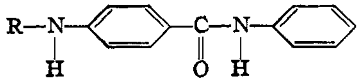
TABLE I



R	Solvent for recrystn.	Cryst. form	Yield, %	M. p., °C.	Empirical formula	N Analyses, % Calcd.	N Analyses, % Found
Acetyl	Acet. + alc.	Prisms	65	211.5	$C_{15}H_{14}N_2O_2$	11.02	11.05
n-Propionyl	Alcohol	Prisms	100	230 (dec.)	$C_{16}H_{16}N_2O_2$	10.45	10.57
n-Butyryl	Acet. + alc.	Prisms	86	231	$C_{17}H_{18}N_2O_2$	9.93	9.90
iso-Butyryl	Alcohol	Prisms	97	285 (dec.) m. > 360	$C_{17}H_{18}N_2O_2$	9.93	9.81
n-Valeryl	Alcohol	Cluster of needles	78	227	$C_{18}H_{20}N_2O_2$	9.46	9.89
Benzoyl	Acetic acid	Plates	98	323–324 (dec.)	$C_{20}H_{16}N_2O_2$	8.86	8.51
p-Nitrobenzoyl	Pyridine	Needles	100	298 (dec.)	$C_{20}H_{15}N_3O_4$	11.64	11.52
N-Acetyl-4-aminobenzoyl	Acetone	Granules	...	245–246 (dec.)	$C_{22}H_{19}N_3O_3$	11.26	11.13
Benzenesulfonyl	Alcohol	Fine needles	100	210.5 (dec.)	$C_{19}H_{16}N_2O_3S$	7.95	7.75
p-Bromobenzenesulfonyl	Acetone	Needles	74	240–241	$C_{19}H_{15}BrN_2O_3S$	6.50	6.66
2-Naphthalenesulfonyl	Acetone	Cluster of fine needles	95	230	$C_{23}H_{18}N_2O_3S$	6.96	6.94

have been tried. Only the reduction by tin and hydrochloric acid is satisfactory. The picrate of *p*-aminobenzanilide was prepared in a yield of 96%, yellow prisms, m. p. 163–164° (dec.).

Anal. Calcd. for $C_{19}H_{15}N_5O_8$: N, 15.87. Found: N, 15.88%.

A number of acyl and aroyl derivatives were prepared by refluxing equivalent weights of *p*-aminobenzanilide and acyl or aroyl chloride (in the case of acetyl derivative acetic anhydride was used instead) in dry benzene or toluene on a steam-bath for thirty minutes to one hour. The solvent was removed by vacuum distillation. The residue was stirred with cold water, filtered, and then recrystallized from a suitable solvent.

N-(N-Acetyl-*p*-aminobenzoyl)-*p*-aminobenzanilide was prepared by reduction of N-(*p*-nitrobenzoyl)-*p*-aminobenzanilide with stannous chloride and hydrochloric acid and subsequent acetylation.

Several aromatic sulfonyl derivatives were similarly prepared. The properties of these compounds are listed in the table.

Since Hirsch[4] demonstrated that *p*-aminobenzamide possessed bacteriostatic properties, it would be interesting to see whether these derivatives are bacteriostatic or not. Only a few more soluble ones have been tested on *Lactobacillus arabinosus* 17–5. N-Acetyl-*p*-aminobenzanilide, N-propionyl-*p*-aminobenzanilide, N-*n*-butyryl-*p*-aminobenzanilide, N-isobutyryl-*p*-aminobenzanilide and N-*n*-valeryl-*p*-aminobenzanilide are toxic at a concentration of 500 γ per 10 ml. of medium, but the toxic action is not reversed by addition of *p*-aminobenzoic acid. However, *p*-aminobenzanilide possesses slight growth-promoting action similar to that of *p*-aminobenzoic acid.

THE BIOCHEMICAL INSTITUTE AND
THE CLAYTON RESEARCH FOUNDATION
UNIVERSITY OF TEXAS EDITH JU-HWA CHU[5]
AUSTIN, TEXAS

RECEIVED JULY 9, 1945

---

(4) J. Hirsch, *Science*, **96**, 140 (1942).

(5) On leave from the University of Peking, Kunming, Yunnan, China. Present address: Department of Medicine, University of Minnesota, Minneapolis, Minnesota.

COMMUNICATIONS TO THE EDITOR

A NEW SYNTHESIS OF MONO SUBSTITUTED CYCLOBUTANES

Sir:

The authors have prepared a tribromide, 1,1,1-tris-(bromomethyl)-propane (I) from a new triol, 1,1,1-tris-(hydroxymethyl)-propane (II), obtained from the Heyden Chemical Corp., Garfield, N. J., Debromination of I by zinc in acetamide, the method of Hass and McBee,[1] gave a mixture of olefins which was separated by distillation at 50-plate efficiency into three distinct fractions. The highest boiling and preponderant fraction has been conclusively identified as ethylidenecyclobutane.

This recalls the fact that methylenecyclobutane[2] is one of the products from the zinc–acetamide debromination of pentaerythrityl tetrabromide, and is the chief product from the zinc–alcohol debromination. On the other hand, the zinc–alcohol debromination of (I) gave no hydrocarbons but chiefly an ether (b. p. 135°, uncor.) which probably was ethyl 1-ethylcyclopropylcarbinyl ether. We believe that in the zinc–acetamide debromination of I a ring closure occurs to give 1-(bromomethyl)-1-ethylcyclopropane which subsequently undergoes dehydrobromination with ring expansion and some ring opening.

The crude brownish triol (II) softened and melted over a wide temperature range; purified by vacuum distillation, and recrystallization from

---

(1) Hass, McBee, Hinds and Gluesenkamp, *J. Ind. Eng. Chem.*, **28**, 1178 (1936).

(2) Murray and Stevenson, THIS JOURNAL, **66**, 812 (1944).

an ether–acetone mixture, it gave white crystals melting at 58.8–59.0°. However, the crude II was found suitable for conversion to the tribromide (I), which was accomplished by melting the II, adding an excess of phosphorus tribromide, and heating to 140° for forty-eight hours. Purified by three crystallizations from 95% ethanol to remove a complex reddish phosphorus compound, the tribromide melted sharply at 94.3° and analyzed correctly for $C_6H_{11}Br_3$. In the ring closure, following a procedure which was essentially that of Murray and Stevenson,[2] use of the crude tribromide was found satisfactory.

The crude olefin mixture (yield 92% based on pure I) was separated into three fractions boiling at 65, 71 and 80.26° in an approximate ratio of 1:2:5, respectively. The highest boiling olefin (III) was proved to be a very pure individual compound by its time–temperature cooling curve, and its molecular refraction checked closely with that calculated for ethylidenecyclobutane.

Over Raney nickel at room temperature III absorbed one equivalent of hydrogen and gave ethylcyclobutane, b. p. 70.64°, f. p. −143.1°; Wibaut[3] found b. p. 70.7°, f. p. −142.9° for ethylcyclobutane prepared by a different method.

Ozonolysis of III gave acetaldehyde which was identified[4] through its 2,4-dinitrophenylhydrazone, m. p. 156–162° after five recrystallizations. An authentic sample of this derivative also melted at 156–162°, and the mixed melting point was identical; a mixed melting point with the corresponding derivative of formaldehyde showed a 20° depression. A second ozonolysis product, probably cyclobutanone, boiled at about 100° and gave a 2,4-dinitrophenylhydrazone which melted at 140–142°.

The other olefins are believed to be 2-ethyl-1-butene and a mixture of vinylcyclobutane with 3-methyl-2-pentene. An attempt is being made to identify these products, and other reactions of this type will be studied.

---

(3) Wibaut, *Rec. trav. chim.*, **58**, 329 (1939).

(4) R. C. Arnold, Master's Thesis, The Ohio State University 1945.

DEPARTMENT OF CHEMISTRY
THE OHIO STATE UNIVERSITY
COLUMBUS, OHIO, AND JOHN M. DERFER
AMERICAN PETROLEUM INSTITUTE
RESEARCH PROJECT 45
WAR RESEARCH BUILDING
OHIO STATE UNIVERSITY KENNETH W. GREENLEE
COLUMBUS, OHIO CECIL E. BOORD

RECEIVED AUGUST 31, 1945

THE ADDITION OF PHOSPHORUS TRICHLORIDE TO OLEFINS

Sir:

No satisfactory method is described in the literature for the preparation of phosphorus compounds of the type $RPCl_2$, where R is an aliphatic radical. The method considered most satisfactory is to heat for many hours a mixture of a mercury dialkyl and phosphorus trichloride in a sealed tube at 250°.[1] We have found that if an unsaturated compound is heated with an excess of phosphorus trichloride, in the presence of a small quantity of a diacyl peroxide (diacetyl or dibenzoyl peroxide), addition of the phosphorus trichloride to the double (or triple) bond takes place readily.[2]

$$RCH{=}CH_2 + PCl_3 \xrightarrow{\text{diacetyl peroxide}} RCHClCH_2PCl_2$$

A description of the experimental details of one example of the reaction is cited.

Octene-1 (0.16 mole) and phosphorus trichloride (1.0 mole) were mixed and placed in a two-necked dry flask equipped with a dropping funnel and a reflux condenser. The latter was connected to a tube immersed into mercury. The air in the flask was displaced by nitrogen, and the mixture heated to 85° under pressure (20 cm. of mercury extra pressure). Acetyl peroxide (0.025 mole) dissolved in octene-1 (0.17 mole) was added (in four equal portions) in the course of two hours. When all the peroxide had been added, the heating was continued for two hours longer.

The excess of phosphorus trichloride was removed from the reaction mixture at atmospheric pressure, and the octene-1, at reduced pressure. The residue was transferred to a small Claisen flask and twice distilled at reduced pressure. A colorless distillate, b. p. 85–88° (0.5 mm.), was collected (13 g.). The high boiling residue weighed about two grams.

Anal. Calcd. for $C_8H_{16}Cl_3P$: Cl, 42.6. Found: Cl, 41.1.

The reaction cited is assumed to proceed *via* a free-radical chain reaction initiated by the free radicals formed by the decomposition of the diacyl peroxide.

$$(CH_3COO—)_2 \longrightarrow CH_3\cdot + CO_2 + CH_3COO\cdot \quad (1)$$

$$CH_3\cdot + PCl_3 \longrightarrow CH_3Cl + \cdot PCl_2 \quad (2)$$

$$RCH{=}CH_2 + \cdot PCl_2 \longrightarrow R\underset{\cdot}{C}HCH_2PCl_2 \quad (3)$$

$$R\underset{\cdot}{C}HCH_2PCl_2 + PCl_3 \longrightarrow RCHClCH_2PCl_2 + \cdot PCl_2 \quad (4)$$

$$R\underset{\cdot}{C}HCH_2PCl_2 + RCH{=}CH_2 \longrightarrow R\underset{\cdot}{C}HCH_2CHRCH_2PCl_2 \quad (5)$$

$$R\underset{\cdot}{C}HCH_2CHRCH_2PCl_2 + PCl_3 \longrightarrow RCHClCH_2CHRCH_2PCl_2 + \cdot PCl_2 \quad (6)$$

Whether reactions (5) and (6) are responsible for the formation of the high boiling residue, or the condensation of the compound $RCHClCH_2PCl_2$ in a manner similar to that indicated in (3) and (4) has not as yet been determined.[3]

For effective propagation of the chain reaction (3 and 4), the radical R must be aliphatic, and the carbon atom to which it is attached must

---

(1) Guichard, *Ber.*, **32**, 1572 (1899); Michaelis, *ibid.*, **13**, 2174 (1880).

(2) The addition of phosphorus trichloride to acetylene compounds will be reported shortly.

(3) The diacyl peroxide catalyzed condensation of compounds of the type $RPCl_3$ with olefins is under way.