degree of enolization of β-diketones. Eistert and Reiss[9] report for benzoylcamphor a band at 247 mμ (ϵ 14,900) for the enol chelate tautomer and 309 mμ (ϵ 7800) for the diketo tautomer. Dimedon[10] absorbs at 1702 and 1724 cm^{-1} (weak), showing the presence of β-diketonic tautomer, and Kirmann and Wakselman[11] give 1500–1650 cm^{-1} (strong) and $\lambda_{\max}^{\text{dioxane}}$ 275 mμ (ϵ 13,950) for large-ring, cyclic β-diketones but 1650 (weak) and 1700 cm^{-1} (strong) for similar compounds bearing a single methyl substituent on the carbon atom between the two carbonyl groups (decreased enolization). The compound 2-acetylcyclohexanone in hexane absorbs at 288 mμ (ϵ 6900), and Nakanishi[12] reports (no references) $\bar{\nu}_{\max}$ 1720 (occasionally a doublet) for β-diketones. In view of the fact that long-chain β-diketones are not previously reported in the literature, there is no reason to doubt the present values but rather to conclude that one has essentially the β-diketo tautomer in hand. The "extra" peak[12] in the infrared spectrum at 1774 cm^{-1} probably reflects the ketone ketone interaction just as the two equal carbonyl groups in symmetrical acid anhydrides produce two bands.[13]

Experimental Section

Heneicosane-2,4-dione. Isomerization of Isopropenyl Stearate in the Presence of Diethyl Malonate.—Isopropenyl stearate (8.03 g), diethyl malonate (10.0 ml), and p-toluenesulfonic acid (100 mg) were heated to the reflux point, 185° pot temperature, using a short, inefficient reflux condenser so that acetone was not trapped and the high-boiling diethyl malonate was condensed and returned to the boiling pot. A second, efficient collection condenser trapped 0.88 g of acetone, identified as the 2,4-dinitrophenylhydrazone derivative. No acetone or other reaction product formed in significant amount in the absence of the acid catalyst. On cooling, the crude dione separated as orange impure crystals. Chromatography on a Florisil column, 4 × 50 cm, gave, on elution with pentane, a colorless solid residue containing the dione and some of the diethyl malonate. Trituration of the solid eluate cuts with ethanol gave the crude dione free of liquid ester. The colorless product recrystallized from pentane melted at 70 and 75° (double melting point): $\lambda_{\max}^{\text{isooctane}}$ 298 mμ (log ϵ 3.48). The dione was much less soluble in pentane than the chief contaminant, ethyl stearate (m.p. 35°). The yield of dione was 70%.

Anal. Calcd for $C_{21}H_{40}O_2$: C, 77.72; H, 12.42. Found: C, 77.90; H, 11.98.

The β-diketone on reaction with hydrazine gave two noncarbonyl-containing compounds, mp 101 and 75°, showing NH absorption bands at 3300 cm^{-1}. Refluxing the diketone in aqueous alcoholic sodium hydroxide gave the cleavage products, stearic acid and a neutral ketone presumed to be methyl heptadecyl ketone.

Duplication of the above rearrangement experiment with the sole variation of substituting 10.0 ml of Nujol for the "inert" diethyl malonate gave no β-diketone after 20 min of 185° and inconsequential amounts of β-diketone and of stearone after heating 1 hr at 200°. In both of these latter cases a substance absorbing intensely at 1815 cm^{-1} and at about 1150 cm^{-1} was produced (stearoketene?).[13a] The characteristic 1030-cm^{-1} band of stearic anhydride was completely absent.

Stearone from Isopropenyl Stearate.—Isopropenyl stearate, 16.1 g, was heated with 100 mg of p-toluenesulfonic acid to 200° for 1 hr. Acetone was liberated, and on cooling crystallization of the melt occurred. Chromatography on Florisil gave 2.87 g of unidentified foreeluate with methylene chloride, and 14 g of stearone eluted with a mixture of benzene–methylene chloride (1:1) fortified with 10% of methanol. The stearone eluted formed rhombic scales, mp 89–90.0°, lit.[14] mp 88°, and had an identical infrared spectrum with that of an authentic specimen. It was converted to the oxime, mp 69.2–70.0°, lit.[15] mp 62–63° (amorphous) for confirmation.

Anal. Calcd for $C_{36}H_{71}NO$: C, 80.98; H, 13.40; N, 2.62. Found: C, 80.74; H, 13.74; N, 2.82.

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[9] B. Eistert, and W. Reiss, *Ber.*, **87**, 92, 108 (1954).

[10] R. S. Rasmussen, D. D. Tunicliff, and R. R. Brattain, *J. Am. Chem. Soc.*, **71**, 1069 (1949).

[11] A. Kirmann and C. Wakselman, *Compt. Rend.*, **261**, 759 (1965).

[12] K. Nakanishi, "Infrared Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, Table 8.

[13] N. O. V. Sonntag, J. R. Trowbridge, and I. J. Krems [*J. Am. Oil Chemists' Soc.*, **31**, 151 (1954)] showed for stearic anhydride $\bar{\nu}_{\max}$ 1735 and 1780 cm^{-1}.

[13a] NOTE ADDED IN PROOF.—This supposition of ester pyrolysis to hexadecylketene appears to be correct and will be the subject of a subsequent paper. The purified substance, mp 75.5–76.3, absorbs at 1752, 1715, 1645, and 1579 cm^{-1} (liquid film) and 1765, 1720, and 1645 cm^{-1} (CS_2) but may be dimeric.

[14] F. Kraft, *Ber.*, **15**, 1715 (1882).

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Enol Esters. III.[1] Preparation of Diisopropenyl Esters of Dicarboxylic Acids

EDWARD S. ROTHMAN,[2] SAMUEL SEROTA, AND DANIEL SWERN

Eastern Regional Research Laboratory,[3]
Philadelphia, Pennsylvania 19118

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In previous publications we have reported the preparation of isopropenyl esters[4] of monocarboxylic, long-chain fatty acids and have shown their usefulness as acylating agents.[5] Acylation occurs even in many unfavorable cases because the evolution of gaseous acetone tends to drive the reaction essentially to completion; for example, N-alkylamides and imidamides such as barbituric acid acylate easily. Not only are clean reaction products obtained in a simple operation, but there is no problem of removing pyridine or emulsified metal soaps as is the case when conventional reagents such as stearoyl chloride or steric anhydride are used.

It occurred to us that by extending this acylation principle to bi- or polyfunctional materials one would have at hand the basis for several polymer-forming reactions.[6] To follow this line, we decided to prepare the difunctional acylating agents, diisopropenyl azelate, diisopropenyl sebacate, and related substances. This goal was not so easy to accomplish as anticipated. At first we were baffled by the apparently great difference in behavior between the monocarboxylic and dicarboxylic acids in isopropenyl ester formation, but gradually we were able to proceed from small yields to useful yields and present a summary of the properties of the compounds prepared in Table I. It is the purpose of the present paper to explain the reasons for the peculiar behavior and to indicate how the deleterious actions can be circumvented by improved techniques.

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[1] For the previous paper in this series, see E. S. Rothman, S. Serota, and D. Swern, *J. Org. Chem.*, **29**, 646 (1964).

[2] To whom correspondence should be addressed.

[3] One of the laboratories of the Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

[4] E. S. Rothman, S. Serota, T. Perlstein, and D. Swern, *J. Org. Chem.* **27**, 3123 (1962).

[5] E. S. Rothman, S. Serota, and D. Swern, *ibid.*, **29**, 646 (1964).

[6] E. S. Rothman, *Tetrahedron Letters*, in press.

TABLE I

Diisopropenyl ester	Bp (mm) or mp, °C	$n^{30}D$	d^{30}_4	Yield, %
Sebacate	140 (0.13)	1.4488	0.9698	80–85
Azelate	103 (0.03)	1.4499	0.9746	75
Suberate	94 (0.025)	1.4470	0.9775	70
Dodecanedioate	...	1.4505	0.9571	40
Tridecanedioate	...	1.4509	0.9464	40
Tetradecanedioate	31.5–33	...	...	40
Adipate	88 (0.11)	1.4453	0.9826	70
Isopropenyl hydrogen sebacate	40–41	...	...	...

There are two main routes[7] that we have studied in diisopropenyl dioate formation. The first involves the direct addition of 1 mole of dioic acid to 2 moles of propyne. The second route involves the acid–ester interchange reaction, utilizing the commercially available isopropenyl acetate, in excess, as the isopropenylating agent. In special cases one procedure may give better yields than the other; for example, the propyne procedure may be preferable for conversions of α-halogenated acids, but in general *the problem to be solved is not that of forming the product in useful yield, but rather that of isolation of the product without destroying it during the isolation procedure.* That is to say, the formation of diisopropenyl ester itself offers no unusual problems, but so many side reactions can carry the already formed product to undesirable material that the yield may be dropped to very small values if these side reactions are allowed to take place.

The major sort of side reaction involves the addition of the intermediate half-ester, *e.g.*, isopropenyl hydrogen sebacate, at the carboxylic acid end to the isopropenyl ester group of another molecule. The resulting unstable geminal diester rapidly collapses, expelling acetone and forming a "dimeric" molecule with an anhydride connecting linkage. The process may be repeated several times and followed by observing the changing infrared carbonyl absorption spectrum. As time progresses, the ester bands increase in intensity to a maximum and then disappear as anhydride bands increase in intensity concurrently. During the work-up, because of the difficulty in removing the catalyst completely, the point in time at which ester function is at a maximum is reached and passed until, sometimes, only anhydride is isolable. For good diester yields it is necessary to freeze all equilibria prior to work-up. Use of salts in heterogeneous phase, such as potassium acetate or potassium bicarbonate, or liquid bases, such as tertiary amines, is helpful in quenching but is not completely reliable.

Absorptive removal through a short clean-up column of Florisil not only removes catalyst and gives clarification of suspended matter including a purple coloration that appears to be colloidal metallic mercury owing to reduction of mercury salts in propyne runs, but also removes a small proportion of contaminant unreacted acid and anhydride. Such a preliminary "chromatography" seems to be innocuous, but standard chromatography procedures using a high ratio of adsorbent to compound are risky. Long-chain isopropenyl esters such as isopropenyl stearate (C_{18}) may be chromatographed, but even isopropenyl laurate (C_{12}) is largely destroyed. In general, the longer the methylene chain the safer the chromatographic procedures. To rationalize its high lability, one may consider that isopropenyl sebacate (C_{10}) behaves like a pair of pentanoic acid molecules. Sometimes the heat of reaction with the column support is so great that the column feels quite hot to the touch.

After such preliminary passage through a short clean-up column, the recommended procedure is a preliminary distillation in a falling-film molecular distillation apparatus. The time of actual heating during such distillation is kept minimal, so that little pyrolysis or artifact anhydride formation occurs. Curiously enough, the appropriate molecular distillate fractions may now be redistilled all day long through a 24-in. spinning-band column with no perceptible decomposition. Attempts to use such spinning-band apparatus directly on crude reaction products occasionally succeed, but, more typically, results are ruinous.

In passing we should like also to call attention to the fact that treatment of the mixture of dioic acid, mercuric salts, and boron trifluoride etherate in methylene chloride solution with propyne always causes some reduction of mercury salts to free mercury, calling to mind analogous reductions of palladium salts by ethylene.[8]

Experimental Section

Diisopropenyl Sebacate. Procedure A (Acid–Ester Interchange).—Sebacic acid (202 g, 1 mole), isopropenyl acetate (1.1 l., 11 moles), mercuric acetate (10.0 g, 0.03 mole), and boron trifluoride etherate (4.6 ml) were mixed at 15° and allowed to warm to ambient temperature of 25°. In 2 hr infrared analysis showed total disappearance of the carboxyl carbonyl band. The mixture was treated with 4.1 ml of triethylamine and concentrated *in vacuo* at 30° to remove most of the excess isopropenyl acetate. The residue was diluted with pentane and filtered through 190 g of Florisil in a short column. The column was rinsed with pentane, and the two percolates were combined. After removing the pentane, the residue was distilled in a falling-film molecular still. The fraction collected at about 50 μ and 100–110° was the required diisopropenyl sebacate (155 g). On redistillation through a 24-in. spinning-band column, a high recovery of diisopropenyl sebacate was obtained: bp 134° (0.06–0.07 mm), 140° (0.13 mm); yield 146 g; $n^{30}D$ 1.4488; $d^{30}_4 = 0.9698$; $\nu_{max}^{CS_2}$ 1751 (CO) and 1673 (C=C) cm^{-1}.

Anal. Calcd for $C_{16}H_{24}O_4$: C, 68.05; H, 9.28. Found: C, 68.04; H, 9.22.

Diisopropenyl Azelate. Procedure B (Addition of Acid to Propyne).—Azelaic acid (100 g, 0.53 mole), methylene chloride (500 ml), and mercuric acetate (18.2 g, 0.057 mole) were treated with 1 ml of boron trifluoride etherate, and propyne gas (freed of anticatalytic matter by passing through Linde Co. Molecular Sieve 4A) was bubbled through the mixture for 3 hr. The reaction, once started, was exothermic and was controlled by the rate of gas feed and/or by the cooling owing to the low boiling point of the methylene chloride solvent. Solid sodium bicarbonate (5 g) was added and the mixture was filtered free of solids and metallic mercury. The filtrate was passed through a short Florisil column which was then washed with additional methylene chloride. The residue obtained by evaporation of the percolate was then submitted to molecular distillation and spinning-band column distillation similar to the operations noted in procedure A. The product boiled at 103° (0.03 mm): $n^{30}D$ 1.4499; d^{30}_4 0.9746; $\nu_{max}^{CS_2}$ 1755, 1675, 1376, 1200, 1150, and 867 cm^{-1}.

Anal. Calcd for $C_{15}H_{24}O_5$: C, 67.13; H, 9.02. Found: C 67.68; H, 9.25.

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(7) *Cf.* R. L. Adelman, *J. Org. Chem.*, **14**, 1057 (1949); and references cited therein.

(8) J. Smidt, W. Hafner, R. Jira, R. Sieber, J. Sedlmeier, and A. Sabel *Angew. Chem.*, **74**, 93 (1962).