Anal. Calcd. for $C_{12}H_{20}N_2O_2$: neut. equiv., 224. Found: neut. equiv., 225.

Summary

1. The recently developed method for the preparation of ketones from aliphatic nitriles and aromatic Grignard reagents has been adapted to the preparation of ketones which may be used as intermediates in the synthesis of potential antimalarial or antitubercular drugs.

2. The mild method of reduction employing zinc dust and acetic acid has been adapted to the reduction of certain oximes to diamines.

3. A number of new intermediates and certain new quinacrine analogs have been synthesized.

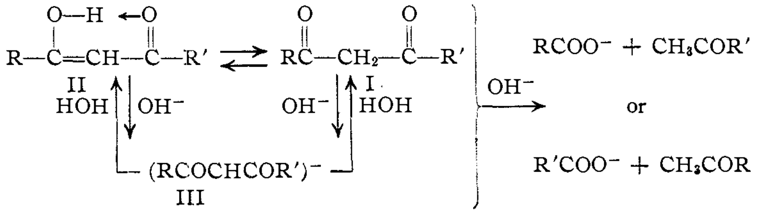
DURHAM, N. C. RECEIVED AUGUST 2, 1948

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, DUKE UNIVERSITY]

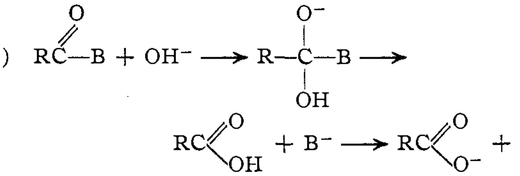
Alkaline Cleavage of Unsymmetrical β-Diketones. Ring Opening of Acylcylohexanones to Form ε-Acyl Caproic Acids[1]

BY CHARLES R. HAUSER, FREDERIC W. SWAMER AND BETTY I. RINGLER

There is evidence[2,3,4] that the cleavage of β-diketones by aqueous alkali to give carboxylic acids and ketones is concerned with the ketonic form (I) rather than with the enolic form (II) or with the anion (III) into which both (I) and (II) are first largely converted reversibly.



Perhaps the best evidence for the cleavage of (I) is that α,α-disubstituted β-diketones, which cannot be enolized or ionized, undergo alkaline cleavage much more rapidly than the unsubstituted compounds[4] and that the relative yields of the two possible acids from the cleavage of *p*-chloro, *p*-bromo and *p*-methoxydibenzoylmethanes are approximately the same as those from the corresponding mono-methylated β-diketones, the enolization of which appears to be almost completely suppressed.[3] Since the cleavage amounts to a reverse Claisen condensation, it is presumably initiated by the attack of hydroxyl ion at the carbonyl carbon. The mechanism for the cleavage[2] and also that for the alkaline hydrolysis of esters,[5] the relationship to which is considered below, may be illustrated by the following general equation in which B represents CH_2COR' or OR', respectively.[6]

(1) 

$$\mathrm{R\overset{O}{\overset{/\!/}{C}}{-}B + OH^- \longrightarrow R{-}\overset{O^-}{\underset{OH}{C}}{-}B \longrightarrow}$$

$$\mathrm{RC}\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{OH}} + \mathrm{B^-} \longrightarrow \mathrm{RC}\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O^-}} + \mathrm{BH}$$

Since the relative yields of the two possible acids, RCOOH and R'COOH, from the cleavage of an unsymmetrical β-diketone (1) would depend on the relative rates of reaction of the two carbonyl groups with hydroxyl ion, a direct relationship might be expected between these yields and the relative rates of alkaline hydrolysis of the corresponding ethyl esters, $RCOOC_2H_5$ and $R'COOC_2H_5$, respectively. Actually such a relationship can be deduced from the results obtained by earlier workers with certain substituted dibenzoylmethanes, such as *p*-methoxy,[3] *p*-chloro[2,3] and *p*-nitro[2] dibenzoylmethanes, and with benzoylacetone.[7] In each case the acid whose ethyl ester undergoes alkaline hydrolysis the more readily is obtained in the greater yield.[8] However, the relationship fails with *o*-chlorodibenzoylmethane,[9,10]

A direct relationship might also be expected between the relative yields of the *p*-substituted benzoic acids produced on the cleavage of a series of *p*-substituted dibenzoylmethanes or of a series of *p*-substituted benzoylacetones and the relative rates of alkaline hydrolysis of the corresponding ethyl esters. In these cases the R group in both (I) and equation (1) is varied while the R' group

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[1] Reported at the Chicago Meetings of the American Chemical Society, September, 1946, and April, 1948.

[2] Bradley and Robinson, *J. Chem. Soc.*, **129**, 2356 (1926).

[3] Bickel, THIS JOURNAL, **67**, 2204 (1945).

[4] Kutz and Adkins, *ibid.*, **52**, 4391 (1930).

[5] See Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 354.

[6] It is possible that, with certain β-diketones which have fixed enolic structures, the enolic form or its anion is cleaved. See Fieser, THIS JOURNAL, **51**, 940 (1929). It is also possible that even with certain ordinary β-diketones the enolic form is cleaved, but, if so, the carbonyl group would presumably be involved (see Beckham and Adkins, *ibid.*, **56**, 1119 (1934)), the mechanism being represented by equation (1) in which B is CH=C(OH)R.

[7] Adkins and Kutz, *ibid.*, **52**, 4036 (1930).

[8] Bradley and Robinson (ref. 2) have pointed out that the relative yields of the two possible acids from substituted dibenzoylmethanes are in general related directly to the strengths of the acids. However, this relationship fails with benzoylacetone (see ref. 7).

[9] Bickel, THIS JOURNAL, **68**, 865 (1946).

[10] The failure of the relationship with the ortho substituted dibenzoylmethane is not surprising since steric factors should be especially operative in such cases and these factors might affect the rates of cleavage of β-diketones and of the alkaline hydrolysis of esters to considerably different degrees. Even with the para-substituted dibenzoylmethanes, the relationship is only qualitative; of course a quantitative relationship could hardly be expected as the two types of reactions have been carried out under different conditions.

in (I) and the B group in equation (1) is kept constant as C_6H_5 or CH_3 and $CH_2COC_6H_5$ or CH_2COCH_3, respectively. Actually this "series" relationship has been realized. In Table I are given the yields of para-substituted benzoic acids obtained by earlier workers from para-substituted dibenzoylmethanes and by us from para-substituted benzoylacetones, together with the rates of alkaline hydrolysis of the corresponding ethyl esters. In both series the yields of the para-substituted benzoic acids increase as the rates of alkaline hydrolysis of the corresponding ethyl esters increase.[11] Also, as with the *p*-substituted dibenzoylmethanes, the relative yields of *p*-substituted benzoic acids and acetic acid (estimated by difference) from the cleavage of each of the *p*-substituted benzoylacetones (Table I) are related directly to the relative rates of alkaline hydrolysis of the two corresponding ethyl esters. However, neither the relationship involving the yields of the two possible acids from a particular β-diketone, nor the "series" relationship appears to hold very well with purely aliphatic β-diketones.[7] We have found that, on alkaline cleavage, caproylacetone and lauroylacetone form mainly caproic and lauric acids although the ethyl esters of these acids might be expected to undergo alkaline hydrolysis less readily than ethyl acetate.

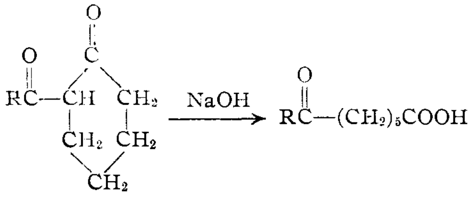
TABLE I

ALKALINE CLEAVAGE OF *p*-$XC_6H_4COCH_2COC_6H_5$ AND *p*-$XC_6H_5COCH_2COCH_3$

X	% Yields of *p*-XC_6H_4COOH from *p*-XC_6H_4-$COCH_2COC_6H_5$	*p*-XC_6H_4-$COCH_2COCH_3$	10^4K^a
CH_3O	42^b	13	1.15
CH_3	...	15	2.51
H	...	28	6.21 (5.50)
Cl	60^b	36	23.7
NO_2	81^c	78	567 (720)

[a] Rate constant (liters per mole sec.) for alkaline hydrolysis of these ethyl esters in 85% ethanol at 25°. From Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., p. 121. [b] See ref. 3. [c] See ref. 2.

Ring Cleavage.—Acylcyclohexanones may undergo alkaline cleavage either at the acyl group or at the ring carbonyl group. Cleavage at the latter position involves ring opening to form ε-acyl caproic acids.



Earlier workers have reported such ring cleavages with benzoyl[12] and acetyl[13] cyclohexanones but no yields were given.[14] We have effected these ring cleavages and also those with propionyl and anisoyl-cyclohexanones in satisfactory yields. Our results are summarized in Table II. As might be expected, the yield of ε-anisoylcaproic acid was somewhat higher than that of ε-benzoylcaproic acid and the yield of ε-propionylcaproic acid was somewhat higher than that of ε-acetylcaproic acid when the reactions were carried out under the same conditions. However, when the reaction was carried out on a 0.5 mole scale the yield for ε-acetylcaproic acid was improved considerably, although that for ε-benzoylcaproic acid was not. Also, the corresponding cleavage of benzoylcyclohexanone with sodium methoxide in absolute methanol to form methyl ε-benzoylcaproate has been effected in good yield. Since the acyl- and aroylcyclohexanones are readily prepared by the acylation or aroylation of cyclohexanone,[15,16] the present method for the preparation of these acyl and aroyl caproic acids appears to be more convenient than those described previously.[17,18]

TABLE II

ALKALINE CLEAVAGE OF RCO-CYCLOHEXANONES

R	$RCO(CH_2)_5COOH$ Yield, %			Neutral equiv. Calcd.	Found
		°C.	Mm.		
CH_3	46 (60^a)	B. 160–162	4^b	158.1	157.5
C_2H_5	60	B. 150–151	2^c	172.1	171.5
C_6H_5	70^e	M. 84–85^d		220.3	220.6
p-$CH_3OC_6H_5$	90	M. 129–130		250.3	249.7

[a] Obtained on a 0.5 mole scale. [b] See ref. 13. [c] Blaise and Koehler, *Compt. rend.*, **148**, 490 (1909). [d] See ref. 12. [e] The yield was the same when the reaction was carried out on the 0.5 mole scale at reflux temperature or on the 0.15 mole scale at room temperature.

Similarly, α-acetylcyclopentanone, on alkaline cleavage, undergoes ring opening to form δ-acetylvaleric acid. Under similar conditions, ring opening occurred to a greater extent with the acetylcyclopentanone than with the acetylcyclohexanone.

In contrast to benzoylcyclohexanone, benzoyltetralone and benzoylhydrindone undergo alkaline cleavage largely at the benzoyl group to form benzoic acid and the corresponding ketone.

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[11] It seems possible that this "series" relationship might be realized even with certain ortho-para-substituted dibenzoylmethanes such as *p*-X—$C_6H_4COCH_2COC_6H_4$—CH_3-*o* or *p*-X—$C_6H_4COCH_2COC_6H_4$—Cl-*o* if the ortho-substituted group is kept constant and the para-substituent is varied.

[12] Bauer, *Ann. chim. phys.*, [9] **1**, 393 (1914).

[13] Leser, *Compt. rend.*, **141**, 1032 (1905).

[14] Bauer (ref. 12) reports a 50% yield of ε-benzoylcaproic acid from benzoyl chloride and sodiocyclohexanone, by alkaline cleavage of the crude intermediate. However, in an attempt to reproduce this result, we have obtained only a poor yield of the acid.

[15] Levine, Conroy, Adams and Hauser, THIS JOURNAL, **67**, 1510 (1945).

[16] Hauser, Ringler, Swamer and Thompson, *ibid.*, **69**, 2649 (1947).

[17] (a) Auger, *Ann. chim.*, [6] **22**, 360 (1891); (b) Etaix, *ibid.*, [7] **9**, 391 (1896); (c) Hill, THIS JOURNAL, **54**, 4105 (1932); (d) Plant and Tomlinson, *J. Chem. Soc.*, 1092 (1935); (e) Billmann and Travis, *Proc. Indiana Acad. Sci.*, **54**, 101 (1945), *C. A.*, **40**, 1826 (1946).

[18] The recently developed method of Papa, Schwenk and Hankin (THIS JOURNAL, **69**, 3018 (1947)) for preparation of ω-aroyl carboxylic acids employing the Friedel-Crafts reaction with ester-acid chlorides of dibasic acids, might also be convenient for the preparation of certain ε-aroyl caproic acids.

Experimental[19]

p-Nitroacetophenone was prepared from *p*-nitrobenzoyl chloride and malonic ester as described previously.[20] Employing this method *p*-methoxyacetophenone (b. p. 150–152° (25 mm.))[21] was obtained in 87% yield from *p*-methoxybenzoyl chloride and malonic ester. Cyclopentanone was prepared according to the method described in "Organic Syntheses."[22] Phenyl anisate (m. p. 73–74°)[23] was prepared by Mr. D. F. Thompson of this Laboratory from anisoyl chloride and phenol according to the general method described previously.[24]

Preparation of β-Diketones.—Benzoylcyclohexanone, benzoyltetralone and benzoylhydrindone were prepared by benzoylation of the corresponding ketones with phenyl benzoate by means of sodium amide as described previously.[25] Employing this same general procedure anisoylcyclohexanone (m. p. 114–116°) was prepared in 46% yield from phenyl anisate and cyclohexanone.

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.37; H, 6.94. Found: C, 72.30; H, 6.77.

The remainder of the β-diketones used in this work have been prepared by acylation of the appropriate ketones with acetic anhydride (or propionic anhydride) by means of boron trifluoride. *p*-Nitrobenzoylacetone was prepared as described previously.[26] Benzoylacetone (m. p. 60–61; yield 50%),[27] *p*-methylbenzoylacetone (b. p. 154–155 (14 mm.), yield 62%),[28] *p*-methoxybenzoylacetone (m. p. 53–54, yield 25%)[29] *p*-chlorobenzoylacetone (m. p. 72–73°), acetylcyclohexanone (b. p. 96-97 (10 mm.), yield 35%),[27] propionylcyclohexanone (b. p. 123–125 (20 mm.), yield 35%),[27] and acetylcyclopentanone (b. p. 71-73 (8 mm.), yield 33%)[30] were prepared according to a modification of a previously described procedure.[26] After saturation with boron fluoride the mixture was stirred for one or two hours at room temperature. The complex was then hydrolyzed by pouring into sodium acetate solution[26] and refluxing the mixture for thirty minutes. The mixture was cooled to room temperature and extracted with two 150-ml. portions of ligroin (30–60°). The ligroin extract was washed with saturated sodium bicarbonate solution until free of acetic acid, then with a little water, and dried over drierite. The ligroin was removed on a steam-bath and the residue was distilled or recrystallized. The *p*-chlorobenzoylacetone is described here for the first time.

Anal. Calcd. for $C_{10}H_9O_2Cl$: C, 61.06; H, 4.61; Cl, 18.05. Found: C, 61.10; H, 4.45; Cl, 18.00.

Cleavage of *p*-Substituted Benzoylacetones.—The diketone (0.01 mole) was weighed into a 125-ml. Erlenmeyer flask and dissolved in 80 ml. of 1% aqueous sodium hydroxide. The resulting solution was kept in an oven at 38° for a period of five days. At the end of this period no precipitate formed when a portion of the solution was saturated with carbon dioxide, and the solution gave no enol test with ferric chloride. The hydrolysate was extracted with two 100 ml. portions of ether to remove the ketone, then heated on the steam-bath to remove dissolved ether. The resulting aqueous solution of the sodium salts of *p*-substituted benzoic acid and acetic acid was acidified with hydrochloric acid and made up to a volume of 200 ml. with water. After standing twenty-four hours at room temperature, the precipitated acid was filtered through a weighed, sintered glass filter plate, washed with a little water, and dried to constant weight in a desiccator. A correction was applied for the solubility of the acid. In the case of benzoylacetone, the benzoic acid was extracted from the acid solution with two 100-ml. portions of ether, the ether removed, and the solid dried to constant weight in a desiccator. The *p*-substituted benzoic acids obtained in this manner were essentially pure, having the melting points reported in the literature. The yields are given in Table I.

Cleavage of α-Acyl and Aroylcyclohexanones and Related β-Diketones.—The diketone (0.15 mole) was dissolved in cold 5% sodium hydroxide solution (10% excess) and the resulting solution refluxed for one and a half hours. The solution was cooled in an ice-bath and the ketone was removed by extraction with ether. In the case of acetyl- and propionyl cyclohexanones the aqueous phase was made acid with concd. hydrochloric acid, saturated with salt, and the desired ε-acylcaproic acid was extracted with ether. The ether extract was dried over drierite, the ether removed, and the residue distilled through a 10-cm. Vigreux column. In the case of benzoyl and anisoyl cyclohexanones, the aqueous solution of the sodium salt, after removal of the ketone, was heated on the steam-bath to remove dissolved ether, then made acid with concd. hydrochloric acid. The precipitated acid was filtered off and recrystallized from dilute ethanol. The yields and physical constants of the products from acyl and aroyl cyclohexanones are given in Table II.

Acetylcyclopentanone was cleaved according to the procedure used for the acylcyclohexanones. The δ-acetylvaleric acid (b. p. 147–149 (3 mm.), neut. equiv., calcd. 144.1, found 144.2) was obtained in yield of 56%.

Caproylacetone, on cleavage according to this same procedure gave a 69% yield of caproic acid, b. p. 140–142 (99 mm.), neut. equiv. calcd. 116.2, found 115.8. Correspondingly, lauroylacetone gave 65% of lauric acid, b. p. 170–171 (12 mm.), neut. equiv. calcd. 200.16, found 203.0.

Alcoholysis of Benzoylcyclohexanone with Sodium Methoxide.—Clean-cut sodium (2.5 g., 0.1 mole + 10%) was dissolved in 100 ml. of absolute methanol and 20.2 g. (0.1 mole) of benzoylcyclohexanone was added. The solution was refluxed on a steam-bath for a period of five hours. The reaction mixture was cooled in an ice-bath and dry hydrogen chloride was passed in until the mixture was just neutral. The precipitated sodium chloride was filtered and washed with ether, the washings being added to the filtrate. Most of the methanol was removed by heating on a steam-bath under aspirator vacuum. Fifty ml. of ether was added to the residue to precipitate all remaining sodium chloride. The product was filtered, the salt washed with ether, washings were added to the filtrate, and the resulting ether solution of the ester was dried over drierite. The ether was removed on a steam-bath and the residue was distilled under reduced pressure. There was obtained a 4.7 g. forecut, consisting mainly of cyclohexanone and methyl benzoate, and 14.0 g. (60%) of methyl ε-benzoylcaproate, b. p. 200–206 (17 mm.).[31] A small amount of the ester was saponified in 20% sodium hydroxide to the ε-benzoylcaproic acid, m. p. 84–85°.

Cleavage of Benzoyltetralone and Benzoylhydrindone.—The cleavage was carried out according to the method of Johnson.[32] To 80 ml. of 1% sodium hydroxide solution was added 1.2 g. of the diketone. The mixture was steam distilled until the drops of distillate were clear. Enough alcohol was added to the heated distillate to render the globules of oil soluble. Semicarbazide hydrochloride (1.0 g.) and 1 g. of sodium acetate were added. On cooling, the

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[19] Analyses are by Oakwold Laboratories, Alexandria, Virginia.

[20] Walker and Hauser, THIS JOURNAL, **68**, 1386 (1946).

[21] Klages and Lickroth, *Ber.*, **32**, 1559 (1899), give 152–154° (26 mm.), for this compound.

[22] "Organic Syntheses," Coll. Vol. I, Ed. by Gilman and Blatt, John Wiley and Sons, Inc., New York, N. Y., p. 192.

[23] Nencki, German Patent, 46,756; Friedlander, "Fortschritte der Teerfarbenfabrication," **2**, 137 gives m. p. 75–76°.

[24] Baumgarten, Walker and Hauser, THIS JOURNAL, **66**, 303 (1944).

[25] Hauser, Ringler, Swamer and Thompson, *ibid.*, **69**, 2649 (1947).

[26] Walker and Hauser, *ibid.*, **68**, 2742 (1946).

[27] Adams and Hauser, *ibid.*, **67**, 284 (1945).

[28] Meerwein and Vossen, *J. prakt. Chem.*, **141**, 149 (1943).

[29] This diketone has been prepared by Dr. H. G. Walker in this Laboratory by the acetylation of anisole with excess acetic anhydride in the presence of boron trifluoride. The results will soon be published.

[30] Blaise and Koehler, *Compt. rend.*, **148**, 1402 (1909). The diketone forms a grey-green copper salt which decomposes without melting at about 240°.

[31] Bauer, *Ann. chim. phys.*, [9] **1**, 403 (1914).

[32] Johnson, THIS JOURNAL, **65**, 1317 (1943).

semicarbazone of tetralone precipitated as white crystals (87%). The homogeneous alkaline residue, on acidification, precipitated benzoic acid, m. p. 119–120°, mixed m. p. 119–120°. In the case of benzoylhydrindone the diketone was not so soluble, however, and after 300 ml. of distillate had been collected, the undissolved diketone was filtered and weighed. The semicarbazone (77%) melted at 230–231° (reported m. p. 233°).[33] Acidification of the alkaline residue gave a 10% yield of a compound melting at 88–89° after recrystallization from alcohol, and which is presumed to be 1-benzoyl-2-(2-carboxyphenyl)-ethane.

Summary

1. The relative yields of the two possible acids and the relative yields of the series of para-substituted benzoic acids from the alkaline cleavage of para-substituted dibenzoylmethanes and para-substituted benzoylacetones have been related to the relative rates of alkaline hydrolysis of the corresponding ethyl esters.

2. Certain ϵ-acyl and ϵ-aroyl caproic acids have been prepared in satisfactory yield by the alkaline cleavage, involving ring opening, of α-acyl and α-aroyl cyclohexanones. Similarly, δ-acetylvaleric acid has been obtained from α-acetylcyclopentanone.

DURHAM, NORTH CAROLINA RECEIVED AUGUST 2, 1948

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[33] Huntress and Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 361.

[CONTRIBUTION FROM KOPPERS COMPANY, INC., MULTIPLE FELLOWSHIP ON TAR SYNTHETICS, MELLON INSTITUTE]

Catalytic Alkylation of Indan and Tetralin by Olefins, Alcohols and Diethyl Ether

BY WALTER M. KUTZ, J. E. NICKELS, J. J. MCGOVERN AND B. B. CORSON

This paper describes the alkylation of indan and tetralin by olefins, alcohols and diethyl ether in the presence of typical alkylation catalysts. The alkylation of tetralin by cyclopentene and cyclohexene[1] in the presence of aluminum chloride, and by ethylene[2] with phosphoric acid as catalyst has been reported; the alkylation of both indan[3] and tetralin[4] is claimed in patents.

The catalysts employed in the present work were alumina–silica, "solid phosphoric acid," aluminum chloride, sulfuric acid and hydrogen fluoride—continuous operation with the first two catalysts and batch operation with the last three.

Indan and tetralin underwent extensive condensation reactions under the influence of alumina–silica and aluminum chloride.[5] The high boiling products contained condensed ring systems as evidenced by their high refractive indices. This new condensation reaction of indan is being studied.

Monoalkyl indans and monoalkyltetralins can exist in two isomeric forms depending upon the location of the alkyl group with respect to the cycloparaffinic ring. All the monoalkylated products obtained in this investigation were isomer mixtures, and the isomer distribution in the mixtures depended upon the catalyst and/or conditions. For example, isopropylation of tetralin at 5° with concentrated sulfuric acid yielded approximately equal amounts of the 5- and 6-isomers, whereas isopropylation at 300° over alumina–silica produced mainly the 6-isomer.

The conventional method of establishing the structure of an organic compound involves the assumption that the sample contains only one species, and the acceptance of a minor yield of a known derivative as indicative of the structure of the original compound. Boiling point is often accepted as criterion of homogeneity without proof that the possible mixture is separable by the distillation employed. In the case of an acknowledged isomer mixture, the unjustified assumption is often tacitly made that the original isomer composition is preserved in the derivative, regardless of yield. We have attempted to avoid these suppositions.

The isomeric compositions of the monoalkylindan mixtures obtained in the present study were established by the ultraviolet absorption spectra of the mixed benzenetricarboxylic acids produced by permanganate oxidation. Inasmuch as the average yield of acid was 80%, the isomer composition of the mixed acids was fairly representative of the isomer composition of the antecedent hydrocarbon mixture. The composition of the monoalkyltetralins could not be established in similar manner because of poor oxidation yields. For example, a fifty–fifty mixture of 5- and 6-isopropyltetralins gave a 25% yield of mixed acids containing 80% of hemimellitic acid and 20% of trimellitic acid. The isomer compositions of the monoalkyltetralins were established by the ultraviolet and infrared absorption spectra of the monoalkylnaphthalenes obtained by sulfur dehydrogenation of the alkyltetralins (also by the melting point of the picrate in the case of the *t*-butylnaphthalenes). Spectroscopic technique is ideally suitable for the analysis of isomer mixtures, a task which is usually difficult and often impossible by conventional methods.

Incidentally, the statement of Tsukervanik and Terent'eva[6] that 1-monoalkylnaphthalenes are

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[1] Pokrovskaya and Suschik, *J. Gen. Chem.* (*U. S. S. R.*), **9**, 2291 (1939); Pokrovskaya and Stephantseva, *ibid.*, **9**, 1953 (1939).

[2] Ipatieff, Pines and Komarewsky, *Ind. Eng. Chem.*, **28**, 222 (1936).

[3] German Patent 80,158 (1895).

[4] U. S. Patents 1,667,214 (1928); reissue 17,548 (1928); 1,741,472 (1929); 1,766,344 (1930).

[5] Schroeter (*Ber.*, **57**, 1990 (1924)) reported that aluminum chloride converted tetralin into a variety of products including anthracene, hydrogenated phenanthrene and ditetralyl.

[6] Tsukervanik and Terent'eva, *J. Gen. Chem.* (*U. S. S. R.*), **7**, 637 (1937).