Photoacylation. II. Intramolecular Photoacylation of Enolates[1]

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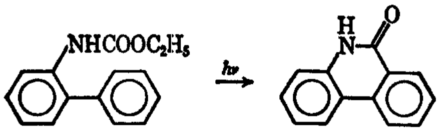
Under the influence of ultraviolet light, the sodium enolate of diethyl *o*-biphenylylmalonate (**5**) in ethanol undergoes intramolecular photoacylation to give ethyl 9-phenanthrol-10-carboxylate (**6**) in 70% yield. The reaction had been extended to the enolates of phenylethylidenemalonate (**7**) and phenylethylidenecyanoacetate (**8**) systems. They cyclized to give the corresponding naphthol derivatives. The reaction represents a new type of photochemical process of organometallic compounds which may have synthetic applications.

In an earlier communication from this laboratory,[1] we reported that ethyl N-*o*-biphenylylcarbamate (**1**) and ethyl *o*-biphenylylcarbonate (**2**) underwent intermolecular photoacylation to give tricyclic products (reactions 1 and 2). The reaction had been extended to a number of other systems.[3] The pathway of this reaction may be visualized as the photoactivation of the aromatic system followed by the ring closure. In contrast to the Lewis acid catalyzed acylatin of aromatic compounds, the reaction may be carried out in neutral media and under mild conditions. The scope and limitation of this process were examined, and the current report deals with the intramolecular photoacylation of enolates.



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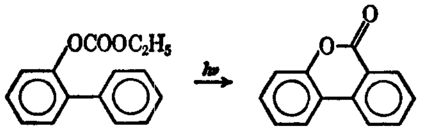

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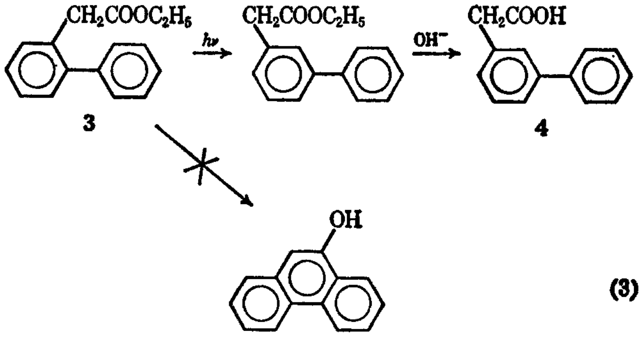
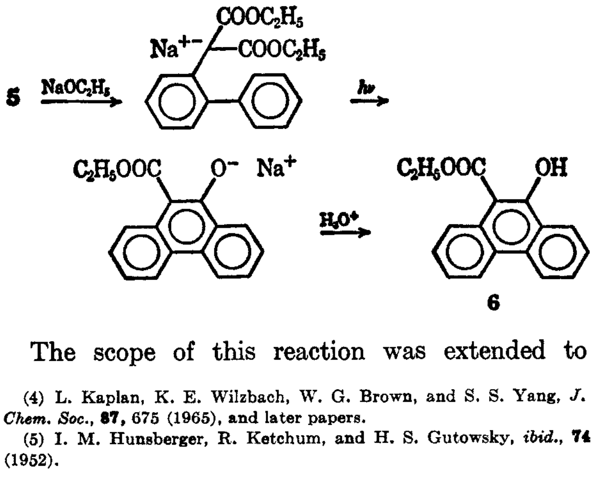
Results and Discussion

In contrast to ethyl *o*-biphenylylcarbamate (**1**) and ethyl *o*-biphenylylcarbonate (**2**), ethyl *o*-biphenylylacetate (**3**) does not undergo intramolecular photoacylation to give a tricyclic product. When a benzene solution of **3** was irradiated with a Hanovia medium-pressure mercury arc, the uv absorption spectrum of the system gradually shifted to longer wavelength, the nmr spectrum underwent no appreciable change except in the aromatic proton region, while the ir spectrum remained essentially unchanged. These results indicated that **3** might be undergoing a molecular rearrangement to give a less-hindered isomeric biphenyl derivative. Chromatography, saponification and recrystallization of the irradiated mixture yielded *m*-biphenylylacetic acid (**4**). Therefore instead of undergoing intramolecular photoacylation, **3** rearranges to give the less-hindered *meta* isomer (reaction 3). Although the mechanism of this rearrangement was not examined in detail, it may well be analogous to the position isomerization of simple substituted benzene derivatives under the influence of light which proceeds *via* a benzvalene derivative as the intermediate.[4]



(3)

The photobehavior of **3** suggests that systems containing nonbonding 2p electrons conjugated with the aromatic nucleus are necessary for the intramolecular photoacylation. In compounds **1** and **2**, these electrons derive from the heteroatom, nitrogen or oxygen. The photochemistry of the enolate of diethyl *o*-biphenylylmalonate (**5**), which also possesses nonbonding 2p electrons as carbamate **1** and carbonate **2**, was subsequently examined. When an ethanolic solution of **5** was irradiated in the presence of sodium ethanolate, a facile cyclization occurred (reaction 4). Only a single product was detected by tlc which is less polar and fluoresces more strongly than **5**. Ethyl 9-phenanathrol-10-carboxylate (**6**) was isolated in 70% yield by chromatography, and its structure was established by spectroscopic determinations. The properties of **6** parallel closely to those reported for the corresponding methyl ester.[5] We also found that **5** does not undergo intramolecular photoacylation in the absence of sodium ethanolate, neither does it undergo thermal cyclization below 185°.



(4)

The scope of this reaction was extended to the

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(1) Paper I: N. C. Yang, A. Shani, and G. R. Lenz, *J. Amer. Chem. Soc.*, **88**, 5369 (1966).

(2) On leave of absence from the Department of Chemistry, National Taiwan University, Taipei, Taiwan, China.

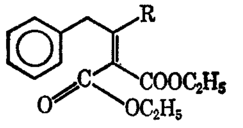
(3) G. R. Lenz and N. C. Yang, *Chem. Commun.*, 1136 (1967); G. R. Lenz, Ph.D. Thesis, University of Chicago, 1967.

(4) L. Kaplan, K. E. Wilzbach, W. G. Brown, and S. S. Yang, *J. Amer. Chem. Soc.*, **87**, 675 (1965), and later papers.

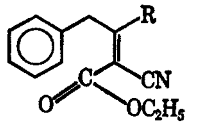
(5) I. M. Hunsberger, R. Ketchum, and H. S. Gutowsky, *ibid.*, **74**, 4839 (1952).

enolates of phenylethylidene malonate (**7**) and phenylethylidene cyanoacetate (**8**) systems. Both ethyl 2-carbethoxy-3-methyl-4-phenyl-2-butenoate (**7a**) and ethyl 2-cyano-3-methyl-4-phenyl-2-butenoate (**8a**) were prepared by the Knoevanagel reaction between phenylacetone and diethyl malonate or ethyl cyanoacetate according to the method of Marion and McRae (reaction 5).[6]

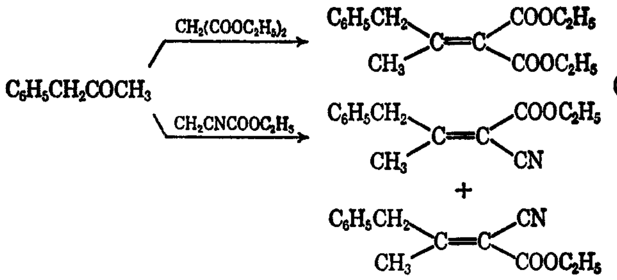
When the same reaction was applied to prepare ethyl 2-carbethoxy-4-phenyl-2-butenoate (**7b**) from phenylacetaldehyde and diethyl malonate, considerable experimental difficulty was encountered. Following a published procedure,[7] only ethyl 4-phenyl-2-butenoate (**9**) was isolated as the product. By modifying the reaction conditions and reducing the reaction time, a mixture of **7b** and **9** was isolated in a relative ratio of 1:4 which could not be separated by repeated distillation or by chromatography. The mixture was used for irradiation without further purification.



7a, R = CH_3
b, R = H

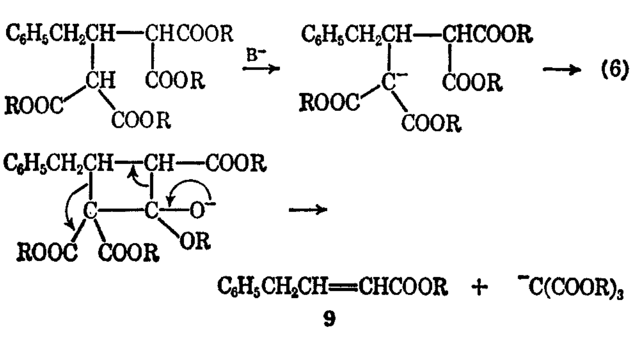


8a, R = CH_3



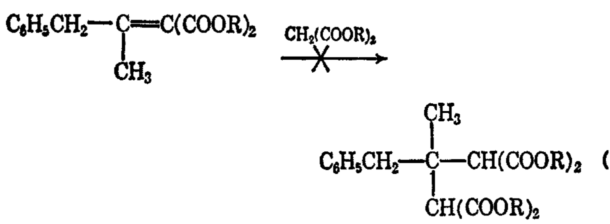
(5)

A rational explanation for our difficulty in the preparation of **7b** is that **7b** may undergo Michael addition with the excess malonate present in the reaction medium after it is formed. The formation of **9** as the major product in the condensation may be rationalized through the following pathway analogous to the abnormal Michael addition (reaction 6).



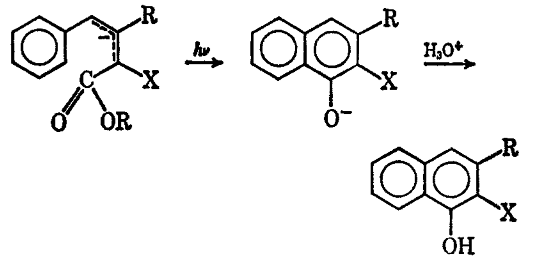
We were unsuccessful in preparing ethyl 2-cyano-4-phenyl-2-butenoate (**8b**) from phenylacetaldehyde and ethyl cyanoacetate following a published procedure.[8] The material obtained showed the absence of any olefinic proton in the nmr spectrum, and we concluded that secondary reaction may have occurred in this condensation.

In contrast to compounds **7b** and **8b**, compounds **7a** and **8a** prepared from phenylacetone will undergo Michael addition much more slowly or not appreciably under the same reaction conditions. In **7a** and **8a**, since the site of addition of a carbanion in the Michael addition is an sp^2 carbon bearing two substituents (C_6H_5– and CH_3–), the product formed would be a highly hindered one with a quarternary carbon atom at position 3 (reaction 7).



$$C_6H_5CH_2-\underset{CH_3}{\underset{|}{C}}{=}C(COOR)_2 \xrightarrow{CH_2(COOR)_2} \not\to \quad C_6H_5CH_2-\overset{CH_3}{\overset{|}{\underset{CH(COOR)_2}{\underset{|}{C}}}}-CH(COOR)_2 \qquad (7)$$

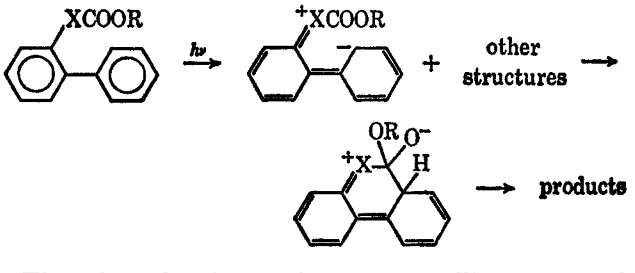
From compounds **7a**, **8a** and **7b**, the enolates undergo intramolecular photoacylation smoothly to give naphthol derivatives **9**, **10** and **11** (reaction 8).



(8)

9, R = CH_3; X = $COOC_2H_5$
10, R = CH_3; X = CN
11, R = H; X = $COOC_2H_5$

The principal transition in the biphenyl system is the L_a transition which exhibits considerable charge-transfer character.[9] When systems containing nonbonding 2p electrons such as carbonions or heteroatoms are conjugated with the biphenyl system, the nonbonding electrons will delocalize into the biphenyl system in the electronic excited state. There will be an increase in electron density at the *o′* positions in the excited state of **1**, **2** and the enolate of **5** which will facilitate the cyclization to give the tricyclic products. The electronic transition in the enolates of **7** and **8** has not been characterized, however, a similar process apparently applies here also.



The photochemistry of organometallic compounds has not been systematically investigated. The princi-

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[6] L. Marion and J. A. McRae, *Can. J. Res.*, **18**, **B**, 265 (1940).

[7] D. Vorländer, *Ann.*, **345**, 245 (1906).

[8] R. P. Linstead and C. T. D. Williams, *J. Chem. Soc.*, 2745 (1962).

[9] H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley & Sons, New York, N. Y., 1962, pp 273–276, 389–407.

pal photochemical reaction of simple organometallic compounds such as organolithium reagents is the formation of radicals.[10] This investigation represents a new photochemical reaction of organometallic compounds which has possible synthetic applications. The investigation is being continued.

Experimental Section

General Procedure.—The light source used was a Hanovia 450-W medium-pressure mercury arc. Irradiations were carried out in an apparatus consisting of two parts, an outer jacket and a dipper well. The dipper well was a water-cooled Hanovia 5-l. flask immersion well made of quartz. The outer jacket was made of Pyrex glass fitted with a fritted nitrogen inlet at the bottom and septum-covered inlet in the midsection for withdrawing aliquots during an irradiation. Different jackets varying in capacity from 150 to 250 ml were used. The solution level was always kept above the top of the mercury arc to prevent pyrolysis. Melting points and boiling points were uncorrected. Mass spectra were recorded with an AEI MS-9 high-resolution mass spectrometer, uv spectra with a Cary 14 spectrometer, and ir spectra with a Perkin-Elmer Infracord or a Beckman IR-7 spectrometer. Nmr spectra were obtained on a Varian A-60 or A-60A spectrometer in CCl_4 or $CDCl_3$ with TMS as an internal standard. Microanalyses were carried out by the Micro-Tech, Inc. of Skokie, Ill., or by Dr. A. Bernhardt of Mülheim, Germany.

Ethyl *o*-biphenylylacetate (3) was prepared by the esterification of the corresponding acid.[11]

Diethyl *o*-biphenylylmalonate (5) was prepared from 3 following the method of Carissimi and coworkers.[11]

Ethyl 2-carbethoxy-3-methyl-4-phenyl-2-butenoate (7a) was also prepared by the method of Marion and McRae.[6] A mixture of phenylacetone (67 g), diethyl malonate (80 ml), aniline–$ZnCl_2$ complex (from 10 ml of aniline and 25 g of freshly dried $ZnCl_2$) and acetic anhydride (60 ml) was heated at 100° for 75 hr. The crude products (34 g) were obtained after the usual work-up and vacuum distillation, bp 140–194° (0.4 mm). Acetanilide (8.3 g) which crystallized upon standing was removed by filtration. The filtrate was fractionally distilled to yield a constant-boiling fraction (20 g), bp 116° (0.05 mm). This fraction was shown to be a mixture by tlc on a Kodak alumina strip developed with ethyl acetate. In addition to the main spot (R_f 0.60), two other impurities (R_f 0.29 and 0.04) were found. A part of this fraction (14.5 g) was chromatographed over basic alumina (200 g, Merck). The second fraction eluted with ethyl acetate showed only a single spot on tlc was concentrated to yield an oily liquid (7.1 g). It was distilled under reduced pressure to give pure **7a** (6.0 g): bp 116° (0.05 mm); ir (neat) 1715 cm^{-1} (conjugated ester C=O); nmr (CCl_4) δ 1.25 (t, 6, J = 7.2 Hz, OCH_2CH_3), 1.92 (s, 3, allylic, CH_3), 3.69 (s, 2, $ArCH_2$), 4.20 (q, 2, J = 7.2 Hz, OCH_2CH_3), 4.23 (q, 2, J = 7.2 Hz, OCH_2CH_3), and 7.25 ppm (s, 5, ArH).

Ethyl 2-cyano-3-methyl-4-phenyl-2-butenoate (8a) was prepared according to the method of Marion and McRae.[6] Phenylacetone (40.2 g), ethyl cyanoacetate (33.9 g), and piperidine (1.5 ml) were stirred at room temperature for 2 days. After the work-up, the mixture was distilled under reduced pressure to yield a fraction boiling at 120–128° (0.05–0.10 mm) (25 g). This fraction was fractionally redistilled to give **8a** (20 g): bp 126° (0.05 mm); ir neat 2220 (CN) and 1720 cm^{-1} (conjugated ester C=O).

The nmr spectrum of **8a** revealed that it was a mixture of two geometrical isomers in a ratio of 4:5: nmr (CCl_4) δ 1.31 (t, 3, J = 7.1 Hz, OCH_2CH_3), 2.10 and 2.21 (s, 3, allylic, CH_3), 3.82 and 4.17 (s, 2, $ArCH_2$), 4.21 and 4.25 (q, 2, J = 7.1 Hz, OCH_2CH_3), and 7.18 and 7.20 ppm (s, 5, ArH). Assuming the ester function is a more effective deshielding group than the nitrile function, the major isomer was assigned the structure with the 3-methyl group *cis* to the ester group on the basis of nmr.

Condensation of Phenylacetaldehyde with Diethyl Malonate.—The method of Vorländer[7] was followed exactly in an attempted preparation of ethyl 2-carbethoxy-4-phenyl-2-butenoate (**7b**). To a mixture of phenylacetaldehyde (25 g) and diethyl malonate (68 g) maintained at 5°, diethylamine (2 ml) was added with stirring. Additional diethylamine was added daily over a period of 7 days (total 5 g) while the stirring continued. After the usual work-up, a portion of the reaction mixture (4.5 g) was distilled to yield a fraction (130 mg), bp 127–130° (0.6 mm). The ir and nmr spectra of this fraction indicated that it was essentially pure ethyl 4-phenyl-2-butenoate (**9**) instead of the desired product. The procedure was then modified. To a mixture of phenylacetaldehyde (25 g) and diethyl malonate (68 g) and glacial acetic acid (3 ml) maintained at 5°, diethylamine (7.5 ml) was added slowly and the stirring was continued at room temperature for 16 hr. The reaction mixture was fractionally distilled under reduced pressure three times to yield a fraction (5.46 g), bp 124–126° (0.05 mm). On the basis of the ratio of olefinic protons to other protons in the nmr, the mixture was shown to be a mixture of **9** and **7a** in a relative ratio of 4:1. The purity of this fraction was not improved either by column chromatography or by further distillation under reduced pressure.

Condensation of Phenylacetaldehyde with Ethyl Cyanoacetate.—The condensation was attempted according to the method of Linstead and Williams.[8] From phenylacetaldehyde (18 g), ethyl cyanoacetate (17.4 g) and diethylamine (1.5 ml), a fraction (7.3 g) boiling at 120–140° (0.15 mm) was obtained after the work-up and distillation under reduced pressure. The fraction was redistilled to yield a mobile mass (4.1 g), bp 124° (0.05 mm). The nmr spectrum of these fractions showed the absence of any olefinic proton, and we concluded that no desired product was formed in this reaction.

Irradiation of Ethyl *o*-Biphenylylacetate (3).—Ethyl *o*-biphenylylacetate (0.30 g) in 100 ml of benzene was irradiated under nitrogen for 16 hr. The ir spectrum of the crude mixture was virtually the same as that of the starting material but the uv spectrum showed a significant red shift to 248 mμ (log ϵ = 4.04) and the nmr spectrum showed a different aromatc resonance pattern and the ethoxyl group protons were shifted slightly downfield. Chromatography on acid-washed alumina gave 0.22 g (ether–hexane 1:19) of a 9:1 mixture of ethyl *m*-biphenylylacetate and the starting material. Saponification of 90 mg of this mixture in 100 ml of 2% ethanolic KOH for 1 hr gave, after dilution with water and acidification, 70 mg of crude acid, mp 95–105°. Recrystallization of the acid from benzene–petroleum ether (bp 30–60°) gave pure *m*-biphenylylacetic acid: mp 135° (lit.[12] mp 133–135°); uv max (C_2H_5OH) 249 mμ (log ϵ = 4.03) [lit.[12] 249 mμ (log ϵ = 4.12)].

When the irradiation of 3 (400 mg in 150 ml) was carried out in methanol for 13 hr, a dark residue was obtained from the irradiated solution after the solvent was removed. Chromatography of the residue on acid-washed alumina yielded only about 30 mg of the *meta* isomer (7.5%). No other well-defined products could be isolated.

When the irradiation was carried out in a solution of sodium ethanolate in ethanol for 6 hr, the acetate was recovered in 60% yield while the balance was the hydrolyzed acid.

Irradiation of Diethyl *o*-Biphenylylmalonate (5).—A solution of the malonate (625 mg, 2 mmol) in 145 ml of absolute ethanol containing 80 mg of Na (3.5 mmol) was irradiated for 2 hr. Aliquots of the mixture were removed, neutralized and monitored by tlc. Tlc showed the presence of a new product (less polar and strongly fluorescent) and some of the starting material. Most of the solvent was removed under reduced pressure. The concentrated solution was diluted with 50 ml of water and extracted with three 50 ml of ether. The crude mixture was chromatographed over 80 g of acid-washed alumina. A portion of the malonate (205 mg) was recovered and 255 mg of the product was isolated (70% based on the malonate reacted). The compound exhibits mp 119–120° (petroleum ether); uv max (C_2H_5OH) 246 mμ (ϵ 42,200), 255 (22,800), 261 (21,200), 270 (13,300), 292 (7100), 314 (5850), 326 (7100), 324.5 (5050), 360 (5000); ir (KBr) 6.11 and 6.17 μ; nmr δ 1.50 (t, 3, J = 7 Hz, OCH_2CH_3), 4.52 (q, 2, J = 7 Hz, OCH_2CH_3), 7.17–1.80 (m, 4, ArH), 8.25–8.75 (m, 4, ArH), and 13.23 ppm (s, 1, ArOH).

Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.67; H, 5.30; mass spectrum, 266.0943. Found: C, 76.54; H, 5.18; mass spectrum, 266.0942.

The malonate was then treated with Na in ethanol under the same conditions as above in the absence of uv light. No reaction took place after 6 days at room temperature and the malonate was recovered in 95% yield. Irradiation of the malonate in the

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(10) H. J. S. Winkler and H. Winkler, *J. Org. Chem.*, **32**, 1695 (1967).

(11) M. Carissimi, I. Grasso, E. Gumelli, E. Milla, and F. Ravenna, *Farmaco, Ed. Sci.*, **18** (10), 705 (1963); see *Chem. Abstr.*, **60**, 1742*b* (1964).

(12) D. L. Turner, *J. Amer. Chem. Soc.*, **72**, 3823 (1950); D. D. Phillips and D. N. Chatterjee, *ibid.*, **80**, 1360 (1958).

absence of Na gave no product after 4 hr and the malonate was recovered unchanged. Heating of the malonate at 180° for 1.5 hr caused a slight decomposition without cyclization.

Irradiation of Ethyl 2-Carbethoxy-3-methyl-4-phenyl-2-butenoate (7a) in the Presence of Sodium Ethanolate.—A solution of **7a** (1.38 g, 5 mmol) in 80 ml of absolute ethanol containing sodium ethanolate (from 0.23 g of sodium, 10 mmol) was deaerated and irradiated through a Corex filter at room temperature for 6.5 hr. Tlc on silica gel showed an intense new spot (R_f 0.55) in addition to **7a** (R_f 0.25) when developed with benzene. After the solvent was removed under reduced pressure, water (40 ml) and ether (30 ml) was added to the reaction mixture. It was then acidified with 10% HCl, the layers were separated, and the aqueous layer was extracted with five 30-ml portions of ether. The combined ethereal extracts were dried over Na_2SO_4 and evaporated to give a crude mixture (1.27 g). The crude mixture was extracted with five 10 ml portions of hexane. The hexane-soluble part (968 mg) was chromatographed over silica gel (40 g) to yield ethyl 1-hydroxy-3-methyl-2-naphthoate (**9**, 497 mg) by eluting with hexane. **7a** (396 mg) was recovered from the column by eluting with benzene and from the hexane-insoluble residue. The yield of **9** was 57% based on the malonate reacted. **9** gives a positive maroon $FeCl_3$ test and after recrystallization from hexane and then ethanol exhibits white prisms: mp 67°; ir (KBr) 3400 (broad, OH) and 1640 cm^{-1} (intramolecularly H-bonded C=O); nmr (CCl_4) δ 1.43 (t, 3, J = 7.1 cps, OCH_2CH_3), 2.60 (s, 3, $ArCH_3$), 4.44 (q, 2, J = 7.1 cps, OCH_2CH_3), 6.94 (s, 1, ArH), 7.18–7.60 (m, 3, ArH), 8.37 (m, 1, ArH) and 12.79 ppm (s, 1, H-bonded ArOH); mass spectrum, parent ion, 230.

Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.02; H, 6.13. Found: C, 72.91; H, 6.25.

Irradiation of Ethyl 2-Cyano-3-methyl-4-phenyl-2-butenoate (8a) in the Presence of Sodium Ethanolate.—Ethyl 2-cyano-3-methyl-4-phenyl-2-butenoate (**8a**, 2.29 g, 10 mmol) in a freshly prepared sodium ethanolate solution (0.40 g of sodium in 90 ml of absolute ethanol) was deaerated with high purity nitrogen for 30 min and irradiated with the light source through a Pyrex filter at room temperature under a slow stream of nitrogen. Aliquots of the solution were taken during the irradiation, neutralized with dilute HCl, and monitored with tlc. When they were spotted on a Kodak silica gel strip and developed with EtOAc–ethanol (5:1), the R_f value of **8a** was 0.73 and a new spot having a R_f value of 0.30 appeared. The new spot became more intense upon further irradiation. After 7 hr of irradiation, ethanol was removed from the mixture under reduced pressure, water (60 ml) was added, and the mixture was extracted with five 30-ml portions of benzene. The benzene extracts were combined, dried and evaporated to give the recovered **8a** (665 mg). The aqueous layer was acidified with 10% HCl and extracted with six 30-ml portions of benzene. The combined benzene extracts were dried and evaporated to give a crude mixture (1.20 g). The product, 3-methyl-2-cyano-1-naphthol (**10**, 370 mg), crystallized out from the mixture on standing which gave a positive green $FeCl_3$ test. The filtrate (690 mg) was chromatographed over silica gel (20 g) and eluted successively with benzene, chloroform, and chloroform–ethanol (1:1) to give crude **10** (390 mg). Crude **10** was recrystallized from benzene to give an additional amount of **10** (310 mg). The yield of **10** based on the ester consumed was 57%. The product was further purified by recrystallization from benzene containing a little ethanol and sublimation to give white prisms: mp 202°; ir (KBr) 3210 (OH) and 2210 cm^{-1} (CN); nmr [$(CD_3)_2SO$] δ 2.53 (s, 3, $ArCH_3$), 3.73 (s, broad, 1, OH), 7.32 (s, 1, ArH), 7.38–7.93 (m, 3, ArH) and 8.56 ppm (m, 1, ArH); mass spectrum, parent ion, 183.

Anal. Calcd for $C_{12}H_9ON$: C, 78.67; H, 4.95; N, 7.65. Found: C, 78.47; H, 5.10; N, 7.84.

Irradiation of the Condensation Products from Phenylacetaldehyde and Diethyl Malonate in the Presence of Sodium Ethanolate.—The condensation products from phenylacetaldehyde and diethyl malonate [1.31 g of ethyl 2-carbethoxy-4-phenyl-2-butenoate (**7b**)–ethyl 4-phenyl-2-butenoate (**9**) 1:4] in a freshly prepared sodium ethanolate solution (0.23 g of sodium in 80 ml of absolute ethanol) was deaerated and irradiated through a Corex filter at room temperature for 12 hr. Tlc on silica gel showed the presence of a new product which has R_f 0.56 in benzene relative to that of the starting material of 0.26. The reaction mixture was concentrated at room temperature, water (60 ml) and ether (30 ml) were added, the mixture was acidified with 10% HCl, layers were separated, and the aqueous layers were extracted with three 25-ml portions of ether. The combined ether extracts were dried and evaporated to yield a residue (1.08 g). The residue exhibited an ir spectrum virtually identical with that of starting material and was digested with hexane. The hexane soluble part (48 mg) was chromatographed over silica gel (2 g). The fraction which was eluted with hexane was crystallized from ethanol to give ethyl 1-hydroxy-2-naphthoate (20 mg), mp 45° (lit.[13] 47°) which gives a blue $FeCl_3$ test. It exhibits ir (KBr) 3410 (broad, H-bonded OH) and 1660 cm^{-1} (intramolecularly H-bonded C=O); nmr (CCl_4) δ 1.40 (t, 3, J = 7.0 cps, OCH_2CH_3), 4.41 (q, 2, J = 7.0 cps, OCH_2CH_3), 6.90–7.90 (m, 5, ArH), 8.25–8.65 (m, 1, ArH) and 12.16 ppm (s, 1, H-bonded ArOH); mass spectrum, parent ion, 216.

Irradiation of the Condensation Products from Phenylacetaldehyde and Ethyl Cyanoacetate in the Presence of Sodium Ethanolate.—The polymeric material prepared equivalent to 5 mmol of the monomer was irradiated in the procedure previously described through a Corex filter. After 24 hr, the reaction mixture showed no appreciable change by tlc, and the starting material was quantitatively recovered.

Registry No.—**6**, 19293-78-8; **7a**, 19293-79-9; **8a** (*cis*),[14] 19293-80-2; **8a** (*trans*),[14] 19317-72-7; **9**, 19293-81-3; **10**, 5333-06-2.

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[13] "Elsevier's Encyclopedia of Organic Chemistry," Vol. 12B, 4283.

[14] Note that the 3-methyl group is *cis* or *trans* to the ester group.