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of IV) was isolated as the di-*n*-butylamine salt, which when recrystallized from acetone afforded 4.05 g. (94% yield) of glistening needles, m.p. 141–144°, [α]D +31° (found for C₂₈H₄₉NO₂: C, 77.96; H, 11.34; N, 3.26). The m.p. and optical rotation were unchanged by further recrystallization. Treatment of the salt with acetic acid in dilute ethanol² yielded, after recrystallization from ethanol-water, 2.42 g. (80%) of $\Delta^{8,12}$ abietadienoic acid (III) (steroid-triterpene numbering) as fine plates, m.p. 160–162°, [α]D +55°. The ultraviolet spectrum (only end-absorption in the low wave length region), the n.m.r. spectrum⁷ in CDCl₃ (single vinyl proton, 4.55 τ), and the mode of formation support the assignment of structure III.



When heated under reflux for 2 hr. in ethanol with concd. hydrochloric acid,² recrystallized III furnished, in 90% vield, abietic acid (II) of an estimated purity of 80-85%.⁸ which was isolated as the diisoamylamine salt, m.p. $133-136^{\circ}$, $[\alpha]_{D}$ -47° (decreased to $-61^{\circ 2}$ after three recrystallizations from acetone), or as the di-n-butylamine salt, m.p. 152–155°, $[\alpha]_D$ – 33° (rotation not altered appreciably by further recrystallization; found for $C_{28}H_{49}NO_2$: C, 77.92; H, 11.30; N, 3.41). The physical properties of the regenerated, recrystallized² acid, including crystallization behavior,² m.p. and mixed m.p. (167-172°), optical rotation² $([\alpha]D - 106^{\circ})$, infrared spectrum (CS₂ and KBr disk), ultraviolet absorption² [λ_{max} 235 (ϵ 21,500), 241.5 (23,000) and 250 mµ (15,500)], and n.m.r. spectrum⁷ (two vinyl protons, 4.26 and 4.66τ), were identical with those of authentic abietic acid.^{2,9,10}

(7) This determination was obtained through the courtesy of Professor Ernest Wenkert at Iowa State University.

(8) Calculated on the basis of the observed extinction at 241.5 $m\mu$.² The presumed impurity, Δ^{3} -abietenoic acid (IV), arising from a small amount of over-reduction of I, is reported to have m.p. $174-176^{\circ}$, $[\alpha]p + 104^{\circ}$ [E. E. Fleck and S. Palkin, J. Am. Chem. Soc., **59**, 1593 (1937)]. A 4:1 mixture of pure abietic acid and IV ($[\alpha]p + 85^{\circ}$), obtained by partial hydrogenation of III, showed spectral and optical rotational properties virtually identical with those of the acid isomerization product of III.

(9) Kindly supplied by Dr. Ray V. Lawrence, Naval Stores Research Laboratory, Olustee, Fla. We thank Dr. Lawrence for this courtesy and also for sending a supply of WW gum rosin from which additional pure abietic acid was isolated.²

(10) An alternative pathway from dehydroabietic acid to abietic acid also has been realized in our Laboratories: The acetoxy keto ester (i), m.p. 120-130°, $[\alpha]_D$ +5°, prepared by chromic acid oxidation of methyl dehydroabietate (T. F. Sanderson, U. S. Patent 2,750,368,

When heated at 210° with potassium hydroxide in ethylene glycol, III was partially isomerized to palustric acid ($\Delta^{8,13}$ -abietadienoic acid), λ_{max} $265-266 \text{ m}\mu$ (single vinyl proton in the n.m.r. spectrum,⁷ 4.54 τ). The further isomerization of palustric acid to abietic acid¹¹ and the conversion of abietic acid to neoabietic acid² and to dihydroand tetrahydroabietic acids¹² have been reported previously.

Interestingly, in the absence of an alcohol, the lithium-in-ethylamine reduction of dehydroabietic acid gave a mixture of non-aromatic *aldehydic* products in about 80% yield. From this mixture, Δ^{8} -abietenal (V) was isolated in 20% yield by alumina chromatography of the 2,4-dinitrophenyl-hydrazone (m.p. 158–159°; found for C₂₆H₃₆N₄O₄: C, 66.69; H, 7.88; N, 11.85). The position of the double bond in V was verified by the n.m.r. spectrum¹³ of the 2,4-DNP and by the method of Castells and Meakins¹⁴ as applied to the corresponding carbinol.

issued June 12, 1956), was subjected to Wolff-Kishner reduction and hydrolysis. The resulting hydroxy acid. n.p. 186-187°, $[\alpha]p + 49°$ (84% yield), was esterified (diazomethane) and converted via the corresponding hydroperoxide (cf. T. F. Sanderson, U. S. Patent 2,750,367, issued June 12, 1956) to the phenolic ester (ii). m.p. 149.5-150°. O-Methylation, ester hydrolysis, Benkeser-Birch reduction.4 esterification (diazomethane), and then reaction of the resulting keto ester, m.p. 127-128° [G. C. Harris and T. F. Sanderson. J. Am. Chem. Soc., **70**, 339 (1948); cf. ref. 3], with isopropylmagnesium bromide in benzene-ether, followed by dehydration and hydrolysis, furnished abietic acid.



Recently, we have learned that a similar sequence, based on the transformation of desisopropyldehydroabietic acid [E. Wenkert and J. W. Chamberlin, J. Am. Chem. Soc., **81**, 688 (1959); cf. M. Ohta and L. Ohmari, Pharm. Bull. (Tokyo). **5**, 91, 96 (1957)] to the phenolic ester (ii), also has been carried out in the Iowa State Laboratories (private communication from Professor Wenkert, with permission to quote).

(11) V. M. Loeblich, D. E. Baldwin and R. V. Lawrence, J. Am. Chem. Soc., 77, 2823 (1955).

(12) Cf. J. L. Simonsen and D. H. R. Barton, "The Terpenes," Vol. 11I, Cambridge Univ. Press, New York, N. Y., 1952, pp. 407-418.

(13) We thank Dr. James N. Shoolery for this determination.
(14) J. Castells and G. D. Meakins, *Chemistry & Industry*, 248
(1956).

(15) The senior author gratefully acknowledges the inspiration and encouragement of Professors Gilbert Stork and D. H. R. Barton. We both thank the University of Kansas for a grant from the General Research Fund.

DEPARTMENT OF CHEMISTRY

THE UNIVERSITY OF KANSAS ALBERT W. BURGSTAHLER¹⁵ LAWRENCE, KANSAS LEONARD R. WORDEN RECEIVED APRIL 8, 1961

THE SYNTHESIS OF ORTHOAMIDES AND THEIR CONVERSION TO FORMAMIDINIUM SALTS

Sir:

We wish to report the synthesis of a series of orthoamides, I. These materials are the first examples of compounds having three basic nitrogens attached to a single carbon atom.¹ They are

(1) Bredereck, et al., Ber., 92, 329 (1959), and 93, 1398 (1960), recently have reported the preparation of a series of triacylaminomethanes. The chemistry of these materials is quite different from that of the orthoamides. particularly useful because of their ready conversion to formamidinium salts, an extremely interesting class of compounds.

$$\begin{pmatrix} Ar \\ R \end{pmatrix}_{3}CH \xrightarrow{HX} Ar \\ R \xrightarrow{HX} R \xrightarrow{HX} R \xrightarrow{HX} R \xrightarrow{R} R$$

The sodium salt of N-methylaniline on treatment with gaseous chlorodifluoromethane in 1,2-dimethoxyethane produced Ia (Ar = C₆H₅; R = CH₃), m.p. 263–265° dec. (anal. Calcd. for C₂₂H₂₅N₃: C, 79.72; H, 7.60; N, 12.68. Found: C, 79.43; H, 7.65; N, 12.82) in 58% yield. Similarly were prepared Ib (Ar = C₆H₅; R = C₂H₅), m.p. 183– 186° (21%) (anal. Calcd. for C₂₅H₃₁N₃: C, 80.38; H, 8.37; N, 11.25. Found: C, 80.13; H, 8.38; N, 11.03) and Ic (Ar = p-NO₂C₆H₄; R = CH₃), m.p. 260–265° dec. (23%) (anal. Calcd. for C₂₂H₂₂-N₆O₆: C, 56.64; H, 4.76; N, 18.02. Found: C, 56.30; H, 4.96; N, 17.73).

The orthoamide Ia (Ar = C_6H_5 ; R = CH₃) also was prepared by heating ethyl orthoformate and N-methylaniline at reflux (21%) and by the reaction of II (Ar = C_6H_5 ; R = CH₃; X = I) with the sodium salt of N-methylaniline.

The orthoamides I react smoothly with strong acids, alkyl halides and acyl halides to produce formamidinium salts. IIa (Ar = C₆H₅; R = CH₃; X = BF₄), m.p. 117–119° (anal. Calcd. for C₁₅H₁₇N₂BF₄: C, 57.72; H, 5.49; N, 8.98. Found: C, 57.90; H, 5.29; N, 8.98) was prepared in 75% yield by heating 30 g. of I (Ar = C₆H₅; R = CH₃) with 200 cc. of water and 60 cc. of 48% fluoroboric acid, then diluting and crystallizing. In a similar manner were prepared IIb (Ar = p-NO₂C₆H₄; R = CH₃; X = BF₄), m.p. 159–161° and IIc (Ar = C₆H₅; R = CH₃; X = DF₄), m.p. 162–164°.

The formamidinium salts undergo a variety of reactions, most of which involve attack of nucleophilic species on the central carbon atom.



For example, on stirring IIa (Ar = C_6H_5 ; R = CH_3 ; X = BF₄) with sodium methoxide, isopropoxide or *t*-butoxide the corresponding diaminoalkoxymethane III is formed in good yields. Treatment of IIc (Ar = C_6H_5 ; R = CH_3 ; X = I) with phenyllithium produced IV, m.p. 127–130°, identified by an analysis in agreement with formula and by hydrolysis to benzaldehyde. It is interesting that reduction of IIa (Ar = C_6H_5 ; R = CH_3 ; X = BF₄) to V, m.p. 33–34° (reported² 35°) was achieved easily with sodium hydride in 1,2-dimethoxyethane.

(2) J. V. Braun, Ber., 41, 2147 (1908).



Nitration of IIa gave a 63% yield of IIb, an extremely interesting result in view of the fact that only para substitution was observed. Other reactions of the orthoamides and formamidinium salts are being examined and will be reported in a later issue of THIS JOURNAL.

Rohm and Haas Company Philadelphia, Pennsylvania Received May 1, 1961

PERFLUOROTHIOCARBONYL COMPOUNDS Sir:

We have found the C=S group in fluorothiocarbonyl compounds has exceptional ability to undergo a variety of addition reactions. This reactivity is best exemplified in hexafluorothioacetone (I), the simplest member of a new class of compounds, the perfluorothioketones.



The remarkable reactivity of fluorothiocarbonyl compounds is illustrated by the ease with which hexafluorothioacetone (I) combines with olefins possessing allyl hydrogen atoms. For example, I reacts very rapidly at -78° with tetramethyl-ethylene to give the allyl sulfide II, b.p. 61° (20 mm.), n^{25} D 1.3960, infrared bands at 6.1 μ (C==C) and 11.3 μ (terminal CH₂), (Anal. Found: S, 11.82).



In many of the reactions of fluorothiocarbonyl compounds, the C=S group behaves as though the sulfur is more electrophilic than the carbon, a situation opposite to that of a C=O group. For example, hexafluorothioacetone reacts in a reverse manner with aqueous bisulfite ion to give a Bunté salt, isolated as the tetramethylammonium salt III, m.p. 196–198° (Anal. Found: F, 33.91; N, 4.26; S, 18.92).

I + HSO₃ -
$$\xrightarrow{+N(CH_3)_4}$$
 H - C - SO₃ - +N(CH₃)₄
CF₃ III

Another example of reverse addition is reaction of hydrogen chloride with I, which gives the disulfide IV, b.p. 67° (48 mm.), n^{26} D 1.3598 (*Anal.* Found: Cl, 8.69; S, 16.08).

$$H = \begin{bmatrix} CF_3 & CF_3 \\ -C-S & -C-Cl & IV \\ -CF_3 & CF_3 \end{bmatrix}$$