Indirect Identification of *A* as the Meso Ester, *l*-Menthyl *d*-Menthyl Terephthalate. Terephthaloyl chloride and *l*-menthol were converted to bis(*l*-menthyl) terephthalate by the method of Cohen and de Pennington (*1*). The crude product was recrystallized from ethanol to give the pure ester, m.p. 76–78° C. [lit. (*1*) m.p. 77–78° C.]. Terephthaloyl chloride and *d*-menthol treated in the same manner yielded bis(*d*-menthyl) terephthalate, m.p. 76–79° C. An equal quantity of each ester was dissolved in ethanol, and then this solution was evaporated to dryness. The resulting racemic modification melted at 111–112° C. Fraction *B*, then, was the racemic diester, while the higher melting fraction *A* was the meso diester.

Partial Saponification of Diesters Made from Menthol and Terephthaloyl Chloride. In testing Cohen and de Pennington's method for partial saponification of bis(*l*-menthyl) terephthalate, some monoethyl terephthalate was isolated along with the *l*-monomenthyl terephthalate. This result was similar to that reported by Hearst and Noller (*2*) who obtained some monomethyl ester during the partial saponification of bis(*l*-menthyl) nitroterephthalate using methanolic potassium hydroxide. They presumed the methyl half ester was formed by ester exchange from the methanolic potassium hydroxide solution.

Because monomethyl terephthalate is soluble in hot water and can be readily separated from the monomenthyl terephthalates with this solvent, methanol was used in later partial saponifications. To reduce the amount of ester exchange and to increase the solubility of the diesters, especially the meso isomer, dioxane was added as a diluent. Under these conditions, the half esters were obtained as crystalline rather than resin-like materials.

A 100-gram sample of the diester was dissolved in 200 ml. of hot dioxane. To this was added 200 ml. of a methanolic solution containing 18 grams of potassium hydroxide and 18 ml. of water. A magnetic stirrer was added, and the cloudy solution was refluxed for 2 hours. A precipitate formed during this time. Most of the solvent was then evaporated and 850 ml. of water was added. The mixture was extracted twice with 200-ml. portions of benzene to remove menthol and unreacted diester. The water layer was acidified with 6*N* hydrochloric acid to precipitate crude monomenthyl terephthalate. The half ester was extracted with hot water to remove monomethyl terephthalate and dissolved in hot benzene to remove relatively insoluble terephthalic acid. Crystals were obtained from the benzene by the addition of petroleum ether and cooling.

***l*-Monomenthyl Terephthalate.** When bis(*l*-menthyl) terephthalate was used as starting material in the partial saponification procedure the product was *l*-monomenthyl terephthalate, m.p. 126–128° C., $[\alpha]_D^{24}$ −86.3° (c 2, benzene) [lit. (*1*) $[\alpha]_D^{18}$ −85.1° (c 2, benzene)]. Anal. Calcd. for $C_{18}H_{24}O_4$: C, 71.06; H, 7.89. Found: C, 70.90; H, 8.00.

***dl*-Monomenthyl Terephthalate.** When a mixture of racemic and meso diesters was used as starting material in the partial saponification procedure, the product was *dl*-monomenthyl terephthalate, m.p. 135.5–137° C. Anal. Calcd. for $C_{18}H_{24}O_4$: C, 71.06; H, 7.89. Found: C, 70.87; H, 7.78.

***l*-Menthyl Terephthaloyl Chloride.** A 5-gram sample of *l*-monomenthyl terephthalate was refluxed with 10 ml. of thionyl chloride for 1.5 hours. Most of the thionyl chloride was then removed under reduced pressure. Final traces of chloride were removed by adding benzene and evaporating and then by adding petroleum ether and evaporating. The resulting sirup had $[\alpha]_D^{21}$ − 85.4° (c 2, benzene). Anal. Calcd. for $C_{18}H_{23}O_3Cl$: C, 66.97; H, 7.18; Cl, 10.98. Found: C, 67.04; H, 7.28; Cl. 10.73.

***dl*-Menthyl Terephthaloyl Chloride.** The same procedure was used for the preparation of the racemic acid chloride as was used for the optically active acid chloride. In this case, however, the sirup soon crystallized, m.p. 55–58° C. Anal. Calcd. for $C_{18}H_{23}O_3Cl$: C, 66.97; H, 7.18; Cl, 10.98. Found: C, 66.72; H, 6.98; Cl, 10.91.

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Association of Diphenylketene

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The association of solutions of diphenylketene in cyclohexane and benzene has been determined. It is found to be that expected from the dipole moment and it remains constant with time, within the limitations of the experimental method used.

STUDY of the degree of association of diphenylketene was undertaken to explain several unusual properties of diphenylketene. First, diphenylketene and ketenes in general undergo several types of addition (*7*) and cycloaddition (*8*) reactions in which two molecules of the ketene add to one molecule of the other reactant, even though the other reactant is present in excess. Second, diphenylketene and ketenes, in general, dimerize readily (*3*). Third, samples of diphenylketene which have been kept under nitrogen, either as a liquid at room temperature or as a solid at −78° C., have been observed to become less soluble in petroleum hexane and to require hours or days to react under conditions where freshly distilled material reacted in minutes. (The yields of products in the reactions were the same.) The possibility that this behavior could be explained on the basis of a type of dimeric association, as observed in sulfoxides (*11*), was investigated.

The degree of association of diphenylketene, both freshly distilled and stored for 4 to 5 days after distillation, in cyclohexane, an aliphatic solvent, and in benzene, an aromatic solvent, was determined from freezing point depression. For comparison, similar determinations were run on benzophenone, a compound of higher dipole moment, and on diphenyl, a compound of lower dipole moment.

The results with freshly distilled diphenylketene are shown in Figures 1 and 2. The results using material stored under nitrogen for 4 to 5 days, as a liquid at room temperature, as a solid at −78° C., and as a solution in the solvents used, were essentially the same.

Apparently diphenylketene is monomeric in dilute benzene solutions and its association in cyclohexane or in more concentrated benzene solutions is that expected from consideration of its dipole moment and its aromatic nature. Further, the degree of association remains constant on standing, within the limits of the experimental method used. Hence, the unusual properties of diphenylketene mentioned above must be due to factors other than dimeric association.

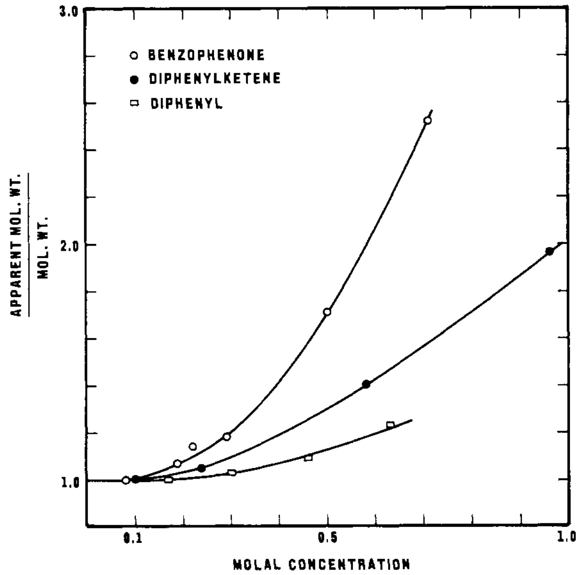

Figure 1. Association in cyclohexane

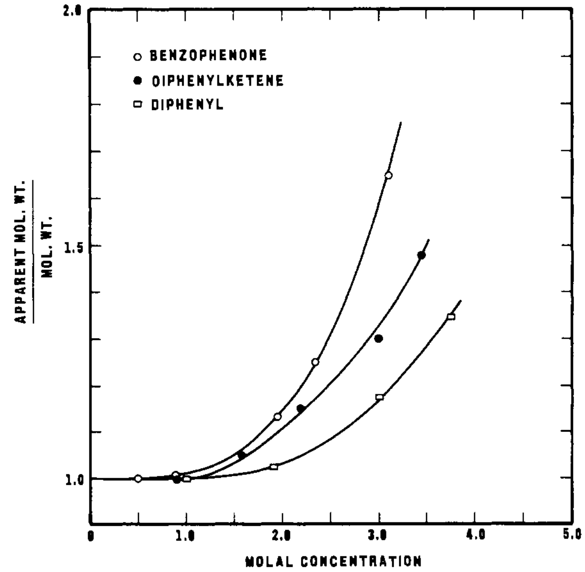

Figure 2. Association in benzene

Samples of diphenylketene that had been kept for 4 to 5 days in cyclohexane solution became very slightly cloudy, presumably because of the formation of a trace of the diphenylketene-oxygen polymer (*10*); however, the quantity of diphenylketene thus used up was not enough to change the freezing point of the solution. This polymer, which would be present in higher concentration in stored material than in the experiments described here where the only oxygen was that trace in the nitrogen, may be the reason for the decreased activity of the diphenylketene observed on storing. In experiments with diphenylketene that had been kept 4 to 5 days, monomeric diphenylketene was recovered quantitatively as the dihydropyran adduct (*6*) on addition of excess dihydropyran. None of the diphenylketene oligomers reacts with dihydropyran.

EXPERIMENTAL

Materials. The solvents were distilled and stored in an atmosphere of nitrogen. The middle fractions were used where the boiling points were essentially constant. Both the melting points and the boiling points agreed with the literature values. The benzophenone and diphenyl were Eastman white label. The melting points agreed with the literature values and the melting point ranges were less than 1°. The diphenylketene (*9*) was redistilled in nitrogen (b.p. 2 mm. 114–15°), and stored under nitrogen.

Dielectric constants (*4*)	
Cyclohexane	2.1
Benzene	2.3

Dipole moments	
Diphenylketene	1.9 (*5*)
Benzophenone	2.9 (*2*)

Method. A modified Beckmann apparatus was used (*1*). Solvent (20.0 ml.) was added from a pipet and samples of solute were added cumulatively. The glass sample container in a second glass container for insulation was placed in an ice-salt water mixture 5° to 10° below the freezing point of the solution. A magnetic stirrer was used. Temperature readings were recorded every 8 seconds. The cooling curves thus obtained were of the expected shape (*1*). In the determinations with diphenylketene, the apparatus was fitted with a T-bore stopcock and the apparatus was evacuated and filled with nitrogen before solvents were added. During the addition of solvent and solute samples, a stream of nitrogen was passed through the apparatus. All pipet operations were in an atmsophere of nitrogen.

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