TABLE I

Compound	No.	Recrystallized[a] from	M.p., °C.	Analyses, %[b] Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
1-Methyl-1,2,3-triazole-4,5-dicarboxylic acid	1	W	179–180	...	..	24.56	...	..	24.30[c]
1-Butyl-1,2,3-triazole-4,5-dicarboxylic acid	2	W	136–136.5 d.	45.07	5.20	...	45.18	5.23	[d]
1-Benzyl-1,2,3-triazole-4-carboxaldehyde	3	E–W	89–90	...	..	22.45	...	..	22.33
1-Benzyl-4,5-bis-(1-hydroxy-1-methylethyl)-1,2,3-triazole	4	A	151–153	65.45	7.69	15.26	66.43	7.78	15.37
β-4-(1-Methyl-1,2,3-triazolyl)-acrylic acid	5	W	218–220	47.05	4.60	...	47.09	4.71	[e]
β-4-(1-Benzyl-1,2,3-triazolyl)-acrylic acid	6	E	216–219	62.87	4.84	...	62.72	4.93	[f]
1,2,3-Triazole-4-carboxaldehyde oxime	7	W	207–209	32.14	3.59	...	32.41	3.85	...
1,2,3-Triazole-4-carboxaldehyde 2,4-dinitrophenylhydrazone	8	E–A	270–271	38.99	2.54	...	39.28	2.60	...
1,2,3-Triazole-4-carboxaldehyde phenylhydrazone	9	E–W	160–162	...	..	37.39	...	..	37.25
1-Benzyl-1,2,3-triazole-4-carboxaldehyde 2,4-dinitrophenylhydrazone	10	E	228–230	...	..	26.70	...	..	26.70

[a] W, Water; E, ethanol; A, ethyl acetate. [b] C, H and N analyses by Micro Tech Laboratories, Skokie, Ill. [c] Neut. equiv.: calcd. 171, found 169. [d] Neut. equiv.: calcd. 106.6, found 107.4. [e] Neut. equiv.: calcd. 153.1, found 156.8. [f] Neut. equiv.: calcd. 229, found 226.

and 6, were prepared by the condensation of the triazolecarboxaldehydes with malonic acid. The aldehyde derivatives, compounds 7, 8, 9 and 10, were prepared by standard methods from the aldehydes. Attempts to prepare a pure thiosemicarbazone of 1,2,3-triazole-4-carboxaldehyde were unsuccessful.

The first compound listed has been reported recently[1] as an oxidation product of 1-methylbenzotriazole. The other compounds have not been described previously in the literature.

The benzyl azide,[2] methyl azide[3] and 1,2,3-triazole-4-carboxaldehyde[4] were made by literature methods; the butyl azide from butyl iodide and sodium azide. The 2,5-dimethyl-3-hexyne-2,5-diol was generously supplied by Air Reduction Chemical Company and the acetylenedicarboxylic acid was generously supplied by the National Aniline Division of Allied Chemical and Dye Corp. All other reactants were purchased from commercial sources.

Acknowledgment.—This research was completed under Contract DA-33-008 ord-734 between the Office of Ordnance Research and the University of Louisville. The authors gratefully acknowledge this support.

(1) W. E. Plaut, THIS JOURNAL, **76**, 5801 (1954).

(2) T. Curtius and G. Erhart, *Ber.*, **55**, 1565 (1922).

(3) O. Dimroth and W. Wislicenus, *ibid.*, **38**, 1573 (1905).

(4) R. Hüttel, *ibid.*, **74**, 1680 (1941).

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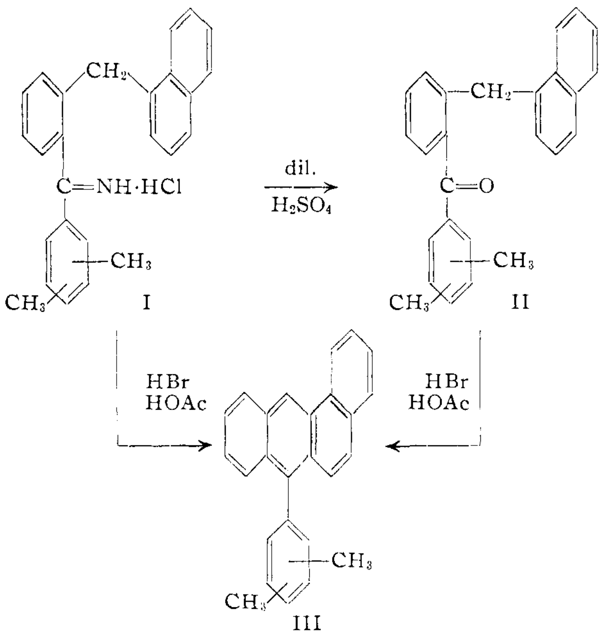
The Synthesis of the Six Isomeric 10-Dimethylphenyl-1,2-benzanthracenes[1,2]

BY FRANK A. VINGIELLO AND ALEXEJ BOŘKOVEC

RECEIVED FEBRUARY 2, 1955

Bradsher's method of aromatic cyclodehydration[3] for the preparation of hydrocarbons was introduced in 1940. Later publications extended the usefulness of this synthesis. So for example Bradsher and Vingiello[4] prepared a series of 9-(*p*-monosubstituted phenyl)-anthracenes and Vingiello and Bořkovec[5] recently prepared 10-phenyl-1,2-benzanthracene and the three isomeric 10-monomethylphenyl-1,2-benzanthracenes. We now have extended Bradsher's aromatic cyclohydration reaction to the preparation of dimethyl substituted hydrocarbons.



Treatment of 1-(*o*-cyanobenzyl)-naphthalene with the appropriate Grignard reagents led to the corresponding ketimines, isolated as the hydrochlorides I, usually in high yield. The salts were hydrolyzed to the corresponding ketones II by refluxing with 25% sulfuric acid. In the case of the 2,6-dimethyl compound (II, 2,6-dimethyl), hydrolysis could not be effected under the specified conditions, but

(1) Presented before the Section of Organic Chemistry at the Sixth Southeastern Regional Meeting of the American Chemical Society, Birmingham, Alabama, October, 1954.

(2) This paper has been abstracted in part from the Masters thesis presented to the Virginia Polytechnic Institute by Alexej Bořkovec in 1953.

(3) C. K. Bradsher, THIS JOURNAL, **62**, 486 (1940).

(4) C. K. Bradsher and F. A. Vingiello, *ibid.*, **71**, 1434 (1949).

(5) F. A. Vingiello and A. Bořkovec, presented before the Division of Organic Chemistry at the 126th Meeting of the American Chemical Society, New York, N. Y., September 1954.

heating with 40% sulfuric acid in a sealed tube at 180° was successful.[6]

The hydrocarbons were prepared by cyclizing either the corresponding ketimine hydrochloride or the ketone using the usual[5] acid mixture but at high temperatures.

The ultraviolet spectra of the new hydrocarbons are shown in Table III. As found in earlier work[5] it seems that the 10-phenyl group is not coplanar with the benzanthracene nucleus and that the picrates are difficult to prepare. If the 10-phenyl group were coplanar with the benzanthracene system we would expect the spectra of these compounds to be different from the spectrum of benzanthracene itself due to the participation of the 10-phenyl group in the resonance of the benzanthracene system. Since the spectra are similar, we assume that the 10-phenyl group is not coplanar with the benzanthracene system. This also is suggested by the model of the molecule made with the Fisher-Hisrchfelder-Taylor kit.

Acknowledgment.—This work was sponsored by the Office of Ordnance Research, U. S. Army.

Experimental[7]

2-(1-Naphthylmethyl)-2',5'-dimethyl Diphenylketimine Hydrochloride (I, 2',5'-Dimethyl).—A Grignard reagent was prepared from 3.5 g. (0.15 mole) of magnesium, 28.0 g. (0.15 mole) of 1-bromo-2,5-dimethylbenzene and 150 ml. of ether. The mixture was stirred under reflux for one hour and a solution of 12.2 g. (0.05 mole)[8] of 2-(1-naphthylmethyl)-benzonitrile[5] in 250 ml. of dry toluene was added dropwise. During the addition the flask was heated gently, and the ether was slowly distilled away. When the temperature of the vapor reached 105°, and all the nitrile had been added, the solution was heated under reflux for 18 hours with stirring and then decomposed with 20% ammonium chloride solution. The clear red liquid was separated and the residue[9] in the flask was washed twice with benzene. The combined benzene and toluene solutions were washed with water and acidified with concentrated hydrochloric acid. After the walls of the flask had been scratched with a glass rod, the crude ketimine hydrochloride crystallized, was separated, washed with water and boiled for one hour with a 20% sodium hydroxide solution. The free imine was extracted with benzene, washed with water and again precipitated with concentrated hydrochloric acid; yield 13.5 g. (70%). The analytical sample was prepared by again decomposing the ketimine hydrochloride with sodium hydroxide, precipitating with hydrochloric acid and recrystallizing the solid from a mixture of one part of ethanol and nine parts of acetone. The resulting white crystals melted at 176–179° dec.

TABLE I

NEW KETIMINE HYDROCHLORIDES[a] I

Methyl groups at	Yield, %	M.p., °C.	Analyses,[b] % Found Carbon	Hydrogen
2,3	92	185[c]	[d]	
2,4	62	179	81.05	6.38
2,5	70	176	80.72	6.53
2,6	76	182	80.49	6.42
3,4	58	180	[e]	
3,5	75	185	[f]	

[a] Calculated for $C_{26}H_{24}NCl$: C, 80.91; H, 6.27; N, 3.63. [b] All analyses were carried out by the Micro-Tech Laboratories, Skokie, Ill. [c] All melted with decomposition. [d] Found: N, 3.91. [e] Found: N, 3.50. [f] Found: N, 3.92.

The other ketimine hydrochlorides were prepared in a similar way.

2-(1-Naphthylmethyl)-2',5'-dimethylbenzophenone (II, 2',5'-Dimethyl).—A mixture of 2 g. of the ketimine hydrochloride, 40 ml. of 25% sulfuric acid and 35 ml. of toluene was heated under reflux for 3 hours. The organic layer was separated, washed three times with water, and dried with calcium chloride; after filtration of the solution through charcoal, the toluene was replaced by 30–60° petroleum ether. The solution then was chromatographed on a column (12 mm. × 300 mm.) packed with Fisher Alumina (80–200 mesh) using a mixture of seven parts of 30–60° petroleum ether and three parts of carbon tetrachloride as the eluent. On evaporation of the solvent from the percolate the ketone was obtained as a colorless, very viscous oil; yield 1.6 g. (88%). Our attempts to crystallize this oil failed.

The other ketones were prepared in a similar way.

TABLE II

NEW KETONES[a] II

Methyl groups at	Yield, %	M.p., °C.	Analyses, % Found Carbon	Hydrogen
2,3	64	72.5–73.5[b]	88.77	6.38
2,4	93	65–66[b]	89.07	6.29
2,5	88	[c]	89.02	6.66
2,6	77	124.5–125[d]	89.47	6.39
3,4	88	93.5–94[b]	89.00	6.49
3,5	87	93–94[b]	88.74	6.20

[a] Calculated for $C_{26}H_{22}O$: C, 89.10; H, 6.33. [b] Recrystallized from ethanol. [c] A viscous oil. [d] Obtained by heating the ketimine hydrochloride with 40% H_2SO_4 for 6 hr. in a Carius tube at 180°, chromatographing in the usual way and recrystallizing from ethanol.

10-(2',5'-Dimethylphenyl)-1,2-benzanthracene (IV, 2',5'-Dimethyl).—A mixture of 2 g. of the corresponding ketimine hydrochloride, 30 ml. of glacial acetic acid and 15 ml. of 48% hydrobromic acid was sealed in a glass tube and heated in a Carius furnace for 5 hours at 180°. The green, viscous oil which appeared on top of the solution was separated, dissolved in benzene, washed with water and dried over calcium chloride. The benzene was replaced with 30–60° pe-

TABLE III

NEW HYDROCARBONS[a,b] III

Methyl groups at	Yield, %	M.p., °C.	Analyses, % Found Carbon	Hydrogen
2,3	41	175–176[c]	94.04	6.27
2,4	59	116–118[d]	93.79	6.01
2,5	53	116–117	93.70	6.15
2,6	32	135.5–136.5[e]	93.57	6.07
3,4[f]	77	126–127	93.99	6.37
3,5[f]	96	118–120	93.95	6.23

[a] Calculated for $C_{26}H_{20}$: C, 93.93; H, 6.07. [b] The ultraviolet spectra of the hydrocarbons were determined with a Beckman spectrophotometer (model DU, 1 cm. silica cell) at a concn. of 10 mg./l. using 95% EtOH as the solvent. The curves for all six hydrocarbons are practically identical. The optical density values at the wave length maxima for III where the methyl groups are at the 3'- and 4'-positions are: λ 222 mμ, 1.60; λ 259 mμ, 0.92; λ 271 mμ, 1.15; λ 281 mμ, 1.83; λ 292 mμ, 2.21; λ 321 mμ, 0.13; λ 336 mμ, 0.22; λ 351 mμ, 0.28; λ 366 mμ, 0.22. [c] Sublimes. [d] Two polymorphic forms grew from solution: first, small needles, m.p. 107.5–108.5°; second, large prism, m.p. 116–118°. A composite sample was taken for analysis. [e] This value is included only to complete the table. The hydrocarbon *could not* be prepared as were its isomers but was successfully cyclized by a new method currently being investigated. [f] Only these two hydrocarbons gave a red color with concd. sulfuric acid.

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[6] J. B. Culbertson's results in a study on the factors affecting the rates of hydrolysis of substituted diphenylketimines, THIS JOURNAL, **73**, 4818 (1951), clearly imply that the difficulty is due to steric hindrance.

[7] All melting points are corrected.

[8] A three molar excess of Grignard reagent was used in most cases; however, it was observed in later experiments that a 1.5 molar excess gave equally good yields.

[9] The hard residue was completely soluble in dil. HCl, which was a satisfactory check that all of the ketimine had been extracted.

troleum ether and the solution chromatographed[10] on a column (12 mm. × 300 mm.) packed with Fisher Alumina (80–200 mesh) using 30–60° petroleum ether as the eluent. On evaporation of the solvent from the percolate the hydrocarbon was obtained as a slightly yellow strongly fluorescent oil which was crystallized from a mixture of ethanol ether and water.[11] The crystals which formed were colorless prisms, m.p. 116–117°.

The other hydrocarbons except for the 2,6-isomer, were prepared in a similar way.

10-(3′,4′-Dimethylphenyl)-1,2-benzanthracene (IV, 3′,4′-Dimethyl).—A mixture of 2 g. of the ketone, 15 ml. of 48% hydrobromic acid and 30 ml. of glacial acetic acid was sealed in a Carius tube and heated in a Carius furnace for 6 hours at 180°. The whole was extracted with benzene, washed in water and dried over calcium chloride. The benzene then was replaced with a solution of ethanol containing a small amount of acetone. When this was seeded with a few crystals of the hydrocarbon (obtained from cyclizing the ketimine hydrochloride as described above) there was obtained a first crop of crystals weighing 1.3 g. and a second crop of 0.2 g.; total yield 1.5 g. (79%), m.p. 122–126°.

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[10] Since the hydrocarbons are sensitive toward light, the chromatography is best performed in the absence of strong light. The progress of the hydrocarbon down the column is observed easily by illuminating the column with ultraviolet light from time to time.

[11] The oil was dissolved in a minimum volume of boiling ether, twice this volume of ethanol was added and the solution brought to a boil again. Water was then added dropwise until the turbidity which immediately formed just disappeared.

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Reversible Dimerization of 2,6-Dibenzylidenecyclohexanone

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RECEIVED JANUARY 5, 1955

In the course of a study of the aromatization of 2,6-dibenzylidenecyclohexanone (I), to be published later, colorless fiber-like crystals (hereafter called "2,6-dibenzylidenecyclohexanone dimer") were obtained, having a molecular weight twice that of 2,6-dibenzylidenecyclohexanone. This compound reverted to 2,6-dibenzylidenecyclohexanone when its ethanolic solution was refluxed.

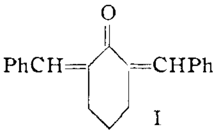
As far as we know, the dimerization of ketones containing a $Ph{-}C{=}C{-}CO{-}C{=}C{-}Ph$ system has been studied only starting from dibenzylideneacetone,[1] and the structure of a dimer has been reported as (II).[1b]

2,6-Dibenzylidenecyclohexanone dimer gave a dioxime and, furthermore, a tetrahydro derivative upon catalytic hydrogenation. When 2,6-dibenzylidenecyclohexanone was oxidized with permanganate, benzoic and glutaric acids (the latter isolated in the form of its diphenacyl ester) were obtained. In contrast, a similar treatment of the dimer did not yield either of the two acids mentioned. This shows the absence of the PhCH= group in the dimer. The location of the spectral maximum of the dimer (ε 42,500 at 293 mμ, in ethanol) is very close to that of 2-benzylidenecyclohexanone (III) (ε 11,200 at 290 mμ, in ethanol)[2] and differs from that of 2,6-dibenzylidenecyclohexanone (I) (ε 25,100 at 330 mμ, in ethanol),[2] and from that of *cis*- or *trans*-stilbene.[3]

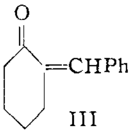
On the basis of the above observations we believe that the dimer (colorless) contains two —CO—C=C groups which are not conjugated with each other, in contrast to the structure of the yellow 2,6-dibenzylidenecyclohexanone (I).

The strong bands (1695, 1608, 754 and 697 cm.$^{-1}$) in the infrared spectrum of the dimer (in carbon disulfide) also show the presence of α,β- (or α,β,γ,δ)-unsaturated carbonyl group and monosubstituted phenyl group.[4]

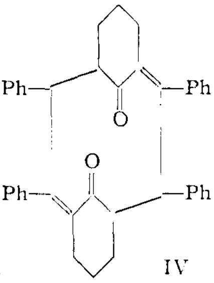
A possible structure for the dimer that satisfies all experimental findings is IV, *i.e.*, 2,3,9,10-tetraphenyltricyclo - $(9,3,1,1^{4,8})$ - 15,16 - diketohexadeca-1,8-diene.



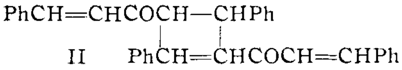
I



III



IV



$$\begin{array}{l} PhCH{=}CHCOCH{-}CHPh \\ \qquad\qquad\quad\;\; | \qquad\; | \\ PhCH{=}CHCOCH{=}CHPh \end{array}$$

II

According to Fawcett,[5] bicyclo(*x,y,z*)alkene structures containing a double bond at a "bridgehead" are strainless when $x + y + z = 11$ which is the case in IV.

Experimental

2,6-Dibenzylidenecyclohexanone Dimer (IV).—An ethanol (400 ml.) solution of 2,6-dibenzylidenecyclohexanone (10 g.) was refluxed for 120 hours. After cooling the crystals thus obtained were recrystallized from ethanol; colorless fiber-like crystals, m.p. 187–188° (cor.); yield 9 g., 90%.

Anal. Calcd. for $C_{40}H_{36}O_2$: C, 87.56; H, 6.61; mol. wt., 549. Found: C, 87.15; H, 6.52; mol. wt., 545 (cryoscopically in benzene).

Dioxime.—A solution of the dimer (0.55 g.) and hydroxylamine hydrochloride (0.28 g.) in 100 ml. of ethanol was refluxed for 24 hours, then concentrated to half its volume and diluted with 600 ml. of 0.5% sodium carbonate. The precipitate was recrystallized from ethanol; colorless needles, m.p. 197–198°, yield 0.08 g.

Anal. Calcd. for $C_{40}H_{38}N_2O_2$: C, 83.01; H, 6.62. Found: C, 82.65; H, 6.34.

Tetrahydro Derivative of the Dimer.—A solution of 0.55 g. of the dimer in 300 ml. of ethanol absorbed, in the presence of 0.02 g. of Adams platinum oxide, 43.2 ml. of hydrogen (0°, 760 mm., corrected). Calcd. for 2 double bonds 44.8 ml. The filtrate was concentrated to about 50 ml. and the crystals thus obtained recrystallized from ethanol; colorless needles; m.p. 217–218°; yield, 0.44 g.

Anal. Calcd. for $C_{40}H_{40}O_2$: C, 86.93; H, 7.30. Found: C, 86.73; H, 7.21.

Oxidation of 2,6-Dibenzylidenecyclohexanone (I) with Permanganate.—To a solution of 3 g. of I in 60 ml. of chloroform a solution of 9 g. of potassium permanganate in 500 ml. of water was added dropwise at 5° with mechanical stirring. After 4 hours the manganese dioxide was filtered off and extracted with boiling water; this extract was com-

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[1] (a) G. Ciamician and P. Silber, *Ber.*, **42**, 1388 (1909); (b) P. Praetorius and F. Korn, *ibid.*, **43**, 2744 (1910).

[2] H. S. French and L. Wiley, THIS JOURNAL, **71**, 3702 (1949).

[3] R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, Figs. 125 and 126; R. N. Beale and E. M. F. Roe, *J. Chem. Soc.*, 2755 (1953).

[4] F. A. Miller, in H. Gilman, "Organic Chemistry," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 172.

[5] F. S. Fawcett, *Chem. Revs.*, **47**, 219 (1950).