The phase diagram of the methylene chloride–triethylamine system has been determined by cooling rate curves. A 1 to 2 compound (1 methylene chloride, 2 triethylamine) melted at 168° K. Eutectic compositions were found at 0.42 and 0.90 mole fraction triethylamine. The corresponding eutectic temperatures were 157° and 153° K.

compositions for study by adiabatic cryogenic calorimetry.

EXPERIMENTAL

The triethylamine was taken from the center cut (b.p. 88–89° C.) of an Eastman Organic material fractionally distilled from a slurry with $Ba(OH)_2$. No differences in melting point, boiling point, or refractive index were observed between this sample and other samples further treated by vacuum distillation or by formation, recrystallization, and decomposition of the amine hydrochloride. The observed melting point, −115° ± 0.5° C., is in accord with the literature (*1*). Fisher Analysed Reagent methylene chloride (dichloromethane) gave a satisfactory melting point, −95° ± 0.5° C., and was used without further purification.

Cooling rate curves over the entire composition range were obtained using an apparatus similar to that used in the chloroform-triethylamine system (*1*). The sample, about 40 to 80 ml., was contained in an evacuable Dewar vessel, the cap of which was fitted with inlets for a motor driven stirrer, a temperature sensing device, and a stream of dry N_2 gas to prevent condensation of moisture on the sample. Cooling was provided by placing this vessel in a liquid N_2 bath and adjusting the vacuum. Temperatures were sensed by a two-junction copper-constantan thermocouple (referenced to an ice-bath) the e.m.f. of which was monitored by a Honeywell 2773 potentiometer and a Keithley 147 null detector. The imbalance of the null detector was recorded, through a suitable voltage divider, on a Heathkit EUW-20A servo-recorder. Checks of the thermocouple calibration at the ice-point and at the boiling point of liquid N_2 were satisfactory.

As in the previous study (*1*), mixtures on the triethylamine rich side of the composition range were extremely viscous and tended to supercool readily. Experimental variations in sample size, stirrer design and stirring rate, and cooling rate did not solve this problem, and it was necessary to introduce seed crystals to obtain equilibrium freezing temperatures. The high viscosities made it impossible to obtain reliable eutectic halts for triethylamine rich mixtures.

RESULTS

The experimental results are depicted as the phase diagram in Figure 1. Clearly, methylene chloride and triethylamine form a 1 to 2 binary compound with a congruent melting point of 168° ● 1° K. Eutectic compositions were observed at 42 ± 2 and 90 ± 2 mole % of triethylamine. The corresponding eutectic temperatures were 157° ± 2° and 153° ± 2° K. Because of the obvious nonideality of this system, no attempt was made to calculate the thermodynamic parameters of melting (formation) of the binary compound. This system should be investigated by cryogenic calorimetry to deduce the thermodynamics of melting and the strengths of the presumed hydrogen bonds.

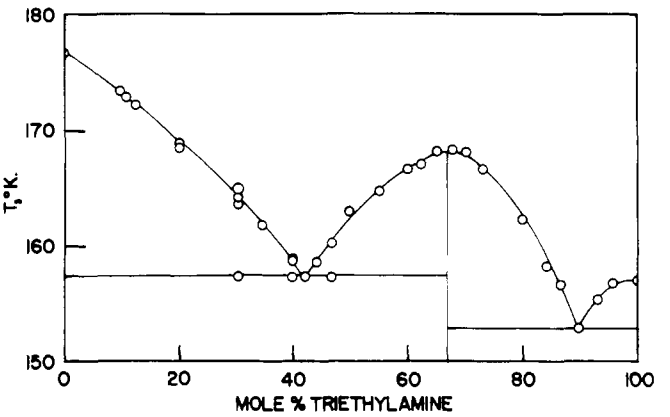

Figure 1. Phase diagram of the system methylene chloride–triethylamine

ACKNOWLEDGMENT

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Some New Derivatives of Maleopimaric Acid

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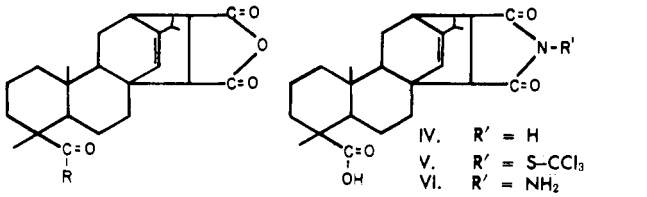
A number of new derivatives of maleopimaric acid have been prepared and characterized.

MALEOPIMARIC ACID (I) is a readily obtainable compound, made by the reaction of maleic anhydride with pine gum, rosin, or the various pure conjugated dienic resin acids, namely, levopimaric, palustric, neoabietic, and abietic acids (*3*). The pure compound finds use in photographic processes while maleated rosin in used as a paper size and in varnishes and surface coatings. A number of new derivatives of maleopimaric acid have been prepared in the present work and are under test as agricultural chemicals. Test results will be published elsewhere. The acid chloride of maleopimaric acid (II) previously reported as a crude unstable intermediate (*4*) has been prepared as a stable



I. R = OH
II. R = Cl
III. R = OCH_3

IV. R′ = H
V. R′ = S–CCl_3
VI. R′ = NH_2
VII. R′ = N = $C(CH_3)_2$
VIII. R′ = $N(CH_3)_2$
IX. R′ = $(CH_2)_3N(CH_3)_2$
X. R′ = CH_3

crystalline compound. Refluxing the acid chloride for a short time in methanol gives the monomethyl ester (III) plus the trimethyl ester. The isolation of the monomethyl ester (III) plus the infrared spectrum of the monoacid chloride unequivocally establish the location of the acid chloride group in the molecule. No diester was isolated from the reaction. Apparently, the liberated hydrogen chloride catalyzes the esterification of the half acid ester, which reaction then proceeds at a rate roughly comparable to the opening of the anhydride ring under the acid conditions which prevail.

The reaction of maleopimaric acid with aqueous ammonia gave the expected imide (IV). The structure was confirmed by preparing the same compound via reaction of levopimaric acid with maleimide in a Diels-Alder reaction. The imide was reacted with trichloromethylsulfenyl chloride to give a compound (V) analogous to the fungicide, Captan.

Maleopimaric acid was condensed with a excess of hydrazine to give the *asym*-aminomaleopimarimide (VI). This compound, on recrystallization from acetone, gave the hydrazone of same (VII). 1,1-Dimethyl hydrazine and maleopimaric acid yielded the expected *N,N*-dimethylaminomaleopimarimide (VIII). Dimethylaminopropylmaleopimarimide (IX) was prepared by the reaction of maleopimaric acid with dimethylaminopropylamine, confirming a patent example (2) in this area. Levopimaric acid was reacted with *N*-methylmaleimide to give the corresponding *N*-methylmaleopimarimide (X).

EXPERIMENTAL

Melting points were taken with a Thomas Hoover capillary melting point apparatus and are uncorrected. The ultraviolet spectra were taken on a Bausch & Lomb Spectronic 505 spectrophotometer and the infrared spectra determined on a Perkin-Elmer Model 21 spectrophotometer. The measurements of optical activity were made on a Franz Schmidt & Haensch precision polarimeter.

Monoacid Chloride of Maleopimaric Acid (MAC, II). A solution of 20 grams of maleopimaric acid in 40 ml. of thionyl chloride was allowed to stand at room temperature overnight and then stripped under reduced pressure to a slush. The crystalline solid was collected on a sintered glass funnel and triturated with dry ethyl ether; yield 16.8 grams (80%); $[\alpha]_D^{25}$ −44.4° (C = 2.4 in chloroform). Recrystallization from dry benzene gave 11.0 grams of acid chloride of unchanged optical rotation; m.p. 190° C. decomposed with evolution of gas; no characteristic absorption from 220 to 320 μ, high end absorption; λ max (Nujol mull) 5.44 (m) (anhydride), 5.63 (broad and very strong) (anhydride), 8.17 (s) (anhydride) μ.

Anal. Calcd. for $C_{24}H_{31}O_4Cl$: C, 68.8; H, 7.46; O, 15.3; Cl, 8.46; neutral equivalent 104.7. Found: C, 68.7; H, 7.39; O, 15.1; Cl, 8.36; neutral equivalent 104.9 (in acetone).

Reaction of MAC with Methanol. A solution of 10 grams of MAC in 200 ml. of methanol was refluxed for 1.5 hours. The excess alcohol was stripped off under reduced pressure to dryness, the residue was dissolved in ether and washed with water until neutral, the ether was removed under reduced pressure, and the residue was crystallized from methanol. The first crop weighed 1.60 grams (16%); m.p. 211–213° C. On recrystallization from benzene, the compound exhibited m.p. 215–216° C.; $[\alpha]_D^{25}$ −29.2 (C = 5.1 in chloroform); reported (*5*) for methyl maleopimarate (III) m.p. 214–215° C. and $[\alpha]_D^{25}$ −26° (C = 10 in chloroform); mixed melting point with authentic sample undepressed.

The mother liquor from the methanol recrystallization was diluted with water and 5.65 grams (51%) of crude trimethyl ester of maleopimaric acid was obtained, m.p. 98° C. On recrystallization from methanol, the ester melted at 101° C. [reported (*6*) 103° C.] and exhibited an NMR spectrum essentially identical to that reported (*1*) for this compound; $[\alpha]_D^{25}$ +13.6 (C = 0.60 in chloroform); $[\alpha]_D^{25}$ +2.9 (C = 0.60 in 95% ethanol).

Maleopimarimide (IV). PROCEDURE A. A slurry of 10 grams of maleopimaric acid in 27 ml. of concentrated aqueous ammonia was charged to a 500-ml. round-bottomed flask and immersed in an oil bath. The temperature was slowly raised until all the solid dissolved (67° C.). The excess ammonia was boiled off at 100° C., and the contents were then heated over a period of 1.5 hours to 170° C. The dry solid was dissolved in hot dioxane, a few drops of 5*N* hydrochloric acid were added, and 6.8 grams (68%) of crude product were obtained when the solution was cooled. This was recrystallized from aqueous ethanol to give 3.84 grams (38%) of imide of unchanged optical rotation on further recrystallization from aqueous acetone; $[\alpha]_D^{25}$ −46.2° (C = 1.1 in chloroform); m.p. 279–280.5° C. with decomposition; no characteristic absorption from 220 to 320 mμ, high end absorption; λ max (Nujol mull) 3.19(s) (NH), 5.68 (m) (imide), 5.88 (s) (imide) μ.

Anal. Calcd. for $C_{24}H_{33}O_4N$: C, 72.2; H, 8.33; N, 3.51; O, 16.0; neutral equivalent 399.5. Found: C, 72.0; H, 8.36; N, 3.47; O, 15.9; neutral equivalent 400.0 (in acetone).

PROCEDURE B. A solution of 1.51 grams of levopimaric acid (0.005 mole) and 0.485 gram of maleimide (0.005 mole) in 15 ml. of dioxane was allowed to stand for 3 days at room temperature. Excess water was then added and the precipitate collected; weight 1.8 grams (90%). The crude imide was recrystallized from aqueous acetone to give 0.63 gram (32%) of pure imide; m.p. 278–281° C. decomposed; $[\alpha]_D^{25}$ −47.3° (C = 0.89 in chloroform); infrared spectrum identical to the spectrum of the imide made by procedure A above. A second crop of imide weighing 0.83 gram (41%) of $[\alpha]_D^{25}$ −41.6° (C = 1.2 in chloroform) was obtained.

Reaction of Maleopimarimide with Trichloromethylsulfenyl Chloride (V). To a solution of 1.0 gram of maleopimarimide (0.0025 mole) in 2.6 grams (0.065) of sodium hydroxide in 50 ml. of water was slowly added 0.84 ml. (0.0075 mole) of trichloromethylsulfenyl chloride with magnetic stirring. After 25 minutes at room temperature, 1.0 ml. of 10% sodium hydroxide was added and 15 minutes later the solution had fallen to pH 6. The gummy solid which came out of solution was collected and dried to give a quantitative yield of crude product. This was crystallized from methanol to give 0.58 gram (41%); $[\alpha]_D^{25}$ −39.8° (C = 0.95 in chloroform), rotation unchanged on further recrystallization; m.p. 153° C. melted and resolidified, 228–229° C. decomposed; no characteristic absorption from 220 to 320 mμ, high end absorption; λ max (chloroform solution) 2.81 (w), 5.60 (m) (imide), 5.88(s) (imide) μ.

Anal. Calcd. for $C_{25}H_{32}O_4NSCl_3$: C, 54.7; H, 5.88: N, 2.55; O, 11.7; Cl, 19.4; S, 5.84; neutral equivalent 549. Found: C, 54.5; H, 6.03; H, 2.60; O, 11.9; Cl, 19.2; S, 5.64; neutral equivalent 548 (in ethanol).

***Asym*-aminomaleopimarimide (VI).** To a solution of 30 grams of 85% hydrazine hydrate (0.50 mole) in 60 ml. of dioxane was added dropwise with magnetic stirring, a solution of 10 grams (0.025 mole) of maleopimaric acid in 60 ml. of dioxane. The temperature was held at 10° to 20° C. throughout. After standing overnight at room temperature the solution was adjusted to pH 3 with 5*N* hydrochloric

acid and diluted with an excess of water. The product was collected; weight 9.8 grams (94%); $[\alpha]_D^{25}$ −53.2° (C = 1.0 in chloroform). On recrystallization from aqueous ethanol, the rotation remained unchanged; weight 5.9 grams; m.p. 255–257° C. decomposed; no characteristic absorption from 220 to 320 mμ, high end absorption; λ max (chloroform solution) 2.87 (s) (amino), 3.05 (s) (amino), 5.63 (m) (imide) μ.

Anal. Calcd. for $C_{24}H_{34}O_4N_2$: C, 69.54; H, 8.27; N, 6.76; O, 15.4; neutral equivalent 415. Found: C, 69.55; H, 8.39; N, 6.80; O, 15.7; neutral equivalent 414 (in ethanol).

A 3.54-gram sample of *asym*-aminomaleopimarimide was recrystallized from aqueous acetone to give 3.31 grams (85%) of acetone condensation product (VII); $[\alpha]_D^{25}$ −12.8° (C = 0.63 in chloroform), rotation unchanged on further recrystallization from acetone, m.p. 281–283° C. decomposed; no characteristic absorption from 220 to 320 mμ, high and absorption; λ max (chloroform solution) 5.66 (m) (imide), 5.88 (s) (imide) μ.

Anal. Calcd. for $C_{27}H_{38}O_4N_2$: C, 71.3; H, 8.43; N, 6.16; O, 14.1; neutral equivalent 455. Found: C, 71.2; H, 8.39; N, 6.24; O, 13.9; neutral equivalent 456 (in ethanol).

1,1-Dimethylaminomaleopimarimide (VIII). To a solution of 4.0 grams (0.01 mole) of maleopimaric acid in 15 ml. of dioxane was added slowly a solution of 1.20 grams (0.02 mole) of 1,1-dimethylhydrazine in 5 ml. of dioxane. After the solution stood overnight at room temperature, a small amount of 3*N* hydrochloric acid was added to bring the solution to pH 2. Excess water was introduced, and the solid was collected (2.16 grams) and crystallized from aqueous ethanol; yield 1.56 grams (36%) $[\alpha]_D^{25}$ −40.6° (C = 0.92 in chloroform), no change in rotation on further recrystallization; m.p. 254–257° C. decomposed; no characteristic absorption from 220 to 320 mμ, high end absorption; λ max (chloroform solution) 5.67 (m) (imide), 5.88 (s) (imide) μ, no band in 3 μ region.

Anal. Calcd. for C, 70.6; H, 8.65; N, 6.33; O, 14.5; neutral equivalent 443. Found: C, 70.5; H, 8.42; N, 6.37; O, 14.3; neutral equivalent 443 (in ethanol).

1,1-Dimethylaminopropylmaleopimarimide (IX). Preparation essentially according to Clinton and Manson (*2*). A solution of 40 grams (0.10 mole) of maleopimaric acid and 11.24 grams (0.12 mole) of 1,1-dimethylaminopropylamine in 500 ml. of benzene was set up under reflux, and in 12 minutes, a solid mass of crystals filled the flask. The theoretical amount of water was liberated in 1.5 hours, and refluxing was continued for a total of 4 hours. The crystals were collected; weight 36.5 grams. An 8.0-gram portion was extracted with ethyl acetate in a Soxhlet-type extractor for 2 hours; weight of remaining solid 7.12 grams. This product was recrystallized from 95% ethanol to give 4.63 grams (41%) of imide; m.p. 237–240° C. unchanged on further recrystallization; $[\alpha]_D^{25}$ −21.0° (C = 1.4 in chloroform); reported (*2*) for 1,1-dimethylaminopropylmaleopimarimide, m.p. 237.4–241.0° C. (corrected) and $[\alpha]_D^{25}$ = −21.8° (1% in chloroform); no characteristic absorption from 220 to 320 mμ, high end absorption; λ max (Nujol mull) 5.68 (m) (imide), 5.88 (s) (imide) μ.

Anal. Calcd. for $C_{29}H_{44}N_2O_2$: C, 71.9; H, 9.15; N, 5.78; O, 13.2; neutral equivalent 485. Found: C, 72.0; H, 9.02; N, 5.72; O, 13.3; neutral equivalent (base) 479, acid (485) (in acetone).

***N*-methylmaleopimarimide (X).** A solution of 9.06 grams (0.03 mole) of levopimaric acid in 40 ml. of dioxane was added to a solution of 3.33 grams (0.03 mole) of *N*-methylmaleimide in 20 ml. of dioxane. After 2 days at room temperature, the specific rotation became constant and the adduct was watered out; yield 11.7 grams (94%); $[\alpha]_D^{25}$ −48° (C 1.8 in 95% ethanol). An analytical sample was recrystallized from methanol to a constant rotation of $[\alpha]_D^{25}$ −55° (C 1.15 in 95% ethanol); m.p. 254–255° C.; λ max ($CHCl_3$) 5.67 (m), 5.80–5.95(s) (both imide).

Anal. Calcd. for $C_{25}H_{35}O_4N$: C, 72.6; H, 8.53; O, 15.5; N, 3.39; neutral equivalent 414. Found: C, 72.8; H, 8.41; O, 15.5; N, 3.46; neutral equivalent 415 (in ethanol).

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Ternary Systems of Furfural and Several Alcohols

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In graphic form 26 systems of furfural, four of furfuryl alcohol, eight of ethyl alcohol, seven of isopropyl alcohol, 15 of butyl alcohols, 12 of methoxyethanol, and 17 of other higher alcohols are presented. Methanol and glycols (previously published) are not included. The graphs show two isopycnics, two twin density lines, two iso-optics, a solutrope, and four systems each having three liquid layers. Most of the other systems have two liquid phases in certain compositions.

FURFURAL (b.p. 161.7° C.) is a widely used selective solvent for hydrocarbons because of its low cost and high selectivity for the hydrocarbons of the light gas oil range (*12, 13*). The low solubility of lubricating oils in furfural makes it less applicable to them unless they are highly aromatic. Experimental studies of furfural are handicapped by its sensitivity to oxidation, causing sludge and necessitating frequent redistillation, although on exclusion of air its heat stability is high.

Critical solution temperatures (CST) of furfural have been compiled (*1*, p. 97; *11*, p. 227) for 32 lighter hydrocarbons; those for 261 pure higher hydrocarbons have been

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