From the residue the 2,4-dinitrophenylhydrazone (m.p. 238–239°) of benzophenone was prepared. From the aqueous alkali *m*-toluic acid (m.p. 111–112°) was precipitated.

Oxidation of triarylethylene glycols with selenium dioxide. The following technique yielded a crystalline benzoin (II) from triphenylethylene glycol and from 1,1-diphenyl-2-*o*-tolylethylene glycol, but not from any of the other glycols in Table I. A molten mixture of 5 g. of 1,1-diphenyl-2-*o*-tolylethylene glycol and 1.5 g. of selenium dioxide was stirred and maintained at a temperature of 200° for 5 min. The cooled mixture was triturated with ether which was in turn washed with aqueous sodium bicarbonate, dried, and evaporated. The residue was recrystallized twice from hexane-benzene to give 3.2 g. (65%) of α-phenyl-2-methylbenzoin, m.p. 116–117° with or without admixture of authentic material.[1]

α-Phenylbenzoin from benzoyl cyanide. To the Grignard reagent prepared from 94 g. of bromobenzene and 1.5 g. of magnesium in 75 ml. of ether there was added dropwise over a period of 30 min. a solution of 2.6 g. of benzoyl cyanide[14] in 40 ml. of ether. A granular precipitate appeared in the stirred reaction mixture as rapidly as the cyanide was added. The reaction mixture was poured into a vigorously stirred mixture of ice and dilute hydrochloric acid contained in a separatory funnel. As soon as the layers separated the aqueous layer was quickly drawn off and allowed to stand at room temperature overnight. The ether layer was worked up in the usual manner to yield 4.3 g. (85%) of triphenylmethanol, m.p. 162–163°. The aqueous layer, after standing overnight, was extracted with ether which was in turn washed, dried, and evaporated. The residue was recrystallized from ligroin to give 0.27 g. (5%) of α-phenylbenzoin, m.p. 87–88° (lit.[15] value 87–88°).

α-o-Tolylbenzoin. The procedure employed was that described above. After reaction between Grignard reagent (from 18.2 g. of bromobenzene and 2.9 g. of magnesium) and *o*-toluyl cyanide (4.2 g., b.p. 202–204°/750 mm., prepared from *o*-toluyl chloride as described for benzoyl cyanide[14]) the reaction mixture was distributed between ether and aqueous acid. The ether layer was discarded and the aqueous acid, after standing overnight, worked up as before. Recrystallization of the crude product gave 0.70 g. (8%) of α-o-tolylbenzoin, m.p. 81–82° with or without admixed authentic material.[1]

KNOXVILLE, TENN.

(14) T. S. Oakwood and C. A. Weisgerber, *Org. Syntheses,* Coll. Vol. III, 114 (1955).

(15) S. F. Acree, *Ber.,* 37, 2753 (1904).

Base-Catalyzed Alkylations with Alcohols. IV

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Refluxing a mixture of indene with sodium benzylate in benzyl alcohol produced dibenzylindene. With added Raney nickel 3-benzyl-1-benzylideneindene was obtained. A third hydrocarbon, believed to be 1-benzylideneindane, was also isolated.

Fluorene was alkylated with 2-diethylamino- and 2-dimethylaminoethanol to give the corresponding 9-(2-dialkylaminoethyl)fluorenes. With ethoxyethanol 9-(2-ethoxyethyl)fluorene was obtained.

The purpose of the present investigation was to determine whether indene, with two potentially active positions, would be alkylated twice with benzyl alcohol and sodium benzylate, and to determine whether fluorene could be alkylated with substituted alcohols as extensions of previous work in this field.[3,4]

The first attempt to alkylate indene was carried out with *n*-propyl alcohol and sodium *n*-propylate in a reaction bomb at 210°, or under reflux, but no isolable product was obtained. However, upon employing benzyl alcohol and sodium benzylate, which has been exploited successfully by Sprinzak and his co-workers,[5] with or without diisopropylbenzene as a solvent, dibenzylindene (I), m.p. 60.3–62.0°, was obtained as the major product. When a mixture of indene with a small amount of sodium benzylate in a large excess of benzyl alcohol in the presence of Raney nickel was refluxed with or without di-isopropylbenzene as a solvent 3-benzyl-1-benzylideneindene (II), a yellow solid, m.p. 137.4–138.4°, was obtained.

In the first reaction, using UOP nickel instead of Raney nickel, a small amount of a white solid (III), believed to be 1-benzylideneindane, m.p. 73.4–74.4°, was isolated. The proofs of structure for the three products follow.

Dibenzylindene. The melting point and the melting point of the dibromo derivative agreed with the reported values.[6] Additional information was added when the molecular weight and the ultimate analysis agreed with those expected for the hydrocarbon. The nuclear magnetic resonance spectrum was also confirmatory: Band 1, 90 cycles on the low field side of water (aromatic CH); Band 2, 49 cycles on the low field side of water (=CH); Band 3, 43 cycles on the high field side of water (=C—CH₂—C=); Band 4, peaks at 47 and 54 cycles on the high field side of water (H in the 1-position); Band 5, peaks at 72, 76 and 83 cycles

(1) From the B.S. theses of S. S. Hirsch and D. H. Lorenz, Polytechnic Institute of Brooklyn, 1958.

(2) To whom inquiries should be sent.

(3) M. Avramoff and Y. Sprinzak, *J. Org. Chem.,* 22, 571 (1957).

(4) I. D. Rubin and E. I. Becker, *J. Org. Chem.,* 22, 1623 (1957).

(5) See footnote 3 and papers cited therein.

(6) J. Thiele and A. Buhner, *Ann.,* 347, 249 (1906).

on the high field side of water (—C—CH₂—C=). Finally, the ultraviolet absorption maximum at 257 mμ (Log ε 3.994) was in agreement with an indene structure and not with a stilbene or fulvene structure.[7,8]

3-Benzyl-1-benzylideneindene. The melting point agreed with the literature value.[6] The infrared spectrum confirmed a hydrocarbon structure by the absence of any peaks in the OH, CO, or COC regions. Ultimate analysis and molecular weight were also in agreement with the expected values. The nuclear magnetic resonance spectrum further confirmed the structure: Band 1, peaks at 95 and 99 cycles on the low field side of water (aromatic CH); Band 2, 81 cycles on the low field side of water (=CH—, olefinic); Band 3, 32 cycles on the high field side of water (=C—CH₂—C=).

In addition, the series of reactions reported for the compound[6] were carried out: Benzylbenzylideneindene was first reduced to dibenzylindene by means of aluminum amalgam in moist ether. Bromine was then added to give a dibromide. Dehydrobromination of the dibromide gave benzylbenzylideneindene once again (see Chart). Melting points of the several compounds agreed with those reported, and melting points of mixtures of corresponding hydrocarbons obtained from the alkylation and from the reduction and dehydrobromination were not depressed.

Benzylideneindane. The infrared spectrum indicated that III was a hydrocarbon and the ultimate analysis agreed with the values expected. Plentl and Bogert[9] have reported III as a liquid, but they mention in the experimental section that the compound is probably a mixture with 3-benzylindene. For this reason the nuclear magnetic resonance spectrum was obtained.

Band 1, peaks at 98 and 102 cycles on the low field side of water (aromatic CH); Band 2, 85 cycles on the low field side of water (—CH=, conjugated); Band 3, 69 cycles on the high field side of water (—CH₂—C=).

No other proton types were indicated. Furthermore, the area under band 3 is about four times that under band 2. This is in agreement with the proposed structure for III.
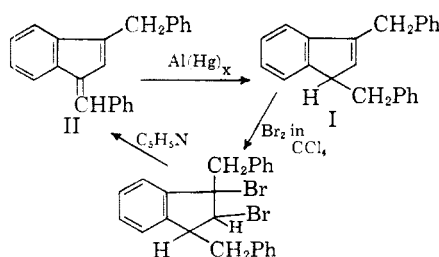
(7) R. A. Friedel and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*, John Wiley & Sons, Inc., New York, N. Y., 1951.

(8) J. H. Day, *Chem. Revs.*, **53**, 167 (1953).

(9) A. A. Plentl and M. T. Bogert, *J. Am. Chem. Soc.*, **63**, 989 (1941).

The formation of benzylbenzylideneindene by alkylation with an alcohol under basic conditions represents the first instance of the alkylation of a hydrocarbon with more than one unsubstituted corner in the ring being alkylated. Since resonance structures for the anion of indene, or of a monosubstituted indene, show the negative charge localized principally at 1 and 3, and further, since the mechanism for the alkylation requires an unsaturated intermediate, the substituents have been placed at the 1- and 3-positions of indene.

In the second part of this investigation an attempt was made to determine whether substituted alcohols could be employed in the alkylation of hydrocarbons. Dimethylaminoethanol, diethylaminoethanol, 3-diethylaminopropanol, ethoxyethanol, and methoxyethanol were each tried as alkylating agents.

Alkylation of fluorene with the two dialkylaminoethanols in the presence of their sodium salts and Raney nickel in *p*-cymene gave the corresponding dialkylaminoethylfluorenes. Each was characterized by its neutral equivalent, ultimate analysis, and preparation and ultimate analysis of the methiodides and picrates. The boiling point and index of refraction for the dimethyl compound agreed with the literature values.[10] The boiling point of the diethyl compound and the melting point of its methiodide also agreed with literature values.[11]

$$IV, Y = -N(CH_3)_2$$
$$V, Y = -N(C_2H_5)_2$$
$$VI, Y = -OC_2H_5$$
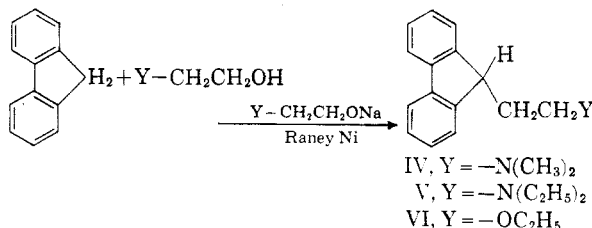
It is interesting that 3-diethylaminopropanol did not give an alkylated product. This fact is analogous to the behavior of 1,3-diols in the alkylation reaction.[4]

When a solution of fluorene in *p*-cymene containing ethoxyethanol, some sodium ethoxyethylate, and suspended Raney nickel was refluxed, a light yellow compound (VI) was obtained. Strong, but not conclusive, proof for the ether were its correct ultimate analysis and a strong band at 1140–1090 cm.⁻¹

The formation of the dialkylaminoethyl and ethoxyethylfluorenes represents the first uses of substituted alcohols in the alkylation with alcohols under basic conditions.

EXPERIMENTAL

Dibenzylindene (I). *A. Without solvent.* Twenty-nine grams

(10) C. J. Cavallito, A. P. Gray, and E. E. Skinner, *J. Am. Chem. Soc.*, **76**, 1862 (1954).

(11) G. M. Badger, J. W. Cook, and F. Schwartz, *J. Chem. Soc.*, 117 (1952).

TABLE I
ALKYLATED INDENES AND FLUORENES

Compound	B.P. (M.P.), °C (Mm. of Hg)	n_D^{25}	d_4^{25}	R_D^{25}	Yield, %	Empirical Formula	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
I	60.3–62.0					$C_{23}H_{20}$	93.20	93.11	6.80	6.75[a]		
II	137.4–138.4					$C_{23}H_{18}$	93.84	93.72	6.16	6.34[b]		
III	73.4–74.4					$C_{16}H_{14}$	93.16	92.98	6.84	6.98		
IV	134–137 (2)[c]	1.5987[c]	1.0352	78.31[d]	48	$C_{17}H_{19}N$	86.03	85.96	8.07	8.20	5.90	5.76[e]
IV-methiodide	205–207 (dec.)				96	$C_{18}H_{22}IN$	57.00	56.92	5.85	5.74	3.69	3.72[f]
IV-picrate	181.5–182.0				62	$C_{23}H_{22}N_4O_7$	59.22	59.16	4.76	4.90	12.01	11.90
V	167–169 (1)[g]	1.5863	1.0178	87.54[h]	69	$C_{19}H_{23}N$	85.99	85.89	8.74	8.62	5.28	5.16[i]
V-methiodide	159.5–160.5[j]				53							
V-picrate	127.2–127.4				64	$C_{25}H_{26}N_4O_7$	60.72	60.72	5.30	5.34	11.33	11.31
VI	145–150 (1)	1.5975	1.0604	76.63[k]	38	$C_{17}H_{18}O$	85.67	85.89	7.61	7.65		

[a] Calcd. for $C_{23}H_{20}$: molecular weight, 296. Found: mol. wt., 282 (cryoscopic, benzene). [b] Calcd. for $C_{23}H_{18}$: molecular weight, 294. Found: mol. wt., 292 (cryoscopic, benzene). [c] Footnote 10 reports b.p. 126–129° (1.5 mm.), n_D^{24} 1.5987. [d] Calcd. for $C_{17}H_{19}N$: R_D^{25}, 77.84. [e] Calcd. for $C_{17}H_{19}N$: neut. equiv., 237. Found: neut. equiv., 234, 238. [f] Calcd. for $C_{18}H_{22}IN$: I, 33.46, Found: I, 33.53. [g] Footnote 11 reports 156–158° (0.8 mm.). [h] Calcd. for $C_{19}H_{23}N$: R_D^{25}, 87.08. [i] Calcd. for $C_{19}H_{23}N$: neut. equiv., 265. Found: 267, 257, 253. [j] Footnote 11 reports 157°. [k] Calcd. for $C_{17}H_{18}O$: $R_{,D}^{25}$ 75.39.

(0.25 mole) of indene was added to a solution of 130 g. (1 mole) of sodium benzylate in 216 g. (2 moles) of benzyl alcohol (made by adding 23 g. of sodium to 3 moles of benzyl alcohol) in a 1-l. three-neck flask. The flask was provided with a mechanical stirrer and a Soxhlet apparatus containing 100 g. of barium oxide. Prepurified nitrogen was passed into the three-neck flask throughout the experiment. The mixture was refluxed for 100 min. whereupon a gelatinous precipitate formed. After cooling and dilution with 400 ml. of benzene, the precipitate was collected and the filtrate was distilled to give a light yellow oil, b.p. 240–247° (5 mm.). Upon standing for three days with occasional stirring, it solidified to a thick mass with crystals dispersed throughout. This was vigorously stirred in small portions with methanol to remove the oil. The crude product was a dark cream-yellow solid, m.p. 58–62°. Three recrystallizations from methanol followed by three recrystallizations from 80% methanol–20% chloroform gave 6 g. (0.020 mole, 8.1%) of a light cream solid, m.p. 60.3–62.0°.

The precipitate obtained from the crude reaction mixture was soluble in water. Acidification gave a colorless precipitate, 10 g. (0.082 mole), m.p. 120.6–122.4°. No depression of the melting point was observed when admixed with authentic benzoic acid.

B. Using solvent. The same reaction mixture as above was used with the addition of 300 ml. of diisopropylbenzene. A Dean-Stark trap replaced the Soxhlet apparatus. The mixture was refluxed for 16 hr. during which 11 ml. of water layer were collected. The sodium benzoate was filtered and the mixture distilled until about 125 ml. remained. This was cooled and seeded giving 10 g. of crude product, m.p. 57.8–59.6°. One recrystallization from ethanol gave 7.3 g. (0.025 mole, 10%) of light cream crystals melting at 60.1–61.7°.

3-Benzyl-1-benzylideneindene (II). A. Without solvent. Twenty-nine grams (0.25 mole) of indene was added to a

solution of 22.6 grams (0.174 mole) of sodium benzylate in 305 g. (2.82 moles) of benzyl alcohol [made by adding 4 grams (0.174 atom) of sodium to 3 moles of benzyl alcohol] and 4 g. of suspended Raney nickel. The mixture was refluxed for 16 hr. Upon standing for eight days orange crystals deposited. The mixture was washed with water to remove sodium benzoate. The orange crystals were dissolved in the minimum quantity of hot 50% benzene–50% acetone mixture and filtered to remove the catalyst. Cooling gave 21 g. (28.6%) of yellow crystals, m.p. 133–136.8°. Two recrystallizations from ethanol afforded 12.5 g. (17.2%) of II, m.p. 137.4–138.4° (reported² 137–137.5°).

B. Using solvent. The same reaction mixture as above was employed, with the addition of 300 ml. of diisopropylbenzene. Only 8.5 ml. of water layer were collected in the trap which was provided. The contents of the flask were diluted with 250 ml. of benzene, and the sodium benzoate was filtered. The solution was distilled to one-half its volume and the residual liquid was cooled and seeded to give 21 g. (28.6%) of yellow 3-benzyl-1-benzylideneindene. After washing with 25 ml. of petroleum ether (b.p. 60–70°) the melting point was 116–133°. Five grams of this material was recrystallized twice from ethanol giving 3.0 g. (60% recovery) of product melting at 133.1–136.9°.

Dibenzylindene (I) from 3-benzyl-1-benzylideneindene.[6] Forty grams of amalgamated aluminum was added to a solution of 5 g. (0.017 mole) of 3-benzyl-1-benzylideneindene dissolved in the minimum amount of wet ether. The mixture was stirred overnight whereupon the yellow color of the original hydrocarbon disappeared. The ether solution was dried with sodium sulfate and carefully distilled to dryness. The white residue was recrystallized twice from 80% methanol–20% chloroform giving 2.6 g. (0.0088 mole, 51.6%) of dibenzylindene, m.p. 59.2–61.2° (reported⁶ 62–63°). A mixed melting point determination with dibenzylindene

(prepared by direct alkylation), m.p. 60.5–61.7°, melted 59.5–60.5°.

1,3-Dibenzyl-2,3-dibromoindane.[6] From 3 g. (10 mmole) of dibenzylindene there was obtained 1.4 g. (3.07 mmole, 30%) of 1,3-dibenzyl-1,2-dibromoindane, m.p. 99–100° (dec., heated at a rate of 1°/min.) (reported[6] 103–104°).

3-Benzyl-1-benzylideneindene from 1,3-dibenzyl-2,3-dibromoindane.[6] From 0.75 g. (1.64 mmole) of 1,3-dibenzyl-2,3-dibromoindane in 3 ml. of pyridine there was obtained 0.25 g. (0.85 mmole, 52%) of yellow 3-benzyl-1-benzylindeneindene, m.p. 137.6–138.7°.

1-Benzylideneindane (III). Fourteen and one-half grams (0.125 mole) of indene was refluxed with a solution of 5.2 g. (0.040 mole) of sodium benzylate in 22.7 g. (0.21 mole) of benzyl alcohol (made by adding 0.92 g. of sodium to 27 g. of benzyl alcohol) in the presence of 1.0 g. of UOP nickel for 16 hr. Two volumes of benzene were added, the mixture filtered, washed with water, and dried over sodium sulfate. Distillation of the benzene solution gave a fraction b.p. 148–185° (1 mm.). Upon standing for one week crystals deposited. Three recrystallizations from acetone-water and then two from ethanol-water afforded 0.20 g. (0.00097 mole, 0.8%) of colorless product, m.p. 73.4–74.4°.

9-Dimethylaminoethylfluorene (IV). To 42 g. (0.252 mole) of fluorene and 2 g. of Raney nickel in 250 ml. of *p*-cymene was added a solution of 38.6 g. (0.348 mole) of sodium dimethylaminoethylate in 167 ml. of dimethylaminoethanol (made by adding 8.0 g. of sodium to 202 ml. of dimethylaminoethanol). A condenser and Dean-Stark trap were attached to the flask and the contents were heated at reflux for 16 hr. The cooled reaction mixture was extracted with 1:1 hydrochloric acid, the aqueous layer basified and then extracted with benzene. After washing the benzene layer with water and drying it, it was distilled and redistilled to give a purified fraction, b.p. 134–137° (2 mm.).

9-Diethylaminoethylfluorene (V). This alkylation reaction was carried out in the same manner, except that a Soxhlet extractor filled with barium oxide was used in place of the Dean-Stark trap to remove the water. The pure product was vacuum distilled and boiled at 167–169° (1 mm.).

The *methiodides* and the *picrates* of IV and of V were prepared according to standard procedures.[12] From 1.471 g. of IV, 2.251 g. of methiodide was obtained and from 0.975 g., 1.201 g. of picrate. From 1.207 g. of V, 0.966 g. of methiodide

(12) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds,* Fourth Edition, John Wiley & Sons, Inc., New York, N. Y., 1956, pp. 227, 228.

was obtained and from 1.112 g., 1.315 g. of picrate. The methiodides were first recrystallized from acetone, then from water and finally from ethanol–ethyl acetate (1:8). The picrates were recrystallized twice from ethanol and once from methanol. The yields (see Table) are for the final products.

9-Ethoxyethylfluorene (VI). To 42 g. (0.252 mole) of fluorene in 200 ml. of *p*-cymene was added a solution of 39 g. (0.348 mole) of sodium ethoxyethylate in 160 ml. of ethoxyethanol (made by adding 8.0 g. of sodium to 194 ml. of ethoxy ethanol). A Soxhlet extractor filled with barium oxide and reflux condenser were attached and the contents were heated under reflux for 16 hr. After washing the cooled reaction mixture with water, dilute hydrochloric acid, and water again, the aqueous layer was extracted once with benzene. The combined organic layers were concentrated and vacuum distilled twice to give the product fraction, b.p. 145–150° (1 mm.).

Reaction of fluorene with methoxyethanol. The same procedure as that of the other ether alkylation was used except that on vacuum distillation a white solid crystallized from a yellow liquid. After crystallization from acetone, the white solid melted 112–113°. A mixture melting point with fluorene gave no depression. Only fluorene could be isolated in a pure state, the liquid always containing some fluorene. The yellow liquid did not have any ether peaks on infrared analysis.

Spectra. Infrared spectra were obtained as liquid films and in potassium bromide pellets with a Perkin-Elmer Infrared Spectrophotometer, Model 21, using sodium chloride optics. Nuclear magnetic resonance spectra were recorded on a Varian Associates 40-Megacycle Nuclear Magnetic Resonance Spectrometer. Methylene chloride was the solvent and water the reference. Ultraviolet spectra were obtained on a Beckman DK-2 Ultraviolet Spectrophotometer using isooctane as solvent.

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[CONTRIBUTION FROM THE MCPHERSON CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

A New Method for Introducing a Two Carbon Acid Side Chain into Ketones

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The alkali-catalyzed condensation of glyoxylic acid, or esters thereof, with α-tetralone (and other α-tetralones) to yield 1-keto-1,2,3,4-tetrahydro-2-naphthylideneacetic acid, III (and similar acids), is described. The reasons for assigning a trans structure to III are given. The reductions of III to 1,2,3,4-tetrahydro-2-naphthylacetic acid, V, and to the cyclopropanecarboxylic acid, VI, are described.

Several methods have found use in the conversion of compounds containing a cyclohexanone

moiety into compounds containing an acetic acid side chain adjacent to the carbonyl function. One method involves conversion of cyclohexanone to cyclohexanone glyoxalate; decarbonylation to 2-carbethoxycyclohexanone; alkylation to ethyl 2-keto-1-carbethoxy-1-cyclohexylacetate; hydrolysis;