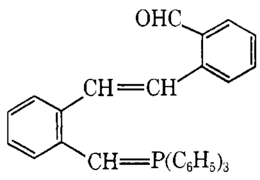


V

to I; the latter process would require *cis* stereochemistry in V.

Recently Shemyakin has shown that the Wittig reaction can be modified to favor the formation of *cis* isomers by conducting the reaction in the presence of a Lewis base and reported that the best results were obtained with lithium bromide or iodide in dimethylformamide.[9] Partial neutralization of the charge on the ylide phosphorus by interaction with the base is postulated as leading to a lessening of the importance of initial ylide–carbonyl dipolar interaction as a determinant in product stereochemistry. Since both of the double bonds to be formed in I are required to be *cis*, the reaction of III and IV was attempted employing conditions similar to those reported by Shemyakin, *i.e.*, the slow addition of a solution of lithium ethoxide in absolute ethanol to a dilute solution of III and IV in dimethylformamide. In this instance, the desired product (I) was isolated from the reaction mixture in 18% yield; since IV can be prepared in 86–89% yield from *o*-xylylene dibromide, an over-all yield of 15–16% of I can be obtained in a two-step process. This yield is comparable to those obtained in the reported four- to five-step procedures.[5–7a]

The successful formation of I by a Wittig procedure indicates that the only probable limitation to effective Wittig cyclization is ring size; the only failures reported to date are in the attempted syntheses of cyclopropenes[3e] and cyclobutenes.[10]

The infrared spectra of samples of I prepared in this study are identical in all respects to the spectrum reported by Wittig[7b] and totally different from that reported earlier by Cope.[6] One of the most prominent features of the spectrum reported by Cope is an intense band at 11.0 μ which is absent in the spectra obtained by Wittig and the present investigators. The ultraviolet spectrum of I shows a single band without fine structure at 239 mμ (ϵ 28,900); Wittig has reported a band at the same wave length of somewhat higher intensity (ϵ 48,000). McEwen and Longuet-Higgins[11] have carried out an LCAO calculation of the electronic transition energies of I; the observed band for I probably corresponds to the calculated $A_1 \rightarrow B_1$ transition at 230 mμ. Because of its high intensity and lack of fine structure, the observed band probably is not related to the calculated forbidden $A_1 \rightarrow A_2$ transition at 239 mμ.

Experimental[12]

***o*-Xylylenebis-(triphenylphosphonium bromide)** (IV) was prepared in 86.5% yield by the reported method.[3d] In the original preparation, IV was reported to have m.p. >340°; however, in subsequent preparations, material decomposing as low as 295° was obtained. The lower melting material was satisfactory in all respects; examination of the infrared spectra of these preparations indicates the melting point depression to be caused by the presence of a trace amount of the monophosphonium salt.[3d]

1,2,5,6-Dibenzocyclooctatetraene (I).—A mixture of 18.1 g. (0.023 mole) of IV and 3.0 g. (0.022 mole) of *o*-phthaldehyde in 400 ml. of dry dimethylformamide (distilled from calcium hydride) was heated to 90° under an atmosphere of dry nitrogen. A solution of 0.059 mole of lithium ethoxide in 100 ml. of absolute ethanol was added to this reaction mixture with rapid stirring over a period of 5 hr. Addition of the basic solution gave a deep orange solution and this color persisted for 4.5 hr. After the addition was completed, the dark reaction mixture was allowed to cool and was diluted with 500 ml. of water. The precipitated material was extracted with ether and the ethereal extracts were washed with water, dried over anhydrous magnesium sulfate, and evaporated to give a dark brown oil. This oil was extracted with boiling petroleum ether (60–70°) to effect separation from triphenylphosphine oxide; evaporation of the petroleum ether extracts gave 5.8 g. of a red oil which was chromatographed on a Florisil column (1.25 × 90 cm.). Elution with 1.4 l. of petroleum ether (30–65°) gave 1.8 g. of a pale yellow crystalline solid which was rechromatographed on Florisil (1.25 × 45 cm. column). Twenty-four 10-ml. fractions were collected by elution with petroleum ether (30–65°). Fraction 1 was an oily mixture which failed to crystallize, but fractions 2–24 gave 1.5 g. of a colorless crystalline product on evaporation of solvent; this product was recrystallized from aqueous ethanol to give 0.8 g. (18%) of I, m.p. 109.2–109.4° (lit. m.p. 108.5–109.2°,[7a] 109°,[8] 106.8–108.1°,[5] 106.2–106.9°[6]).

Anal. Calcd. for $C_{16}H_{12}$: C, 94.08; H, 5.92. Found: C, 94.17, 94.11; H 5.80, 5.93.

The ultraviolet spectrum of I in 95% ethanol showed a maximum at 239 mμ (ϵ 28,900). The infrared spectrum was recorded in carbon tetrachloride and acetonitrile and showed bands at the following wave lengths (μ): 3.27 s, 3.32 s, 6.09 w, 6.73 s, 7.01 m, 7.17 m, 8.68 m, 8.97 w, 9.20 m, 9.65 m, 10.42 w, 10.60 m, 11.52 w, 11.98 s, 12.85 vs, 13.42 s, 14.31 s, 14.45 s, 14.87 w.

Treatment of a methanolic solution of I with saturated aqueous silver nitrate gave a colorless precipitate which was recrystallized from ethanol to give the **silver nitrate complex of I**, m.p. 221–222° (lit. m.p. 222°,[9] 214–215°[3a]).

The reaction of *o*-phthaldehyde and IV in refluxing absolute ethanol for 5 hr. employing sodium ethoxide as base was carried out in a manner analogous to the previous experiment. Careful chromatography of the products led to the isolation of triphenylphosphine oxide and the dialdehyde as the only characterizable materials; examination of the infrared spectra of all fractions showed the presence of only trace amounts of I. When the reaction was carried out for a longer period of time (22 hr.), the major portion of the organic material isolated was polymeric in nature, showing aromatic and both *cis* and *trans* olefinic absorptions in the infrared.

---

[9] M. M. Shemyakin, L. D. Bergelson, and V. A. Vaver, IUPAC International Symposium on Organic Chemistry of Natural Products, Brussels, June 12–15, 1962.

[10] G. Witschard and C. E. Griffin, unpublished results; T. I. Bieber, private communication.

[11] K. L. McEwen and H. C. Longuet-Higgins, *J. Chem. Phys.*, **24**, 771 (1956).

[12] Micronalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Synthesis of 7-Methyl- and 7-Phenylnorbornadiene

Paul R. Story and Susan R. Fahrenholtz

Bell Telephone Laboratories, Inc.,
Murray Hill, New Jersey

Received February 15, 1963

The synthesis of norbornadiene is a relatively straightforward procedure involving the Diels–Alder condensation of cyclopentadiene and acetylene.[1] However, 7-substituted norbornadienes generally are not available by this simple route because the corresponding 5-substituted cyclopentadienes are unstable relative to

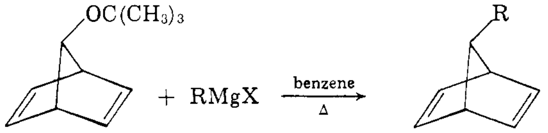
---

[1] J. Hyman, E. Freireich, and R. E. Lidov, U. S. Patent 2,875,256; *Chem. Abstr.*, **53**, 13082 (1959).

their 1 and 2 isomers and at best give a mixture of isomeric products even when generated *in situ*.[2]

7-*t*-Butoxynorbornadiene, prepared by treating norbornadiene with *t*-butyl perbenzoate, has recently proven to be a valuable precursor for the synthesis of several other 7-substituted norbornadienes.[3,4]

We now wish to report the preparation of 7-methyl- and 7-phenylnorbornadiene by treatment of 7-*t*-butoxynorbornadiene with the appropriate Grignard reagent as shown in equation 1.



(1)

I

IIa. R = CH3-
b. R = Ph-

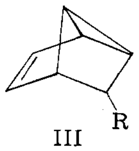
Presumably the reaction could be extended to the synthesis of many alkyl and aryl substituted norbornadienes.

Refluxing the ether (I) with an excess of methylmagnesium iodide in benzene gave a 57% yield of 7-methylnorbornadiene (IIa). Similar treatment of the ether (I) with phenylmagnesium bromide gave 7-phenylnorbornadiene (IIb) in 75% yield. 7-Norbornadienol was not detected among the products; however, it was not rigorously sought. In fact, no other monomeric products were detectable.

The structures of IIa and IIb were established by analysis of their infrared and n.m.r. spectra. Both molecules exhibited the highly characteristic infrared absorptions at 6.5 μ (double bond stretch and at *ca.* 13.6–14.0 μ (*cis* double bond, carbon–hydrogen out-of-plane deformation) indicative of the norbornadiene nucleus.[3] The n.m.r. spectra also were highly characteristic of the norbornadiene nucleus[3] and consistent with the proposed structures. For example, in the 7-methylnorbornadiene spectrum, the methyl group appears as a doublet at $\tau = 9.15$. The bridge hydrogen (7) appears as a complex quartet at $\tau = 7.40$ and the bridgehead hydrogens (1,4) appear as a multiplet at $\tau = 6.82$. In addition, the two pairs of olefinic hydrogens appear as two separate triplets at $\tau = 3.29$ and 3.52 in characteristic fashion.

Several ethers have been cleaved by Grignard reagents to yield analogous hydrocarbons.[5] In most of these examples, at least one moiety was capable of supporting a positive charge. For example, diallyl ether and benzyl ethers are rather easily cleaned to generate hydrocarbons.

The relatively facile cleavage of I is consistent with the stability of the 7-norbornadienyl carbonium ion[4,6] and probably is mechanistically similar to the lithium aluminum hydride reduction of 7-chloronorbornadiene.[7] There is one important exception. The reduction of 7-chloronorbornadiene yielded, in addition to norbornadiene, tricyclo[4.1.0.0^{3,7}]heptene-4 as the major product. The corresponding 2-substituted tricyclo[4.1.0.0^{3,7}]heptene-4 (III) was not observed in the reaction of Grignard reagents with I. However, the tricyclic olefins (III) may have been destroyed under the reaction conditions.



III

Experimental

7-Methylnorbornadiene (IIa).—Following the general procedure of Normant,[8] methylmagnesium iodide was prepared from 57.6 g. (2.4 g.-atoms) of magnesium and 341 g. (2.4 moles) of methyl iodide in 1.5 l. of anhydrous ether. About 1 to 1.5 l. of reagent grade benzene was added in several portions while the ether was removed by distillation. Distillation was continued until the boiling point reached 79°. After the solution was allowed to cool 10–20°, 200 g. (1.22 moles) of 7-*t*-butoxynorbornadiene (I)[3] was added all at once. This mixture was stirred and refluxed for 2.5–3 days. After this time, the excess Grignard was destroyed with about 225 ml. of water and the benzene solution decanted. The solvent was removed at atmospheric pressure with a 24-in. spinning bond distillation column. The product was distilled on the same column to give 74.5 g. (57.6%) of 7-methylnorbornadiene (IIa), b.p. 54.5–55.0° (113 mm.). Infrared (carbon tetrachloride, μ): 3.4 (s), 6.5 (m), 7.6 (s), 13.9 (s). N.m.r. (carbon tetrachloride, τ): 3.29 (3), 3.52 (3), 6.82 (6), 7.40 (4), 9.15 (2), area ratio of 2:2:2:1:3.

Anal. Calcd. for C_8H_{10}: C, 90.50; H, 9.50. Found: C, 90.68; H, 9.43.

7-Phenylnorbornadiene (IIb).—Using the same procedure, 7-phenylnorbornadiene (IIb) was prepared from 14.4 g. (0.6 g.-atom) of magnesium, 94.2 g. (0.6 mole) of phenyl bromide, and 50 g. (0.3 mole) of 7-*t*-butoxynorbornadiene (I) to give 38.9 g. (75.8%) of IIb, b.p. 80–81° (1.7 mm.). This product was about 95% pure. Greater purity was obtained by gas phase chromatography using a 20 ft × 3/8 in. 10% Dow 710 silicone column at 160°. Infrared (neat, μ): 3.2 (m), 6.5 (m), 7.6 (s), 13.5 (m), 13.8 (s), 14.4 (s). N.m.r. (carbon tetrachloride, τ): 2.97 (m), 3.15 (3), 3.5 (m), 6.25 (m), area ratio 5:2:2:3.

Anal. Calcd. for $C_{13}H_{12}$: C, 92.81; H, 7.19. Found: C, 93.07; H, 7.41.

---

(2) R. Vanelli, Ph.D. thesis, Harvard University, 1950.

(3) P. R. Story, *J. Org. Chem.*, **26**, 287 (1961).

(4) P. R. Story and M. Saunders, *J. Am. Chem. Soc.*, **84**, 4876 (1962).

(5) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-Metallic Substances," Chap. XV, Prentice-Hall, New York. N. Y., 1954; C. M. Hill, L. Haynes, D. E. Simmons, and M. E. Hill, *J. Am. Chem. Soc.*, **80**, 3623 (1958).

(6) S. Winstein and C. Ordronneau, *ibid.*, **82**, 2084 (1960).

(7) P. R. Story, *ibid.*, **83**, 3347 (1961).

(8) A. Normant, *Bull. soc. chim. France*, (5) **7**, 371 (1940).

Fluorine-Containing Nitrogen Compounds. V. Difluoronitroacetamidines and Difluoronitromethyl-1,2,4-triazoles[1,2]

Eugene R. Bissell

*Lawrence Radiation Laboratory, University of California
Livermore, California*

Received November 26, 1962

The reaction of ammonia or primary or secondary alkylamines with perfluoroalkylnitriles has been shown to afford good yields of stable perfluoroalkylamidines.[3,4] The stability of the perfluoroalkylamidines, as contrasted with their unfluorinated analogs, was attributed to the electronegativity of the fluorocarbon radical.[4]

---

(1) This work was performed under the suspices of the U. S. Atomic Energy Commission.

(2) For paper number IV of this series, see G. C. Shaw, D. L. Seaton, and E. R. Bissell, *J. Org. Chem.*, **26**, 4765 (1961); for paper number III, see E. R. Bissell, *ibid.*, **26**, 5100 (1961).

(3) D. Husted, U. S. Patent 2,676,985 (April, 1954).

(4) W. L. Reilly and H. C. Brown, *J. Am. Chem. Soc.*, **78**, 6032 (1956).