TABLE VII

SUBSTITUTED TETRAPHENYLCYCLOPENTADIENONES

Benzil[a]		Products						
					Analyses			
					Carbon		Hydrogen	
Y	Grams	Yield, %	M.P., °C.	Empirical formula	Calcd.	Found	Calcd.	Found
						89.89		5.95
n-C_4H_9	6.0	21.8	122.0–122.5	$C_{33}H_{28}O$	89.96	89.76	6.41	6.35
						89.90		6.41
iso-C_4H_9	6.0	27.6	132.5–133.0	$C_{33}H_{28}O$	89.96	90.12	6.41	6.59
						90.22		6.58
neo-C_5H_{11}	6.3	12.7	153.5–154.0[b]	$C_{34}H_{30}O$	89.83	89.80	6.65	6.77
		16.6	169–170[b]	$C_{34}H_{30}O$				
C_2H_5O	1.22	69	171–172	$C_{31}H_{24}O_2$	86.89	86.65	5.65	5.44
n-C_3H_7O	7.0	64.5	182.5–183.5	$C_{32}H_{26}O_2$	86.85	87.28	5.92	6.10
						87.06		5.99
iso-C_3H_7O	7.0	60	176–177	$C_{32}H_{26}O_2$	86.85	87.25	5.92	6.01
n-C_4H_9O	1.2	66	144.5–145.5	$C_{33}H_{28}O_2$	86.81	86.61	6.18	6.27
n-$C_5H_{11}O$	4.26	63.8	184.3–185.1	$C_{34}H_{30}O_2$	86.77	86.82	6.43	6.69
n-$C_6H_{13}O$	4.46	50.2	140.8–141.5	$C_{35}H_{32}O_2$	86.74	86.79	6.66	6.67
n-$C_7H_{15}O$	4.67	29.0	142.1–143.0	$C_{36}H_{34}O_2$	86.71	86.37	6.87	6.97
n-$C_8H_{17}O$	2.0	63	96.5–98.0	$C_{37}H_{36}O_2$	86.68	86.46	7.08	6.94
n-$C_9H_{19}O$	5.07	28.7	115.3–115.7	$C_{38}H_{38}O_2$	86.65	86.55	7.27	7.20
n-$C_{10}H_{21}O$	5.27	40.7	134.0–134.7	$C_{39}H_{40}O_2$	86.62	86.74	7.46	7.58
n-$C_{11}H_{23}O$	2.73	30.1	125.0–126.6	$C_{40}H_{42}O_2$	86.60	86.40	7.63	7.53

[a] An equivalent number of moles of benzyl ketone were employed. [b] Mixture melting point 169–170° with the compound immediately above.

was washed with cold water, dried in a desiccator, and then recrystallized from absolute ethanol.

2,3,4,5-Tetraphenylcyclopentadienones.[9,10] Alkyl or alkoxybenzil and an equivalent quantity of benzyl ketone in 15–25 ml. of absolute ethanol (purified by distillation from either potassium hydroxide or sodium ethoxide) was heated to boiling and a solution of potassium hydroxide in 1–2 ml. of ethanol was added and the mixture was refluxed for 15 min. The crude product was isolated by cooling the reaction mixture in a salt-ice bath. The precipitate which formed was filtered, washed with cold ethanol, and then purified by chromatography from benzene on alumina. The percolates were evaporated to dryness and the residue recrystallized from a benzene-ethanol mixture.

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[CONTRIBUTION FROM THE LABORATORY OF CHEMISTRY, RAMNARAIN RUIA COLLEGE, UNIVERSITY OF BOMBAY]

Effect of Substitution in the Aniline Portion on the Behavior of Semianilides of β-Arylglutaconic Acids

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Semianilides of β-arylglutaconic acids are ordinarily found to exist in the cis form, but if the aniline portion of the semianilide is made to carry a carbomethoxy substituent in the ortho position, then the resulting *o*-carbomethoxysemianilides can be obtained as well-defined cis and trans modifications. The cis *o*-carbomethoxysemianilides are found to lose one molecule of water in two different ways, under different conditions, yielding (a) a lactonic substance and (b) the corresponding hydroxy anil.

The chemistry of substituted and unsubstituted glutaconic acids has been previously studied, principally by Thorpe *et al.*[2,3] and by other workers.[4–6] By analogy with the existence of well defined cis and trans modifications of maleic and fumaric acids, Thorpe postulated that glutaconic acids should exist in three forms namely, cis, trans, and labile.[3] The labile form was, however, found to be nonexistent. Also, attempts to isolate the simple unsubstituted glutaconic acids in cis and trans modifications failed, although Perkin *et al.*[5] were able to obtain some alkyl substituted glutaconic

(1) Present address: Laboratory of Pharmaceutical Chemistry, University of Kansas, Lawrence, Kan.

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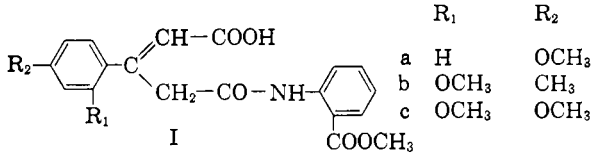
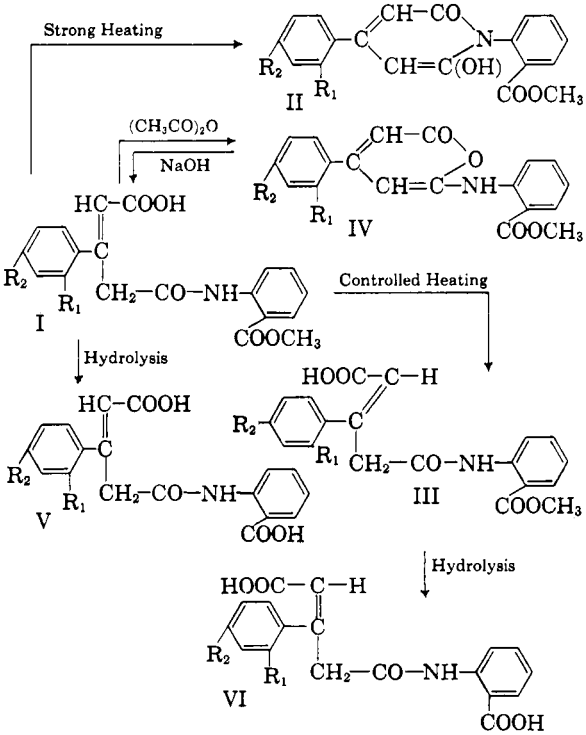
acids in cis and trans modifications. Isolation of stable cis and trans forms of β-arylglutaconic acids was not found possible,[3,7] although separation of these forms in the case of the semianilides of unsubstituted and β-arylglutaconic acids has been reported.[3] This work indicates that perhaps the energy barrier between the cis and trans forms of glutaconic acid itself is too high to permit conversion of the cis to the trans isomer under ordinary conditions. Introduction of bulky groups into the molecule apparently decreases the energy barrier to the extent that conversion from cis to trans modification becomes possible. In the case of semianilides of various β-arylglutaconic acids[8-10] which were initially obtained in cis forms, though milder temperatures brought about no change, strong heating resulted in the formation of the corresponding hydroxy-anils by loss of water.

The objective of the present investigation was to prepare semianilides of β-arylglutaconic acids containing an ortho substituent on the aniline ring, which by virtue of its bulkiness might sterically hinder anil formation and thus permit cis-trans conversion. With this in mind, methyl anthranilate was used instead of aniline in the reaction with the β-arylglutaconic anhydrides as carried out previously by Limaye *et al.*[8] to give the corresponding *o*-carbomethoxy-β-aryl-*cis*-glutaconanilic acids (Ia, Ib and Ic). By analogy with the observation of



the previous workers,[3,8] these *cis*-glutaconanilic acids, on heating at elevated temperature, gave the corresponding hydroxy anils (IIa, IIb, IIc respectively).[11] When they were subjected to prolonged controlled heating at temperatures slightly above their melting points according to Thorpe's method,[3] they underwent a substantial cis to trans conversion giving IIIa, IIIb, IIIc respectively. Unlike the unsubstituted glutaconanilic acids which yield only hydroxy anils in the presence of acetic anhydride,[2] these *o* - carbomethoxy-substituted-*cis*-glutaconanilic acids (Ia, Ib, Ic) on similar treatment gave lactonic compounds, methyl *N*-[4,6-dehydro-4-β-aryl-6-oxo-2-pyranylidene]-anthranilates (IVa, IVb, IVc), which could be reconverted into the original *o*-carbomethoxy-*cis*-glutaconanilic acids (Ia, Ib, Ic) by treatment with alkali. This is apparent from the relative nucleophilicities of the carbonyl oxygen and amide nitrogen of Ia, Ib, and Ic. In the case of these carbomethoxy-*cis*-glutaconanilic acids, either of the two nucleophilic agents, *i.e.* the carbonyl oxygen or amide nitrogen is capable of attack at the carboxyl group. Without the *o*-carbomethoxy substituent, the amide nitrogen is the stronger nucleophilic atom, giving corresponding hydroxy anils by treatment with acetic anhydride. With the *o*-carbomethoxy group as in Ia, Ib, and Ic, the resonance and inductive effects become prominent, causing a decrease in electron density around the amide nitrogen atom. This decrease in nucleophilicity of the nitrogen permits the carbonyl oxygen to be more reactive, giving the corresponding lactones IVa, IVb, and IVc.

The isomeric *o*-carbomethoxy-β-aryl-*trans*-glutaconanilic acids (IIIa, IIIb, and IIIc) were found to be inert to prolonged heating at reflux temperature with acetic anhydride, thereby confirming their trans configurations. The *cis*-(Ia, Ib, and Ic) and *trans*-glutaconanilic acids (IIIa, IIIb, and IIIc), which are also methyl esters, on hydrolysis with alcoholic alkali gave the corresponding dicarboxylic acids (Va, Vb, Vc, and VIa, VIb, VIc) which may be considered respectively, as *o*-carboxy-β-aryl-*cis*-glutaconanilic acids and *o*-carboxy-β-aryl-*trans*-glutaconanilic acids. The *cis*-acids (Va, Vb, Vc) could also be obtained by the action of alcoholic alkali on the neutral lactones (IVa, IVb, and IVc).



Methyl anthranilate was also made to condense with the β-arylglutaric acids (VIIb, VIIc) or their anhydrides (VIIIb, VIIIc) to give the corresponding carbomethoxy-β-arylglutaraninilic acids (IXb,

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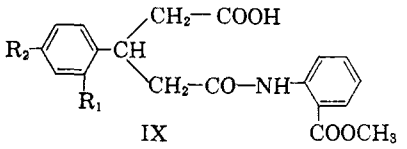
(11) To be published.

IXc). These monobasic glutaraninilic acids (IXb, IXc), on hydrolysis with alkali, gave the corresponding dibasic *o*-carboxy-β-arylglutaraninilic acids (Xb, Xc).



IX

EXPERIMENTAL

o-Carbomethoxy-β-(4-methoxyphenyl)-cis-glutaconanilic acid (Ia). A solution of 18.8 g. (0.1 mole) of β-(4-methoxyphenyl)-glutaconic anhydride[8] and 15.1 g. (0.1 mole) of methyl anthranilate in 800 ml. of warm benzene was heated at reflux temperature on a steam bath for about 30 min. Upon removal of the benzene, a pale yellow solid separated. It was collected by filtration, washed with water, and purified by dissolution in sodium bicarbonate solution and reprecipitation with dilute hydrochloric acid. Further purification by repeated recrystallizations from alcohol gave 22.6 g. (61% yield) of Ia as pinkish white needles, m.p. 146–146.5°.

Anal. Calcd. for $C_{20}H_{19}O_6N$: C, 65.03; H, 5.19; N, 3.79. Found: C, 65.24; H, 5.14; N, 3.80.

o-Carbomethoxy-β-(4-methoxyphenyl)-trans-glutaconanilic acid (IIIa). In a clean dry flask, 1 g. of Ia was heated in a paraffin bath at 150° for 0.5 hr. The resulting resinous mass was washed first with ether and then with water, giving a crystalline yellow solid. It was purified by being dissolved in dilute sodium bicarbonate solution and precipitation with dilute hydrochloric acid. Further purification by repeated recrystallizations from 50% alcohol gave 0.6 g. (60% yield) of IIIa as pale yellow needles, m.p. 185–186°.

Anal. Found: C, 65.28; H, 5.11.

Methyl N-[4,6-dehydro-4-(4-methoxyphenyl)-6-oxo-2-pyranylidene]-anthranilate (IVa). A mixture of 1 g. of Ia and 5 ml. of acetic anhydride was heated at reflux temperature for 1 hr. on a steam bath. The clear red liquid so obtained was poured into about 25 ml. of cold water, giving an orange colored solid material. This solid was collected on a filter, washed several times with water, triturated with sodium bicarbonate solution to remove any unchanged semianilide and filtered. Upon drying, the residue was recrystallized from ethyl alcohol yielding 0.4 g. (45% yield) of pale yellow crystals, m.p. 135–135.5°. This material was found to be insoluble in cold dilute sodium hydroxide solution. However, upon warming this suspension, solution was effected regenerating the semianilide (Ia) after neutralization.

Anal. Calcd. for $C_{20}H_{17}O_5N$: C, 68.36; H, 4.88. Found: C, 68.06; H, 5.08.

o-Carboxy-β-(4-methoxyphenyl)-cis-glutaconanilic acid (Va). To a solution of 1 g. of Ia in 15 ml. absolute alcohol, 2 ml. of 12.5*N* sodium hydroxide solution was added and the mixture heated at reflux temperature for about 2 hr. Removal of the solvent and neutralization of residual sodium salt with concentrated hydrochloric acid gave a pale yellow solid mass. Repeated crystallizations from alcohol gave 0.63 g. (67% yield) of faint, yellow crystals, m.p. 172° dec.

Anal. Calcd. for $C_{19}H_{17}O_6N$: C, 64.21; H, 4.82. Found: C, 64.46; H, 4.87.

o-Carbomethoxy-β-(2-methoxy-4-methylphenyl)-cis-glutaconanilic acid (Ib). The procedure used in making this compound was the same as that used for Ia. From 23 g. (0.1 mole) of β-(2-methoxy-4-methylphenyl)-glutaconic anhydride,[9] 28 g. (70% yield) of Ib, m.p. 132–132.5°, was obtained.

Anal. Calcd. for $C_{21}H_{21}O_6N$; C, 63.16; H, 5.26. Found: C, 63.30; H, 5.47.

o-Carbomethoxy-β-(2-methoxy-4-methylphenyl)-trans-glutaconanilic acid (IIIb). The procedure used in making this compound was the same as that described for IIIa. From 1 g. of Ib, 0.56 g. (56% yield) of IIIb, m.p. 162–163° was obtained.

Anal. Found: C, 63.32; H, 5.38.

Methyl N-[4,6-dehydro-4-(2-methoxy-4-methylphenyl)-6-oxo-2-pyranylidene]-anthranilate (IVb). This compound was prepared by the same procedure described for IVa. From 3.8 g. (0.01 mole) of Ib, 2 g. (57% yield) of IVb was obtained, m.p. 152–153°.

Anal. Calcd. for $C_{21}H_{19}O_5N$: C, 69.04; H, 5.2; N, 3.63. Found: C, 69.23; H, 5.36; N, 3.48.

o-Carboxy-β-(2-methoxy-4-methylphenyl)-cis-glutaconanilic acid (Vb). The procedure used in making Vb was the same as described for Va except that it was purified by crystallization from 80% acetic acid. From 4 g. (0.01 mole) of Ib, 2.8 g. (75% yield) of Vb was obtained, m.p. 200° (dec.).

Anal. Calcd. for $C_{20}H_{19}O_6N$: C, 65.03; H, 5.15; neut. equiv., 184.5. Found: C, 65.24, H, 5.30; neut. equiv., 184.7.

o-Carboxy-β-(2-methoxy-4-methylphenyl)-trans-glutaconanilic acid (VIb). To a solution of 4 g. (0.1 mole) of IIIb in 50 ml. of alcohol, 7.5 ml. of 12.5*N* NaOH was added and the whole mixture heated at reflux temperature on the water bath for 3 hr. Upon removal of the solvent, the residue was dissolved in water, filtered, and the filtrate neutralized with hydrochloric acid at 0°, giving VIb as a pale yellow mass. Crystallization from 80% alcohol gave 2 g. (52% yield) of colorless crystals VIb, m.p. 225° (dec.).

Anal. Calcd. for $C_{20}H_{19}O_6N$: C, 65.43; H, 5.15. Found: C, 64.82; H, 5.28.

o-Carbomethoxy-β-(2,4-dimethoxyphenyl)-cis-glutaconanilic acid (Ic). The same procedure as was used in making Ia was used for the preparation of this compound. From 21.6 g. (0.1 mole) of 2,4-dimethoxyphenylglutaconic anhydride,[10] 29.1 g. (73% yield) of Ic was obtained in the form of pinkish white needles, m.p. 132–134°.

Anal. Calcd. for $C_{21}H_{21}O_7N$: C, 63.16; H, 5.26. Found: C, 63.30, H, 5.47.

o-Carbomethoxy-β-(2,4-dimethoxyphenyl)-trans-glutaconanilic acid (IIIc). This compound was obtained from Ic by heating it at a temperature just above its melting point (*i.e.*, 135°) for 1 hr. From 2.0 g. of Ic, 1.2 g. (60% yield) of IIIc was obtained, m.p. 158°–159.5°.

Anal. Found: C, 63.32; H, 5.39.

Methyl N-[4,6-dehydro-4-(2,4-dimethoxyphenyl)-6-oxo-2-pyranylidene]-anthranilate (IVc). This compound was prepared by the same method described for the preparation of IVa. From 4.0 g. (0.1 mole) of Ic, 2.6 g. (70% yield) of IVc was obtained in the form of yellow plates, m.p. 146°. Upon treatment with cold dilute sodium hydroxide solution, solution was gradually effected. Acidification regenerated the semianilide Ic. Treatment of IVc with boiling dilute sodium hydroxide solution and subsequent acidification, however, gave the dibasic acid Vc, m.p. 196.5° (dec.).

Anal. Calcd. for $C_{21}H_{19}O_6N$: C, 66.15; H, 4.99. Found: C, 65.97; H, 5.21.

o-Carboxy-β-(2,4-dimethoxyphenyl)-cis-glutaconanilic acid (Vc). This dibasic acid was prepared from Ic by heating it with alcoholic alkali at reflux temperature or from IVc by boiling with decinormal sodium hydroxide solution. From 4 g. of Ic, 2 g. (55% yield) of Vc was obtained. Crystallization from 80% acetic acid gave pure Vc, m.p. 196–197° (dec.). From 3.8 g. (0.1 mole) of IVc, 1.6 g. (41% yield) of Vc was obtained.

Anal. Calcd. for $C_{20}H_{19}O_7N$: C, 62.33; H, 4.93. Found: C, 62.55; H, 4.77.

o-Carboxy-β-(2,4-dimethoxyphenyl)-trans-glutaconanilic acid (VIc). This compound was prepared from IIIc by treatment with alcoholic alkali. From 4 g. (0.1 mole) of IIIc, 1.7 g. (46% yield) of colorless VIc, m.p. 215° (dec.) was obtained.

Anal. Found: C, 62.03; H, 5.11.

β-(2-Methoxy-4-methylphenyl)-glutaric anhydride (VIIIb). A mixture of 2.5 g. (0.01 mole) of β-(2-methoxy-4-methyl-

phenyl)glutaric acid[12] VIIb, and 2 ml. of acetic anhydride was heated at reflux temperature for about an hour. The resinous mass obtained upon cooling was crystallized by the addition of ether. Crystallization from dry benzene gave 1.9 g. (72% yield), of brilliantly shining colorless plates (VIIIb), m.p. 104–105°.

o-Carbomethoxy-β-(2-methoxy-4-methylphenyl)glutaraninilic acid (IXb). This compound was prepared by the same procedure as previously described for the preparation of Ia, except that glutaric anhydride (VIIIb) was used instead of glutaconic anhydride. From 2.3 g. (0.01 mole) of VIIIb, 2.6 g. (60% yield) of IXb, m.p. 135–136°, was obtained.

Anal. Calcd. for $C_{21}H_{23}O_6N$: neut. equiv., 385.0. Found: neut. equiv., 389.1.

o-Carboxy-β-(2-methoxy-4-methylphenyl)glutaraninilic acid (Xb). This dicarboxylic acid was prepared by the alkaline hydrolysis of IXb. From 3.9 g. (0.1 mole) of IXb, 2.6 g. (71% yield) of Xb was obtained. Repeated crystallizations from dilute acetic acid and finally from alcohol gave the pure product, m.p. 165–165.5°.

Anal. Calcd. for $C_{20}H_{21}O_6N$: C, 64.69; H, 5.66; neut. equiv., 185.5. Found: C, 64.82; H, 5.51; neut. equiv., 186.5.

β-(2,4-Dimethoxyphenyl)glutaric acid (VIIc). This acid was prepared by the reduction of β-(2,4-dimethoxyphenyl)-glutaconic acid,[13] m.p. 174° (dec.) with sodium amalgum according to the method described by Chitre.[14] From 26.6 g. (0.1 mole) of β-(2,4-dimethoxyphenyl)-glutaconic acid, 21.8 g. (81% yield) of crude reduced acid was obtained, as a white mass. Crystallization from water gave 20.2 g. (76% yield) of VIIc as colorless needles, m.p. 158–159°.

Anal. Calcd. for $C_{13}H_{16}O_6$: neut. equiv., 134.0. Found: neut. equiv., 135.8.

β-(2,4-Dimethoxyphenyl)glutaric anhydride (VIIIc). This compound was prepared from VIIc by heating at reflux temperature with acetic anhydride. The yield was 82% of white crystals, m.p. 122–122.5°.

Anal. Calcd. for $C_{13}H_{14}O_5$: C, 62.4; H, 5.6. Found: C, 62.5; H, 5.8.

o-Carbomethoxy-β-(2,4-dimethoxyphenyl)glutaraninilic acid (IXc). This monobasic acid was prepared from the corresponding glutaric anhydride (VIIIc) by heating it in boiling benzene solution with a molecular quantity of methyl anthranilate. Repeated crystallizations from 50% alcohol gave pure IXc, in 72% yield, m.p. 136–136.5°.

Anal. Calcd. for $C_{20}H_{23}O_7N$: neut. equiv., 401.0. Found: neut. equiv., 398.7.

o-Carboxy-β-(2,4-dimethoxyphenyl)glutaraninilic acid (Xc). This dicarboxylic acid was obtained in 61% yield from IXc by hydrolysis with alcoholic alkali. It was purified by crystallization from acetic acid giving dull crystals, m.p. 128–128.5°.

Anal. Calcd. for $C_{21}H_{21}O_7N$: neut. equiv., 193.5. Found: neut. equiv., 195.2.

BOMBAY, INDIA

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[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

Psoralene. II. Certain Reactions of Xanthotoxin[1]

MERVIN E. BROKKE AND BERT E. CHRISTENSEN

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The behavior of 9-methoxypsoralene under the conditions of oxidation, chlorination, sulfonation, and ether cleavage is described. Chromium trioxide converted 9-methoxypsoralene I into psoralenequinone II. Chlorination with chlorine produced 2,3-dihydro-9-methoxy-2,3,4-trichloropsoralene VII while chlorination with sodium hypochlorite formed 4-chloro-9-methoxypsoralene VIII. Chlorosulfonic acid attacked the 4-position forming both the free sulfonic acid and the acid chloride. The conversion of 9-methoxypsoralene to 9-hydroxypsoralene was accomplished in good yield by heating with anhydrous aluminum chloride.

Xanthotoxin I (9-methoxypsoralene) is a furocoumarin that occurs in a number of plants indigenous to the Eastern Hemisphere. As its name implies xanthotoxin is a fish poison and is, in general, toxic to cold-blooded animals while it is relatively nontoxic to mammals. Current interest in this material stems from its photodynamic activity, which causes the skin to "tan" as opposed to "burn" if the drug is administered orally prior to exposure to the sunlight.

The behavior of 9-methoxypsoralene under the conditions of nitration, bromination, hydrogenation, ozonization, thionation, and various ring-opening procedures has been previously described by this laboratory.[2] This paper is concerned with the oxidation, ether cleavage, chlorination, and sulfonation of this molecule.

Schonberg has reported[3] that oxidation of 4-methoxypsoralene (bergaptene) with sodium dichromate attacked the furan double bond and formed 6-formyl-7-hydroxy-5-methoxycoumarin. His work has been confirmed in this laboratory.

It seemed unusual, therefore, that the isomer of bergaptene, 9-methoxypsoralene, was unaffected by sodium dichromate under identical conditions. Treatment with chromium trioxide in acetic acid,

(1) This work was supported in part by grants from the Division of Research Grants and Fellowships, National Institutes of Health, Public Health Service. Published with the approval of the Monographs Publications Committee, Oregon State College as Research Paper No. 351, School of Science, Department of Chemistry.

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