

flashed to the cold trap at 1 mm. pressure. The products were worked up in the usual manner to give a 23% yield of 1-chloro-3-ethoxy-1-propyne.

*cis*-1-Bromo-1-chloro-1-propene (H,Br). Bromine was added to a mixture of 90% *trans*-1-chloro-1-propene and 10% *cis*-1-chloropropene (0.77 mole) in carbon tetrachloride (400 ml.) at  $-10^{\circ}$  over a period of 1 hr. followed by 3 hr. at the same temperature. The reaction mixture was worked up in the usual manner and distilled to give a 75% yield of 1,2-dibromo-1-chloropropene boiling at  $56^{\circ}$  (9 mm.). The physical properties of this compound were the same as those obtained for the 1,2-dibromo-1-chloropropene from *cis*-1-chloro-1-propene and its infrared spectrum was essentially the same.

This 1,2-dibromo-1-chloropropene (0.17 mole) and potassium acetate (0.51 mole) in acetic acid (100 ml.) were heated for 16 hr. at reflux temperature. Work up of the reaction mixture gave a 30% yield of 1-bromo-1-chloro-1-propene. A 56% yield was obtained by using potassium hydroxide (12%) in glycerol at  $80^{\circ}$  and a pressure of 113 mm. Under these conditions the product flashed to a cold trap as soon as formed. Physical properties of this material are given in Table I.

The *cis*-1-bromo-1-chloro-1-propene (H,Br) was dehydrobrominated by dropping it into a 12% solution of potassium hydroxide in glycerol under nitrogen at a temperature of  $76^{\circ}$ . There was a 26% conversion and a 25% yield of 1-chloro-1-propyne boiling at  $31-31.5^{\circ}$  (755 mm.). The identity of the 1-chloro-1-propyne was checked by comparing its infrared spectrum with that of an authentic sample.

*trans*-1-Bromo-1-chloro-1-propene (H,Br). *cis*-1-Chloro-1-propene with a boiling point of  $30.5^{\circ}$  at 733 mm. pressure ( $n_D^{20}$  1.4061) was obtained from Columbia Organic Chemicals Co. The material had been purified by distillation through a 100-plate column at a reflux ratio of 100:1. The distillation was made by Arthur Rose, Applied Science Laboratories, Inc., State College, Pa. Gas chromatography indicated a purity of 99+%.

Bromine was added to the *cis*-1-chloro-1-propene in a manner similar to that used for the *trans*-1-chloro-1-propene. Sixty-three hours were required to effect the addition. A 70% yield of 1,2-dibromo-1-chloropropene was obtained. The physical properties were essentially the same as those of the 1,2-dibromo-1-chloropropene from *trans*-1-chloro-1-propene (Table I).

It was not possible to dehydrobrominate this compound with potassium acetate in acetic acid in a manner similar to that used for the bromine addition product of *trans*-1-chloro-1-propene. *trans*-1-Bromo-1-chloro-1-propene(H,Br) was obtained by using potassium hydroxide in glycerol and the same procedure as that used for the production of *cis*-1-

bromo-1-chloro-1-propene(H,Br) from the 1,2-dibromo-1-chloropropene from *trans*-1-chloro-1-propene. A 60% yield was obtained.

This 1-bromo-1-chloro-1-propene was not dehydrohalogenated by potassium hydroxide in glycerol under the same conditions used to dehydrobrominate the 1-bromo-1-chloro-1-propene from *trans*-1-chloro-1-propene. It was dehydrobrominated by powdered potassium hydroxide at  $130^{\circ}$  to give a 33% yield of 1-chloro-1-propyne. No 1-bromo-1-propyne was detected. The unreacted 1-bromo-1-chloro-1-propene was shown by its infrared spectrum to be the same as that of the isomer from *trans*-1-chloro-1-propene.

*Infrared spectra.* The infrared spectra were obtained using a Baird Associates Double-Beam Recording Infrared Spectrophotometer equipped with sodium chloride optics. The following are the principal bands in microns.

*cis*-1-Chloro-1-propene: 3.41; 6.10; 6.92; 7.23; 7.60; 10.68; 13.2-13.3; 14.4-14.7.

*trans*-1-Chloro-1-propene: 3.41-3.45; 6.12; 6.94; 8.09; 10.55; 10.8-10.9; 12.6.

1,2-Dibromo-1-chloropropene (from *cis*-1-chloro-1-propene): 3.33; 6.91; 7.25; 7.60; 7.99; 8.30; 8.53; 9.51; 9.96; 11.21; 13.08; 13.4-13.9; 14.7.

1-Bromo-1-chloro-1-propene (from *cis*-1-chloro-1-propene): 3.41; 5.61; 6.17; 6.91; 7.25; 7.87; 9.04; 10.02; 10.2-10.3; 10.73; 11.7-12.1; 12.3-12.4; 14.20.

1-Bromo-1-chloro-1-propene (from *trans*-1-chloro-1-propene): 3.46; 6.22; 6.97; 7.30; 7.91; 9.10; 10.3-10.4; 11.9-12.1; 12.4.

2,3-Dibromo-2-propen-1-ol: 2.92-3.10; 3.21; 3.41; 3.50; 6.20; 6.90; 8.00; 8.15; 9.4-9.8; 10.42; 12.56; 14.0-14.2.

3-Bromo-3-chloro-2-propen-1-ol: 3.0-3.1; 3.40; 3.48; 6.21; 6.9-7.1; 7.4; 8.2; 9.5-9.9; 11.9-12.2.

1-Bromo-1-chloro-3-ethoxy-1-propene: 3.40; 3.50; 6.21; 6.92; 7.18; 7.42; 7.90; 8.9-9.1; 12.0-12.1.

1,1-Dibromo-3-ethoxy-1-propene: 3.34; 3.47; 6.21; 6.92; 7.31; 7.43; 7.87; 8.29; 9.0-9.1; 9.8; 11.25; 11.9; 12.5-12.8.

1,1-Dibromo-3-phenoxy-1-propene: 3.28; 3.41; 3.48; 6.12; 6.25; 6.68; 6.85; 7.29; 7.70; 8.0-8.3; 8.52; 9.27; 9.63; 9.8; 10.05; 11.32; 11.9; 12.5-12.7; 13.2-13.3; 14.54.

3-Chloro-2-propyn-1-ol: 3.0-3.1; 3.42; 3.48; 4.48; 6.9-7.1; 7.40; 8.18; 9.9-10.1.

3-Bromo-2-propyn-1-ol: 2.9-3.1; 3.43; 3.51; 4.52; 6.9-7.1; 7.41; 8.18; 9.4-9.6; 10.1-10.3; 12.6-12.7.

1-Chloro-3-ethoxy-1-propyne: 3.38; 3.48; 4.45; 6.92; 7.18; 7.42; 7.95; 8.9-9.1; 11.9; 15.1.

1-Bromo-3-ethoxy-1-propyne: 3.35; 3.47; 4.50; 6.72; 6.93; 7.31; 7.42; 7.94; 8.9-9.2; 9.76; 10.01; 11.88.

1-Bromo-3-phenoxy-1-propyne: 2.99; 3.24; 3.39; 3.44; 4.46; 6.22; 6.67; 6.86; 7.25; 7.70; 7.92; 8.1-8.3; 8.49; 9.23; 9.5; 9.7; 10.08; 11.28; 11.99; 12.82; 13.1-13.3; 14.54.

AUSTIN, TEX.

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES OF THE ETHYL CORPORATION]

## Catalytic Graphite Inclusion Compounds. II. Potassium Graphite as an Alkylation Catalyst

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Potassium graphite has been found to catalyze both the nuclear and side-chain alkylation of aromatic hydrocarbons with ethylene.

While attempting to catalyze the polymerization of ethylene with potassium graphite,  $KC_8$ ,<sup>1</sup> in ben-

zene and in toluene, it was found that alkylation of these hydrocarbons occurred instead. A study was therefore undertaken of the potassium graphite-catalyzed alkylation of aromatic hydrocarbons with olefins. The results are shown in Table I.

(1) H. E. Podall, W. E. Foster, and A. P. Giraitis, *J. Org. Chem.*, **23**, 82 (1958).

TABLE I  
CATALYTIC ALKYLATION OF AROMATICS USING POTASSIUM GRAPHITE (KC<sub>8</sub>) CATALYST

Solvent or Substrate	KC <sub>8</sub> (g.)	Temp. Time	Pressure, C <sub>2</sub> H <sub>4</sub> (psig)	Products
Benzene 0.28 mole	1.4	102–112° 2–3 hr.	700	1.7 g. <i>sec</i> -butylbenzene, 2.6 g. higher mono-substituted benzenes + <i>m</i> -disubstituted benzene, 0.6 g. residue
Benzene 0.34 mole	3	200° 20 hr.	900	9.6 g. liquid, b.p. > 150°, containing 23% <i>sec</i> -butylbenzene and 19% diphenyl
Benzene 0.23 mole	2	250° 26 hr.	150	None
Toluene 0.24 mole	9	120–130° 7–9 hr.	800	16.4 g. 3-phenylpentane (50% conversion) + 5–10 g. higher boiling material
Toluene 0.24 mole	2	150–155° 30 hr.	970	28% toluene recovered, 34% conversion to <i>n</i> -propylbenzene (48% yield), 12% conversion to 3-phenylpentane (17% yield) and 0.7 g. high-boiling material
Isopropylbenzene 0.18 mole	2	200° 24 hr.	700	21.9 g. liquid, b.p. 172–267° (corr.), containing <i>tert</i> -amylbenzene (42% conversion) and 11% unreacted isopropylbenzene, 3.9 g. residue

It was found that ethylene was readily absorbed in benzene in the presence of catalytic amounts of potassium graphite at 100–110°. This temperature was considerably lower than that required for the polymerization of ethylene in the presence of potassium graphite in aliphatic hydrocarbons. Workup of the reaction mixture yielded about 3 grams of alkylated benzene per gram of potassium. *Sec*-butylbenzene was the predominant product (35% by weight) with higher monoalkylbenzenes and some *m*-dialkylbenzene as the remainder. No significant quantity of ethylbenzene could be detected. This contrasts with the results obtained with organosodium catalysts by Pines and Mark.<sup>2</sup> Apparently with KC<sub>8</sub> as catalyst, the ethylbenzene immediately reacts further with ethylene.

In an effort to obtain a higher conversion of benzene to *sec*-butylbenzene, a run was made at 200° and an ethylene pressure of 900 psig. It was found that although the yield of products boiling above benzene increased to 11 grams per gram of potassium, the product now contained only 23% *sec*-butylbenzene. The remainder consisted of 19% of a rather surprisingly pure white solid [b.p. 257–260°/760 mm. (corr.), m.p. 66.5–68.5°] and higher monoalkylbenzenes. The white solid was identified as diphenyl from its mixed melting point and infrared spectrum.<sup>3</sup>

In an effort to decrease the chain growth leading to higher monoalkylbenzenes, another run was made at 250° and an ethylene pressure of only 150 p.s.i.g.<sup>4</sup> No significant reaction occurred. Appar-

ently under these conditions the initiation and/or propagation reactions were too slow to compete with the termination reactions.

An attempt was made to alkylate benzene with isobutylene using the KC<sub>8</sub> catalyst at 200°, 330 p.s.i.g. A high yield of *tert*-butylbenzene was expected, since it does not contain  $\alpha$ -hydrogens to lead to transmetallation and further alkylation. It was found, surprisingly, that no reaction occurred; only benzene and isobutylene were recovered from the reaction mixture.<sup>5</sup>

Reaction of ethylene with KC<sub>8</sub> in toluene gave alkylation of the side chain. A 50% conversion of toluene to 3-phenylpentane was obtained together with some higher alkylbenzenes. It has been reported by Pines and coworkers<sup>6</sup> that the alkylation of toluene with ethylene is effectively catalyzed by the use of a mixture of sodium and a "promoter" such as anthracene or *o*-chlorotoluene. They suggest that the reaction occurs *via* an organosodium compound, which is formed *in situ*.

The use of KC<sub>8</sub> as a catalyst for the side-chain alkylation of toluene was apparently novel and rather interesting because of its high catalytic activity. A "promotor" was not required.<sup>7</sup> In an effort to increase the conversion of toluene to 3-phenylpentane, another reaction was carried out at a somewhat higher temperature, 150° instead of 120°,

(2) H. Pines and V. Mark, Abstracts of Papers, 127th Meeting AMERICAN CHEMICAL SOCIETY, Cincinnati, Ohio, March 29 to April 7, 1955, p. 21N.

(3) Diphenyl might arise from the coupling of phenyl radicals formed by a radical-transfer reaction.

(4) Data obtained for the KC<sub>8</sub> catalyzed polymerization of ethylene (see ref. 1) indicate that an increase in temperature and a decrease in the ethylene pressure both tend to decrease the chain length of the resulting polymer.

(5) The absence of any reaction here might be interpreted as being due either to the unreactivity of isobutylene towards phenylpotassium (which may be formed from the interaction of benzene with KC<sub>8</sub>), or to the unreactivity of isobutylene towards KC<sub>8</sub>. In the latter case, it would be assumed that the first step in the alkylation of benzene involves formation of an *alkyl*-potassium compound, from the olefin and KC<sub>8</sub>, and that the latter transmetallates benzene.

(6) H. Pines, J. A. Vesely, and V. N. Ipatieff, *J. Am. Chem. Soc.*, **77**, 554 (1955).

(7) It has been found in our laboratories that sodium or potassium alone is considerably less effective than potassium graphite as an aromatic alkylation catalyst.

and with a smaller concentration of suspended  $KC_8$  catalyst. Surprisingly, the main product now was *n*-propylbenzene instead of 3-phenylpentane; the product mixture contained a 48% yield of *n*-propylbenzene, a 17% yield of 3-phenylpentane, and a small quantity of higher alkylated products. The product distribution in the side-chain alkylation of toluene is thus apparently quite sensitive to changes in the reaction conditions.

In order to establish the generality of the  $KC_8$  catalyzed side-chain alkylation reaction, an attempt was made to ethylate isopropylbenzene with ethylene. A 42% conversion to *tert*-amylbenzene was obtained.

It thus appears that the potassium graphite inclusion compound,  $KC_8$ , is a powerful and effective catalyst for the side-chain alkylation of aromatic hydrocarbons with ethylene and possibly with other olefins. It appears to be particularly useful for side-chain ethylations of aromatic hydrocarbons, containing at least one  $\alpha$ -hydrogen, leading to highly branched alkylbenzenes.

#### EXPERIMENTAL

*Materials.* The materials used were all C.P. reagents and/or were rectified followed by drying with sodium ribbon.

*General procedure<sup>8</sup>—ethylation of isopropylbenzene.* Two grams of  $KC_8$  and 25 ml. of isopropylbenzene (dried over sodium ribbon) were charged into a 100 ml. Magne-Dash autoclave. The system was purged and then pressurized with ethylene to 300 p.s.i.g. It was then heated to 200° and repressurized to 700 p.s.i.g. with ethylene. The reaction was carried out for 24 hr. at 200°. The system was then cooled to room temperature, quenched with 50 ml. of water, and filtered. The organic layer was red-brown in color. On rectification it gave 2.3 g. of isopropylbenzene (11% recovery), 21.9 g. of fractions b.p. 172–267°/760 mm. (corr), and 3.9 g. of residue, b.p. >267°/760 mm. (corr). The fractions of b.p. 172–267° contained principally a pure fraction of *tert*-amylbenzene, b.p. 192°/760 mm; the total *t*-amylbenzene, estimated from an analysis of the rectification data, amounted to 11.1 g, or a 42% conversion. The graphite filter cake, 3.3 g., was extracted with 100 ml. of *m*-xylene for 6 hr. in a Soxhlet extractor. The extract was then cooled to room temperature, and about 25–50 ml. of 2B ethanol was added to precipitate a very small quantity of a gelatinous white solid. This material was not investigated.

The alkylations of benzene and toluene were carried out by similar procedures, except for the temperature and time employed (see Table I).

*Acknowledgment.* The authors wish to thank Dr. R. L. Hudson and Mr. J. B. Sigrest for the infrared and rectification work, respectively.

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(8) See ref. 1 for procedure used to prepare  $KC_8$ .

[CONTRIBUTION FROM AVERY LABORATORY, THE UNIVERSITY OF NEBRASKA]

## An *O*-Aroylgllycollate and Carboxylic Anhydrides from the Attempted *C*-Aroylation of Methyl Diazoacetate<sup>1</sup>

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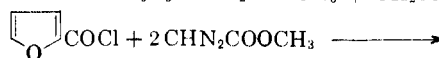
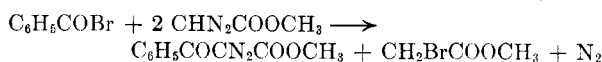
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3,5-Dinitrobenzoyl chloride reacts with methyl diazoacetate containing water to give methyl *O*-(3,5-dinitrobenzoyl)glycollate. Under similar conditions,  $\alpha$ - and  $\beta$ -naphthoyl chloride, and *o*-iodobenzoyl chloride give carboxylic anhydrides. Possible mechanisms are discussed.

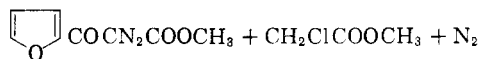
In a previous communication from this laboratory,<sup>3</sup> it was shown that reduction of methyl benzoyldiazoacetate affords DL-erythro- $\beta$ -phenylserine (allophenylserine) in good yield. Extension of this reaction would require synthesis of additional aroyldiazo esters. The present paper describes the attempted synthesis of the latter class by the action of four aromatic carboxylic acid chlorides on methyl diazoacetate, prepared in the usual manner and used without distillation.

Previous work indicates that benzoyl bromide reacts smoothly with methyl diazoacetate (I) to

give the crystalline methyl benzoyldiazoacetate,<sup>4</sup> whereas benzoyl chloride gives with I an oily product which was not identified.<sup>4</sup> In other instances, acid chlorides react with I to give the acyl- or aroyldiazo ester. Thus several aliphatic acid chlorides give liquid diazo esters,<sup>4</sup> and  $\alpha$ -furoyl chloride<sup>5</sup> gives the crystalline methyl  $\alpha$ -



I



(1) Taken in part from a portion of a thesis submitted by Donald Nixon Thatcher in partial fulfillment of requirements for the Ph. D. degree, 1954.

(2) Du Pont Teaching Assistant, 1953–1954.

(3) J. H. Looker and D. N. Thatcher, *J. Org. Chem.*, **22**, 1233 (1957).

(4) H. Staudinger, J. Becker, and H. Hirzel, *Ber.* **49**, 1978 (1916).

(5) T. Reichstein and H. J. Morsman, *Helv. Chim. Acta*, **17**, 1120 (1934).