

lated in 12% yield and boiled at 46–49° (0.1 mm.). The heart-cut had a refractive index of 1.5520 at 25°.

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37; sapon. equiv., 164.2; quant. hydrogenation, 0.0488 g. hydrogen/g. sample. Found: C, 72.78, 72.99; H, 7.30, 7.10; sapon. equiv., 161.1, 168.9; quant. hydrogenation, 0.0492, 0.0482 g. hydrogen/g. sample.

2,4,6-Heptatrienol.—Commercial lithium aluminum hydride (16.7 g.) in 300 ml. of anhydrous ether was stirred under nitrogen for 300 minutes and then filtered from 2.1 g. of insoluble material into a separatory funnel. The ethereal solution of 14.6 g. (0.38 mole) of lithium aluminum hydride was added dropwise with stirring at 0° to a solution of 95.3 g. (0.69 mole) of methyl 2,4,6-heptatrienoate in 300 ml. of anhydrous ether at such a rate that the temperature was kept below 10°. After the addition was completed (3 hours), the mixture was stirred for 30 minutes at 0–10°. A solution of 44 ml. of concentrated sulfuric acid in 185 ml. of water was then added with stirring so that the temperature did not exceed 15°. The ether layer was separated and the aqueous layer extracted several times with ether. The combined ether extracts were washed with aqueous 5% sodium bicarbonate and then with water. After drying over magnesium sulfate, the ether was removed by distillation under reduced pressure and the residual oil was stirred with a solution of 28 g. of sodium hydroxide in 160 ml. of water under nitrogen for 4 hours to remove any ester. The mixture was extracted with ether and the combined extracts dried over magnesium sulfate. After removal of the ether under reduced pressure, the residual oil was distilled through a helix-packed column. The main fraction distilled at 44–47° (0.02 mm.) and weighed 49.1 g. (65% yield).

Anal. Calcd. for $C_{10}H_{10}O$: C, 76.32; H, 9.15; quant. hydrogenation, 0.0549 g. hydrogen/g. sample. Found: C, 75.88, 76.13; H, 8.98, 9.20; quant. hydrogenation, 0.0502, 0.0512 g. hydrogen/g. sample.

Hydrogenation of 2,4,6-Heptatrienol to *n*-Heptyl Alcohol.—2,4,6-Heptatrienol (17.4 g.) in absolute alcohol (50 ml.) was hydrogenated using 5% palladium-on-carbon (1 g.) at 40–50° under 1000 lb./sq. in. of hydrogen for 2 hours. The solution was filtered from catalyst and alcohol was distilled from the filtrate. Distillation of the residual oil gave 12.7 g. of product, b.p. 82–84° (16 mm.). The *N*-phenylcarbamate was prepared by heating this compound (1 g.) with phenyl isocyanate (0.5 ml.) on the steam-bath for 5 minutes. Recrystallization of the carbamate from alcohol-water gave colorless crystals, m.p. 57.5–58°. In the same manner *n*-heptyl *N*-phenylcarbamate, m.p. 58–58.5°, was prepared from *n*-heptyl alcohol, b.p. 83–83.5° (16 mm.). There was no depression in melting point on admixture of the two carbamates. Therefore, the hydrogenated product is *n*-heptyl alcohol.

Absorption Spectra.—The infrared spectra of heptatrienenitrile and methyl heptatrienoate are given in Fig. 1 and the ultraviolet absorption spectra of the nitrile and heptatrienol in Fig. 2. These spectra show bands at 3.2, 6.1, 10.2 and 10.8 microns from the $-\text{CH}=\text{CH}_2$ group, slightly shifted from the position for this group in simple olefins such as 1-octene. The lack of absorption band for the $-\text{C}\equiv\text{C}-\text{H}$ groups at 3.0 microns shows the absence of a terminal acetylenic CH bond. Absorption bands at 3.4 and 6.8 microns are not of sufficient intensity to allow CH_2 groups as a major constituent in either structure. The ultraviolet spectrum of the nitrile showed a series of strong bands about 2800 Å. while a similar absorption, shifted to the shorter wave lengths, is evident for the corresponding alcohol. The Raman spectrum of methyl heptatrienoate failed to show the characteristic lines near 2200 cm^{-1} for an internal triple bond. An exceedingly strong Raman line at 1630 cm^{-1} , indicative of conjugated double bonds, was observed.

WILMINGTON, DELAWARE

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

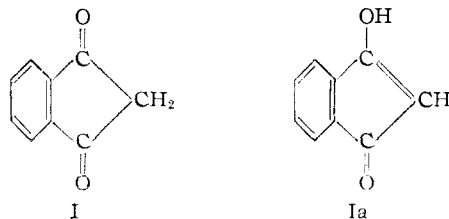
Some Adsorption Colors and Their Significance for Thermochromic and Tautomeric Effects. III. Experiments with Anthrone Derivatives, Nitrotoluenes, Spiropyran and Xanthydrols

BY ALEXANDER SCHÖNBERG, AHMED MUSTAFA AND WAFIA ASKER

RECEIVED MARCH 17, 1952

Activated alumina acquires a deep orange color when added to a cold colorless solution of 10-nitroanthrone, presumably because of the formation of the colored 10-nitroanthranol. Similar results are obtained in the case of 10-anilinoanthrone (orange color). Adsorptiochromism was also observed with the colorless 10,10-bianthronyl and with 2,4-dinitrotoluene and 5-nitroacenaphthene. Benzene solutions (cold or hot) of dibenzospiropyran are colorless; a deep violet adsorption color is produced with activated alumina or dried silica gel. Adsorptiochromism, piezochromism and thermochromism are discussed in the case of some pyrans and pyrones and their sulfur analogs: replacement of the oxygen by sulfur is detrimental to the development of color.

Recently,¹ it has been shown that when activated alumina is added to a colorless cold solution of 1,3-diketohydrindene (I), the inorganic material acquires a violet color at once. The theory was advanced that the violet color was due to the enolic form; in the colorless benzene solution, there exists an equilibrium ($\text{I} \rightleftharpoons \text{Ia}$) which strongly



(1) A. Schönberg, A. Mustafa and W. Asker, *THIS JOURNAL*, **73**, 2876 (1951).

favors the left-hand side, but the activated alumina preferentially adsorbs Ia, producing the adsorption color. It is also possible that the enol form (Ia) is produced by the action of the activated adsorbent. Ia has never been isolated as such, and it seems desirable to investigate the behavior of pairs of keto-enol tautomers toward activated alumina.

(1) **Experiments with (a) 10-Nitroanthrone.**—When to the colorless benzene solution of 10-nitroanthrone² is added a piece of activated alumina, a deep orange color is produced on the surface immediately. When the dried colored inorganic material is treated with aqueous ferric chloride solution, a green color is produced. 10-Nitroanthranol forms red needles; its yellow, alcoholic solution gives a green color with aqueous ferric chloride solution.

(b) **10-Anilinoanthrone (IIa).**—When the pale yellow benzene solution of IIa is treated with activated alumina, a yellowish-orange adsorption color is observed and the solution becomes yellow with a green fluorescence and then after

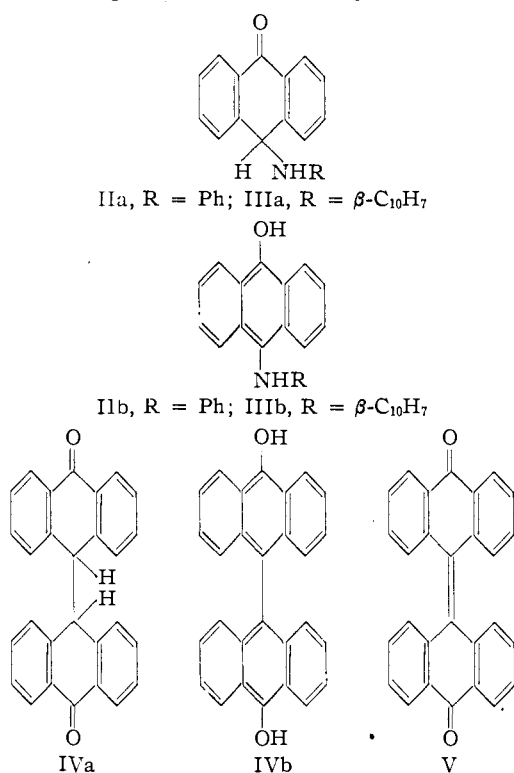
(2) Meyer and Sander, *Ann.*, **396**, 133 (1913).

some time orange. A similar color phenomenon is observed when dried silica gel is used. 10-Anilinoanthranol (IIb) forms an orange red solution in benzene which exhibits a yellowish-green fluorescence.

(c) 10- β -Naphthylaminoanthrone (IIIa).—This substance when treated as described in the case of IIa gives similar results.

(d) 10,10'-Bianthranyl (IVa) and Bianthranol (IVb).—The benzene solutions of IVa are colorless. When the freshly prepared solutions in alcohol are treated with aqueous ferric chloride, no color is observed. The benzene solutions of IVb are yellow and when the yellow alcoholic solutions are treated with aqueous ferric chloride, a vivid but transient green color³ is produced.

Activated alumina added to the colorless benzene solutions of IVa acquires an orange color, and when the alumina is allowed to dry and then immediately treated with an aqueous ferric chloride solution, a vivid but transient green color is observed. An orange color of the adsorbent was observed when activated alumina was added to the yellow benzene solutions of IVb and the experiment with aqueous ferric chloride gave the same transient green color.



When yellowish-green benzene solutions of bianthrone (V) were treated with activated alumina or silica gel as described in the case of IVa, no color phenomenon was observed.

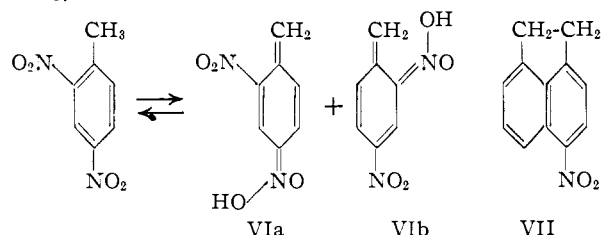
Discussion

We believe that in all cases, the enol form on the surface of the activated alumina is responsible for the adsorption color. With IIa or IIIa, the benzene solutions containing activated alumina acquire gradually the color of the enol forms. It is believed that IIb or IIIb, after being formed on the surface of the activated inorganic material, goes gradually into solution, enabling the activated material to convert another crop of molecules from the keto form to the enol form. Repetition of these processes leads to the formation of the enol form in quantity.

(2) Experiments with Aromatic Nitrohydrocarbons.—When the benzene solutions of *o*-nitrotoluene, *p*-nitrotoluene,

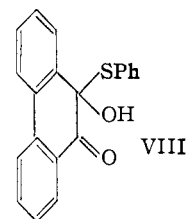
p-chloronitrobenzene, *m*-dinitrobenzene, *m*-nitrobenzaldehyde, ω -nitrostyrene, ethyl *p*-nitrocinnamate, α -nitronaphthalene and nitromethane,⁴ which are yellow or almost colorless, are treated with activated alumina, no color phenomenon is observed. When, however, the yellow benzene solutions of 2,4-dinitro- and 2,4,6-trinitrotoluene are treated with activated alumina, an immediate brownish-violet color is produced on the surface of the adsorbent.

We believe that the violet-brown color is connected with the change of the nitro to the aci-nitro form (*cf.* VIa and VIb in the case of 2,4-dinitrotoluene), the color change being due to the change from the benzenoid to the quinonoid system. A similar explanation is offered for the following. Activated alumina added to the yellow benzene solution of 5-nitroacenaphthene (VII) acquires a brown color changing to brownish-green after some time.



That the methyl group plays a role is seen from the fact that, *inter alia*, *m*-dinitrobenzene does not show the color phenomenon with activated alumina, but we do not want to state that the formation of adsorption colors of aromatic nitro compounds on alumina is restricted to those capable of forming an aci-form.

(3) Experiments with 10-Hydroxy-10-phenylmercapto-phenanthrone (VIII) and with 1,5-Dihydroxyanthraquinone.—When the pale yellow benzene solution of VIII⁵ is treated with activated alumina, a deep yellowish-brown color is developed immediately on the surface of the alumina. This color is identical with the adsorption color produced when working with phenanthraquinone solutions. One possible explanation of the phenomenon is that VIII is decomposed to phenanthraquinone on the surface of the activated alumina (head of adsorption) (*cf.* the decomposition of VIII at *ca.* 100° into phenanthraquinone and thiophenol⁵).



When alumina, not freshly activated, is added to the yellow chloroform solution of 1,5-dihydroxyanthraquinone, no color phenomenon is observed. However, freshly activated alumina becomes deep red immediately.

(4) Adsorption Colors of Spiroprans.—Many spiroprans give deep colors when adsorbed on silica gel or alumina. The majority of these com-

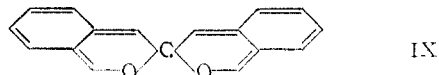
(4) *o*- and *p*-nitrotoluene do not condense with certain benzaldehydes or with *p*-nitrosodimethylaniline under the same conditions (*e.g.*, in the presence of piperidine) under which 2,4-dinitrotoluene (see Ullmann and Geschwind, *Ber.*, **41**, 2292 (1908); Skrap and Böhm, *ibid.*, **59**, 1007 (1926)) and 5-nitroacenaphthene (see Löhe, *Chem. Ber.*, **82**, 213 (1949)) condense. It seems from the above that *o*- and *p*-nitrotoluene have a smaller tendency to form "aci" compounds or the corresponding ions than 2,4-dinitrotoluene, or VII which is in accordance with adsorption behavior of *o*- and *p*-nitrotoluene on the one hand and 2,4-dinitrotoluene and VII on the other.

(5) Schönberg and Schütz, *Ber.*, **60**, 2344 (1927).

(3) Meyer, *Ber.*, **42**, 143 (1909); *Monatsh.*, **30**, 165 (1909).

pounds show a similar color when their colorless solutions (inert solvents, *e.g.*, anisole) are heated. One exception is 3'-methylbenzo- β -naphthospiropyran which dissolves in hot inert solvents without developing color. Nevertheless, this substance gives, as do related compounds, a colored adsorbate on silica gel and alumina.¹ This phenomenon has been recently discussed by Knott.⁶

We have now found a second example of this type. Dibenzospiropyran (IX) gives almost colorless solutions in boiling anisole or benzene. If, however, the cold benzene solutions are treated with dried silica gel or activated alumina, a deep violet color is produced at once on the surface.



(5) **Adsorption Colors of Some Arylated Xanthohydrols.**—The substances listed in Table I develop adsorption colors, as indicated in brackets, when their colorless or almost colorless benzene solutions are treated with dried silica gel. The color is presumably due to the formation of ions (*cf.* X, only one of the possible resonance structures is shown). No color phenomena were observed in the following cases: diphenyl-2-naphthylcarbinol (see Acree, *Ber.*, **37**, 625 (1904)); *p*-tolylidiphenylcarbinol (see Bistrzycki and Gyr, *Ber.*, **37**, 655 (1904)); and *p*-methylmercaptophenyldiphenylcarbinol (see Bistrzycki and Kuba, *Helv. Chim. Acta*, **4**, 969 (1921)).

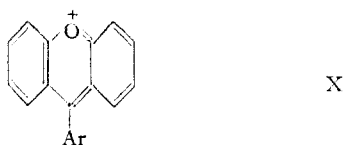


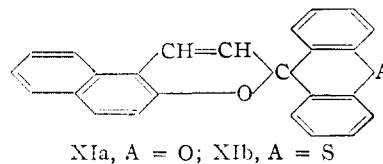
TABLE I

9-Phenylxanthohydrol ^a	(Yellowish-orange)
9- <i>p</i> -Methoxyphenylxanthohydrol ^b	(Orange)
9-Phenyl-3,4-benzoxanthohydrol ^c	(Orange)
9-Phenyl-1,2-benzoxanthohydrol ^c	(Orange)

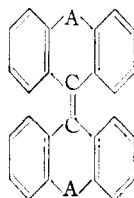
^a Ullmann and Engi, *Ber.*, **37**, 2371 (1904). ^b Gomberg and West, *This Journal*, **34**, 1528 (1912). ^c Mustafa and Hilmy, *J. Chem. Soc.*, 1343 (1952).

(6) **Thermochromic Properties of Oxygen Compounds as Compared with the Sulfur Analogs.**—Xantho- β -naphthospiropyran (XIa) dissolves in hot anisole (b.p. 153°) with a pink color which disappears on cooling. When to the cold, benzene solution of (XIa) is added activated alumina or dried silica gel, a vivid blue color is developed on the surface of the adsorbents.¹ In contrast, the hot, anisole solutions of the sulfur analog (XIb) were colorless, though in boiling diphenyl ether (b.p. 259°) or tetralin (b.p. 207°) a pink color was obtained which disappeared on cooling.⁷ When the cold benzene solutions of β -naphthothiaspiropyran (XIb) are treated with activated alumina or dried silica gel, only a very pale green adsorption color or no adsorption color is developed, respectively. This effect may be paralleled by the observation that dixanthylene (XIIa) is a strongly

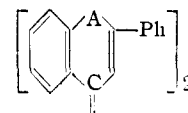
thermochromic substance,⁸ whereas the colorless dithiodixanthylene (XIIb) shows no striking thermochromic effect. Attention is also drawn to the piezochromism of the solid diflavylene⁹ (XIIIa), whereas the dithiodiflavylene (XIIIb) does not exhibit this property or only to a very slight degree.



XIa, A = O; XIb, A = S



XIIa, A = O; XIIb, A = S

XIIIa, A = O;
XIIIb, A = S

Experimental

The benzene used was dried over metallic sodium, the silica gel was Protek-Sorb, grade A or B; the alumina was obtained from Peter Spence and Sons, Ltd., London. When used as such, it is described as "not freshly activated." The activation of Protek-Sorb and the fresh activation of the alumina was carried out by heating in a small test-tube, using a free flame until the formation of water-drops on the cooler parts of the tube ceased (about one minute); the drops were then evaporated by heating with a free flame. The activated material was then placed on a filter paper, allowed to cool (about one minute) and used directly. The volume of the solutions (the authors worked with concentrated solutions) was about 1 cc. and the weight of the pieces of alumina and Protek-Sorb (grade B) was about 0.1 g.

In some cases, the activation of alumina was carried out in a vacuum and the material was allowed to cool also in a vacuum, but no difference was observed.

In all cases, decolorization was effected by treating the colored surface of the active material, benzene-wet, with methyl alcohol (elution).

The experiments were carried out at room temperature.

The experiments with aqueous ferric chloride solution and the colored, activated alumina were carried out by removing it from the benzene solution, washing and drying in the open on a filter paper and then directly treating it with a small drop of dilute, aqueous ferric chloride solution delivered from a melting point tube, open at both ends.

Experiments¹⁰ with 10-Anilinoanthrone (IIa) and 10- β -Naphthylaminoanthrone (IIIa). (a) **With Activated Alumina.**—When freshly prepared, pale yellow or almost colorless benzene solutions of (IIa) were treated with activated alumina, a yellowish-orange adsorption color was developed, which changed to a deep orange color (after about 3/4 hour depending on the concentration of the solutions) and the benzene solution acquires a deep yellowish-orange color starting from the benzene layer next to the surface of the inorganic material. In a parallel experiment without alumina, the benzene solution was pale yellow.

Working with saturated benzene solutions (containing undissolved solid IIa), the orange color of the inorganic material became more pronounced in a shorter time.

The experiments with (IIIa), which is difficultly soluble in benzene at room temperature, were carried out in saturated benzene solutions (containing IIIa in the solid state).

(b) **With Dried Silica Gel Grade "A".**¹¹—When the

(8) Schönberg and Schütz, *Ber.*, **61**, 478 (1928); Theilacker, Kortüm and Friedheim, *Chem. Ber.*, **83**, 508 (1950).

(9) Schönberg and Nickel, *Ber.*, **64**, 2323 (1931); **67**, 1795 (1934); Schönberg, Ismail and Asker, *J. Chem. Soc.*, 442 (1946).

(10) These experiments were carried out in the absence of light or in the presence of diffused sunlight.

(11) About 440 particles contained in 0.1 g. before heating.

(6) Knott, *J. Chem. Soc.*, 3043 (1951).

(7) Mustafa, *ibid.*, 2295 (1949).

above experiments were repeated with dried silica gel Grade "A" in place of activated alumina, the color of the adsorbates on the silica gel was deep red (after 24 hours) and the benzene solution acquired a deep, orange color. In a paral-

lel experiment without silica gel, the color of the benzene solution was a very pale yellow and yellow in the case of (IIa) and (IIIa), respectively.

GIZA, CAIRO, EGYPT

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, KANSAS STATE COLLEGE]

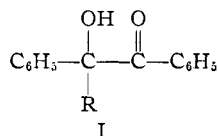
The Rearrangement and Cleavage of Benzoïn and α -Substituted Benzoins by Alkali¹

BY DEXTER B. SHARP² AND EDESEL L. MILLER

RECEIVED JULY 23, 1952

The cleavage by alkali of benzoïn and six α -substituted benzoins has been examined in detail. α -Phenylbenzoïn gave quantitative yields of benzhydrol and benzoic acid. α -(*o*-Tolyl)-benzoïn gave quantitative yields of benzhydrol and *o*-toluic acid. Benzoïn, α -methyl-, α -benzyl-, α -(*m*-tolyl)- and α -(*p*-tolyl)-benzoïn each gave varying quantities of four products, which indicated partial rearrangement prior to cleavage. Mechanisms are suggested for these reactions.

Acree³ observed that α -phenylbenzoïn (I, R = C₆H₅) was cleaved by hot alcoholic alkali and gave

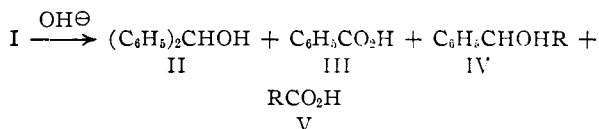


benzhydrol (II) and benzoic acid (III) in unspecified amounts. He reported also^{3b} that α -(1-naphthyl)-benzoïn gave benzoic acid and α -naphthylphenylcarbinol upon alkaline cleavage. Roger and McGregor⁴ reported similar scissions in which R was *o*- and *m*-tolyl and methyl. Pascual and Cerezo⁵ reported the alkaline cleavage of α -benzylbenzoïn to benzoic acid and phenylbenzylcarbinol. The results of Roger and McGregor⁴ suggested that a rearrangement may have occurred, but more complete studies of this reaction were lacking in the literature. In contrast, Temnikova⁶ reported that tri-substituted α -ketols (R₂COHCOR', R and R' alternatively methyl and phenyl) did not isomerize in alkali. Our interest in this reaction developed when Acree's³ cleavage of α -phenylbenzoïn was repeated and found to give quantitative scission into benzhydrol and benzoic acid. Since detection of rearrangement is impossible with α -phenylbenzoïn, attention was directed toward an examination of the cleavage of representative examples of I.

Preparation of α -Substituted Benzoins.—Excepting benzoïn itself, the starting compounds (I) were prepared by addition of the appropriate Grignard reagent to benzil. Benzoïn, α -methyl-, α -benzyl-, α -phenyl- and α -(*o*-tolyl)-benzoïn were crystalline solids and appeared to be single molecular species. The samples of α -(*m*-tolyl)- and α -(*p*-tolyl)-benzoïn were viscous liquids obtained by fractional distillation at reduced pressure. It seemed unlikely that the crystalline α -substituted benzoins were mixtures of isomeric α -ketols formed

during the Grignard reaction, and benzoïn itself is known to be one molecular species only. Reduction products of α -(*o*-tolyl)- and α -(*m*-tolyl)-benzoïn corresponded with compounds previously reported, and Zerewitinoff determinations of active hydrogen and carbonyl group content checked reasonably well for α -ketol structures. The homogeneity of the liquid α -substituted benzoins is probably subject to question.

Cleavage Reaction.—The α -arylbenzoins were cleaved easily in refluxing methanolic alkali and gave total product quantities accounting for 70–100% of the initial amount of α -ketol. Benzoïn, α -methyl- and α -benzylbenzoïn were unaffected under these conditions, but were cleaved at 160° in alkali-containing diethylene glycol with total product quantities accounting for 80–100% of the initial amount of α -ketol. The following formulation represents the general cleavage reaction, and all corresponding products were obtained from five of the seven compounds examined (R = H, CH₃, C₆H₅CH₂, *m*- and *p*-CH₃C₆H₄). The products



from α -phenylbenzoïn were mentioned above. Cleavage of α -(*o*-tolyl)-benzoïn gave only benzhydrol and *o*-toluic acid, confirming the report by Roger and McGregor.⁴ This suggests that complete rearrangement occurred, or that the starting compound was diphenyl-*o*-toluylcarbinol rather than the expected α -(*o*-tolyl)-benzoïn. The identities and relative quantities of the cleavage products from each reaction are summarized in Table I.

The cleavage of benzoïn itself to give benzhydrol, benzoic acid, benzyl alcohol and formic acid is evidence indicating partial rearrangement prior to cleavage. Knoevenagel and Arndts⁷ reported the cleavage of benzoïn to benzoic acid and benzyl alcohol in concentrated alkali, but apparently did not obtain benzhydrol or formic acid.

Roger and McGregor⁴ reported that α -methylbenzoïn gave only trace amounts of benzhydrol, whereas our results indicate that approximately

(7) E. Knoevenagel and J. Arndts, *Ber.*, **35**, 1982 (1902).

(1) Abstracted in part from the Ph.D. thesis submitted by Edsel L. Miller to the Graduate Faculty of Kansas State College, January, 1952. Contribution no. 281 from the Department of Chemistry.

(2) Monsanto Chemical Co., Dayton, Ohio.

(3) (a) S. F. Acree, *Am. Chem. J.*, **29**, 588 (1903); (b) *Ber.*, **37**, 2753 (1904).

(4) R. Roger and A. McGregor, *J. Chem. Soc.*, 442 (1934).

(5) J. Pascual Vila and J. Cerezo, *Anales. soc. espan. fis. quim.*, **24**, 395 (1926); *C. A.*, **21**, 3798 (1927).

(6) T. I. Temnikova, *Vestnik Leningrad Univ.*, 138 (1947); *C. A.*, **42**, 4155f (1948).