solution of III or IV in ethanol with dry hydrogen chloride, diluting with water to the point of turbidity and storing for 24 hr. at 5–10°. This procedure yielded 88 to 90% of the desired material; m.p. 79–81°.

Dimethyl 3-indolesuccinate[2] was prepared either from the diacid or the dinitrile by treating them with dry hydrogen chloride in methanol. The dimethyl ester was obtained in yields of 85–95% and melted at 73–76° after recrystallization from a benzene-*n*-pentane mixture: reported m.p. 74°.[2]

Anal. Calcd. for $C_{14}H_{15}NO_4$: C, 64.36; H, 5.79. Found: C, 64.65; H, 6.06.

3-Indolesuccinimide. The following modification of the method used by Shaw[10] for the preparation of 3-indoleacetamides was employed. An intimate mixture of 35 g. (0.15 mole) of 3-indolesuccinic acid (V) and 70 g. (0.46 mole) of urea in a flask fitted with an air condenser was introduced into an oil bath at 160°. The bath temperature was raised to 185° during 30 min. and maintained at 180–190° for 2.5 hr. Brisk evolution of ammonia was evident during the first part of the final heating period. The hot melt was diluted to 250 ml. with water, cooled and filtered. The crude product was recrystallized from methanol with charcoaling, yielding 17 g. (53%) of white crystals of m.p. 197–198°. A mixed m.p. between this product and V gave considerable depression.

Anal. Calcd. for $C_{12}H_{10}N_2O_2$: C, 67.29; H, 4.67; N, 13.1. Found: C, 67.33; H, 4.70; N, 12.8. Infrared (KBr) (μ): 2.92 (indole NH); 5.50, 5.65, 5.86, and 5.95 ($C{=}O$).

A small amount of 3-indolesuccinimide was also obtained by gradually heating a sample of 3-indolesuccinic acid (V) to 240° in concentrated ammonium hydroxide; it had m.p. 194–195°. The m.p. of a mixture of this material with that prepared from V and urea was not depressed.

Diethyl 3-indolylmethyl malonate (VII). Hydrogenation of a sample of II in ethanol over platinum oxide at 50 p.s.i. gave a 62% yield of diethyl 3-indolylmethylmalonate (VII)[8], m.p. 61–63° (recrystallized from benzene-*n*-pentane). An analytical sample was recrystallized from ethanol-water and had m.p. 63–65°; reported 62°.[8a,b]

Anal. Calcd. for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62. Found: C, 66.68; H, 6.76. Infrared (KBr) (μ): 2.97 (NH); 5.77 and 5.83 ($C{=}O$).

3-Indolylmethylmalonic acid (VIII). A 2.8-g. (0.01 mole) sample of diethyl 3-indolylmethylmalonate (VII) was heated under reflux for 1 hr. in 25 ml. of 15% potassium hydroxide solution. The solution was charcoaled, filtered, cooled, and acidified to *p*H 2 with concentrated hydrochloric acid to yield 1.6 g. (89%) of reddish 3-indolylmethylmalonic acid (VIII);[8] m.p. 182–184° (dec., with evolution of gas). An analytical sample, recrystallized from water, was still reddish; m.p. 185–187° (dec., gas evolution); reported 178° (dec.).[8a]

Anal. Calcd. for $C_{12}H_{11}NO_4$: C, 61.80; H, 4.74. Found: C, 62.08; H, 4.94.

3-Indolepropionic acid (VI). Pyrolysis of a sample of 3-indolesuccinic acid (V) for 2–3 minutes at 205° gave a vigorous evolution of carbon dioxide; the residue was cooled and recrystallized from 20% ethanol (charcoal). The colorless crystals thus obtained melted at 133–134° either alone or upon admixture with an authentic sample of 3-indolepropionic acid.

3-Indolylmethylmalonic acid (VIII) was pyrolyzed at 190–200° to yield VI in a yield of 46%, m.p. 132–134° either alone or upon admixture with authentic VI.

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[10] E. Shaw, *J. Am. Chem. Soc.*, **77**, 4319 (1955).

Metalation of Polystyrene[1]

AVERY A. MORTON AND LLOYD D. TAYLOR

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This metalation of polystyrene was done in the hope of developing a method for introducing metal atoms on the alpha (to phenyl) carbon atoms of the chain. The reaction proved easier than expected. Under some conditions or in some fractions, 86 to 94% of the maximum possible amount of metalation on a chain was realized. The project was terminated before the fine conditions for control could be worked out, but the results deserve mention because they represent a new chemical attack at specific points on this polymer. The reaction also provides a new base for graft polymerization or chemical processes on polystyrene.

The reagent was potassium metal and sodium oxide[2] although the very recent experience[3] with amyl- and phenyl-potassium suggests that those reagents might be equally good or even better because they are finely divided and leave no inorganic residue other than potassium chloride or an alkoxide. Benzene was the medium, that solvent having been found satisfactory in a series of preliminary experiments with cumene, a low molecular weight pattern molecule. After a stipulated time the mixture was carbonated. Then the solid was digested with hot water to remove the carboxylate. Mineral acid precipitated the carboxylated polymer. The dried polymer was weighed, titrated with alkali to determine the neutralization equivalent, and mixed with potassium bromide for infrared measurements.

Metalation was about as easy as with cumene itself. Time was very important. At the end of three hours, under approximately comparable conditions, the weights of carboxylic acid were 0.7 and 0.5 gram for cumene and the polymer, respectively. The neutralization equivalent of the polymer carboxylate indicated that 94% of the available positions on the metalated chain had been occupied. In a longer time (15 hr.) the polymer took up 42% of the potassium, and 36% of the polymer was recovered as carboxylate (14.4 g.) for which 89% of the maximum possible metalation had taken place.

The potassium ion should be on the carbon alpha to the phenyl group because metalation of alkylaryl hydrocarbons by this reagent has occurred[2] only at that place. The absorption at 1700 cm.$^{-1}$ in the infrared (Fig. 1) accorded with this view. The position of absorption was similar to that found for other acids of that type. The intensity of absorption was very high, being much greater at

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[1] This work was performed as part of a research project sponsored by the National Science Foundation.

[2] C. E. Claff, Jr., and A. A. Morton, *J. Org. Chem.*, **20**, 444, 981 (1955).

[3] A. A. Morton and E. J. Lanpher, *J. Org. Chem.*, **23**, 1639 (1958).

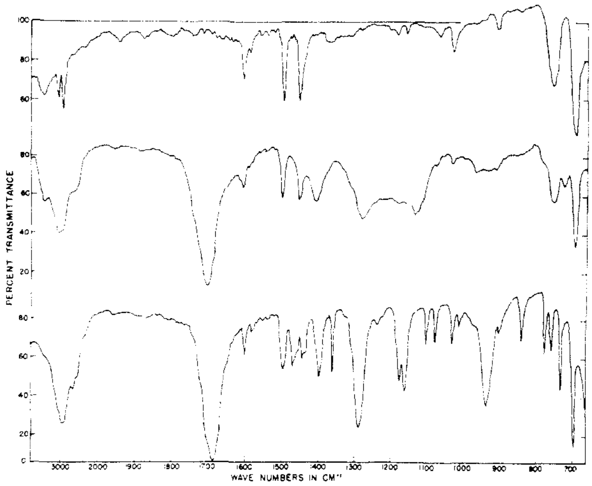

Fig. 1. *Comparison of the infrared absorption of polystyrene, carboxylated polystyrene, and α-phenylisobutyric acid as shown by the top, middle, and bottom lines, respectively. The intensity of the absorption of the carbonyl of the carboxyl group at 1700 cm.$^{-1}$ should be compared with that for monosubstitution on the benzene ring at 700 cm.$^{-1}$ The strong bands at 1290 cm.$^{-1}$ for a carboxyl group and at 935 cm.$^{-1}$ for OH deformation in the low molecular weight carboxylic acid (lowest line) are greatly reduced in intensity in the polymer carboxylic acid*

that wave length than at any other place in the spectrum.

EXPERIMENTS

The reagent and general conditions. In all experiments 8.5 g. of potassium with 56 g. of sodium oxide was used. Benzene (usually 250–300 ml.) was the medium. The apparatus was a 1-l. creased flask with high speed (5000 r.p.m.) stirring as is the common practice[2,3] in this laboratory for heterogeneous reactions.

Metalation of cumene. Cumene (40 g.), which previously had been treated with amylsodium to remove impurities, was metalated in 300 ml. of benzene for 3 hr. at 75–80°. The color of the mixture changed progressively from grey to pinkish brown to dark tan to blackish brown. After being carbonated, the mixture was allowed to stand overnight before addition of water. The hydrocarbon layer was separated and the aqueous portion was extracted twice with ether before being acidified. The carboxylic acids were recovered by extraction with ether. The yield was 0.7 g. or 2% calculated on the metal. The crude acid melted at 72–78° and had a neutralization equivalent of 165.1 (theory 164). Recrystallization from water raised the melting point to 80–81°, identical with the value obtained from previous metalations in heptane.[2,4]

A similar experiment with 95 g. of cumene in 250 ml. of benzene yielded 1.0 g., or 3.4%. In 15 hr. with 200 g. of cumene the yield was 6.3 g. or 24%. Metalation of cumene in benzene was less than it was in cumene itself as might be expected; under conditions similar to the 3-hr. experiment the yield was 3 g. or 11%, and similar to the 15-hr. run it was 14 g. or 40%. The melting points of all of these products were similar to that described for the first experiment in this section.

Metalation of polystyrene. Polystyrene (40 g.) in 500 ml. of benzene was metalated for 3 hr. at 75–80°. The color changed from light brown to tan to chocolate brown. The carbonated product was treated with water as in the case of the metalated cumene, but the benzene was removed by warming on a steam bath. Then the solid was digested for a day with a liter of water to which a few pellets of sodium hydroxide had been added. The aqueous extract was acidified and the recovered polymer was washed and dried. The yield was 0.5 g. and the neutralization equivalent was 234, a value which showed that the metalation of this water-soluble fraction had been 59% complete.

This experiment was repeated with 95 g. of polymer. The yield was 0.2 g. and the neutralization equivalent was 161.5 which corresponded to 94% complete metalation of that fraction.

Several metalations were carried out for 15 hr. With 29 g. of polystyrene in 300 ml. of benzene the yield after three extractions of the carboxylated polymer was 14.4 g. which had a neutralization equivalent of 172 corresponding to 89% complete metalation of that fraction. With 62.5 g. of polystyrene the yield was 17.1 g. of carboxylated polymer which had a neutralization equivalent of 178, corresponding to 86% metalation of the available positions in that fraction. With 200 g. of polymer the yield was 3 g. and the neutralization equivalent was 220, corresponding to 65% complete metalation in a chain.

The reduction in yield as larger quantities of polystyrene were used may be an illusion caused by distribution of the metalating action to other chains and failure to extract polymer which contained only a few carboxyl groups per chain. No claim is made that the extraction removed all of the carboxylated polymer. However, in one instance where the yield was very low, the residue was given an additional extraction with alcoholic sodium hydroxide without removal of any more carboxylated polymer.

Infrared measurements. The polymer was ground with potassium bromide in proportion to make a 1% pellet. The spectrum is shown in Fig. 1 together with one of polystyrene (top) and of α-phenylisobutyric acid (bottom) made under the same conditions and at the same concentration. The absorption at 1700 cm.$^{-1}$ is characteristic[5] for the carbonyl of the carboxyl group and its intensity confirms the finding of a large amount of metalation on each chain. Its position accords with other evidence that the carboxyl is on a carbon atom adjacent to the phenyl group, the absorption for that position being a little different from that shown by a carboxyl on the ring. Table I shows a comparison of the polymer carboxylic acid with other acids which have a somewhat similar structure and have been observed[4] in this laboratory.

TABLE I

INFRARED COMPARISON OF ABSORPTIONS BY THE CARBONYL OF THE CARBOXYL GROUP IN VARIOUS CARBOXYLIC ACIDS OF SOMEWHAT SIMILAR STRUCTURES

Hydrocarbon Metalated	Aliphatic Carboxyl, cm.$^{-1}$	Carbon Component of Acid	Aromatic Carboxyl, cm.$^{-1}$
Cumene	1691	$-(CH_3)_2CC_6H_5$	
Cumene		$(CH_3)_2CHC_6H_4-$	1681
n-Butylbenzene	1705	$-(C_3H_7)CHC_6H_4-$	1685
p-Cymene	1712	$-CH_2C_6H_3CH(CH_3)_2$	
Polystyrene	1700	$-(RCH_2)_2CC_6H_5$[a]	

[a] R symbolizes a section of the polystyrene chain.

Acknowledgments. The authors are greatly indebted to James Howard for carrying out all of the metalations described in this note, to Marianne

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(4) A. A. Morton and J. L. Eisenmann, *J. Org. Chem.*, **23**, 1469 (1958).

(5) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, Inc., New York, N. Y., 1954.

Taylor for the infrared measurements, to the Dow Chemical Company for the polystyrene used in most of the experiments, and to the E. I. du Pont de Nemours & Co., Inc. for the sodium oxide.

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Preparation of D-Propylene Glycol and Oxide

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By the reduction of acetol benzoate, readily prepared from chloroacetone and sodium benzoate, with fermenting yeast solution, optically pure D-propylene glycol 1-benzoate was obtained in 65% yield. Saponification produced D-propylene glycol in 60% yield. This contrasts to yeast reduction of acetol itself, which yields L-propylene glycol.[1]

Treatment of the D-glycol with anhydrous hydrogen bromide gave the bromohydrin, $[\alpha]^{24}_{D}$ +9.90° (in $CHCl_3$), which was converted by alkali to D-propylene oxide, $[\alpha]^{21}_{D}$ −6.21° (2% in $CHCl_3$).

EXPERIMENTAL

D-*Propylene glycol 1-benzoate.* Into a 3-l. two-necked round-bottomed flask, provided with a gas trap and a mechanical stirrer, a solution of 100 g. of sucrose in 450 ml. of tap water was placed. To this solution, a paste of 40.6 g. of Fleischmann's dry yeast in 140 ml. of tap water was added. The mixture was allowed to stand at room temperature until a lively evolution of gas started. To this vigorous fermenting solution, 4.5 g. of acetol benzoate[2] was added and the mixture was allowed to stand at room temperature until the reaction subsided. The flask was then transferred to an incubator at 32° (or at room temperature for a longer time). The reaction was generally completed when all of the yeast had settled. Most of the clear solution was separated from the yeast by a siphon. The last portion of the solution was filtered. The combined solution was extracted with ether (3 × 150 ml., tech. grade) and the ethereal solution was washed with 3% aqueous sodium carbonate solution, water, and dried. After the removal of the solvent, the yellowish oil was distilled under reduced pressure, b.p. 139–140° (5 mm.). The distillate solidified after cooling. It was recrystallized from ether (Mallinckrodt, anhyd.) as white needles by dissolving the crude product in ether at room temperature and cooling the ethereal solution with an acetone–Dry Ice bath, m.p. 42–42.5°; yield, 64–66%, $[\alpha]^{24.2}_{D}$ + 21.8° (in $CHCl_3$).

The compound obtained did not give a good analysis, even after it had been purified alternatively by vacuum distillation and recrystallization (each twice).

Anal.: Calcd. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 67.17, 67.32, 67.39; H, 6.87, 6.84, 6.77.

D-*Propylene glycol.* Optically-active propylene glycol 1-benzoate (40 g.) was added gradually with constant shaking to 20 g. of 50% alkali solution. An additional 10–15 ml. of water was added and the cakelike sodium benzoate was mashed with a spatula. The reaction mixture was refluxed in an oil bath at 125° for 3 hr. After cooling, 100 ml. of ether was poured in and the mixture was filtered. The precipitate was washed with 10 ml. of absolute ethanol. The filtrate was extracted with ether for 9 hr. The ethereal layer obtained was dried over anhydrous magnesium sulfate and evaporated to yield 10.1 g. (60%) of propylene glycol, b.p. 92° (14 mm.), $n^{26.7}_{D}$ 1.4334, $[\alpha]^{24.2}_{D}$ + 30.0° (in $CHCl_3$). (For *l*-propylene glycol, b.p. 86–88° (9–10 mm.), $[\alpha]^{24.4}_{D}$ −28.6° (in $CHCl_3$); −14.9° (pure state, dm.), d^{24} 1.030, n^{24}_{D} 1.4355.)

D-*Propylene oxide.* Levene's synthesis[3] for L-propylene oxide was used. D-Propylene bromohydrin was prepared by passing dry hydrogen bromide through D-propylene glycol at 0°; yield, 60%, b.p. 57–58° (19 mm.), n^{25}_{D} 1.4765 $[\alpha]^{24}_{D}$ +9.90° (in $CHCl_3$). (For L-propylene bromohydrin, n^{25}_{D} 1.4775, $[\alpha]^{24}_{D}$ −10.53° (in $CHCl_3$) or −3.37° (pure bromohydrin), $d^{24.5}$ 1.541.)

The D-propylene bromohydrin was then cyclized to D-propylene oxide with 45% (by weight) aqueous potassium hydroxide, b.p. 35°, $[\alpha]^{21}_{D}$ −6.21° (2% in $CHCl_3$). [*l*-Propylene oxide, $[\alpha]^{21}_{D}$ +7.05° (2% in $CHCl_3$); +14.5° (38% in ether)].

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[1] The reduction of the benzoate in the opposite sense to the glycol was predicted by Dr. V. Prelog (private communication).

[2] For the preparation of acetol benzoate, Adams and Govindacharis' procedure was followed [*J. Am. Chem. Soc.*, **72,** 158 (1950)] with the following modification. The combined ethereal solution was washed with ice-cold 3% sodium carbonate solution, water, and dried. It is very important that no trace of benzoic acid remain in the acetol benzoate. Otherwise the yeast will be killed during the fermentation.

[3] P. A. Levene and A. Walti, *J. Biol. Chem.*, **68,** 415 (1926).

Relative Reactivities of Toluene and Toluene-α,α,α-d_3 in Hydrogen-Deuterium Exchange

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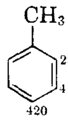
March 2, 1959

Recent exchange studies[2] carried out in this laboratory have led to the following values for the partial rate factors for hydrogen-deuterium exchange in the case of toluene:



These exchange studies were conducted at 70° in a trifluoroacetic acid medium. Under these conditions, exchange occurs only in the aromatic nucleus. This fact was demonstrated by oxidizing a sample of randomly deuterated toluene to benzoic acid with aqueous alkaline permanganate. There was no loss of deuterium in this transformation. Infrared absorption studies, though less sensitive, also indicated the absence of side-chain deuterium in the randomly deuterated toluene samples. These

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[1] Abstract of part of Ph.D. thesis submitted to the University of Minnesota, June 1958.

[2] W. M. Lauer, G. Matson, and G. Stedman, *J. Am. Chem. Soc.*, **80,** 6433, 6437, 6439 (1958).