

solution was allowed to stand overnight at room temperature. Dilute H_2SO_4 (650 ml, 6 *N*) was added slowly with stirring to the reaction mixture; the temperature was maintained at 20° or below with an ice bath. During the addition of the acid the color changed from amber to bright yellow to white. The mixture appeared to be an emulsion. By adding 5 ml of concentrated H_2SO_4 and shaking, the emulsion was broken and a white solid was observed. The solid was removed by vacuum filtration yielding 166 g of crude material (mp 84–87.5°).

The two phases in the filtrate were separated; the aqueous one was xylene extracted three times (150 ml each). These extracts were combined with the organic layer. The combined extracts were washed first with 200 ml of water and then with 200 ml of saturated NaCl solution. The organic layer was dried over anhydrous Na_2SO_4 , filtered, and distilled on a Todd 42-in. Vigreux column, yielding 73 g of material boiling at 68–125°. Water (25 ml) was added to the distillate and the mixture was allowed to stand overnight. The resulting crystals were filtered and dried: yield, 40 g. The total yield of **3** was 206 g (56%). A small portion of the compound was purified by sublimation at 85°, mp 60–61°.

Anal. Calcd for $C_6H_6O_4F_8$: C, 24.50; H, 2.06; F, 51.68. Found: C, 24.31; H, 1.94; F, 51.49.

A portion (50 g) of **3** was placed in a 500-ml erlenmeyer flask and ~50 g of $P_{2}O_{10}$ was added with stirring in 10–15-g portions. Gummy semisolids resulted and liquid **1** was released. The remaining **3** was dehydrated. All liquid product was decanted, combined, and twice distilled, yielding 77.5 g (53%) of **1**: bp 85–86° (atm); n_D^{25} 1.3260; d_4^{25} 1.538; nmr (downfield from tetramethylsilane, internal) δ 12.9 (s, 1, enol OH), 6.49 (s, 1, CH=C); nmr (fluorine resonance upfield from trifluoroacetic acid, external) δ +48.4 (m, 2, $J = 1$ Hz, CF_3CF_2), +6.9 (t, 3, $J = 1$ Hz, CF_3CF_2), +0.9 (s, 3, CCF_3).

Anal. Calcd for $C_6H_6O_2F_8$: C, 27.92; H, 0.78; F, 58.90. Found: C, 27.71; H, 0.78; F, 59.06.

1,1,1,2,2,3,3,3,7,7,7-Decafluoro-4,6-heptanedione (2).—Sodium methoxide (78 g, 1.45 mol) was suspended in 478 ml of hexane with vigorous stirring. Ethyl heptafluorobutyrate (Pierce Chemical Co., 323 g, 1.33 mol) was added to the flask from a dropping funnel over a 30-min period with vigorous stirring. After an additional 30-min stirring almost all of the sodium methoxide was dissolved. Following the addition of the ester, 172 g, 1.53 mol, of trifluoroacetone was added dropwise over a 1-hr period. The solution was allowed to stand overnight. During addition of the ester and the ketone, a Dry Ice condenser was connected to the flask to prevent the escape of volatile materials.

Two phases were apparent after standing overnight. The mixture was acidified with 500 ml of 6 *N* H_2SO_4 with vigorous swirling in an ice bath. The two phases were separated in a 2-l. separatory funnel. The aqueous phase was washed twice with 100-ml portions of hexane, and the hexane extracts were added to the original hexane phase. The hexane phase was extracted five times with 200-ml portions of aqueous sodium acetate (260 g/l.). The third extraction produced a third phase (on the bottom) of a dark yellow–orange color. The first three aqueous extracts were added with vigorous stirring to a solution of 126 g of $CuSO_4 \cdot 5H_2O$ dissolved in 750 ml of water. A green precipitate formed as the extracts were added to the copper sulfate solution. This precipitate was collected on a Büchner funnel, washed sparingly with ice–water, and air-dried overnight.

The solid (331 g) was powdered and placed in a 2-l. flask and cooled in an ice bath. Cold concentrated H_2SO_4 was added in three 50-ml portions to the copper chelate, resulting in a green liquid with white solids. The liquid was distilled through a glass helices-packed column. The forecut (cloudy) consisted of material(s) boiling up to 100°. After the forecut was taken, the distillation was stopped, and the condenser was rinsed with acetone to remove white solids and was air-dried. The distillation was then continued. The principal cut (214 g) boiled between 100 and 104°.

After storage for 5 days at –25°, white solid material was observed in the product. This was removed by filtration. The filtrate was redistilled yielding 166 g (40%) of **2**: bp 103–104° (atm); n_D^{25} 1.3243; d_4^{25} 1.592; nmr (downfield from tetramethylsilane, internal) δ 13.3 (s, 1, enol), 6.50 (s, 1, CH=C); nmr (fluorine resonance upfield from trifluoroacetic acid, external) δ +50.8 (m, 2, $J \cong 1$ Hz, $CF_3CF_2CF_2$), +45.8 (m, 2, $J = 9$ Hz, $CF_3CF_2CF_2$), +4.6 (t, 3, $J = 9$ Hz, $CF_3CF_2CF_2$), +0.7 (s, 3, CCF_3).

Anal. Calcd for $C_7H_2O_2F_{10}$: C, 27.29; H, 0.65; F, 61.67. Found: C, 27.07; H, 0.70; F, 61.78.

Registry No.—**1** (keto form), 20825-07-4; **2** (keto form), 20583-66-8; **3**, 23405-28-9.

Carbanions in Dimethyl Sulfoxide. II.¹ Dimerization During the Base-Catalyzed Disproportionation of 1,4-Dihydronaphthalene

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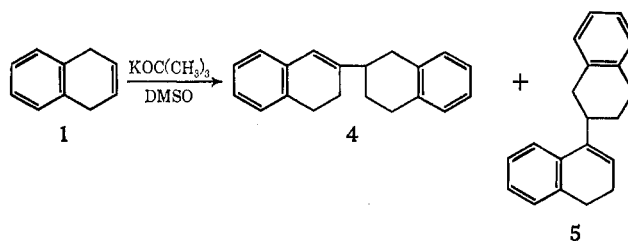
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Recently the base-catalyzed disproportionation of cyclohexadiene to give benzene and cyclohexene was reported.² Disproportionation was effected with potassium *t*-butoxide in dimethyl sulfoxide (DMSO) and went equally well for the 1,3- or 1,4-dienes, which readily isomerize in base.^{2,3}

In our investigation of DMSO and 1,4-dihydronaphthalene, we observed a similar disproportionation that gave naphthalene and tetralin (**3**) in the $KOC(CH_3)_3$ -DMSO system at 25°. In contrast, however, the disproportionation accounted for only 37% of the reaction product. The main reaction was a dihydronaphthalene–anion addition to afford a 58% yield of a crystalline dimer **4** (Scheme I) that analyzed for $C_{20}H_{20}$

SCHEME I



with a molecular ion at m/e 260.1565 (theory 260.1565). The nmr spectrum showed the presence of eight aromatic protons (singlet at δ 7.00), eleven aliphatic protons in a broad multiplet at δ 1.60–3.00, and one unsplit olefinic proton that is assigned as being conjugated at δ 6.22. Evidence that the two ring systems are joined at the 2,2' positions is obtained from the dehydrogenation product. When **4** is heated in the presence of palladium on charcoal, 2,2'-binaphthyl is obtained as the only product.

Two other dimers (**5** and **6**), isomeric with **4** ($C_{20}H_{20}$), were also found but in much smaller amounts. Compound **5** (5% yield) has an nmr spectrum showing an unsymmetrical aromatic multiplet at δ 6.75–7.38 within which is a sharp singlet at δ 6.96 (8 H), an olefinic triplet (1 H) centered at δ 5.81 ($J = 4.3$ Hz), and a

(1) Part I: S. B. Hanna and L. G. Wideman, *Chem. Ind.* (London), 486 (1968).

(2) J. E. Hofmann, P. A. Argabright, and A. Schriesheim, *Tetrahedron Lett.*, No. 17, 1005 (1964).

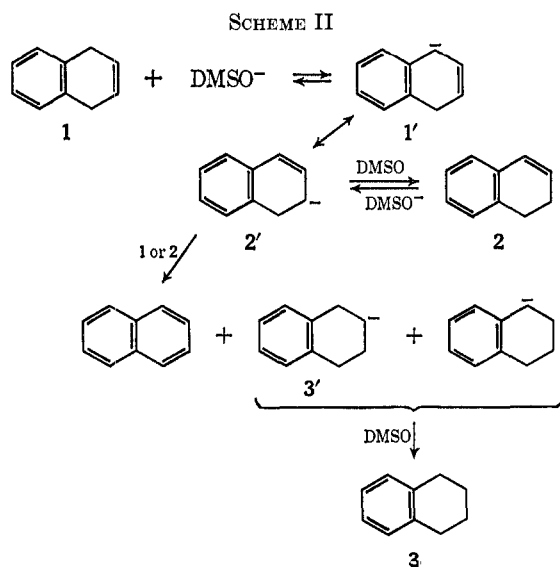
(3) A. T. Bottini and W. Scheer, *J. Org. Chem.*, **30**, 3205 (1965); D. P. Wyman and I. H. Song, *ibid.*, **32**, 4139 (1967).

broad poorly resolved multiplet ranging from δ 0.70 to 3.34 (11 H). Ultraviolet analysis shows a system of extended conjugation similar to that of 4.

The third dimer (6) in 1% yield appears to be a 1,2-bisdialin. Its nmr spectrum shows no protons in the olefinic region, and its uv spectrum shows no extended conjugation.

There was little effect on the products when the reaction mixture was heated at 100°. However, no disproportionation or addition products resulted when *t*-butyl alcohol was used as the solvent even upon heating.

The proposed reaction mechanism for disproportionation is shown in Scheme II and based on the formation



of carbanions 1' and 2'. The isomerization of 1,4- to 1,2-dihydronaphthalene in the presence of base is quite facile.⁴ Carbanion 2' may then accept a proton from DMSO⁵ and form 2, or liberate a hydride ion to 1 or 2 to effect the disproportionation. Dimer 4 may form by the attack of 2' on 1 or 2 followed by protonation and double bond isomerization. The favored reaction mechanism, however, is the attack of 3' on 2 followed by liberation of a hydride ion, which may also account for 5. In order to account for the formation of more product from the addition reaction than disproportionation it is also necessary to assume that 3' is a better nucleophile than proton acceptor. Similar nucleophilic additions of anions have been observed in other systems.⁶

Experimental Section

DMSO was obtained from Eastman Organics and was dried over Linde 13X Molecular Sieves, filtered, and then distilled through more 13X Molecular Sieves at reduced pressure. Potassium *t*-butoxide was sublimed material of reagent grade purchased from Alpha Inorganics.

The melting points were determined on a Fisher-Johns apparatus and are uncorrected. The elemental analyses were performed by the Goodyear Research Analytical Section. The analytical and preparative glpc were carried out on an F & M (Model 500) chromatograph using a 12-ft column packed with 10% SE-30 on Diatoport W at 150 and 300°. Infrared spectra,

obtained on a Perkin-Elmer (Model 137) spectrometer with a polystyrene reference, are reported as KBr pellets and melts for the solids and as films for the liquids. The nmr spectra (CCl₄) were obtained on a Varian A-60 spectrometer (TMS reference), and the mass spectra on an AEI MS-9 spectrometer.

1,4-Dihydronaphthalene (1).—Naphthalene was reduced with sodium metal in *t*-butyl alcohol and toluene by the method of Hansley.⁷ The product is free of the 1,2 isomer and analyzed 99+ % pure by glpc after fractional distillation (bp 58° at 2.8 mm, *m/e* 130). The ir spectrum was identical with that of redistilled authentic 1,4-dihydronaphthalene.⁸

1,2,3,3',4,4'-Hexahydro-2,2'-binaphthyl (4).—A flask containing 11.2 g (0.1 mol) of potassium *t*-butoxide (under nitrogen) in 200 ml of DMSO was charged with 13.0 g (0.1 mol) of 1,4-dihydronaphthalene in 100 ml of DMSO which gave an instantaneous orange-red carbanion that turned green within a few minutes. The reaction mixture was periodically shaken during the 24-hr reaction time and held at 25° with a water bath. The reaction mixture was then poured into 300 ml of H₂O and the resulting mixture was extracted three times with ether. The ether portion was removed and back extracted with water to remove DMSO. After drying (CaCl₂) and removal of the solvent (steam bath), the thick oil was chromatographed (1 × 24 in. column) over neutral alumina (dry-column technique⁹) obtained from Matheson Coleman and Bell, activity I. Naphthalene (*m/e* 128, mp 79–80°) and tetralin (*m/e* 132, bp 206–207°) were eluted first with petroleum ether (bp 36–47°) and were further purified by preparative glpc. The ir spectra and glpc retention times were identical with those of reagent samples. Continued elution with petroleum ether afforded ca. 8.0 g of a white crystalline solid. The solid was recrystallized several times from methanol to give a constant melting compound (4) at 77–78° (99+ % pure by glpc): $\lambda_{\max}^{\text{cyclohexane}}$ 218 m μ (ϵ 33,480), 226 (22,925), 263 (15,715), and 273 (15,030); ir (melt) ν_{\max} 3070, 2990, 2910, 2860, 1620, 1490, 1450, 1430, and 785 cm⁻¹.

Anal. Calcd for C₂₀H₂₀: C, 92.31; H, 7.69. Found: C, 92.09; H, 7.83.

2,2'-Binaphthyl.—Compound 4 (1.0 g) and 5% Pd-C (0.1 g) were heated to 200° in a 50-ml 1-neck round-bottom flask. The pressure inside the flask was 0.40 mm. White crystals begin to condense at the top of the flask and heating was continued until no more solid formed. After cooling, the flask was washed with boiling benzene. The hot benzene was filtered and the clear solution taken to dryness. Recrystallization from hexane gave white crystals (0.9 g): mp 185–187° (authentic material, mp 185–187°); mmp 185–187°; ir (KBr): ν_{\max} 3090, 1600, 1390, 1370, 1275, 884, 855, 812, and 736 cm⁻¹; nmr (50° in CCl₄) broad singlet at δ 7.43 (2 H), multiplet at 7.18 (8 H), and multiplet at 6.76 (4 H).

Anal. Calcd for C₂₀H₁₄: C, 94.48; H, 5.51. Found: C, 94.15; H, 5.85.

1,2,3,3',4,4'-Hexahydro-1',2'-binaphthyl (5) and Compound (6).—The methanolic mother liquor, from which compound 4 was recrystallized, was shown by glpc analysis to contain two other compounds. When the solution was concentrated and acetone added (50 ml), 6 precipitated and was recrystallized from acetone: mp 179–180°; ir (KBr) ν_{\max} 3090, 3050, 2970, 2910, 1480, 1445, 1420, 753, and 739 cm⁻¹; nmr (CCl₄) singlet at δ 7.00 (8 H), multiplet from 3.50 to 2.59 (6 H), and multiplet from 2.30 to 1.12 (6 H); *m/e* 260.1569; $\lambda_{\max}^{\text{cyclohexane}}$ 260 m μ (ϵ 1010), 266 (1565), and 273 (1790).

Concentration of the remaining solution and separation by preparative glpc gave a thick liquid: bp 175–180° at 1–2 mm; $\lambda_{\max}^{\text{cyclohexane}}$ 214 m μ (ϵ 28,800), 219 (26,780), 226 (15,750), and 262 (9315); ir (film) ν_{\max} 3090, 3050, 2940, 2900, 2860, 1630, 1494, 1445, 1425, 808, 770, and 740 cm⁻¹.

Anal. Calcd for C₂₀H₂₀: C, 92.31; H, 7.69. Found: C, 92.03; H, 7.81.

Registry No.—1, 612-17-9; 4, 23405-30-3; 5, 23439-78-3.

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(4) R. C. Fuson, "Reactions of Organic Compounds," John Wiley & Sons, Inc., New York, 1966, p 469; F. Straus and L. Lemmel, *Ber.*, **54**, 25 (1921).

(5) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **84**, 866 (1962).

(6) P. R. Stapp and R. F. Kleinschmidt, *J. Org. Chem.*, **30**, 3006 (1965).

(7) V. L. Hansley, U. S. Patent 2,473,997 (1949).

(8) Obtained from K & K Laboratories.

(9) B. Loev and M. M. Goodman, *Chem. Ind. (London)*, 2026 (1967).