARIOUS ALDEHYDES



R	Empirical formula	Yield, %	Solvent of crystallization	M.p., °C.	Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N	Infrared absorption of lactone C═O (μ)	
Phenyl	$C_{15}H_9NO_4$	25, 65[a]	AcOH	232[b,c]							5.62	
4-Methylphenyl	$C_{16}H_{11}NO_4$	24	CH_3NO_2	204–205	68.32	3.94		67.99	4.12		5.65	
2-Hydroxyphenyl	$C_{15}H_9NO_5$	14	$CHCl_3$	205[d]							5.59	5.83[i]
4-Hydroxyphenyl	$C_{15}H_9NO_5$	23	$CHCl_3$	258–259			4.95			5.13	5.64	
2-Nitrophenyl	$C_{15}H_8N_2O_6$	10	o-$C_6H_4Cl_2$	216	57.70	2.50		57.64	2.66		5.60	5.90[i]
3-Nitrophenyl	$C_{15}H_8N_2O_6$	15	CH_3NO_2	251			8.97			8.91	5.60	
4-Nitrophenyl	$C_{15}H_8N_2O_6$	17	CH_3NO_2	292			8.97			9.01	5.60	
4-Methoxyphenyl	$C_{16}H_{11}NO_5$	44	AcOH	199[e]							5.62	
4-Isopropylphenyl	$C_{18}H_{15}NO_4$	31	CH_3NO_2	221–222	69.89	4.89		70.00	4.85		5.64	
3,4-Methylenedioxyphenyl	$C_{16}H_9NO_6$	86	Dioxane	243–244[f]							5.63	
3-Methoxy-4-hydroxyphenyl	$C_{16}H_{11}NO_6$	20	o-$C_6H_4Cl_2$	274	61.34	3.54	4.47	61.12	3.79	4.66	5.65	
4-Dimethylaminophenyl	$C_{17}H_{14}N_2O_4$	52, 83[a]	o-$C_6H_4Cl_2$	272–273[g,h]							5.65	
4-Diethylaminophenyl	$C_{19}H_{18}N_2O_4$	55	o-$C_6H_4Cl_2$	270	67.44	5.36	8.28	67.46	5.50	8.49	5.66	
1-Naphthyl	$C_{19}H_{11}NO_4$	18	o-$C_6H_4Cl_2$	292–293	71.92	3.49		71.48	3.35		5.59	
1-Furfuryl	$C_{13}H_7NO_5$	18	CH_3NO_2	206	60.71	2.74		60.57	2.89		5.63	

[a] 1,2,4-Trichlorobenzene as solvent. [b] Ref. 4, m.p. 236–237°. [c] Derivatives: 4-benzyl-7-nitrophthalaz-1-ol, m.p. 206°; 2-phenyl-6-nitroindan-1,3-dion, m.p. 212°. [d] Ref. 4, m.p. 210°. [e] Ref. 4, m.p. 201.5°. [f] Ref. 4, m.p. 244°. [g] Ref. 6, m.p. 283–284°. [h] Ref. 4, m.p. 270°. [i] R. N. Jones and B. S. Gallagher, *J. Am. Chem. Soc.*, 81, 5242 (1959), also report two CO-peaks, for unsaturated γ-lactones.

clearly show that the reaction is applicable to a wide range of aldehydes.

The procedure described in the literature[4–6] involved melting together 6-nitrophthalide and the aldehyde in the presence of a catalytic amount of piperidine at 180–200° for about twenty minutes. More conveniently, this reaction is run in a solvent. A good solvent for this reaction seemed to be 1,2,4-trichlorobenzene which gave a higher yield and purer product in the condensation with benzaldehyde, although a longer reaction time was necessary.

For all of the products the *trans* configuration is assigned. This assignment is based on the fact that phthalic anhydride and phenylacetic acid gave almost exclusively *trans*-3-benzylidenephthalide and the corresponding *cis* isomer (formed in small yield) was not stable.[7,8] The instability of the *cis* isomer is further attested by examination of models.

Experimental

Melting points are uncorrected. Micro analyses by A. Bernhardt, Mikroanatylisches Laboratorium im Max-Planck-Institut, Mülheim, Ruhr, Germany. The infrared spectra were determined on a Baird double beam spectrophotometer using Nujol as a medium.

Preparation of 3-Arylidene-6-nitrophthalides without Solvent.—The procedure of Borsche[4] was followed, and the product was subsequently recrystallized from acetic acid, chloroform, nitromethane, or o-dichlorobenzene.

Preparation of 3-Benzylidene-6-nitrophthalide with 1,2,4-Trichlorobenzene as Solvent.—A mixture of 179 g. (0.1 mole) of 6-nitrophthalide,[9] 250 ml. of 1,2,4-trichlorobenzene, 159 ml. (1.5 moles) benzaldehyde, and 2 ml. of piperidine was refluxed for 3 hr. with removal of the benzaldehyde, water, and 1,2,4-trichlorobenzene azeotrope (50 ml. total removed) intermittently. The dark colored mixture was cooled and treated with 500 ml. of hexane. The crystals were collected, washed with 100 ml. of ethanol, and dried furnishing 174 g. (65%) m.p. 234–236° (yellow crystals).

4-Benzyl-7-nitrophthalaz-1-ol.—A mixture of 5.3 g. (0.024 mole) of 3-benzylidene-6-nitrophthalide, 20 ml. of 95% ethanol, and 4 ml. of 85% hydrazine hydrate was refluxed 1.5 hr. then cooled and crystals which separated were collected; yield of 4-benzyl-7-nitrophthalaz-1-ol 2.1 g. (31%), m.p. 206°.

Anal. Calcd. for $C_{15}H_{11}N_3O_3$: C, 64.05; H, 3.94; N, 14.94. Found: C, 64.11; H, 3.94; N, 14.99.

2-Phenyl-6-nitroindan-1,3-dione.—A solution of 4.6 g. (0.2 g.-atom) of sodium in 100 ml. of anhydrous methanol was treated with 5.3 g. (0.02 mole) of 3-benzylidene-6-nitrophthalide and stirred 20 min. The mixture was acidified with 150 ml. of hydrochloric acid and the purple precipitate of 2-phenyl-6-nitroindan-1,3-dione, m.p. 212° (from o-dichlorobenzene), was collected; yield 3.4 g. (64%); (lit., m.p. 199–200.5).[5]

Anal. Calcd. for $C_{15}H_9NO_4$: C, 67.41; H, 3.39; N, 5.24. Found: C, 67.20; H, 3.32; N, 5.22.

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