formed, the heating was continued for 4 hours at 240–250°. The reaction mixture was cooled, diluted with water, acidified and extracted with ether; b.p. 98° (0.25 mm.), yield 7 g. (93%), $n^{26}_D$ 1.5450, $d^{26}_4$ 0.9820; *MR* calcd. 68.77, found 68.94; ultraviolet spectrum (in ethanol) 252 mμ (3.26).

*Anal.* Calcd. for $C_{16}H_{22}$: C, 89.7; H, 10.3. Found: C, 89.6; H, 10.0.

**4-Phenylazulene (XVIII).**—The dehydrogenation of 4-phenylbicyclodecane (6.5 g.) was carried out in the usual manner[17] at 350–360° and the product taken up in petroleum ether from which the azulene formed was extracted with 85% phosphoric acid. The material was recycled 12 times. The acid solutions were combined, diluted with water and extracted with ether. After treatment with water, dilute bicarbonate solution and again water, the product was purified by distillation. It formed a deep-blue oil of b.p. 120–130° (0.8 mm.), yield 2.2 g. (34%). **The trinitrobenzene derivative** was prepared in alcohol and recrystallized from the same solvent. It formed needles of m.p. 86°, as indicated in the literature.

*Anal.* Calcd. for $C_{22}H_{15}N_3O_6$: C, 63.3; H, 3.6. Found: C, 62.8; H, 4.0.

The trinitrobenzene compound was decomposed by chromatography of its benzene solution on activated alumina; the hydrocarbon so purified was used for the determination of the spectrum.

JERUSALEM, ISRAEL

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE FLORIDA STATE UNIVERSITY]

# Azulenes. IX.[1] Migration of the Isopropyl Group during the Synthesis of 1-Isopropyl-8-methylazulene

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Treatment of 1-isopropyl-7-methylindan with ethyl diazoacetate followed by hydrolysis and dehydrogenation gave 1-isopropyl-8-methylazulene and 2-isopropyl-4-methylazulene, the latter by migration of the isopropyl group. The rearrangement product was synthesized independently from 2-isopropyl-4-methylindan.

Earlier work dealing with alkyl group migrations in the azulene series was reviewed in the previous paper.[1] Isopropyl group migration, presumably due to interference between alkyl groups in the 1- and 8-positions of the azulene nucleus, was observed when attempts were made to synthesize 1-isopropyl-4,8-dimethyl-[2] and 3-isopropyl-4,5-dimethylazulene.[3] The present paper reports an analogous migration during the preparation of 1-isopropyl-8-methylazulene, the simplest member of this group.

Authentic 2-isopropyl-4-methylazulene was prepared from *o*-methylbenzyl chloride by a standard series of reactions involving condensation with diethyl isopropylmalonate, hydrolysis and decarboxylation, cyclization of the resulting acid to 2-isopropyl-4-methylindanone, Clemmensen reduction to 2-isopropyl-4-methylindan, ring expansion with ethyl diazoacetate, saponification and dehydrogenation with palladium–charcoal. The azulene, a violet liquid, was characterized through its trinitrobenzene complex and exhibited the expected[4] peaks in the visible and ultraviolet spectrum (Figs. 1 and 2).

1-Isopropyl-7-methylindan was synthesized by alkylation of *o*-tolylacetonitrile with isopropyl bromide, saponification, homologation by the method of Newman and Beal,[6] hydrolysis and cyclization and Clemmensen reduction of the resulting 3-isopropyl-4-methylindanone. Treatment of the indan with diazoacetic ester, saponification and dehydrogenation with 10% palladium–charcoal gave a mixture of 1-isopropyl-8-methylazulene and 2-isopropyl-4-methylazulene. The mixture was separated into its constituents by taking advantage of the somewhat lower basicity of 1-alkylazulenes[7] and the greater solubility of their trinitrobenzene complexes in ethanol.[1,3] Isolated in this fashion the violet 2-isopropyl-4-methylazulene which constituted the major part of the azulene mixture was identical in all respects with the authentic sample.

1-Isopropyl-8-methylazulene, a *blue* liquid, was isolated in small amount only. Its trinitrobenzene complex melted over a 3° range, which may indicate the presence of a contaminant, but the visible spectrum (Fig. 1) was sharp and exhibited bands at or near the wave lengths reported for 1,8-dimethylazulene.[4,8] Similarly, the ultraviolet spectrum (Fig. 2) exhibited a medium-intensity band at a wave length higher than 360 mμ, which seems to be characteristic of 1-alkyl substituted azulenes.[1,10]

No evidence was found for the presence of 4-methylazulene and 1,3-diisopropyl-4-methylazulene, products which might have been formed by dealkylation accompanied, or followed, by disubstitution. Although these substances might have escaped detection, their apparent absence supports the earlier suggestion[1] that migration and

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[1] Paper VIII, W. Herz, THIS JOURNAL, **80**, 1243 (1958).

[2] W. Herz, *ibid.*, **75**, 73 (1953).

[3] W. Herz and B. E. Cleare, *ibid.*, **77**, 2318 (1955).

[4] For a review, see M. Gordon, *Chem. Revs.*, **50**, 127 (1952). There appears to be some question about the accuracy of the spectral data reported for 2-ethyl-4-methylazulene, the only previously synthesized 2,4-dialkylated azulene.[5]

[5] T. Wagner-Jauregg, H. Arnold, F. Hüter and J. Schmidt, *Ber.*, **74**, 1522 (1941); T. Wagner-Jauregg and H. Hippchen, *ibid.*, **76**, 694 (1943).

[6] M. S. Newman and P. F. Beal, THIS JOURNAL, **72**, 5163 (1950).

[7] Indications of this are found in the distribution studies of Pl. A. Plattner, E. Heilbronner and S. Weber, *Helv. Chim. Acta*, **32**, 574 (1949); **33**, 1663 (1950). Quantitative separation by this method is generally not feasible, but a small amount of pure 1-alkylazulene may usually be obtained by repeated extraction of the azulene mixture, dissolved in cyclohexane, with phosphoric acid (see also ref. 1).

[8] Differences in the m.p.'s of the complexes and the absorption maxima suggest that a blue azulene obtained by Hafner and Weldes[9] on treatment of 1-isopropylazulene with methyllithium and dehydrogenation with chloranil is 1-isopropyl-4-methylazulene, as might conceivably be expected by analogy with the behavior of 1-methylazulene,[9] and not 1-isopropyl-8-methylazulene.

[9] K. Hafner and H. Weldes, *Ann.*, **606**, 90 (1957).

[10] Pl. E. Plattner and E. Heilbronner, *Helv. Chim. Acta*, **31**, 804 (1948).

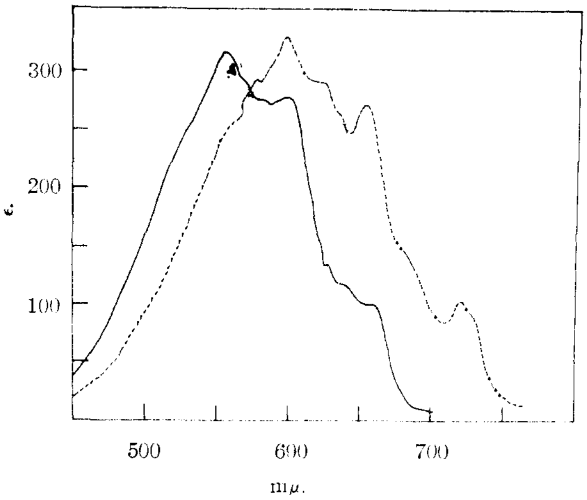

Fig. 1.—Visible spectra: --------, 1-isopropyl-8-methylazulene; ———, 2-isopropyl-4-methylazulene.

1,3-disubstitution are entirely separate, independent reactions.

**Acknowledgment.**—This work was supported in part by a grant from the National Science Foundation, for which I express my thanks.

## Experimental[11]

**Diethyl Isopropyl-2-methylbenzylmalonate.**—To 37 g. of powdered sodium and 800 ml. of dry benzene was added slowly, with stirring and heating, 312 g. of diethyl isopropylmalonate. After 5 hours of stirring at reflux, there was added slowly 204 g. of 2-methylbenzyl chloride.[12] After an additional 12 hours of stirring at reflux, the mixture was cooled, diluted with water and acidified with acetic acid. The organic layer was separated, washed, dried and distilled; wt. of crude product, b.p. 131–165° (2.3 mm.), 247 g. (56%). A middle cut, b.p. 150–151° (2.3 mm.), was used for analysis.

*Anal.* Calcd. for $C_{18}H_{26}O_4$: C, 70.56; H, 8.55. Found: C, 70.97; H, 8.92.

**$\alpha$-Isopropyl-$\beta$-(2-methylbenzyl)-propionic Acid.**—The crude ester, wt. 247 g., was saponified by refluxing for three days with 130 g. of KOH, 175 ml. of water and 400 ml. of ethanol. Water was added, the alcohol was removed by distillation, the residue was extracted with ether and acidified. The acid fraction was distilled *in vacuo*, b.p. 140–148° (1.6 mm.), yield 134 g. (83%, based on the recovery of 9 g. of material from the neutral fraction). It solidified on standing. Recrystallization from petroleum ether furnished colorless needles, m.p. 66.5–68°.

*Anal.* Calcd. for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 76.03; H, 8.94.

**2-Isopropyl-4-methylindanone.**—A mixture of 132 g. of the preceding acid and 150 ml. of thionyl chloride was warmed on the steam-bath for three hours. Excess thionyl chloride was removed *in vacuo* and the residue diluted with 600 ml. of thiophene-free benzene. After cautious addition of 95 g. of anhydrous aluminum chloride, the violet-black mixture was allowed to stand for four hours and then decomposed by pouring over ice–hydrochloric acid. The organic layer was washed, dried and distilled. The neutral fraction boiled at 117–128° (2.5 mm.), wt. 99 g. (82%). The analytical sample boiled at 105–106° (1.1 mm.), $n^{21}D$ 1.5403.

*Anal.* Calcd. for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.85; H, 8.19.

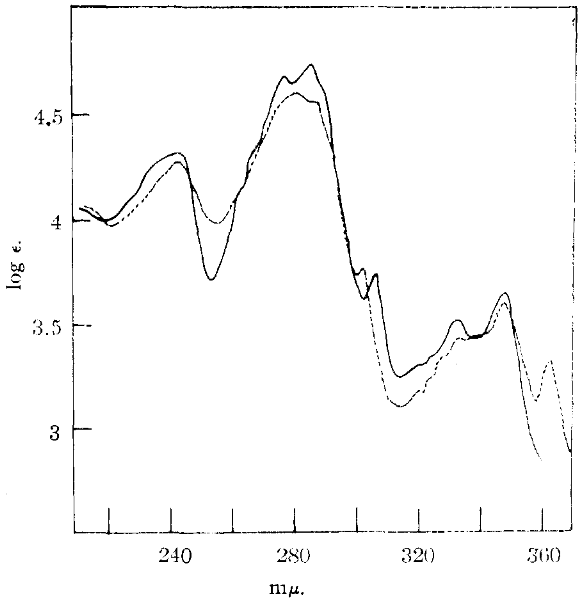

Fig. 2.—Ultraviolet spectra: --------, 1-isopropyl-8-methylazulene; ———, 2-isopropyl-4-methylazulene.

The dinitrophenylhydrazone was recrystallized several times from ethyl acetate. The scarlet crystals melted at 209–210° dec.

*Anal.* Calcd. for $C_{19}H_{20}N_4O_4$: C, 61.94; H, 5.47; N, 15.2. Found: C, 62.27; H, 5.29; N, 15.4.

**2-Isopropyl-4-methylindan.**—A mixture of 32 g. of 2-isopropyl-4-methylindanone, 140 g. of freshly cleaned and amalgamated zinc, 100 ml. of water and 200 ml. of concentrated hydrochloric acid was refluxed for 24 hours, fresh 100-ml. portions of hydrochloric acid being added at six-hour intervals. The mixture was cooled, diluted with water and extracted with ether. The ether extracts were washed, dried and distilled. The product was collected at 80–83° (2.5 mm.), the higher boiler, b.p. 84–105° (2.5 mm.), was combined with another batch of indanone and rereduced. In this manner, 97 g. of indanone furnished 73 g. of indan, $n^{25}D$ 1.5150.

*Anal.* Calcd. for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.33; H, 10.14.

**2-Isopropyl-4-methylazulene.**—Treatment of 53 g. of 2-isopropyl-4-methylindan with eight portions of ethyl diazoacetate in the usual manner furnished 36 g. of red distillate, b.p. 125–170° (2 mm.), which was hydrolyzed with 25 g. of potassium hydroxide, 45 ml. of water and 60 ml. of ethanol. The acid fraction was distilled, b.p. 160–180° (2 mm.), yield 22 g. Decarboxylation and dehydrogenation was carried out by mixing this material with 3.5 g. of 10% palladium-on-charcoal in a small distilling flask and heating over an open flame. The violet-blue distillate was taken up in low-boiling petroleum ether. The azulene was extracted with four 25-ml. portions of 85% phosporic acid, regenerated by diluting the acid extracts with water, and taken up in petroleum ether. Removal of solvent yielded 3.1 g. of crude azulene. A solution of 2.5 g. of this material in 50 ml. of ethanol was added to a solution of 6 g. of trinitrobenzene in 400 ml. of hot ethanol. Upon cooling there precipitated 4.1 g. of trinitrobenzene complex which was decomposed by chromatography over alumina (solvent and eluent cyclohexane). The residual violet azulene, wt. 1.3 g., was distilled *in vacuo*, b.p. 116–121° (2 mm.).

*Anal.* Calcd. for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.18; H, 8.84.

The trinitrobenzene complex, violet-black needles from ethanol, melted at 129.5–131° with indications of sublimation below the m.p.

*Anal.* Calcd. for $C_{20}H_{19}N_3O_6$: C, 60.45; H, 4.82; N, 10.6. Found: C, 60.48; H, 5.11; N, 10.7.

Solutions for spectral measurements were prepared by decomposing 20.1 mg. of the pure trinitrobenzene complex

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[11] M.p.'s and b.p.'s are uncorrected. Analyses by Dr. Weiler and Strauss, Oxford. Infrared spectra were determined by Miss M. T. Esquivel on a Perkin–Elmer model 21 recording spectrometer; ultraviolet and visible spectra were run on a Beckman model DU spectrometer.

[12] L. I. Smith and L. J. Spillane, THIS JOURNAL, **62**, 2639 (1940).

over alumina (solvent and eluent spectral grade isoöctane). Maxima in the visible were at 660 mμ (ε 99), 630 (127, shoulder), 625 (134), 598 (278), 580 (275), 566 (292, shoulder), 556 (313) and a weak shoulder near 525 mμ. Ultraviolet maxima were at 347 (log ε 3.65), 332 (3.52), 325 (3.36), 321 (3.32), 306 (3.74), 286 (4.73), 278 (4.67) and 242 mμ (4.33).

**α-(*o*-Tolyl)-isovaleronitrile.**—To 248 g. of *o*-tolylacetonitrile, b.p. 82–85° (2.5 mm.), lit.[13] 123.5–125° (14 mm.), in 1 l. of anhydrous toluene was added 73.8 g. of sodamide with stirring and heating. After 12 hours at reflux, 240 g. of isopropyl bromide was added dropwise at such a rate that refluxing continued. The mixture was stirred and heated for an additional 12 hour period. Following the addition of a little methanol, water was added and the neutral fraction separated in the usual way. Fractional distillation furnished a fraction boiling up to 90° (1.8 mm.), which was largely starting material, and the desired product, b.p. 91–98° (1.8 mm.), $n^{24}_{D}$ 1.5125, wt. 183 g. (56%).

*Anal.* Calcd. for $C_{12}H_{15}N$: C, 83.19; H, 8.73. Found: C, 82.83; H, 8.90.

**α-(*o*-Tolyl)-isovaleric Acid.**—A mixture made from 113 g. of α-(*o*-tolyl)-isovaleronitrile, 225 g. of potassium hydroxide, 160 ml. of water and 1 l. of ethylene glycol was refluxed in a copper flask for three days until ammonia evolution had ceased. A portion of the solvent was removed at reduced pressure. The residue was poured into water, extracted thoroughly with ether and acidified. The acid which separated was filtered and air-dried; yield of crude material 104 g. (83%). A small portion was recrystallized several times by dissolving in methanol, diluting with water at room temperature to incipient cloudiness, adding a little more methanol and allowing the methanol to evaporate slowly at 20°. The colorless crystals melted at 91–92°.

*Anal.* Calcd. for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.76; H, 8.18.

**Methyl β-(*o*-Tolyl)-isocaproate.**—A mixture of 50 g. of the preceding acid and 60 ml. of thionyl chloride was warmed on the steam-bath for three hours. Excess thionyl chloride was removed at reduced pressure and the residual acid chloride was distilled, b.p. 86–88° (1.8 mm.), wt. 50.5 g. It was dissolved in 300 ml. of anhydrous ether and added slowly to a solution of diazomethane in 1 l. of ether prepared from 100 g. of nitrosomethylurea. Nitrogen was evolved briskly. The solution was allowed to stand overnight and the ether was removed *in vacuo* below 30°. The residual diazoketone, wt. 55 g., which did not crystallize, was dissolved in 500 ml. of absolute methanol and treated with a few ml. of a solution of 10 g. of silver benzoate in 100 ml. of triethylamine. When the initial reaction had slackened, the remainder of the silver benzoate solution was added in the course of one hour and the mixture was stirred for an additional four hours. Purification in the usual manner yielded 39 g. (78% based on acid chloride, 72% based on acid) of methyl ester, b.p. 98-106° (1.4 mm.). The analytical sample boiled at 90° (0.6 mm.), $n^{26}_{D}$ 1.4994.

*Anal.* Calcd. for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 76.19; H, 9.08.

**β-(*o*-Tolyl)-isocaproic Acid.**—Saponification of 98 g. of the methyl ester with 60 g. of potassium hydroxide, 80 ml. of water and 300 ml. of ethanol furnished 82 g. (89%) of an acid fraction, b.p. 133–135° (1.3 mm.).

*Anal.* Calcd. for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.62; H, 8.64.

**3-Isopropyl-4-methylindanone.**—Cyclization of 81 g. of the preceding acid in the usual manner yielded 44.5 g. (60%) of the indanone, b.p. 118–126° (2 mm.). The analytical sample boiled at 108–110° (1.2 mm.), $n^{26}_{D}$ 1.5449.

*Anal.* Calcd. for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.79; H, 8.29.

The dinitrophenylhydrazone was recrystallized repeatedly from ethyl acetate and melted at 201–202°, mixed m.p. with dinitrophenylhydrazine 174–179°.

*Anal.* Calcd. for $C_{19}H_{20}N_4O_4$: C, 61.94; H, 5.47; N, 15.2. Found: C, 61.59; H, 5.07; N, 15.0.

**1-Isopropyl-7-methylindan.**—Clemmensen reduction of 43.5 g. of 3-isopropyl-4-methylindanone in the previously described manner furnished 30 g. (75%) of indan, b.p. 80–82° (2.5 mm.), $n^{26}_{D}$ 1.5195, and 6 g. of material, b.p. 83–130° (2.5 mm.), which was largely unreduced indanone.

*Anal.* Calcd. for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.65; H, 10.08.

**1-Isopropyl-8-methylazulene.**—Treatment of 29.5 g. of 1-isopropyl-7-methylindan with eight 10-g. portions of diazoacetic ester in the customary manner furnished 11 g. of material, b.p. up to 125° (1 mm.), which represented largely recovered indan, and 30 g. of crude product, b.p. 125–170° (1 mm.). The higher boiling fraction was hydrolyzed with 25 g. of potassium hydroxide, 40 ml. of water and 150 ml. of ethanol and the resulting acid was distilled, b.p. 180–190° (3 mm.), yield 15 g. The distillate was mixed with 3 g. of 10% palladium–charcoal and distilled over an open flame. The violet-blue distillate was taken up in cyclohexane and extracted with phosphoric acid in five consecutive portions (portions 1 and 4 were 25 ml.; portions 2, 3 and 5 were 50 ml.). Each extract was diluted immediately with water; it was noted that the last two extracts gave an azulene fraction which appeared to be pure blue. These were combined and extracted with petroleum ether. Removal of the solvent furnished 1.2 g. of a blue residue which was mixed with 1 g. of trinitrobenzene in 50 ml. of hot ethanol. The solution was allowed to evaporate to 25 ml. at room temperature, and filtered from trinitrobenzene. The filtrate was evaporated to dryness in an air stream, taken up in petroleum ether, and chromatographed over alumina. The blue eluate, wt. 0.1 g., was taken up in 15 ml. of ethanol, mixed with 0.1 g. of trinitrobenzene, concentrated to 8 ml. and allowed to stand. There precipitated 21 mg. of violet-black needles, m.p. 109–112°. Decomposition of 11.2 mg. of this complex over alumina (solvent and eluent spectral grade isoöctane) yielded a deep blue solution, whose visible and ultraviolet spectrum (Figs. 1 and 2) indicated that the azulene was 1-isopropyl-8-methylazulene. Bands in the visible occurred at 721 mμ (ε 103), 680 (approximate location of a shoulder) 653 (221), 635 (shoulder), 623 (290), 596 (327), 576 (292) and shoulders near 555 and 535 mμ. Ultraviolet maxima were found at 362 mμ (log ε 3.31), 347 (3.60), 339 (3.45), shoulders near 329 (3.35) and 324 (3.25), 320 (3.18), 302 (3.77), 287 (3.56), 280 (3.60) and 244 mμ (3.28).

*Anal.* Calcd. for $C_{20}H_{19}N_3O_6$: C, 60.45; H, 4.82. Found: C, 60.22; H, 4.99.

Phosphoric acid fractions 1–3 were combined also and extracted with petroleum ether. Removal of solvent furnished 2.1 g. of a violet-blue oil, azulene mixture I, which was converted to the trinitrobenzene complex by mixing with 2 g. of trinitrobenzene in 100 ml. of warm ethanol; weight of crude complex (mixed with trinitrobenzene) 2.1 g. This was decomposed over an alumina column. The initial portions of the eluate appeared to contain a mixture of the two azulenes; the later eluates were violet-blue and were collected separately. Removal of solvent from the later fractions furnished 0.25 g. of violet-blue oil which was converted to the trinitrobenzene complex, wt. 0.37 g. One recrystallization furnished material, m.p. 128.5–130°, undepressed on admixture of trinitrobenzene complex of authentic 2-isopropyl-4-methylazulene. The visible spectrum of the azulene regenerated from the complex was identical in every detail with the spectrum of authentic 2-isopropyl-4-methylazulene.

The mother liquors of the preparation of the trinitrobenzene complex from azulene mixture I were allowed to evaporate to dryness in an air stream. The azulene was liberated by decomposition over alumina and rechromatographed over a large column of alumina (eluent petroleum ether). The first portions of the eluate were pure blue and yielded an additional 12 mg. of 1-isopropyl-8-methylazulene–trinitrobenzene complex.

TALLAHASSEE, FLA.

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[13] M. S. Newman, THIS JOURNAL, **62**, 2295 (1940).