NOTE

Boron Arsenate

BY GUSTAV E. R. SCHULZE

Schumb and Hartford in a recent article dealing with boron arsenate,[1] while referring to my publications[2] in this connection, report new values for the density and refractive index of boron arsenate which deviate greatly from those which I reported in the above-mentioned articles, without attempting any explanation of these differences.

Schumb and Hartford found for the density of $BAsO_4$ at room temperature 3.40 and for the refractive index, with the sodium D line, 1.66; I obtained densities by three entirely independent methods of 3.64–3.66, and indices of refraction $\omega = 1.681$ and $\epsilon = 1.690$. While my preparation consisted of single crystals with edges about 0.1 mm. long, that of Schumb and Hartford (according to a private communication) was extremely finely divided, so that the refractive index could only be determined under a microscope for a conglomerate of single particles and could therefore only yield a mean index.

Since the purity both of my preparation and that of Schumb and Hartford was confirmed by analysis, it may be that the discrepancies are to be ascribed to the very different degree of dispersion. A second possibility is that the low values for the density and the indices of refraction resulted from the increasing difficulty of measurement with decreasing size of particles. A third, but quite unlikely possibility, is that the discrepancies are due to the existence of two modifications of $BAsO_4$.

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[1] Schumb and Hartford, THIS JOURNAL, **56**, 2646 (1934).

[2] Schulze, *Naturwiss.*, **21**, 562 (1933); *Z. physik. Chem.*, **B24**, 215 (1934).

[CONTRIBUTION FROM RESEARCH LABORATORIES OF THE SHELL DEVELOPMENT COMPANY]

Direct Alkylation of Aromatic Hydrocarbons by Olefins under the Catalytic Influence of Phosphorus Pentoxide

BY B. W. MALISHEV

The direct alkylation of aromatics with olefins was first accomplished by Balsohn[1] in 1879, *i. e.*, two years after Friedel and Crafts published their synthesis with aluminum chloride. Since Balsohn, other investigators have made developments in this field, using the same catalyst. The present investigation was undertaken with the object of finding a catalyst similar to aluminum chloride for this type of alkylation and it has been found that phosphorus pentoxide is very effective.

Inasmuch as phosphorus pentoxide is insoluble in hydrocarbons, its effectiveness as a catalyst is dependent upon producing and maintaining a large contact surface. Commercial phosphorus pentoxide is in a state of colloidal subdivision but its simple colloidal dispersions in hydrocarbons are not stable and readily coagulate to hard infusible or sticky masses. Consequently in the course of this investigation the necessity to maintain phosphorus pentoxide in its colloidal state was recognized and suitable dispersions were developed through the use of stabilizing colloids and peptizing agents. The best stabilizing colloid for the purpose of this investigation was found to be lampblack. F. S. Brown and C. R. Bury[2] obtained colloidal dispersions of phosphorus pentoxide in nitrobenzene by peptization with alcohols, phenols or organic acids. In this investigation cresol was found to be quite effective for peptizing lampblack–phosphorus pentoxide dispersions in hydrocarbons.

In general the alkylation of aromatic hydrocarbons with olefins in contact with stabilized dispersions of phosphorus pentoxide becomes noticeable at 150°, with the optimum temperature at from 200 to 250°. Pressures up to 40 atmospheres were used in the experimental work, a description of which is given herein.

Phosphorus pentoxide has practically no polymerizing effect on the lower olefins by itself. Higher olefins are polymerized to naphthenes but only to a small degree under the conditions favorable for alkylation of aromatics. In fact, it has

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[1] Balsohn, *Bull. soc. chim.*, [2] **31**, 539 (1879).

[2] Brown and Bury, *J. Phys. Chem.*, **29**, 1312 (1925).

been observed that diisobutylene in benzene solution is depolymerized, as is apparent from the reaction product, which is in the main isobutyl benzenes.

Benzene and ethylene, benzene and isobutylene, toluene and propylene, and naphthalene and ethylene were condensed in the presence of phosphorus pentoxide dispersions.

Experimental Part

(1) **Benzene–Ethylene Condensation.**—A mixture of 708 g. of benzene (10 mols), 50 g. of phosphorus pentoxide, 24 g. of lampblack and 10 g. of cresol was heated in an autoclave for one hundred minutes at 250° with agitation while a pressure of approximately 27 atmospheres was maintained by a periodic introduction of ethylene. The absorption of ethylene was still perceptible but slow at the conclusion of the run. The weight of the liquid in the autoclave was increased by 527.7 g., indicating that 18.86 mols of C_2H_4 had been absorbed.

The reaction product was fractionated into five portions corresponding to: benzene, 1.6%; monoethylbenzene, 23.1%; isomers of diethylbenzene, 42.3%; isomers of triethylbenzene, 24.4%; isomers of higher ethylbenzenes 8.5% by volume.

The monoethylbenzene fraction after refractionation gave 184 cc. or 18.2% of a product of boiling point 135.5–135.6°, sp. gr. 0.8663 15°/4° and analyzed as follows: calcd., C, 90.46; H, 9.44. Found: C, 90.11; H, 9.90.

From the last fraction 34 g. of hexaethylbenzene was isolated by crystallization from ethyl alcohol in the form of large white needle-shaped crystals with a melting point of 128–129°.[3] The elementary analysis gave the following results: Calcd.: C, 87.72; H, 12.38. Found: C, 87.72; H, 12.38.

(2) **Benzene–Isobutylene Condensation.**—The benzene–isobutylene condensation was carried out in the same way as the benzene–ethylene condensation. The isobutylene was made from *t*-butyl alcohol by the Shell Chemical Company and contained 96.0% isobutylene, 3.5% unidentified olefins and a small amount of air. The reaction temperature was between 200 and 240°, maintained for two hours. The reaction product was separated into five portions by fractionation corresponding to: residual butylene 3.3%, residual benzene 20.7%, monobutylbenzene 47.9%, isomers of dibutylbenzene 17.0%, higher butylbenzenes and residue 11.0% by volume.

The monobutyl fraction was refractionated and found to give 65% of a fraction boiling from 165–170°.

The 1,4-*di*-*t*-butylbenzene $C_{14}H_{22}$ = $(CH_3)_3$—C—C_6H_4—C—$(CH_3)_3$ from the dibutylbenzene cut was isolated in the form of white transparent monoclinic crystals. This product analyzed as follows:

	Boedtker[4]	Observed
B. p., °C.	236.5	234–236
M. p., °C.	76	76
Molecular wt.	190	192
Carbon	88.42	88.6
Hydrogen	11.58	11.8

(3) **Toluene–Propylene Condensation.**—*p*-Cymene was obtained by condensation of toluene with propylene. The autoclave was charged with 1000 cc. of toluene (= 9.4 mols), 50 g. of phosphorus pentoxide, 25 g. of lampblack and 5 cc. of cresol and propylene admitted as described below.

In this case the reaction was noticeable at a much lower temperature than with ethylene, a very rapid absorption of propylene having been observed at 150°. Propylene was introduced into the autoclave at about 80 lb. pressure at room temperature. After absorption of the first portion of the propylene at 150°, a fresh portion was introduced at room temperature, following which the autoclave was again heated to 150°. This was repeated several times. The increase in weight finally reached approximately 700 g., equal to 16.6 mols of propylene absorbed. The reaction mixture was distilled directly from the autoclave and 1755 cc. of distillate obtained. Sixteen hundred cc. of this distillate was fractionated and the following cuts were obtained: fraction boiling below cymene, 531 cc.; *p*-cymene fraction 171.5–193.5°, 750 cc.; fraction boiling above cymene, 310 cc.

The *p*-cymene cut was refractionated and 660 cc. of a product obtained which had a boiling point of 177.3°; d^{20}_4 0.8575 and analyzed: C, 89.49; H, 10.51. Found: C, 89.26, H. 10.81.

(4) **Naphthalene–Ethylene Condensation.**—The naphthalene–ethylene condensation was carried out at 250°. The autoclave was charged with 915 g. of technical naphthalene (= 7.1 mols), 50 g. of phosphorus pentoxide, 50 g. of lampblack and 10 g. of cresol.

The autoclave was connected to an ethylene tank and the mixture heated to a maximum temperature of 250° for five hours while a pressure of 40 atmospheres was maintained by regulating the ethylene supply. In the beginning of the reaction the pressure tended to drop very rapidly. The total increase in weight finally obtained was approximately 480 g. equal to 17.2 mols of ethylene. The liquid reaction product contained a small amount of naphthalene. On distillation an almost colorless liquid was obtained boiling without decomposition between 210–322°. A crude fractionation of the material showed the bulk of the product to be a mixture of mono- and diethylnaphthalene.

Summary

1. It has been found that in presence of finely dispersed phosphorus pentoxide, aromatic hydrocarbons are readily alkylated directly by olefins.

2. Benzene is ethylated by means of ethylene at 250° and a pressure of 27 atmospheres. Mono- and hexaethylbenzenes were identified.

3. *t*-Butylbenzenes are formed with benzene and isobutylene.

4. *p*-Cymene is obtained by condensation of toluene with propylene at 150°.

5. Naphthalene is ethylated to a liquid boiling between 210–322°, consisting mainly of mono- and diethylnaphthalene.

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[3] Oscar Jacobsen, *Ber.*, **21**, 2817 (1888), found 129°.

[4] Boedtker (Eyvind Boedtker), *Bull. soc. chim.*, [3] **31**, 965–971 (1904).