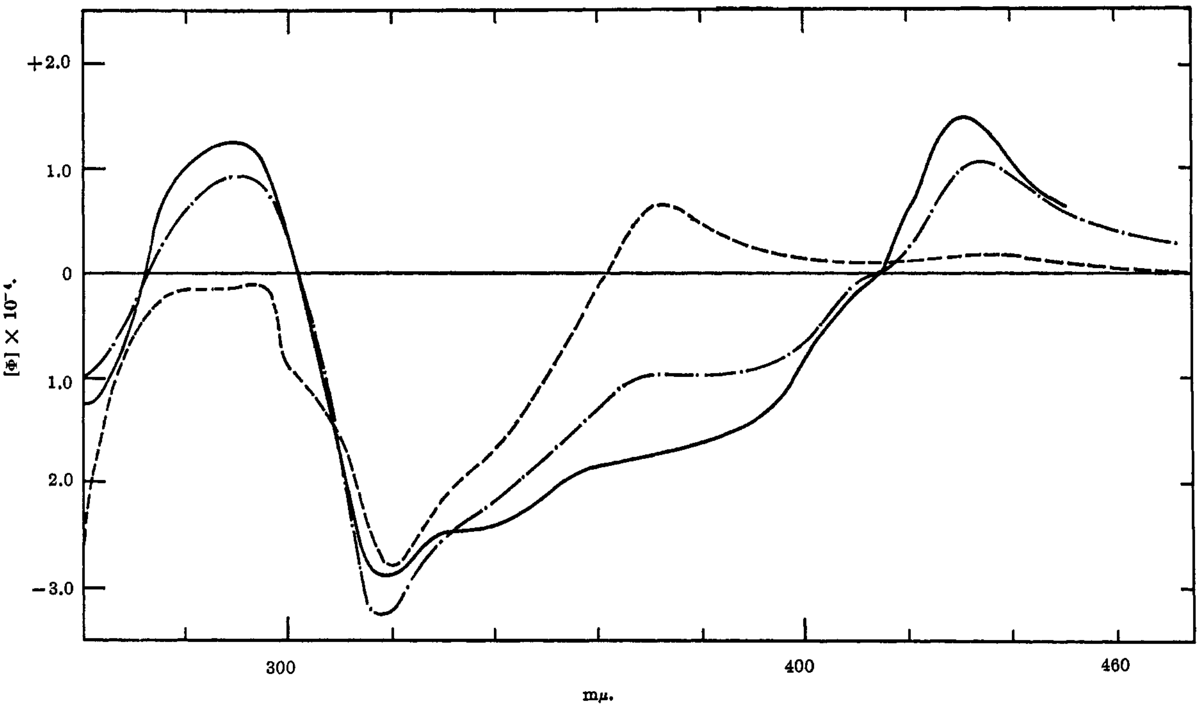

Figure 1.—The optical rotatory dispersion curve of 1-[(*S*)-(+)-α-phenylethylformimidoyl]-2-naphthol in - - - -, hexane; — · — chloroform; and ———, absolute ethanol.

Experimental Section

The compound, N-[(*R*)-(−)-α-phenylethyl]formimidoylnaphthol, was prepared by mixing (*R*)-(+)-α-phenylethylamine ([α] +39.4°) and 2-hydroxy-1-naphthaldehyde. After crystallization from benzene–hexane and then sublimation, it melted at 110.7–111.5°. *Anal.* Calcd for $C_{19}H_{17}NO$: C, 82.88; H, 6.22; N, 5.09. Found: C, 82.63; H, 6.06; N, 5.12.

It should be noted that the DL compound melted at about 82–85° and being a less tractable substance, the analytical data were obtained from the optically active material.

The ORD spectra were obtained from a Cary Model 60 recording spectropolarimeter using 1.0-mm cells. In all cases, ultraviolet spectra were taken of solutions used in the ORD studies to ensure optimum performance of the polarimeter. The solvents used were commercial spectra grade materials.

Registry No.—Ia [R = (*R*)-(−)-α-phenylethyl], 10349-22-1; Ia [R = (*S*)-(+)-α-phenylethyl], 10349-23-2; DL Ia, 10349-24-3; Ib [R = (*R*)-(−)-α-phenylethyl], 10349-25-4; Ib [R = (*S*)-(+)-α-phenylethyl, 10349-26-5; DL Ib, 10406-88-9.

Trimesate Esters by Formylation with Carbon Monoxide

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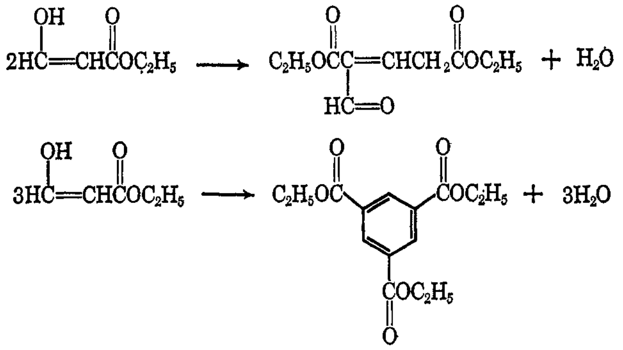
In 1887, Wilhelm Wislicenus first reported the condensation of ethyl formate and ethyl acetate through the action of sodium in ether or benzene.[1] A more thorough report was published in 1901.[2] The product, the sodium salt of formylacetic ester, when acidified gives ethyl formylacetate, which is, however, too unstable to isolate. It condenses with itself, forming ethyl formylglutaconate as the major product, along with small amounts of ethyl trimesate.



The first application of carbon monoxide under pressure in the formylacetic ester synthesis was reported in a patent by Beer and Halbig,[3] and later by Northey.[4] In these patents the usual condensation between a formate and acetate ester is effected, but under carbon monoxide pressure. The formate ester is prevented from decomposing, to an alcohol and carbon monoxide by the sodium alkoxide, and the alcohol that is normally formed in the reaction is converted to a formate ester. Neither of these patents, however, discussed the utility of using the formylacetic ester, obtained by acidifying the sodium salt, to prepare trimesate esters. The trimerization to trimesate esters was only mentioned in passing.

A mechanism for the reaction of carbon monoxide with an alkoxide ion and an alcohol to form a formate

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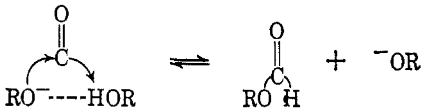
(1) W. Wislicenus, *Ber.*, **20**, 2930 (1887).

(2) W. Wislicenus and W. Bindemann, *Ann.*, **316**, 18 (1901).

(3) L. Beer and P. Halbig, German Patent 708,513 (1941).

(4) E. H. Northey, U. S. Patent 2,394,255 (1946).

ester has been recently proposed.[5] It is pictured as the reaction of carbon monoxide with an alkoxide ion hydrogen bonded to its conjugate acid, in contrast to the carbanionic mechanism previously proposed.[6]

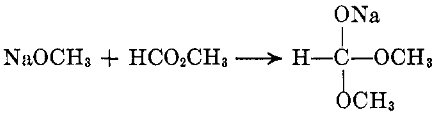


Carbon monoxide has also been used to formylate ketones. Stahler[7] reported the formylation of acetophenone, and a more recent study has investigated this area in detail.[8]

In starting our investigation of the possibility of using formylacetic esters for the intentional preparation of trimesate esters, we first obtained authentic samples of methyl and ethyl trimesates by following the procedures of the earlier workers in this area, using methyl and ethyl esters of formic and acetic acids. No carbon monoxide was used in these preliminary runs.

The highest yield of trimesate ester obtained in these runs was 2.5%. A real difficulty arose in adequately stirring the reactions. The mixed condensation between the formate and acetate esters created a slurry of ice cream consistency. Doubling the volume of solvent (ether) had no effect; the mixture seemed just as thick as before. During the reaction, some carbon monoxide was evolved from decomposition of the formate ester.

The thickening is characteristic of the reaction of a sodium alkoxide with a formate ester. In this reaction an intermediate has been postulated with an ortho ester type of structure, *e.g.*



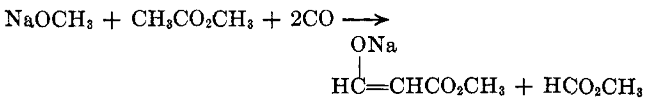
$$NaOCH_3 + HCO_2CH_3 \longrightarrow H{-}\overset{\displaystyle ONa}{\underset{\displaystyle OCH_3}{C}}{-}OCH_3$$

This ultimately decomposes to the alcohol, sodium alkoxide, and carbon monoxide. Supporting evidence for this will be discussed below.

The reactions using carbon monoxide under pressure were done in both rocking and stirred autoclaves. Small-scale reactions gave the best results. Adequate mixing was the most serious problem encountered and was not solved.

Sodium methoxide, and consequently methyl acetate, was used primarily because it is commercially available and relatively easy to handle.

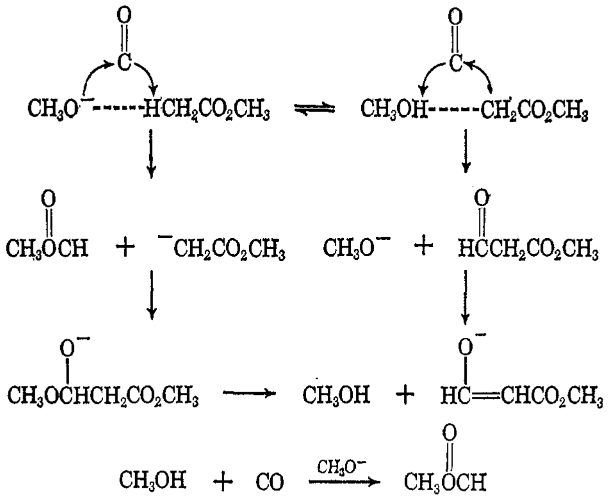
The condensation with carbon monoxide required no methanol or methyl formate. Earlier workers had used either the formate ester or the alcohol, or both, in effecting the condensation in the presence of carbon monoxide. Methyl formate is, however, produced in the following reaction.



$$NaOCH_3 + CH_3CO_2CH_3 + 2CO \longrightarrow H\overset{\displaystyle ONa}{C}{=}CHCO_2CH_3 + HCO_2CH_3$$

The formylation of the methyl acetate may occur by the reaction of the anion with either methyl formate or carbon monoxide. Which path is the more important is impossible to say. A possible mechanism is shown in Scheme I.

SCHEME I



Room temperature condensations appear to be best. Heating the autoclave gave generally lower yields of trimesate ester, but this may have been caused by the decreased solubility of carbon monoxide at the higher temperature. The addition of solvents did not help; better yields were obtained in the absence of solvents. (See Table I.)

TABLE I

METHYL TRIMESATE FROM CARBON MONOXIDE AND METHYL ACETATE[a]

Temp, °C	CO pressure, psig	$NaOCH_3$, mole	CH_3OAc, moles	Solvent	Methyl trimesate,[b] %
30	1000	0.166	0.166	Methanol, 25 ml	20.4[c]
25	1180	0.166	0.166	Methyl formate, 10 g	19.3[c]
50	1080	0.189	0.189	None	28.8[c]
25	1000	0.378	0.189	Ether, 100 ml	21.7[c,d]
25	890	0.189	0.189	None	51.7
25	890	0.189	0.189	None	50.9
93	890	0.378	0.378	None	12.0[e]
93	860	0.378	0.378	None	28.8
25	830	0.378	0.378	None	31.3
21	780	0.378	0.378	Toluene, 50 ml	35.4

[a] All runs made overnight, about 16 hr. Stirred autoclave unless otherwise noted. [b] Acidified with 10 *M* acetic acid, heated to 60°, allowing methyl formate to distil out, for 2–3 hr. [c] Rocking autoclave. [d] Based on methyl acetate. [e] Acetic acid added to autoclave. Methyl formate not allowed to escape.

For some unexplained reason, it appears to be important to allow the methyl formate to distil off during the trimerization step. When the acidification and subsequent trimerization was carried out in the autoclave, without allowing the methyl formate to escape, significantly lower yields were obtained. Alternatively, the crude sodium salt can be rapidly vacuum dried prior to the acidification and trimerization step.

We have developed an assay method for the crude sodium salt by the use of nuclear magnetic resonance

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(5) J. C. Powers, R. Seidner, T. G. Parsons, and H. J. Berwin, *J. Org. Chem.*, **31**, 2623 (1966).

(6) (a) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 311; (b) J. Hines, "Divalent Carbon," Ronald Press Co., New York, N. Y., 1964, p 79.

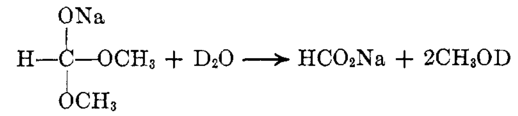
(7) A. Stahler, *Ber.*, **47**, 580 (1914).

(8) A. J. Van der Zeeuw and H. R. Gersmann, *Rec. Trav. Chim.*, **84**, 1535 (1965).

spectroscopy. This method suffers from none of the disadvantages found by earlier workers.[9,10]

A portion of the crude sodio methyl formylacetate was dissolved in heavy water and a portion dissolved in ordinary water. These samples were examined by nmr spectroscopy. The peaks (in Hertz) in heavy water were a, −237 (broad); b, −223; c, 0 (H_2O); d, 63; and e, 79. The peak labeled c was the trace of H_2O present and was used as the reference point. The ratio of a:d was 1:3, and that of b:e was 1:6. In ordinary water the same spectrum was obtained except that peak a became a doublet with a splitting of 11 Hz.

The peaks at b and e were shown to be due to formate anion and methanol, respectively. They resulted from the hydrolysis of the sodium methoxide–methyl formate adduct referred to earlier. To demonstrate this, we



$$H-C(ONa)(OCH_3)-OCH_3 + D_2O \longrightarrow HCO_2Na + 2CH_3OD$$

stirred a mixture of sodium methoxide and methyl formate in an autoclave under carbon monoxide pressure (to prevent decomposition of the methyl formate). The resulting paste was rapidly vacuum dried and dissolved in heavy water. Two peaks (besides the residual H_2O peak) were seen, corresponding in position to peaks b and e above, in the ratio of 1:6.

The formyl hydrogen is assigned to peak a. The adjacent vinyl hydrogen exchanges with the solvent. When it is D, the peak at a is broad. In ordinary water, where it is H, it splits peak a by 11 Hz. The vinyl hydrogen in this latter case is obscured by the large water peak. Peak d is, of course, the methyl hydrogen of the ester, and the ratio of a:d of 1:3 is as is to be expected.

The ratio of a:b, or of d:e, then, affords an analysis of the mixture. It was about 75% sodio methyl formylacetate.

Interestingly, *no* evidence was seen for any sodio methyl acetoacetate which would be a likely impurity formed by the self-condensation of two molecules of methyl acetate in the presence of sodium methoxide.

Experimental Section

Methyl Trimesate.—A 300-ml stirred autoclave was charged with 10.2 g (0.189 mole) of sodium methoxide (Matheson Coleman and Bell) and 15.0 ml (0.189 mole) of methyl acetate (Matheson Coleman and Bell). The autoclave was rapidly sealed, pressurized with carbon monoxide (Matheson, CP grade), vented several times to purge air from the system, pressurized to 890 psig with carbon monoxide, and stirred at 1000 rpm overnight (about 16 hr). The thick, almost solid, residue was acidified with 20 ml of 10 *M* acetic acid and heated, with stirring, in a water bath at 50° for 3 hr. The buff ester was filtered and dried: 8.20 g, 51.7% yield, mp 137–140°. Recrystallization from methanol gave colorless material, mp 142–144°.

Nuclear magnetic resonance assay was performed with a Varian A-60 spectrometer. The heavy water used was 99.5 mole % D_2O minimum (Matheson Coleman and Bell). The crude sodio methyl formylacetate used was prepared as above and vacuum dried to remove volatile methyl formate.

Registry No.—Carbon monoxide, 630-08-0; methyl trimisate, 2672-58-4.

[9] M. Cogan, *Bull. Soc. Chim. France*, **8**, 125 (1941).

[10] S. M. McElvain and R. C. Clarke, *J. Am. Chem. Soc.*, **69**, 2657 (1947).

The Enthalpy of Sublimation of Adamantane[1a]

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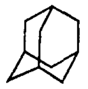
Adamantane (tricyclo[3.3.1.1.^{3,7}]decane, I) possesses a unique diamondoid structure which may be formally derived from the rigid fusion of three chair-form cyclohexane rings. A recent review on adamantane suggests that this geometry should result in an essentially strain-free molecule.[2] However, experimental verification for this hypothesis has been unavailable since no value for the enthalpy of sublimation has been reported. We have recently measured the sublimation pressure of adamantane between 40 and 80° and have calculated the enthalpy of sublimation from these data using the integrated form of the Clausius–Clapeyron equation. The data represent the arithmetic mean of three independent measurements on a dibutylphthalate manometer which agreed within 0.3 mm. The readings from the oil manometer were converted to Torrs by using 1.048 g/cm^3 as the density of the dibutylphthalate and 13.595 g/cm^3 as the density of mercury.



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These data, by means of a least-squares fit, yield the following expression for the temperature dependence of

$$\log p = 9.40 - 3054.2/T$$

the sublimation of adamantane. Calculated standard deviations are

$$\log p = 0.01, \text{ slope} = 31.3, \text{ intercept} = 0.09$$

Although there are a number of assumptions involved in the use of the Clausius–Clapeyron equation to derive the enthalpy of sublimation from the above data, more rigorous calculations[3] require physical data which are not available. Estimation of the critical properties of adamantane in order to apply a reduced equation of state is precluded by its unusually high melting point, the lack of a reliable value for its normal boiling point,[2] and its unique structure. As a result, we have calculated the following value for the enthalpy of sublimation of adamantane at 333.2°K from the Clausius–Clapeyron equation with no correction for nonideality of the gas phase. (See Table I.) The standard

$$\Delta H_{\text{sub}} = 14.0 \text{ kcal/mole}$$

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[1] (a) Supported by the National Science Foundation, Grant No. GP-4329; (b) The Royal Institute of Technology, Stockholm, Sweden; (c) to whom correspondence should be addressed.

[2] R. Fort and P. v. R. Schleyer, *Chem. Rev.*, **64**, 277 (1964).

[3] A. J. Gottschal and A. E. Korvezee, *Rec. Trav. Chim.*, **72**, 465 (1953).