of pyridazine-3-carboxylic acid was collected and air-dried, m.p. 201° (dec.), yield 22 g. (81%).

Pyridazine-4-carboxylic Acid.—A solution of 3.35 g. of pyridazine-4,5-dicarboxylic acid in 300 ml. of water was heated in a bomb at 200° for two hours. The resulting tan solution was boiled with Darco and filtered. The filtrate was evaporated to 70 ml., acidified to *p*H 2.5 and chilled, yielding a precipitate of pyridazine-4-carboxylic acid as white crystals, m.p. 230–235° (dec.); yield 1.4 g. (56%). An analytical sample recrystallized twice from water decomposed at 239–240° (slow heating).

Anal. Calcd. for $C_5H_4N_2O_2$: C, 48.39; H, 3.25; N, 22.57. Found: C, 48.78; H, 3.42; N, 22.40.

3-Carbethoxypyridazine.—Pyridazine-3-carboxylic acid (17.7 g.) was esterified by refluxing for six hours with 177 ml. of absolute alcohol and 18 ml. of concentrated sulfuric acid. The reaction mixture was concentrated *in vacuo* to 75 ml. and poured into a cold saturated solution of sodium carbonate. The ester was extracted from the aqueous solution with benzene and crystallized from benzene–petroleum ether. Recrystallization from absolute alcohol gave 11.1 g. of product, m.p. 68.0–68.5°, and a second crop of 2.8 g., slightly yellow, m.p. 65–67° (64% yield).

Anal. Calcd. for $C_7H_8N_2O_2$: C, 55.25; H, 5.30; N, 18.41. Found: C, 55.52; H, 5.01.

4-Carbethoxypyridazine.—Pyridazine-4-carboxylic acid (6.5 g.) was esterified in a similar manner. The ester was obtained as a straw-colored oil which was distilled under vacuum; b.p. 125° (13 mm.), yield 4 g. (60%).

Anal. Found: C, 55.78; H, 4.97; N, 18.33.

Pyridazine-3-carboxamide.—A suspension of 109 g. of 3-carbethoxypyridazine in 800 ml. of absolute alcohol was treated with anhydrous ammonia. The mixture became warm, the ester dissolved and amide began to deposit. Gas introduction was halted after three hours when the reaction mixture had cooled to room temperature. The filtered crystals were recrystallized from water with charcoaling, giving 83.6 g. (95%) of colorless amide, m.p. 182–182.5°.

Anal. Calcd. for $C_5H_5N_3O$: C, 48.78; H, 4.09; N, 34.13. Found: C, 49.17; H, 3.92; N, 34.03.

Pyridazine-4-carboxamide.—Treatment of an alcoholic solution of 4-carbethoxypyridazine with ammonia gave the corresponding amide which when recrystallized from water melted at 191–192°.

Anal. Found: C, 48.77; H, 3.83; N, 33.96.

Pyridazine-3-carbohydrazide.—A mixture of 6 g. of 3-carbethoxypyridazine, 4.6 g. of 85% hydrazide hydrate and 35 ml. of alcohol was refluxed for one hour, then cooled. The hydrazide deposited as pale yellow crystals, m.p. 151–152°, yield 5.2 g. (95%). After recrystallization from alcohol, the product was cream-colored; the melting point was unchanged.

Anal. Calcd. for $C_5H_6N_4O$: C, 43.47; H, 4.38; N, 40.56. Found: N, 39.73.

Pyridazine-4-carbohydrazide.—Reaction of 4-carbethoxypyridazine with hydrazine hydrate as above gave the hydrazide, m.p. 124–125° (recrystallized from alcohol).

Anal. Found: C, 43.99; H, 4.13; N, 40.52.

RESEARCH & DEVELOPING DIVISION
MERCK & CO., INC.
RAHWAY, NEW JERSEY

Characterization of Some Alkylbenzenes through their Phthalic Anhydride Derivatives[1]

BY GEORGE F. LEWENZ AND KASPER T. SERIJAN[2]

RECEIVED FEBRUARY 27, 1953

The identification of aromatic hydrocarbons has generally been possible only by physical methods such as examination of absorption spectra and comparison of the physical properties of unknown with authentic compounds. Identification based on the melting points of solid derivatives offers several advantages, especially in those instances where sufficient quantities of the hydrocarbons or equipment necessary for physical examination are unavailable. Consequently, an investigation of solid derivatives of aromatic hydrocarbons was begun at this Laboratory in order to ascertain the usefulness of certain derivatives in identifying the hydrocarbons.

While several types of solid derivatives of aromatic hydrocarbons are known, most of them have proved to be unsuitable for identification purposes, for one reason or another. Picric acid derivatives are frequently unstable,[3] while styphnic acid[4] and 2,4,7-trinitrofluorenone[5] derivatives have been prepared only from fused ring aromatics. The mono- and diacetamino as well as the benzamino derivatives have been prepared only from monoalkylbenzenes.[6,7] Trinitrobenzene derivatives from fused ring aromatics are stable,[4] but those from single-ring aromatics are not.[8]

The *o*-aroylbenzoic and *o*-aroyltetrachlorobenzoic acids, prepared by the condensation of aromatic hydrocarbons with phthalic and tetrachlorophthalic anhydride, respectively, have been proposed by Underwood and Walsh[9] as suitable crystalline derivatives for the identification of aromatic hydrocarbons. In the present investigation phthalic anhydride derivatives of 25 mono-, di- and trialkylbenzenes have been prepared, and the melting points of the derivatives have been compared to determine the usefulness of these compounds in distinguishing the hydrocarbons. The keto acid of *i*-propylbenzene could not be obtained in sufficient purity. In addition the 1,4-substituted alkylbenzenes formed derivatives only with difficulty and none could be obtained in the cases of the *o*-aroylbenzoic acid derivatives of 1-methyl-4-ethylbenzene and 1,4-diethylbenzene.

The melting points, carbon–hydrogen analyses and neutralization equivalents of 25 *o*-aroylbenzoic acids are presented in Table I; fourteen of these keto acids are reported for the first time. All the derivatives were recrystallized until successive recrystallizations gave no significant change in melting point. The melting points available from the literature are indicated in the tables and are generally in good agreement with the values obtained in the present work. In those instances where the melting points of derivatives of isomeric hydrocarbons were similar, mixed melting points were determined. In this way it was found that a common derivative was obtained from the three isomeric methyl-*t*-butylbenzenes.

In two other cases the mixed melting points taken with the derivatives of two isomeric hydrocarbons showed slight depressions; however, the degree of depression was not sufficient to permit a definite conclusion as to whether rearrangement of the hy-

---

[1] Presented at the Buffalo meeting of the American Chemical Society, March 24, 1952.

[2] Armour and Company, Chicago, Illinois.

(3) O. L. Baril and E. S. Hauber, THIS JOURNAL, 53, 1087 (1931).

(4) W. J. Hickinbottom, "Reactions of Organic Compounds," 2nd Edition, Longmans Green and Co., London, 1948, p. 76.

(5) M. Orchin and E. O. Woolfolk, THIS JOURNAL, 68, 1727 (1946).

(6) V. N. Ipatieff and L. Schmerling, *ibid.*, 59, 1056 (1937).

(7) V. N. Ipatieff and L. Schmerling, *ibid.*, 60, 1476 (1938).

(8) L. Triandaf, *Ann. sci. Univ. Jassy*, 26, I, 155 (1940).

(9) H. Underwood, Jr., and W. Walsh, THIS JOURNAL, 57, 940 (1935).

TABLE I

THE *o*-AROYLBENZOIC ACID DERIVATIVES OF BENZENE AND VARIOUS MONO-, DI- AND TRIALKYLBENZENES

o-Aroylbenzoic acid	Molecular formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Neut. equiv. Calcd.	Neut. equiv. Found	Melting point (°C.) Obsd.	Melting point (°C.) Lit.
Benzene	$C_{14}H_{10}O_3$	74.34	74.46	4.46	4.50	226	225	129.2–130.0	127–128[9]
Toluene	$C_{15}H_{12}O_3$	74.98	75.07	5.03	5.04	240	239	139.6–140.5	137–138[9]
Ethylbenzene	$C_{16}H_{14}O_3$	75.57	75.40	5.55	5.62	254	254	130.7–131.6	122[16]
1,2-Dimethylbenzene	$C_{16}H_{14}O_3$	75.57	75.65	5.55	5.64	254	251	166.7–168.1	162[17]
1,3-Dimethylbenzene	$C_{16}H_{14}O_3$	75.57	75.51	5.55	5.64	254	254	142.5–142.8	
1,4-Dimethylbenzene	$C_{16}H_{14}O_3$	75.57	75.71	5.55	5.63	254	256	148.0–149.1	149[18]
n-Propylbenzene	$C_{17}H_{16}O_3$	76.10	75.84	6.01	5.97	268	263	125.4–126.2	125–126[9]
1,2,3-Trimethylbenzene	$C_{17}H_{16}O_3$	76.10	76.05	6.01	5.84	268	268	173.4–173.8	
1,3,5-Trimethylbenzene	$C_{17}H_{16}O_3$	76.10	75.92	6.01	6.19	268	267	216.3–216.9	211–212[9]
1,2,4-Trimethylbenzene	$C_{17}H_{16}O_3$	76.10	75.99	6.01	5.98	268	261	148.9–150.5	
1-Methyl-2-ethylbenzene	$C_{17}H_{16}O_3$	76.10	76.16	6.01	5.99	268	269	129.8–131.4	
1-Methyl-3-ethylbenzene	$C_{17}H_{16}O_3$	76.10	76.34	6.01	6.09	268	268	104.1–105.7	
1,2-Diethylbenzene	$C_{18}H_{18}O_3$	76.57	76.30	6.43	6.34	282	283	141.8–142.7	
1,3-Diethylbenzene	$C_{18}H_{18}O_3$	76.57	76.66	6.43	6.38	282	276	121.8–122.5	114–116[9]
n-Butylbenzene	$C_{18}H_{18}O_3$	76.57	76.62	6.43	6.29	282	282	100.8–101.8	97–98[9]
s-Butylbenzene	$C_{18}H_{18}O_3$	76.57	76.84	6.43	6.74	282	282	129.0–129.6	
i-Butylbenzene	$C_{18}H_{18}O_3$	76.57	76.26	6.43	6.46	282	272	125.2–126.8	
t-Butylbenzene	$C_{18}H_{18}O_3$	76.57	76.47	6.43	6.44	282	277	143.8–144.7	
1,3-Dimethyl-5-ethylbenzene	$C_{18}H_{18}O_3$	76.57	76.29	6.43	6.42	282	287	210.1–212.1	
1-Methyl-4-*i*-propylbenzene	$C_{18}H_{18}O_3$	76.57	76.49	6.43	6.47	282	282	125.8–126.6	123–124[9]
1-Methyl-2-*t*-butylbenzene	$C_{19}H_{20}O_3$	77.00	76.84	6.80	6.80	296	293	134.3–135.5	
1-Methyl-3-*t*-butylbenzene	$C_{19}H_{20}O_3$	77.00	76.82	6.80	6.78	296	292	135.6–136.4	
1-Methyl-4-*t*-butylbenzene	$C_{19}H_{20}O_3$	77.00	76.72	6.80	6.91	296	295	136.0–136.8	
1-Methyl-3,5-diethylbenzene	$C_{19}H_{20}O_3$	77.00	76.89	6.80	6.80	296	298	145.2–146.7	
1,3,5-Triethylbenzene	$C_{20}H_{22}O_3$	77.39	77.42	7.15	7.12	310	306	(19)	129.5–130.5[9]

drocarbon had or had not occurred. Compounds in this category were the keto acids of *s*- and *i*-butylbenzene.

One derivative was also observed to have at least two crystalline modifications, and the change from one modification to another could be seen at certain temperatures on the hot stage of a microscope. The compound which was observed to exhibit this phenomenon was the keto acid of 1,3,5-triethylbenzene. An examination of the data of Table I shows that the keto acids of the three trimethylbenzenes, the two methylethylbenzenes, the two diethylbenzenes, and three of the four butylbenzenes distinguish well between these isomeric hydrocarbons.

Experimental

General.—In preparing the *o*-aroylbenzoic acids, previously described procedures[9,10,11] which involved the application of heat during the condensation reaction, were found to give poor yields of the acids, and often non-crystallizable products, especially where higher alkylated benzenes were involved. This may be due to the fact that on heating alkylbenzenes with aluminum chloride, rearrangement of the alkyl groups and isomerization can occur,[12,13] changing the originally pure hydrocarbon to a mixture, so that the resulting derivatives would be difficult to crystallize and separate. By cooling the reaction flask in an ice-bath for the first 3 to 4 hours and then allowing the reactants to warm to room temperature until the evolution of hydrogen chloride had ceased, these difficulties were alleviated. Although solvents such as benzene or mixtures of ethanol and water were tried for the recrystallization of the derivatives, the *o*-aroylbenzoic acids were most satisfactorily recrystallized from a mixture of toluene and petroleum ether.

Starting Materials.—The hydrocarbons used in this investigation were of 99 mole % purity or better and had previously been prepared and purified in conjunction with a program concerned with the evaluation of aviation fuel components at this Laboratory.[14] The aluminum chloride used was J. T. Baker Reagent grade, anhydrous, sublimed, and the phthalic anhydride was Eastman Kodak Co. Reagent grade.

***o*-Aroylbenzoic Acids.**—As a typical preparation the synthesis and purification of *o*-benzoylbenzoic acid is given. A mixture of 14.8 g. (0.1 mole) of phthalic anhydride (m.p. 130.8-131.6°) and 29.4 g. (0.22 mole) of aluminum chloride[15] was intimately ground in a mortar, and the mixture then placed in a 500-ml. 2-necked flask which was equipped with a stirrer and a small reflux condenser. The flask was cooled in an ice-bath while 39.1 g. (0.5 mole) of benzene was added with stirring, the excess of hydrocarbon serving as solvent. The reaction mixture was vigorously stirred at the ice-bath temperature for 3 to 4 hours, during which time a continuous evolution of hydrogen chloride was observed. The ice-bath was then removed and stirring continued until the evolution of gas ceased. The product was hydrolyzed by gradually pouring the reaction mixture into a beaker containing dilute hydrochloric acid and ice. The hydrolyzed mixture was refrigerated at about 0° for 5 hours and the solid product was filtered off, washed several times with petroleum ether, and dried in a vacuum oven at 50°. The

---

(10) C. R. Rubidge and N. C. Qua, THIS JOURNAL, **36**, 732 (1914).

(11) W. A. Lawrance, *ibid.*, **43**, 2577 (1921).

(12) J. F. Norris and D. Rubinstein, *ibid.*, **61**, 1163 (1939).

(13) D. V. Nightingale, *Chem. Revs.*, **25**, 347 (1939).

(14) (a) L. Gibbons, *et al.*, THIS JOURNAL, **68**, 1130 (1946); (b) J. Karabinos, K. Serijan and L. Gibbons, *ibid.*, **68**, 2107 (1946); (c) K. Serijan, H. Hipsher and L. Gibbons, *ibid.*, **71**, 873 (1949); (d) T. Reynolds, *et al.*, *Ind. Eng. Chem.*, **40**, 1751 (1948); (e) E. Ebersole, "Natl. Advisory Comm. Aeronaut.," Tech. Note 1020, January 1946; (f) C. Buess, *et al.*, *ibid.*, 1021, June 1946; (g) J. Karabinos and J. Lamberti, *ibid.*, 1019, January 1946; (h) unpublished work.

(15) Careful adjustment of the quantities of the reactants and control of other factors helps to avoid the formation of substituted phthalides, as discussed in detail by C. Thomas in "Anhydrous Aluminum Chloride in Chemistry," American Chem. Soc. Monograph Series No. 87, Reinhold Publ. Corp., New York, N. Y., 1941, pp. 511–548, and by P. Groggins, *Ind. Eng. Chem.*, **23**, 152 (1931).

(16) R. Scholl, J. Potschewanscheg and J. Lenko, *Monatsh.*, **32**, 687 (1912).

(17) H. Limpricht, *Ann.*, **312**, 99 (1900).

(18) E. de Barry Barnett and J. A. Low, *Ber.*, **64B**, 49 (1931).

(19) Two crystalline modifications were observed: (1) 122.8–123.6°, (2) 131.0–132.0°.

weight of the crude product was 22 g. By adding petroleum ether to the hydrocarbon portion of the filtrate, additional solid product could be obtained to slightly increase the yield.

The *o*-benzoylbenzoic acid was recrystallized by dissolving it in a small volume of hot toluene and then adding just enough petroleum ether to cause precipitation as the solution cooled. The yield of purified acid obtained in this way was 16.8 g., m.p. 128.8–129.8°. The product was further recrystallized to constant melting point.

Neutralization Equivalents.—The neutralization equivalent for each acid was determined by dissolving a 50- to 80-mg. sample in 50 ml. of 95% ethyl alcohol. The solution was titrated with aqueous sodium hydroxide (approx. 0.03 *N*) using phenolphthalein as the indicator. Previous to the titration a blank was determined for the alcohol.

Melting Point Determinations.—The melting ranges given in Tables I and II were taken from the point where the compound first wetted the side of the capillary tube to the point where only a clear liquid was observed. The rate of temperature rise near the melting point was a maximum of $^{1}/_{2}$° per minute. The values were determined by the use of calibrated Anschütz precision thermometers of the total immersion type. The melting point apparatus was similar to that described by Merriam.[20]

---

(20) F. Merriam, *Anal. Chem.*, **20**, 1245 (1948).

NACA Lewis Flight Propulsion Lab.
Cleveland 11, Ohio

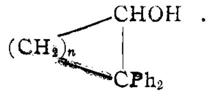
Molecular Rearrangements. III. The Retropinacolone Rearrangement of 2,2-Diphenylcycloalkanols[1]

By Robert E. Lyle, Nathan B. Martin, Jr.,[2] and Herbert L. Fielding[2]

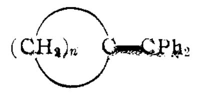
Received April 3, 1953

The retropinacolone rearrangement of several diarylalkylmethyl alkyl carbinols has been reported in the literature,[3] and in each case the symmetrical diaryldialkylethylene was obtained as the major product. By analogy to these compounds, the cyclic alcohols, 2,2-diphenylcycloheptanol (Ia) and 2,2-diphenylcyclohexanol (Ib), would be expected to produce the 1,2-diphenylcycloalkenes as the product of this type of reaction. On the other hand, Mueller and co-workers[4] have shown that 1,2-diphenylcyclohexene is unstable because of steric interference of the phenyl groups, and if 1,2-diphenylcyclohexene were formed, it could rearrange to the more stable 2,3-diphenylcyclohexene. Phenyl migration, however, might be retarded altogether in the retropinacolone rearrangement and the product of alkyl migration, cyclohexylidene diphenylmethane (IIa), would result. Thus a study of the retropinacolone rearrangement of two diphenyl cyclic alcohols was initiated in order to determine which of the groups migrated during the reaction and thus the influence of the cyclic system on the rearrangement.

The dehydration of 2,2-diphenylcycloheptanol (Ia) was effected by thermal dehydration on distillation at atmospheric pressure or by reagents such as phosphorus pentoxide, phosphorus tribromide or thionyl chloride. In each experiment the only product isolated, cyclohexylidene diphenylmethane (IIa), was that resulting from migration of the alkyl group. The identity of this material was confirmed by conversion to the epoxide.



Ia,b



IIa,b

a, $n = 5$
b, $n = 4$

2,2-Diphenylcyclohexanol (Ib) was dehydrated by treatment with phosphorus tribromide yielding cyclopentylidene diphenylmethane (IIb), identified by melting point and ultraviolet spectrum showing a maximum at 250 mμ with a molar extinction coefficient of 2.10×10^4. These values are quite similar to those obtained for cyclohexylidene diphenylmethane, maximum at 246 mμ with a molar extinction coefficient of 1.49×10^4. Thus the retropinacolone rearrangement proceeded with alkyl migrations in both cases. Unlike 2,2-diphenylcycloheptanol (Ia), the six-membered ring alcohol (Ib) was stable to atmospheric pressure distillation.

It is evident from these results that in the six- and seven-membered ring compounds studied ring contraction occurs in preference to migration of an aryl group. This preferential alkyl migration may well be related to the similar reaction noted in the pinacol rearrangement of unsymmetrical cyclic diaryl glycols.[5,6]

Experimental

Dehydration of 2,2-Diphenylcycloheptanol (Ia). a. **With Phosphorus Pentoxide.**—To 5.3 g. (0.02 mole) of 2,2-diphenylcycloheptanol[5] (Ia) in a 50-ml. round-bottom flask was added 3.0 g. (0.021 mole) of phosphorus pentoxide. The mixture was heated on a steam-bath for one hour and then treated with 100 ml. of cold water. The resulting white solid was removed by filtration yielding 3.7 g. (75%) of crude cyclohexylidene diphenylmethane (IIa) which, on recrystallization from low-boiling petroleum ether, melted at 82–83.5° and showed no depression of melting point on mixing with an authentic sample.

b. **With Phosphorus Tribromide.**—To 5.3 g. (0.02 mole) of molten 2,2-diphenylcycloheptanol (Ia) in a 50-ml. round-bottom flask was added dropwise 3.6 g. (0.014 mole) of phosphorus tribromide. After the vigorous reaction had subsided, the mixture was heated for an additional six hours on a steam-bath, poured into 200 ml. of water and the resulting solid removed by suction filtration. After two recrystallizations from ethanol, 2.3 g. (46%) of cyclohexylidene diphenylmethane (IIa), m.p. 81–83°, was obtained. This material showed no depression of melting point on mixing with an authentic sample.

c. **With Thionyl Chloride.**—Following the above procedure, 2.7 g. (0.01 mole) of Ia was treated with 1.2 g. (0.01 mole) of thionyl chloride. This reaction yielded 1.4 g. (56%) of product shown to be cyclohexylidene diphenylmethane (IIa) by mixture melting point.

d. **By Distillation at Atmospheric Pressure.**—After three consecutive distillations, b.p. 368–372°, 10.8 g. (0.04 mole) of Ia gave 8.8 g. of distillate. From a methanol solution this distillate deposited 3.6 g. (36%) of cyclohexylidene diphenylmethane (IIa), m.p. 82.8–83.6° after recrystallization from methanol. The oil remaining after removal of the methanol was oxidized with peracetic acid yielding 1.2 g. of crystalline cyclohexylidene diphenylmethane oxide. The total yield of IIa was 4.8 g. (48%). The remainder of the

---

[1] This work was supported in part by a Frederick Gardner Cottrell Grant from the Research Corporation of New York.

[2] These results were abstracted from the M.S. theses of N. B. Martin, Jr., and H. L. Fielding submitted to the faculty of the University of New Hampshire.

[3] J. Levy, *Bull. soc. chim.*, **29**, 878 (1921); R. Lucas and S. Legagneur, *ibid.*, **45**, 718 (1929); K. Sisido and H. Nozaki, This Journal, **70**, 776 (1948).

[4] G. Mueller, J. Fleckenstein and W. Tallenn, *ibid.*, **73**, 2653 (1951).

[5] R. Lyle and G. Lyle, *ibid.*, **74**, 4059 (1952).

[6] A. Burger and W. Bennet, *ibid.*, **72**, 5414 (1950).