TABLE I

COMPARISON OF CONDENSATION PRODUCTS OF α-, β- AND γ-PICOLINE METHIODIDES WITH p-DIMETHYLAMINO- AND p-DI-
ETHYLAMINOBENZALDEHYDE

Isomer	Para substituent	M.p., °C.	Phillips[8] Yield, %	Doja and Prasad[10] M.p., °C.	Yield, %	Crippa and Verdi[9] M.p., °C.	Yield, %
α	(CH₃)₂N	273–274	98–100	265	83		
	(C₂H₅)₂N	246–247	98–100	240	78		
β	(CH₃)₂N	.....	None obtained	247	82	247	Not stated
	(C₂H₅)₂N	.....	...	222	84		
γ	(CH₃)₂N	258–259	100	262	76		
	(C₂H₅)₂N	221–222	100	232	86		

phenylhydrazine gave 4.8 g. (100%) of yellow crystals of the phenylhydrazone; m.p. 150–151°.

Pure unchanged β-picoline methiodide, 4.7 g. (100%), m.p. 98–99°, was recovered from the ether-insoluble fraction by solution in methanol, treatment with Darco, filtration, evaporation and crystallization.

When the original Reilly 98% β-picoline, purified only by distillation, was used to make the methiodide the condensation reaction with p-dimethylaminobenzaldehyde had a different result. The reaction solution became deep claret colored; after evaporation of the reaction mixture to 10 cc.

and cooling, 0.1–0.2 g. (2%) of deep red crystals was obtained. Recrystallized from methanol, these melted at 258–259° and were shown by melting point, analysis and ultraviolet absorption spectrum to be identical with the γ-(p′-dimethylaminostyryl)-pyridine methiodide described earlier.[6b] Careful working up of the filtrates from these crystals resulted in a 97% recovery of both aldehyde and β-picoline methiodide as described above. This process can be used to obtained the pure β-picoline methiodide from the less pure material.

TUCKAHOE 7, NEW YORK

The Action of N-Bromosuccinimide on Lignin Sulfonates

BY T. L. FLETCHER[1] WITH D. M. RITTER

Lignin sulfonates with essentially one aromatic bromine per aromatic ring have been obtained with the use of N-bromosuccinimide. These derivatives result in good yield and have undergone small methoxyl loss and little other change. The brominated products appear useful for degradative and structural studies because of demonstrable increase in stability of otherwise sensitive aromatic rings.

Introduction

As an approach to elucidation of the structure of lignin sulfonic acid, it seemed desirable to investigate new ways of brominating the material. Stabilization of the aromatic ring and labeling positions for degradative studies are among the results sought in such an approach. One of the methods developed in this study for controlled bromination without significant degradation has been with the use of N-bromosuccinimide.

Much of the reported work on halogenation of lignin derivatives has been carried out under intentionally drastic conditions in order to obtain simple degradation products rather than as a step in controlled degradation.[2] The breakdown of halogenated lignins has usually resulted in low yields or a variety of products by routes that make speculation about the structure of the original lignin preparation hazardous. Lautsch and Piazolo[3] found that a brominated lignin, upon oxidation with cobaltic hydroxide, yielded 8% of 6-bromo-vanillin. They also obtained 10% of 5-iodo-vanillin by degradation of spruce iodolignin (prepared from acetomercurilignin). In each case the position of the major part of the substituted halogen

atom is not certain. In a survey of bromination of lignin sulfonic acid and some model substances, Kratzl and Bleckmann[4] reported loss of about 50% of the sulfur in the lignin derivative, considerable degradation, and evidence of some dibrominated aromatic rings.

Procedure

Buu-Hoï[5] has shown that various alkyl phenyl ethers react with NBS to give good yields of compounds brominated in the nucleus. It was thought, therefore, that aromatic bromination of lignin sulfonic acid might occur. Possible reactions of oxidation (involving carbinol groups or dehydrogenation of neighboring carbon atoms) were not considered. Yields of brominated lignin sulfonates were 10–15% less than quantitative (after dialysis), and the products had suffered a small reduction in methoxyl value and sulfur content and there was evidence of some oxidation (infrared spectra). However, the bromination reaction appears quite straightforward and of significant interest with respect to stabilization and amount of bromine introduced.

Attempts to brominate insoluble lignin preparations in chloroform with NBS gave ambiguous results and an incomplete reaction. Further efforts were therefore concentrated on the limited selection of lignin sulfonate derivatives soluble in chloroform or other suitable organic solvents. Among the former are the salts of lignin sulfonic acid and methylated lignin sulfonic acid with dimethyloctadecylamine.[6] These salts in chloroform, upon treatment with NBS at 22–25°.for 48 hours, gave a non-homogeneous product with not more than 0.4 atom of bromine per C₉ unit. Another chloroform-soluble derivative giving more interest-

(1) Department of Surgery. School of Medicine, University of Washington, Seattle 5, Washington.

(2) L. E. Wise. "Wood Chemistry." Reinhold Publishing Corp., New York. N. Y.. 1946, pp. 308–311, contains a summary of many of the reactions of lignins with halogens.

(3) W. Lautsch and G. Piazolo. Ber.. 73 (1), 317 (1940).

(4) K. Kratzl and Ch. Bleckmann. Monatsh., 76, 185 (1947).

(5) Ng. Ph. Buu-Hoï. Ann., 556. 1 (1944).

(6) From studies by Dr. A. E. Markham and Dr. J. L. McCarthy of the Pulp Mills Project. University of Washington.

TABLE I

BROMINE TO $C_9(OCH_3)$ RATIOS

Derivatives	1 Equiv. NBS[m]	a	2 Equiv.	a	2 Equiv. plus peroxide	a	4 Equiv.	a
Lithium lignin sulfonate[h]	0.55	0.40[c]	0.90	0.80	0.91	..	1.06	0.90[c]
Lithium lignin sulfonate (fully methylated)[h]	.66	.58[c,d,e]	0.93	.80⁻	0.90	0.80	0.92	.85--
Me ester of lignin sulfonic acid (fully methylated)[i]	.77	.72[c]	1.02	0.88[c,e]	1.05		1.09	.94[b]
								0.90[c,d]
Lithium lignin sulfonate[j]							1.26[k]	
							1.51[l]	f,g

a Column represents ratio after dehalogenation with b, c, d, e, or f. b Excess NBS and heat. c KOH, 1 hr. (2 samples run for 20 hr.) 25° with no further removal of bromine. d Dimethylaniline. e Collidine. f Lithium hydroxide (0.5 molar, 25°, 1 week) followed by dialysis. g Loss of about one-third of bromine. h In absolute methyl or ethyl alcohol. i In chloroform. j In benzene–absolute methanol. k 48 hr., 25°; 1.5 hr., 55°. l 48 hr., 25°; 2 hr., 65-70°. m $C_9(OCH_3)$ basis.

TABLE II

TYPICAL EMPIRICAL FORMULAS OF LIGNIN SULFONATES AND BROMINATED DERIVATIVES

Derivative	No.	Conditions	Formula (C_9 basis)
Lithium lignin sulfonate			$C_9H_{7.7}O_{2.52}S_{0.46}Li_{0.45}MeO_{0.92}$
	II-60	2 Eq. NBS, 25°, 24 hr., MeOH	$C_9H_{8.3}O_{2.64}S_{0.39}Li_{0.18}MeO_{0.79}Br_{0.90}$
	II-65	4 Eq. NBS. 25°, 24 hr., MeOH	$C_9H_{7.5}O_{2.62}S_{0.41}Li_{0.06}MeO_{0.78}Br_{1.06}$
Lithium lignin sulfonate (fully methylated)			$C_9H_{7.50}O_{1.55}S_{0.42}Li_{0.40}MeO_{1.94}$
	I-285	2 NBS, 25°, plus peroxide in MeOH	$C_9H_{6.65}O_{1.98}S_{0.28}Li_{0.21}MeO_{1.68}Br_{0.93}$
	I-287	2 NBS, 25°, 20 hr. in MeOH plus dimethylaniline	$C_9H_{6.85}O_{2.06}S_{0.27}Li_{0.18}MeO_{1.51}Br_{0.88}$
	II-77	4 NBS, 48 hr., 25° in MeOH	$C_9H_{7.22}O_{1.80}S_{6.33}Li_{0.05}MeO_{1.87}Br_{0.92}$
Me ester lignin sulfonic acid (fully methylated)			$C_9H_{7.52}O_{1.39}S_{0.38}(MeO)^{a}_{0.37}MeO_{1.76}$
	II-75	4 NBS. 25°, 20 hr., CHCl₃	$C_9H_{7.92}O_{1.87}S_{0.32}(MeO)^{a}_{0.20}MeO_{1.35}Br_{1.08}$
	II-76	4 NBS, 25°. 48 hr., CHCl₃	$C_9H_{7.92}O_{1.84}S_{0.32}(MeO)^{a}_{0.18}MeO_{1.34}Br_{1.09}$
	II-115	II-75 plus 2 NBS, 55°. 24 hr., CHCl₃	$C_9H_{8.12}O_{1.77}S_{0.30}(MeO)^{a}_{0.14}MeO_{1.43}Br_{0.94}$
	I-291A	4 NBS, 20 hr., CHCl₃, dehalogenated with KOH	$C_9H_{7.12}O_{1.87}S_{0.20}Li_{0.16}MeO_{1.44}Br_{0.93}$
Lithium lignin sulfonate			$C_9H_{7.7}O_{2.52}S_{0.46}Li_{0.45}MeO_{0.92}$
	II-123	4 NBS in benzene-methanol	$C_9H_{8.7}O_{2.50}S_{0.40}Li_{0.40}MeO_{1.43}Br_{1.26}$
	II-124B	4 NBS in benzene-methanol (more heat than II-123 see Table 1)	$C_9H-O_{3.24}S_{0.35}Li-MeO_{1.07}Br_{1.51}$

a Ester McO: difference between methoxyl analysis of sample before and after alkaline hydrolysis.

ing results was the methyl ester of fully methylated lignin sulfonic acid. When properly prepared, precipitated from ether, and kept in the dark in a vacuum with phosphorus pentoxide this substance is stable and was found, eighteen months after preparation, to have the same analytical values, almost white color, and ready solubility in chloroform as when fresh. Approximately 5% solutions in chloroform were treated with NBS (1 equivalent/C_9, 2 eq., 2 eq. with peroxide, 4 eq., and 6 eq.) as described below (also see Tables I and II).

The effect of NBS on the lithium salts of lignin sulfonic acid and its fully methylated derivative was then investigated in absolute methanol. The results with both of these materials and with the methyl ester are in essential agreement (Tables I and II). Many of the brominated products were treated with cold 15-20% KOH for different lengths of time, or alcoholic solutions of collidine or dimethylaniline at different temperatures. As shown in Table I, there is good agreement between values for unremoved halogen after different dehalogenating treatments of the same derivative, and comparable results with different derivatives.

In general, two to four equivalents of NBS, on a C_9/OCH_3 basis, at 25° for 18-24 hours introduces 0.95-1.20 bromine atoms per C_9 of which 0.05-0.20 atom are removed by the above procedures, leaving 0.95 ± 0.05 atom per C_9 as relatively firmly bound bromine. Recently it has been found that various lignin sulfonate derivatives are soluble in mixtures of benzene and absolute methanol. The freshly prepared lithium salts of lignin sulfonic acid and fully methylated lignin sulfonic acid are soluble in a mixture of four or five parts of benzene to one of absolute methanol, provided the salt is first dissolved in the alcohol. Within a few minutes after addition of NBS, the ratio can be increased to 8 or 10:1. A bromination of the former salt was carried out with four equivalents of NBS. A high yield of

product was obtained which was different in some respects from previous preparations, as described below.

For purposes of rough comparison, infrared spectra of many of the brominated products (as dimethyloctadecylamine salts in CHCl₃) were run (2-16 microns) by Mr. Ernest Wenkert on a Baird spectrophotometer.

Discussion

The conclusion seems reasonable that the bromine introduced is largely aromatic and the small amount of readily removable bromine is aliphatic. Confirmation of this must come from degradative studies and recovery of a major part of the bromine in identifiable compounds. More drastic dehalogenation conditions than described here unfortunately appear to lead to fundamental changes in the brominated products. For example, temperatures of over 40° in KOH solution led to much loss of sulfur. Subsequent dialysis led to considerable loss of material. Treatment with KOH (25°) was followed by small loss on dialysis. Agreement (see tables) between the various dehalogenating procedures on different brominated products gives strong support to the postulated aromatic:aliphatic bromine ratio. The location of the readily removable bromine is unknown. The reaction of NBS on lithium lignin sulfonate in benzene–methanol, as described above, appears to introduce a large amount of aliphatic bromine (see

tables) and a strong band appears at 5.87–5.93 microns in the infrared spectrum. There is some change at about 5.80–5.90 microns in the spectra of lignin sulfonates brominated in alcohol or chloroform with NBS. This is, in general, somewhat more noticeable after dehalogenation. The latter change is by no means as pronounced as in the benzene–methanol reaction, further study of which might lead to an understanding of the side-chain bromination and oxidizing effects of NBS on lignin sulfonates. It can also be seen (Table II) that instead of a small net loss in the methoxyl value, as in the other reactions, there is a net increase. Some of this is labile in the presence of NBS with additional heat. (Compare No. II-123 and II-124b, Table II and compare with heat treatment, II-76.)

It appears that, in addition to alkaline agents, use of excess NBS with a rise in temperature for several hours removes side-chain bromine. The data for II-115 (Table II) indicate that heating the brominated methyl ester, II-76, with two equivalents of NBS and catalytic amounts of benzoyl peroxide for as much as 24 hours results in no appreciable change in the empirical formula except loss of 0.15 atom of bromine per C_9. This brominated product is therefore more stable than the original lignin sulfonate. Heating initially with NBS causes considerable degradation and a non-homogeneous product. The simplest way of obtaining an aromatically brominated lignin sulfonate (0.95 ± 0.05 Br/C_9) with the least loss, degradation, or change, is to combine two, or slightly more than two, equivalents of NBS with the lithium salt of the fully methylated lignin sulfonic acid in absolute alcohol for 15–20 hr. at 20–25° followed by treatment with two more equivalents of NBS for 2 hr. at 50–55°. In most of these brominations (Table II) the loss in methoxyl is balanced, within experimental error, by the gain in non-methoxyl oxygen. An examination of the products by acylation and methylation procedures[7] would be of value in determining the nature of the non-methoxyl oxygen produced in the reaction. Unmethylated lignin sulfonates give the same results, with respect to oxygen balance, as the methylated derivatives. It has not been determined whether the reaction of NBS with lignin sulfonates is affected by traces of water present in some of the starting materials.

Experimental Part

Preparation of Derivatives.—The lignin available as starting material was obtained by dialyzing[8,9] a calcium-base sulfite waste liquor from a commercial cook, largely of Western hemlock, *Tsuga heterophylla.* This high molecular weight sulfonate represented about 45% of the methoxy-bearing material in the cooking liquor. The lithium salt was prepared by passing a solution of the lignin sulfonate through a bed of Ionex #2[10] cation exchange resin, charged

with H⁺ ions, and then through the same type of resin charged with Li⁺ ions[11] and dried (Table II). Fully methylated lignin sulfonate[12] and its methyl ester[13] (Table II) were made according to previous directions. In preparing the latter the freshly freeze-dried methylated lignin sulfonic acid was completely soluble in tetrahydrofuran before addition of diazomethane.

The following reactions are typical (Table II) of the many brominations run. Most yields were about 85–90% of the theoretical. After dehalogenation and dialysis an additional 5–10% was lost.

Reaction of NBS with the Methyl Ester of Methylated Lignin Sulfonic Acid in Chloroform (a).—One equivalent of NBS and 465 mg. of the methyl ester of methylated lignin sulfonic acid were dissolved in alcohol-free chloroform to make an approximately 5% solution. 360 mg. of NBS was added and the solution was kept at 25 ± 2° for 24 hr. The clear reaction mixture was then slowly poured with vigorous stirring into 250 ml. of absolute ether. This was centrifuged and the light tan powdery precipitate washed repeatedly with ether until the washings showed no trace of residue upon evaporation.[14] The yield was 486 mg. and an additional 30 mg. was recovered from the combined first supernatant and the first washing.

Methyl Ester with 4 Equivalents NBS.—One and one-half grams of the methyl ester was dissolved in 25 ml. of alcohol-free chloroform; 4.7 g. of NBS was added and the solution was kept at 25 ± 2° for 20 hr. An aliquot was then removed and precipitated into ether, washed and dried (II-75, Table II). The remainder of the solution was allowed to stand an additional 28 hr. and worked up in the same way (II-76, Table II).

Brominated Methyl Ester with 2 Equivalents NBS and Benzoyl Peroxide.—Three hundred mg. of the (20 hr.) brominated methyl ester was dissolved in 10 ml. of chloroform; 0.43 g. of NBS (2 equivalents on a C_9 basis) and 7.3 mg. of benzoyl peroxide were added and the mixture was heated 24 hr. at approximately 55°. This was worked up as above (II-115, Table II).

Reactions of NBS with the Lithium Salt of Lignin Sulfonic Acid and Its Fully Methylated Derivative.—Some of these reactions were run in absolute ethanol and later ones in absolute methanol. The procedure was the same as described above.

Reactions of NBS with the Lithium Salt of Lignin Sulfonic Acid in Benzene–Methanol.—The lithium salt was dissolved in the least possible amount of absolute methanol. Benzene was then added to make the benzene–methanol ratio 2 or 3:1. NBS was then added and dissolved. The solvent ratio was then brought up to 5–7 benzene:1 methanol without clouding the solution. The reaction was then carried out as before.

Dehalogenation. Aqueous KOH.—Dehalogenation experiments were run on 250–300 mg. samples of brominated lignin sulfonates which were dissolved in a small amount of water and made up to 15–20% KOH (5 ml.). At the end of 1 or 20 hr. the solution was strongly acidified (HCl). The precipitate was centrifuged and washed repeatedly with 6 N HCl and dried in a desiccator with phosphorus pentoxide and sodium hydroxide at 1 mm. For comparison, acid-washed samples were dialyzed against running water in a viscose membrane and the dialyzed solution passed through the ion-exchange resin to make the lithium salt (as described above). There was some loss in the process of dialysis but the product had the same bromine to C_9 ratio as the undialyzed product.

Collidine and Dimethylaniline.—Brominated samples were dissolved in a small amount of alcohol and a two- or threefold excess of the organic base was added. These mixtures were heated for one and two hours and at 60 and 80° under a condenser. The lignin was recovered by diluting with water, extracting with ether, dialyzing the remaining solution against running water for a week, and preparing the lithium salt. The bromine to C_9 ratios were in good agree-

(7) E.g., Freudenberg and Dietrich, *Ann.,* **563,** 146 (1949); *C. A.,* **43,** 6408 (1949).

(8) Peniston and McCarthy, THIS JOURNAL, **70,** 1327 (1948); Markham, Peniston and McCarthy, *ibid.,* **71,** 3599 (1949).

(9) It is now felt that lignin sulfonates carefully prepared in the laboratory would offer many advantages for extension of this work (e.g., Erdtman, Lindgren and Pettersson. *Acta Chem. Scand.,* **4,** 228 (1950); Lindgren, *ibid.,* **5,** 603 (1951)).

(10) Dow Chemical Co., Midland, Mich.

(11) H⁺-Charged resin treated with a slight excess of 5% lithium carbonate solution and thoroughly washed.

(12) King, Brauns and Hibbert, *Can. J. Research,* **13B,** 88 (1935); Tomlinson and Hibbert, THIS JOURNAL, **58,** 340 (1936).

(13) Ritter, Olleman, Pennington and Wright, *ibid.,* **72,** 1351 (1950).

(14) Dumas nitrogen run on several of the brominated (as well as dehalogenated) products showed absence of nitrogen.

ment with each other and with the samples dehalogenated with KOH.[14]

Acknowledgment.—The considerable number of microanalyses on which this work is based were done by Mr. Murray E. Taylor assisted by Miss M.

Styslinger, and by Mr. Werner Mauser, Zürich (carbon and hydrogen, and some of the sulfur and bromine analyses).

SEATTLE, WASHINGTON

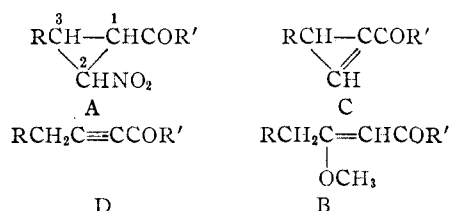[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Cyclopropanes. X.[1] The Reaction between Nitrocyclopropyl Ketones and Sodio Malonic Ester
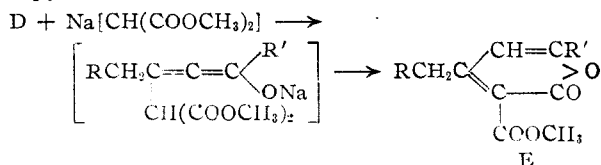
BY LEE IRVIN SMITH AND RALPH E. KELLY[2]

1-Benzoyl-2-nitro-3-phenylcyclopropane I has been subjected to the action of (a) sodio malonic ester and (b) sodium methoxide. Action of the former reagent produced the α-pyrone ester II; action of the latter reagent produced the methyl enol ether VI of the 1,3-diketone VII. Action of sodio malonic ester upon either the enol ether VI or the 1,3-diketone VII failed to produce any α-pyrone; hence, neither of these substances can be a precursor of the α-pyrone formed from I and sodio malonic ester. In an effort to correlate the formation of the pyrone with the mechanism of Smith and Engelhardt (ref. 5), the unsaturated nitro ketone IX has been prepared and subjected to the action of sodio malonic ester. This nitro ketone IX is so constituted that the double bond is α,β- with reference to the nitro group, but is β,γ- with reference to the carbonyl group. Although IX reacts with sodio malonic ester, the products are derived by addition of the reagent to IX acting as an α,β-unsaturated nitro compound, and no α-pyrone is formed. Hence, IX cannot be a precursor of the α-pyrone formed from I. The one remaining compound in the sequence proposed by Smith and Engelhardt which could be the precursor of the α-pyrone is the nitro ketone X which differs from IX in that the double bond is α,β-with reference to both the nitro group and the carbonyl group. A successful synthesis of X was not achieved.
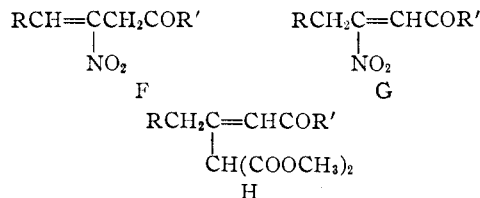
The reaction between nitrocyclopropyl ketones (A) and alkoxides produces, as the first isolable products, enol ethers of 1,3-diketones (B). To account for these products, Kohler and Smith[3] proposed that the initial step in the reaction involved conversion of the nitrocyclopropane, by loss of the elements of nitrous acid, into a cyclopropene (C). The cyclopropene then rearranged into an α,β-acetylenic ketone (D) which, by addition of the solvent alcohol, was converted into (B).

$$\overset{3}{R}\overset{1}{CH}—\overset{}{CH}COR' \qquad RCH—CCOR'$$

(structures A, C, B, D shown)

A   C

$RCH_2C{\equiv}CCOR'$ $RCH_2C{=}CHCOR'$
                                     OCH_3

D   B

Although neither the cyclopropene nor the acetylenic ketone could be isolated, support for the mechanism was obtained when it was found that action of sodio malonic ester upon (A) led to an α-pyrone (E),[3] for it had been shown previously[4] that α,β-acetylenic ketones did in fact react with sodio malonic esters with production of these α-pyrones.

$$D + Na[CH(COOCH_3)_2] \longrightarrow$$

$$\left[\begin{matrix} RCH_2C{=}C{=}C\!\!<^{R'}_{ONa} \\ CH(COOCH_3)_2 \end{matrix} \right] \longrightarrow RCH_2C\!\!<^{CH=CR'}_{C—CO}{>}O$$

                                                  $COOCH_3$

                                                    E

In previous papers of this series[5] it has been shown that an acetylenic ketone is not a likely intermediate in the transformation of a nitrocyclopropyl ketone into the enol ether of a 1,3-diketone, and a new mechanism for this transformation was suggested. One of the key intermediates of this mechanism was the β-nitro-β,γ-unsaturated ketone (F), formed from (A) by a "reverse Michael" reaction; by assuming, for (F), reasonable shifts of the double bond and replacement of the nitro group

$RCH{=}CCH_2COR'$ $RCH_2C{=}CHCOR'$
    NO_2 NO_2
     F   G

           $RCH_2C{=}CHCOR'$
                $CH(COOCH_3)_2$
                    H

by the anion (OR⁻) of a base, it was possible to account for the formation of the enol ethers actually isolated when several nitrocyclopropyl ketones reacted with alkoxides. This same intermediate (F) could also be the precursor of the α-pyrones when nitrocyclopropyl ketones react with sodio malonic ester; thus, a shift of the double bond in (F) into the α,β-position (G), followed by replacement of the nitro group by the malonate anion, would lead to (H) and thence to the α-pyrone (E).

In order to test these ideas the behavior of 1-benzoyl-2-nitro-3-phenylcyclopropane (I) toward sodio malonic esters and other bases has been examined. This cyclopropane was synthesized according to the method of Kohler and Engelbrecht[6]; the yield in the final cyclization was, however, only 33% as compared with 61% reported by the earlier workers. When the cyclopropane I was subjected to action of excess sodio methyl or ethyl malonate, the respective 3-carbalkoxy-4-benzyl-6-phenyl-α-

(1) Paper IX, L. I. Smith and E. R. Rogier, THIS JOURNAL, 73, 4049 (1951).

(2) Abstracted from a thesis by Ralph E. Kelly, presented to the Graduate Faculty of the University of Minnesota, in partial fulfillment of the requirements for the Ph.D. degree, August, 1951. du Pont Fellow, 1950-1951.

(3) E. P. Kohler and L. I. Smith, THIS JOURNAL, 44, 624 (1922).

(4) E. P. Kohler, ibid., 44, 379 (1922).

(5) L. I. Smith and V. A. Engelhardt, ibid., 71, 2671, 2676 (1949).

(6) E. P. Kohler and H. F. Engelbrecht, ibid., 41, 1381 (1919).