Under the same conditions but in the absence of sodium methylate the yields were considerably lower.

The reaction appears to be applicable to simple aliphatic esters as would be expected. With ethyl diethylmalonate the same conditions gave only a small yield of the diamide (3.5%). This parallels the experience of Fischer and Dilthey[3] and of Meyer,[10] the latter was not able to detect any noticeable reaction between the substances while the former workers obtained only a 1.1% yield after standing two months. The purely steric situation with this ester should be no more favorable to reaction than with esters of pivalic acid which have been found[6] to react with about one-sixtieth of the speed shown by esters of isobutyric acid.

Experimental

The conversions of the esters to the corresponding diamides are summarized in Table I. To illustrate both the general method and the effect of sodium methylate conversions of ethyl ethylmalonate to ethylmalondiamide in the presence and in the absence of sodium methylate is described.

TABLE I

Ester, ethyl	Time, hours	Amide	M. p., °C.	Yield, %
Ethylmalonate	96	Ethylmalondiamide	215[3]	91
n-Butylmalonate	72	*n*-Butylmalondiamide[a]	198	87
Benzylmalonate	64	Benzylmalondiamide	224–226[4]	96
Diethylmalonate	336	Diethylmalondiamide	225[3,10]	3.5

[a] *Anal.* Calcd. for $C_7H_{14}O_2N_2$: C, 53.2; H, 8.9. Found: C, 53.2; H, 8.9.

Conversion of Ethyl Ethylmalonate to Ethylmalondiamide.—(a) In the presence of sodium methylate: The ester (10 g.) was dissolved in methanol (50 ml.) and a solution of ammonia in methanol (100 ml. of a solution saturated at 0°) containing sodium methylate (from 0.1 g. of sodium) was added. The mixture was allowed to stand in a stoppered flask at room temperature. The diamide soon began to separate. It melted at 215° (lit. gives 216°[3]) without further purification. After thirty-six hours the amount of diamide corresponded to a 62% conversion while after ninety-six hours the separated diamide together with a further small amount obtained by evaporation and acidification of the residue weighed 6.3 g. representing a yield of 91%. (b) Without sodium methylate: The above experiment was repeated but no sodium methylate was added. After sixty hours the amount of diamide separated corresponded to a conversion of about 33%. The amount separated after eighty-four hours together with a small amount obtained by removal of the solvent was 4.4 g. (62%).

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[10] Meyer, *Ber.*, **39**, 198 (1906).

THE WELLCOME RESEARCH LABORATORIES
TUCKAHOE 7, NEW YORK

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Bromination of 9,10-Dihydroanthracene

BY JOHN R. SAMPEY, ANNE K. MCCUEN AND JESSIE M. COX

There is little information in the literature on the bromination of 9,10-dihydroanthracene. Barnett[1] discusses the *cis–trans* isomerism of 9,10-dibromo-9,10-dihydroanthracene, but gives no preparation of the same. Oda[2] measured the rates of bromination without identifying any products. Graebe[3] prepared a dibromoanthracene, melting 219–220° with no details or yield given. We have studied both the photochemical and dark room bromination of peroxide free samples of this hydrocarbon under anhydrous conditions.

The addition during two hours of 0.10 mole of bromine in 50.00 ml. of carbon disulfide to 0.05 mole of dihydroanthracene in 70.00 ml. of the same solvent at 0° with a small (2″) mercury arc 6″ distant, resulted in a 51% yield of 9,10-anthracene dibromide, melting at 219–220°, and giving 46.8% bromine (theory 47.0%) by a Rosanoff analysis. Repeating the bromination in carbon tetrachloride on a boiling water-bath for forty-five minutes gave a 44% yield. Using a large arc (6″) at 4″ distance for thirty-five minutes on a water-bath with carbon disulfide as solvent, cut the yield to 24%.

The dark room bromination of dihydroanthracene gave a mixture of poly-bromo derivatives. In an overnight run with 0.10 mole of bromine in carbon disulfide with 1 g. of iodine present, 0.05 mole of dihydroanthracene gave 7% of the anthracene dibromide, melting at 220°, and 30% of tribromoanthracene, melting at 170°. Kaufler[4] gives the melting point of 2,9,10-tribromoanthracene as 171°.

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[1] Barnett, *Rec. trav. chim.*, **44**, 218–223 (1925).

[2] Oda, *Sci. Papers, Tokyo*, **33**, no. 728, 129–208 (1937).

[3] Graebe, *Ann. Chem. Phys.*, **7**, 257–306 (1870).

[4] Kaufler, *Ber.*, **37**, 4707 (1904).

FURMAN UNIVERSITY
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Spectroscopic Evidence Concerning the Structure of 2-Phenyl-4,4-dimethyl-5(4)-oxazolone Hydrobromide. A Correction

BY CURTIS W. SMITH

The present note is an attempt to correct a mistaken statement concerning the work of Hunter, Hinman and Carter.[1] In our paper[2] "Spectroscopic Evidence Concerning the Structure of 2-Phenyl-4,4-dimethyl-5(4)-oxazolone Hydrobromide" we stated: "During a study of the reaction of β-methylbenzylpenicilloate with phosphorus tribromide, collaborators from the University of Michigan and the Upjohn Company[1] determined the infrared absorption of a solution of the penicilloate and phosphorus tribromide in carefully dried dioxane immediately after combination and then again at short intervals. The oxazolone hydrobromide shown in the accompanying equation

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[1] Hunter, Hinman and Carter, "Methyl Benzylpseudopenicillinate" in "The Chemistry of Penicillin," Princeton University Press, Princeton, N. J., 1949.

[2] Smith and Rasmussen, THIS JOURNAL, **71**, 1080 (1949).

was considered as a more or less transitory (v) intermediate in the reaction."

This statement was an unintentional oversight on our part of the fact that Hunter, Hinman and Carter[1] had changed their original interpretation as to the significance of this experiment so that in the final draft of their chapter in the Penicillin Monograph the oxazolone hydrobromide was not mentioned as a possible intermediate and no conclusion was drawn as to the structure of the intermediate product. This change in interpretation, of which we had been notified, was at least in part based on data obtained from us after conclusion of the penicillin contract.

SHELL DEVELOPMENT COMPANY
EMERYVILLE, CALIFORNIA
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Azeotrope in the Bromine–Carbon Tetrachloride System[1]

BY WILLIAM M. SPICER AND JEROME KRUGER[2]

In connection with thermal diffusion experiments on azeotropes, it seemed desirable to use a colored azeotrope in order that the separation could be followed visually. This need led to a search for azeotropes of bromine. Since none was found listed in the literature, a systematic experimental investigation was undertaken.

The number of possible second components is limited by the reactivity of bromine. The first system selected as a probable one in which to find an azeotrope was that of bromine with carbon tetrachloride. The boiling points of these liquids are only 18° apart and their solutions show positive deviations from Raoult's law.[3] These deviations would be expected to be rather large since there are large differences in the internal pressures, which are 5700 and 3070 atm. for bromine and carbon tetrachloride, respectively.[4]

Experimental

The carbon tetrachloride was purified by washing with concentrated sulfuric acid, then with water, and drying over phosphorus pentoxide. It was then fractionated in a five-foot glass helix packed column. A center cut of about 80% of the charge was retained. The boiling point was 76.0° at 739.1 mm. Using an Abbe refractometer, the index of refraction was found at 25° to be 1.4576 as compared with 1.4575 from the literature.[5] J. T. Baker analyzed C. P. bromine was used without further purification.

Weighed samples of the bromine–carbon tetrachloride solutions were analyzed for bromine by titration with standardized sodium thiosulfate solution using iodide and starch indicator.

Liquid–vapor equilibrium data as shown in Table I were obtained using an equilibrium still similar to that described by Jones, Schoenborn and Colburn.[6] The heating of the residue chamber and flash boiler was controlled by a Variac connected to a Sola constant voltage transformer. The equilibrium temperatures, which were measured by means of a calibrated copper–constantan thermocouple using a potentiometer reading to one microvolt, were accurate to approximately 0.1°.

This uncertainty in the temperature as well as the variation in the pressure as noted in Table I were tolerated since the object was not to obtain accurate liquid–vapor equilibrium data but to ascertain whether an azeotrope exists in this system.

TABLE I

LIQUID–VAPOR EQUILIBRIUM DATA FOR SYSTEM BROMINE–CARBON TETRACHLORIDE

Temp., °C.	Pressure, mm.	Mole fraction Bromine in liquid	Mole fraction Bromine in vapor
58.0	741.2	1.0	1.0
57.9	738.1	0.969	0.966
57.7	736.8	.940	.927
57.9	736.8	.865	.874
58.1	736.8	.771	.810
59.9	734.6	.558	.690
61.2	734.6	.441	.606
63.1	738.5	.342	.536
68.6	734.3	.151	.353
71.7	736.7	.070	.199
76.0	738.5	.0	.0

A plot of the data of Table I in the form of mole fraction bromine in the vapor *vs.* mole fraction bromine in the liquid indicated an azeotrope with a composition of approximately 0.89 mole fraction bromine. In order to determine more accurately the composition and boiling point of this azeotrope, solutions near the azeotropic composition were distilled through the fractioning column mentioned previously. The azeotrope, which was approached from both sides, was found to boil at 57.7° at 735.6 mm. and have a composition of 0.884 mole fraction bromine.

It was felt that there was little likelihood of reaction between these liquids at the low temperatures used. However, the following experiment was performed to determine whether reaction had taken place. A bromine–carbon tetrachloride solution containing approximately 11% bromine was fractionated. After the bromine, as azeotrope, had been removed as indicated by the fact that the distillate coming off exhibited the boiling point of carbon tetrachloride, the content of the still pot exhibited the refractive index of pure carbon tetrachloride.

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(1) From the thesis submitted by Jerome Kruger in partial fulfillment of the requirements for the M.S. degree, Georgia Institute of Technology, September, 1949.

(2) Present address: Department of Chemistry, University of Virginia, Charlottesville, Virginia.

(3) Lewis and Storch, THIS JOURNAL, **39**, 2544 (1917).

(4) Ewell, Harrison and Berg, *Ind. Eng. Chem.*, **36**, 871 (1944).

(5) Perce and Evdorinnoff, *Gazz. chim. ital.*, **70**, 723 (1940).

(6) Jones, Schoenborn and Colburn, *Ind. Eng. Chem.*, **35**, 666 (1943).