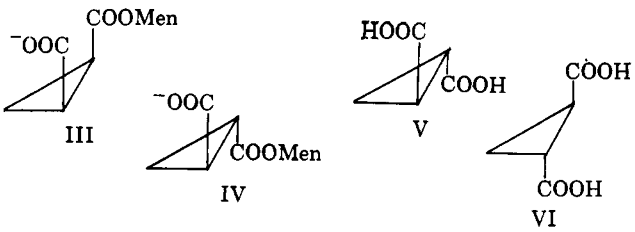

III IV V VI

over *trans* diacid.[6] The menthyl group should hinder saponification of that ester, while the carboxylate anion should stabilize the adjacent position towards isomerization, at least relative to the ease of isomerization of the ester position. These two factors should lead to isomerization at the next step to produce IV. When the menthyl group eventually is saponified, the resulting *trans* diacid V will be the enantiomer of *trans* diacid VI, obtained directly by saponification of the *trans* diester.

Some isomerization of the *cis* diester undoubtedly will occur, but this should lead to *racemic* diacid. The rotations of the *trans* diacids obtained should be roughly proportional to the excess of one isomer over the other. For the present system, it is probably true that the *cis* to *trans* ratio in benzene will always be less than the *trans* to *cis* ratio in dimethylformamide. These two factors, isomerization of the diester and difference in the relative isomer ratios, should both operate so as to make the optical yield in benzene smaller than that in dimethylformamide. This is consistent with observation.[7]

In summary, it is suggested that partial asymmetric synthesis of the 1,2-cyclopropanedicarboxylate system is independent of the solvent, but that the solvent does control the *cis* to *trans* isomer ratio; and that the observed formation of enantiomeric *trans*-1,2-cyclopropanedicarboxylic acids can be accounted for by an asymmetric *cis* to *trans* isomerization during saponification.[7]

Experimental[8]

(−)-Menthyl chloroacetate was prepared in 87% yield, b.p. 125–126° (10 mm.).[9,10] *cis*-1,2-Bis(acetoxymethyl)cyclopropane, b.p. 115–120° (13–14 mm.), 46% yield, and *trans*-1,2-bis(acetoxymethyl)cyclopropane, b.p. 125–128° (17–18 mm.), m.p. 43–45° (petroleum ether, b.p. 30–60°), 67% yield, were prepared from the pure *cis* and *trans* dimethyl cyclopropanedicarboxylates essentially as described by Blomquist and Longone[5] for the *trans* isomer. Gas phase chromatographic analyses were made with a Beckman GC-2A chromatograph operating at 190° with a Beckman Column No. 70026.

Reaction in Benzene Diluent.—Methyl acrylate (10.4 g., 0.24 mole) and (−)-menthyl chloroacetate (28.0 g., 0.12 mole) were added to sodium hydride (2.88 g., 0.12 mole) in benzene (10 ml.). Methanol then was added dropwise very slowly until a convenient, steady rate of gas evolution was obtained. The reaction was maintained between 24–26° by a water bath. Gas evolution stopped after about 4 hr. and after an additional half hour of stirring, water was added, and the organic phase isolated and dried. Removal of the benzene at aspirator pressure left 39.1 g. of crude ester.

A.—Half of the crude ester was saponified with potassium hydroxide (13.4 g., 0.24 mole) in refluxing ethylene glycol (940 ml.).[4] After 72 hr., about 80% of the ethylene glycol was removed by distillation and water was added to the residue which was extracted continuously with ether until no more neutral material was removed. The aqueous solution then was acidified and extracted continuously with ether for 24 hr. Evaporation of the acidic ether extract left a mush which was diluted with a small amount of chloroform and filtered. The solid, 2.7 g., was identified as essentially pure *trans*-1,2-cyclopropanedicarboxylic acid, m.p. 174–176°, by its infrared spectrum; the yield was 35%. No indication for the presence of *cis* isomer was observed.

B.—The second half was reduced and acetylated essentially by the procedure of Blomquist and Longone,[5] but a slight modification of the work-up was used. After filtration of the metal acetate salts, the filtrate was washed with water, and the washes were extracted with ether. The combined ether extracts and organic filtrate were dried and distilled. The product fraction was taken over the range 105–135°(27 mm.) and amounted to 14.2 g.; there was negligible pot residue. This distillate was analyzed by gas phase chromatography; the chromatogram peaks were identified by comparison of retention times with those of known compounds. The analytical results are shown in Table I.

Reaction in Dimethylformamide.—Using dimethylformamide (50 ml.) in place of benzene, the reaction sequence was repeated. The crude ester amounted to 36.2 g. Reduction–acetylation of half of this gave 13.6 g. of product acetates which were analyzed by gas phase chromatography; the results are shown in Table I.

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(6) L. L. McCoy, *J. Am. Chem. Soc.*, **80**, 6568 (1958).

(7) The most obvious way of refuting or establishing a direct "solvent effect" in partial asymmetric synthesis would be to isolate the *trans* diacetate (I) from the reduction–acetylation sequence for each solvent and compare their rotations. The small yield of the *trans* isomer in the benzene solvent and the close boiling points of the *cis* and *trans* isomers almost demands that separation be accomplished by preparative scale gas chromatographic equipment; unfortunately, the author does not have the necessary equipment.

(8) Melting points were taken on a Fisher-Johns hot stage and are corrected; boiling points are uncorrected.

(9) K. Sisido, O. Nakanisi, and H. Nozake, *J. Org. Chem.*, **26**, 4878 (1961).

(10) C. R. Hauser, B. E. Hudson, B. Abramovitch, and J. C. Shivers, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N.Y., 1955, p. 142.

Improved Procedures for Converting Higher α-Olefins to Methyl Ketones with Palladium Chloride

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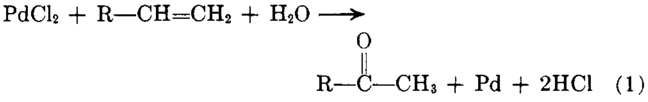
An attractive approach to the synthesis of methyl ketones from normal α-olefins has been described by J. Smidt, *et al.*[3] Their procedure employs an aqueous solution of palladium chloride to oxidize the olefin and utilizes the presence of cupric chloride and oxygen to maintain the palladium in a +2 state. The resulting reactions may be represented by the following equations.



$$PdCl_2 + R{-}CH{=}CH_2 + H_2O \longrightarrow R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3 + Pd + 2HCl \quad (1)$$

$$Pd + 2CuCl_2 \longrightarrow PdCl_2 + 2CuCl \quad (2)$$

$$2CuCl + 1/2O_2 + 2HCl \longrightarrow 2CuCl_2 + H_2O \quad (3)$$

Other investigators have utilized such reagents as *p*-benzoquinone or hydrogen peroxide to reoxidize the palladium.[4] The mechanism of the olefin oxidation step has been discussed in several publications.[5,6]

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(1) Department of Chemistry, University of Cincinnati, Cincinnati, Ohio.

(2) To whom inquiries should be sent.

(3) J. Smidt, *et al.*, *Angew. Chem.*, **71**, 176 (1959).

(4) I. I. Moiseev, M. N. Vargaftik, and Ya. K. Syrkin, *Dokl. Akad. Nauk. SSSR*, **130**, 820 (1960).

(5) M. N. Vargaftik, I. I. Moiseev, and Ya. K. Syrkin, *ibid.*, **139**, 1396 (1961).

(6) J. Smidt, *et al.*, *Angew. Chem. Intern. Ed. Engl.*, **1**, 80 (1962).

Although experimental procedures have been disclosed for the treatment of lower olefins,[4,6-8] no convenient laboratory method is available in the literature for the handling of higher α-olefins. The higher molecular weight α-olefins (hexane-1 and larger) do not readily react with an entirely aqueous solution of palladium chloride as do the lower homologs. In addition to low yields, the product obtained is often highly contaminated with the more internal ketone isomers which are difficult to separate. We wish to describe two efficient procedures, as demonstrated with 1-dodecene, which afford excellent yields of higher molecular weight methyl ketones of high purity.

By employing an aqueous dimethylformamide (DMF) solvent and utilizing a regulated feed of olefin into the catalyst solution, it has been found possible to obtain product yields of greater than 80%.

The ketone which forms is 96%–99% methyl ketone, as determined by v.p.c. Typical results with 1-dodecene are summarized in Table I. The effect of water concentration is seen in the data shown in Table I. Best yields were obtained with solvent systems containing 12–17% water (by volume). When equal volumes of dimethylformamide and water were employed, the conversion dropped drastically (run 9). Undoubtedly, with additional variations in catalyst concentration, oxygen flow, temperature, and rate of feed, the results can be further improved.

TABLE I

CONVERSION OF 1-DODECENE TO 2-DODECANONE[a]

	Solvent			
Run	DMF, ml.	water, ml.	1-Dodecene content of olefin, %	Yield,[b] %
1[c]		25	84	0
2	50	4	96	78
3	50	7	96	78
4	50	7	94	81
5	50	7	84	85
6	50	7	96	87
7	50	10	84	85
8	40	15	96	51
9	25	25	84	20

[a] Each experiment was carried out at 60–70° using 0.020 mole of $PdCl_2$, 0.020 mole of $CuCl_2 \cdot 2H_2O$, 0.20 mole of olefin, and an O_2 flow of 3.3 l./hr. In run 6 the olefin was added over a 3.5-hr. period; in all other cases the time of introduction was 2.5 hr. [b] Determined by v.p.c. [c] This experiment was stopped after 1.5 hr. as no reaction occurred.

The regulated feed of olefin is necessary to prevent build-up of unchanged olefin. When this occurs, the yield is lowered. A partial explanation for this observation lies in the fact that isomerization of the α-olefins is a competing reaction. More intensive research is required before a satisfactory explanation for the improvement obtained with dimethylformamide may be given. Conceivably, the dimethylformamide provides more intimate contact between the olefin and catalyst solution and also may exert a solvent effect which promotes reaction and selectivity. Certainly not all water-miscible solvents are equally applicable. For example, we examined dimethyl sulfoxide, acetone, acetic acid, tetrahydrofuran, dioxane, and acetonitrile and found each to be highly inferior to dimethylformamide. This technique can be used to oxidize olefinic compounds other than hydrocarbons to methyl ketones. The essentially unmodified optimum procedure was used to convert 10-undecenoic acid to 10-ketoundecanoic acid in 83% yield.

Where it is desirous to avoid the use of oxygen and/or copper salts, *p*-benzoquinone may be utilized to reoxidize palladium. In this case a slightly different experimental approach is required. The olefin, palladium chloride, quinone, and dimethylformamide are charged to the reaction flask, and then water is added portionwise at intervals. In this manner, 1-dodecene was converted in a 77% yield to 2-dodecanone.

The results of our investigation suggest that the above procedures may be extremely valuable in laboratory synthesis. Many organic compounds which possess a vinyl radical ($-CH{=}CH_2$) and which do not react to form pure ketones *via* the original Smidt[3] procedure may lend themselves to treatment through application of the modifications which we have described.

Experimental

All melting points and boiling points are uncorrected.

Materials.—Dimethylformamide (Eastman Kodak, White Label), $PdCl_2$ (60.00% Pd, J. Bishop and Co., Malvern, Pa.), $CuCl_2 \cdot 2H_2O$ (Baker and Adamson, Reagent Grade), and *p*-benzoquinone (Fisher Scientific, Purified) were used without further purification. Commercial samples of 1-dodecene (Gulf Oil Corp., Pittsburgh, Pa.) were analyzed by v.p.c. for C_{12} content and by infrared for *n*-1 olefin content.

Identification of 2-Dodecanone.—In an initial experiment, the reaction product was isolated by fractional distillation, b.p., 246–247° (lit. b.p. 246–247°).

Anal. Calcd. for $C_{12}H_{24}O$: C, 78.13; H, 13.13. Found: C, 78.13; H, 13.21.

The semicarbazide derivative melted at 122.5–123.5° (lit.[9] m.p. 122–123°), and the 2,4-dinitrophenylhydrazine derivative melted at 80° (lit.[9] m.p. 81°). The product had the same retention time (v.p.c.) as an authentic sample, and infrared examination further confirmed its structure.

Analytical Method.—Vapor phase chromatographic analyses were carried out on a 17-ft. column packed with tripentaerythritol octaisooctanoate on firebrick at 180° with a helium pressure of 20 p.s.i. (gage) and on a 2-ft. column packed with silicone rubber on firebrick with a helium flow of 125 ml./min. (temperature programmed). A sample of isolated and identified 2-dodecanone was used for tagging purposes and to establish retention times. To permit quantitative evaluation of 2-dodecanone formation, appropriate calibration curves were obtained with known blends of olefin and ketone. The 17-ft. column was capable of resolving a mixture of 2-, 3-, and 4-dodecanone.

2-Dodecanone Using Cupric Chloride and Oxygen (Table I).—The reactions were conducted in a cylindrical 250-ml. glass reactor which had a gas-dispersion inlet tube affixed to the bottom to permit efficient passage of oxygen through the reaction solution. A flowmeter was used to control the amount of oxygen. The reactor was equipped with a stirrer, condenser, and thermowell. A 6-mm. glass delivery tube was set into the flask so that the outlet was well below the surface of the initial solution and dropping funnel was connected to the top of the tube. The reactor was charged with the catalyst salts, DMF, and water, and the oxygen flow was adjusted. The stirred solution was heated at 60°, and the 1-dodecene was then fed dropwise through the delivery tube into the catalyst solution over a period of 2.5 hr. The temperature was maintained between 60° and 70° during the introduction of the olefin and for 0.5 hr. following complete addition. The mixture was cooled, and the upper phase which contained DMF, unchanged olefin, and products was analyzed by v.p.c. Reagent quantities and yields of 2-dodecanone are listed in Table I. To collect the ketone, the product

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(7) Belgian Patent 592,633 (January 5, 1961).

(8) German Patent Application 1,080,994 (May 5, 1960).

(9) I. Heilbron, "Dictionary of Organic Compounds," Vol. III, Oxford University Press, New York, N. Y., 1953, p. 362.

phase was removed, washed several times with water, dried, and fractionally distilled.

10-Ketoundecanoic Acid.—Run 2 described before and in Table I was duplicated except that 27.5 g. (0.15 mole) of 10-undecenoic acid was added over a 2-hr. period in place of dodecene-1. The product was finally poured into excess, cold, dilute hydrochloric acid and the precipitated solid was isolated, dried, and taken up in benzene. After filtration and removal of the benzene the product was extracted with cold pentane to leave 18.0 grams of 10-ketoundecanoic acid, m.p. 52°, while the pentane contained 7.5 g. of cruder product. The keto acid was recrystallized from ethyl acetate, m.p. 57–59° (lit.[10] m.p. 58–60°).

Anal. Calcd. for $C_{11}H_{20}O_3$: neut. equiv., 280. Found: neut. equiv., 282.

2-Dodecanone Using *p*-Benzoquinone.—Palladium chloride (0.020 mole), *p*-benzoquinone (0.10 mole), 1-dodecene 0.10 mole), and 50 ml. of DMF were placed in a 250-ml. round-bottomed flask fitted with a stirrer, condenser, thermometer, and dropping funnel, and 1 ml. of water was added from the dropping funnel. The solution temperature rose to 70°. After 0.25 hr. an additional 1 ml. of water was added, and heat was applied to maintain a 70° temperature. A third milliliter of water was introduced at 0.75 hr. and a milliliter at 2.5 hr. The mixture was cooled and flooded with water after a total reaction time of 3 hr. and the product was extracted with pentane. The pentane solution was washed several times with water and then dried. Removal of the solvent left 17 g. of an oil which was analyzed by v.p.c. and found to contain 13.5 g. of 2-dodecanone (77%). Only trace amounts of other C_{12} ketone isomers were detected.

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(10) J. Casey and F. S. Prout, *J. Am. Chem. Soc.*, **66**, 48 (1944).

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peri-Substituted Naphthalene Compounds. VI.[1,2] Acenaphth[1,2-*a*]acenaphthylene

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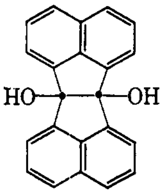
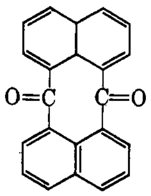
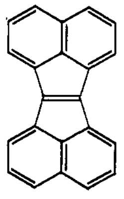
With the availability of 1,8-dilithionaphthalene,[1] a variety of *peri*-substituted naphthalene compounds have become accessible. The present paper reports the preparation of *cis*-6b,12b-dihydroxy-6b,12b-dihydroacenaphth[1,2-*a*]acenaphthylene (I) and conversion of this diol to diketone II and to hydrocarbon III.



I



II



III

Diol I was obtained in 14% yield on hydrolyzing the products from reaction of equimolar quantities of 1,8-dilithionaphthalene and acenaphthenequinone. It is a colorless, crystalline solid melting at 319–321°. The assigned structure is supported by the infrared spectrum (bands attributable to hydrogen bonded O–H at 3.00 and 3.12 μ), the mass spectrum (molecular ion at *m/e* 310), a Zerewitinoff determination (two active hydrogen atoms per molecule), and the elemental analysis. Of the two possible stereoisomeric forms, only that with *cis* fusion of the five-membered rings seems a plausible structure in view of the method of formation and the high degree of strain that would exist in the *trans* isomer. It was indeed found that diol I was produced by oxidation of acenaphth[1,2-*a*]acenaphthylene (III) with osmium tetroxide, a reagent well established to add *cis* to carbon–carbon double bonds. Furthermore, a sharp melting, crystalline ester was obtained from the reaction of I with benzeneboronic acid.

Oxidation of diol I with lead tetraacetate afforded 1,8-naphthalylnaphthalene (II) in 81% yield. A molecular model of this substance indicates that the carbonyl groups would not lie in the plane of either naphthalene ring. In agreement with the expectation that the geometry would lead to inhibition of resonance involving these groups, it was found that the carbonyl stretching frequency for II was 25 $cm.^{-1}$ greater than that for 1,8-dibenzoylnaphthalene and the extinction coefficient for the maximum occurring at 280 mμ was only 1120, as compared to 9680 for 1,8-dibenzoylnaphthalene. Also of interest is the fact that II dissolved in concentrated sulfuric acid to give a colorless solution, whereas naphthalene compounds which possess oxygen functions at the α-position in general give highly colored sulfuric acid solutions.[4] The ion formed from II seems best formulated as one in which hybridization of the carbonium ion is largely sp^3 and conjugation with the aromatic rings is minimal as a consequence of the molecular geometry.

On addition of I to hydrogen fluoride a green solution was obtained. Hydrolysis and chromatography of the resulting dark precipitate afforded in 29% yield a deep purple, sublimable hydrocarbon, $C_{22}H_{12}$. The same compound was obtained in 7% yield when a solution of diol I in sulfuric acid was hydrolyzed. The mass spectrum (molecular ion of mass 276) was consistent with an aromatic hydrocarbon structure, and the infrared spectrum was unusually simple, consisting of three strong bands (6.91, 12.16, and 13.06 μ), three medium intensity bands (6.80, 7.05, and 8.32 μ), and a few very weak bands. Evidence that no rearrangement of the carbon skeleton had occurred was provided by the fact that the purple hydrocarbon was reconverted to diol I by treatment with osmium tetroxide and hydrolysis of the resulting ester. These facts identify the hydrocarbon as acenaphth[1,2-*a*]acenaphthylene (III).

Formation of III from I involves elimination of *cis*-hydroxyl groups. A few other cases of production of olefinic substances from glycols under conditions for the pinacol rearrangement have been reported. For example, Bachmann and Chu[5] obtained 1,2-diarylacenaphthylenes as well as the expected pinacolones on treating 1,2-bis-*p*-chlorophenyl-1,2-acenaphthenediol and the corresponding fluorophenyl analog with iodine in acetic acid. In addition, Gomberg and Bachmann[6] reported that $\Delta^{9,9'}$-bixanthene was formed when 9,9'-bixanthydrol was warmed in an acetic acid–sulfuric acid solution. This result was questioned by Bergmann and Schuchardt,[7] who failed to obtain the bixanthene

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(1) Paper V, R. L. Letsinger, J. A. Gilpin, and W. J. Vullo, *J. Org. Chem.*, **27**, 672 (1962).

(2) This work was supported in part by the National Science Foundation.

(3) Dow Chemical Co. Fellow, 1961–1962.

(4) A solution of 1,8-dibenzoylnaphthalene in sulfuric acid is red (λ_{max} 523 mμ).

(5) W. E. Bachmann and E. J. Chu, *J. Am. Chem. Soc.*, **58**, 1118 (1936).

(6) M. Gomberg and W. E. Bachmann, *ibid.*, **49**, 236 (1927).

(7) E. Bergmann and W. Schuchardt, *Ann.*, **487**, 240 (1931).