heating continued for 1 hr. The mixture was poured into 25 g. of ice and neutralized with solid sodium carbonate. The solution was extracted with chloroform. The chloroform extracts were dried and the chloroform was removed by evaporation. The residue weighed 1.5 g. The residue was stirred with 20 ml. of water, filtered, and dissolved in dilute sulfuric acid. Neutralization with ammonium hydroxide gave a yellow solid which was collected by suction filtration and dried. Crystallization from a chloroform–ether mixture gave 0.24 g. (10%) of material, m.p. 160° dec.

Anal. Calcd. for $C_{12}H_7N_3O_3$: C, 59.74; H, 2.93; N, 17.42. *Found:* C, 59.70; H, 2.99; N, 17.28.

The ammoniacal filtrate from the above reaction was evaporated to dryness. The residue was extracted with chloroform. Removal of the chloroform and examination of the infrared spectrum of the residue indicated that it was mainly unchanged 1,10-phenanthroline 1-oxide.

When the nitration was carried out at 110–115° a 10% yield of 4-nitro-1,10-phenanthroline 1-oxide was again obtained.

4-Chloro-1,10-phenanthroline 1-Oxide.—A solution of 150 mg. (0.625 mmole) of 4-nitro-1,10-phenanthroline 1-oxide in 10 ml. of 50% hydrochloric acid was refluxed for 18 hr. The mixture was cooled, neutralized with solid sodium carbonate, and repeatedly extracted with chloroform. The chloroform extracts were dried over sodium sulfate and the solvent was removed. The yield of pale yellow solid was 100 mg. (69.5%). Recrystallization from benzene furnished the analytical sample, m.p. 139–141°. The compound gave a positive test for chlorine.

Anal. Calcd. for $C_{12}H_7ClN_2O$: C, 62.42; H, 3.03; N, 12.12. Found: C, 62.30; H, 3.24; N, 12.11.

4-Chloro-1,10-phenanthroline.—To a solution of 0.5 g. (2.07 mmoles) of 4-nitro-1,10-phenanthroline 1-oxide in 15 ml. of chloroform was added dropwise a solution of freshly distilled phosphorus trichloride in 5 ml. of chloroform. A precipitate formed which dissolved upon heating. The reaction mixture was refluxed for 2 hr. The solution was cooled, poured onto crushed ice, and treated with solid sodium carbonate. The chloroform was separated and the aqueous layer was extracted with several portions of chloroform. The chloroform extracts were dried and the chloroform was evaporated. The pinkish solid that remained proved to be an acid salt. The salt was dissolved in water and neutralized with ammonium hydroxide; the resulting solution was extracted with chloroform. Drying and removal of the solvent furnished 0.283 g. (63.5%) of white solid, m.p. 159–162°. Recrystallization from benzene raised the melting point to 163–165°. Because of the hygroscopic nature of the compound it was converted to a picrate for analytical purposes. The picrate gave a positive test for chloride.

Anal. Calcd. for $C_{18}H_{10}ClN_5O_7$: C, 48.71; H, 2.27; N, 15.78. Found: C, 48.65; H, 2.42; N, 15.69.

Nitration and Degradation of 1,10-Phenanthroline in Nitric–Sulfuric Acid.—To 5 ml. of concentrated sulfuric acid (sp. gr. 1.84) was added, with cooling, 2.35 g. (0.012 mole) of 1,10-phenanthroline 1-oxide. The mixture was heated on an oil bath to 85–90° during the addition of 1.75 g. of concentrated nitric acid (Spectrograde 1.42). The addition required 40 min.; the reaction was maintained at 85–90° for an additional 3.5 hr. After 2.5 hr. an orange solid began to precipitate from solution. The mixture was cooled and poured onto 45 g. of ice. Neutralization with sodium carbonate followed by filtration gave 0.6 g. of an orange solid. The compound was extremely insoluble in most organic solvents, but could be crystallized from aqueous dimethylformamide. The crystallized material melted at 210–215° dec. and showed infrared bands at 3500 (OH?), 1710 (C=O?), 1550 (NO_2?), and 1360 cm.$^{-1}$ (NO_2). The compound was insoluble in mineral acids and only sparingly soluble in base.

Anal. Found: C, 54.37; H, 2.70; N, 16.87.

The aqueous filtrate from the above reaction was extracted with chloroform. Removal of the chloroform by evaporation gave 0.1 g. of 4-nitro-1,10-phenanthroline 1-oxide, identified by melting point and infrared spectrum.

Acknowledgment.—This work was supported in part by the National Science Foundation (G14473) and a Drexel Institute of Technology Faculty Research Grant.

Addition Reactions of Substituted 1,4-Cyclohexadienes. I. 3,3,6,6-Tetramethyl-1,4-cyclohexadiene[1a]

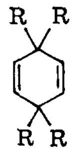
F. W. GRANT,[1b] R. W. GLEASON, AND C. H. BUSHWELLER

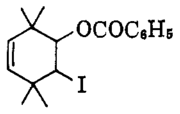
Departments of Chemistry, Hamilton College, Clinton, New York, and Middlebury College, Middlebury, Vermont

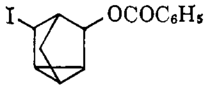
Received September 8, 1964

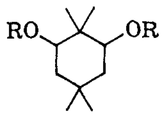
Bicyclo[2.2.1]heptadiene and bicyclo[2.2.2]octadiene are known to undergo a variety of 1,5-homoconjugate addition reactions.[2] Recognizing the unique disposition of the double bonds in these compounds and the spectral evidence demonstrating interaction between them,[4] it was, nonetheless, of interest to determine whether homoconjugate addition might be induced in the related 1,4-cyclohexadiene (I) or its derivatives. Double-bond interaction in I has been inferred from its ultraviolet absorption spectrum.[3] An unsuccessful attempt in this direction was reported by van Tamelen[5] who reinvestigated the controlled Prevost addition of iodine and silver benzoate to I[6] and confirmed that the major product was correctly described as the 1,2-addition product, cyclohexene 4,5-dibenzoate. He extended this work to include the controlled bromination of I which resulted in 4,5-dibromocyclohexene. No trace of a homoconjugate addition product was noted in either case.

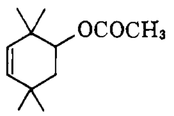
Earlier reports pertinent to this problem have described the halogenation of 1-methyl-,[7] 1,2-dimethyl-,[8] 1,2-dichloro-,[9] and perfluoro-1,4-cyclohexadiene[10] but in none of these cases were homoconjugate addition products isolated, although this possibility may not have been fully explored in the analysis of minor products.


I, R = H
II, R = CH_3


III


IV


V, R = H
VI, R = $COCH_3$


VII

Our interest has been in derivatives of I substituted at the 3- and 6-positions where bulky *cis* and equatorially oriented groups might be expected to favor

---

[1] (a) Taken in part from the Master's Thesis of C. H. B., Middlebury College, 1963. (b) Department of Chemistry, Hamilton College, Clinton, N. Y.

[2] A summary of pertinent publications is found in ref. 3 and should include the work of A. Gagneux and C. A. Grob, *Helv. Chim. Acta*, **42**, 1753; 2006 (1959).

[3] W. Reusch, M. Russell, and C. Dzurella, *J. Org. Chem.*, **29**, 2446 (1964).

[4] C. F. Wilcox, Jr., S. Winstein, and W. McMillan, *J. Am. Chem. Soc.*, **82**, 5450 (1960).

[5] E. E. van Tamelen, *J. Am. Chem. Soc.*, **77**, 1704 (1955).

[6] G. E. McCasland and E. C. Horswill, *ibid.*, **76**, 1654 (1954).

[7] F. A. Haak and J. B. Wibaut, *Rec. trav. chim.*, **69**, 1382 (1950).

[8] W. Hückel and U. Wörffel, *Chem. Ber.*, **88**, 338 (1955).

[9] R. Riemschneider, *Monatsh.*, **86**, 101 (1955).

[10] D. E. Evans and J. C. Taylor, *J. Chem. Soc.*, 3779 (1954).

maximum "folding" of the ring system and, therefore, a high probability of interaction between double bonds. The synthesis and properties of compounds of this type will be the subject of a future communication.

Geminal substitution at the 3- and 6-positions of I should have an inhibitory effect on the "folding" of the ring system and it appears from an examination of models that the compound which forms the subject of this paper, 3,3,6,6-tetramethyl-1,4-cyclohexadiene (II), is very nearly planar in this respect. No evidence of π-system interaction has been noted in its ultraviolet spectrum.[3]

We have found that Prevost addition of iodine and silver benzoate to II proceeds by 1,2-addition to yield 4-iodo-3,3,6,6-tetramethylcyclohexene 5-benzoate (III) in 68% yield with no evidence of a homoconjugate addition product. Presumably because of steric factors, III failed to react further with silver benzoate to form the 4,5-dibenzoate. The structure of III was confirmed by elemental analysis and from infrared and n.m.r. spectral considerations. A strong band at 764 cm.$^{-1}$ has been attributed to vinyl hydrogen in the infrared spectrum of II[3] and we believe this to be associated with a weaker absorption at 796 cm.$^{-1}$. Both of these bands are present but attenuated in III. Olefinic unsaturation was also evident in absorptions at 1650 and 3017 cm.$^{-1}$. Conventional tests for unsaturation such as bromination or oxidation with permanganate required sufficiently vigorous conditions to be ambiguous. These observations parallel those of McCasland and Horswill[6] on the addition reactions of cyclohexene 4,5-dibenzoate. The n.m.r. spectrum of III[11] in deuteriochloroform contained a complex multiplet at τ 1.7–2.6 (phenyl hydrogens), a set of three peaks at 8.72, 8.85, and 8.90 (ratio: 1.0:1.0:2.0, methyl hydrogens), and seven peaks near 5 (ring hydrogens). The relative weights of these three sets of hydrogens were 5.0:12.2:3.8, respectively. The seven peaks near τ 5 constituted two AB quadruplets with one accidental superposition. The second, third, fourth, and fifth peaks from the low-field side were assigned to the vinyl protons at C-1 and C-2 (τ 4.68 and 4.54, J = 10 c.p.s.) and the first, third, sixth, and seventh are assigned to the C-4 and C-5 protons (τ 4.48 and 5.44, J = 12 c.p.s.[12]).

To our knowledge, the Prevost reaction has not previously been employed in a homoconjugate addition reaction[13] and it was, therefore, of interest to establish that the reaction of iodine, silver benzoate, and bicyclo[2.2.1]heptadiene proceeded in this sense. A single crystalline product was isolated in 37% yield and its structure was inferred from its elemental analysis and n.m.r. spectrum.[11] The latter showed no vinyl hydrogen peak such as appears in the spectrum of bicyclo[2.2.1]heptene at τ 4.06.[14] The spectrum consisted of a complex multiplet at τ 1.9–2.8 (phenyl hydrogens), an unsymmetrical triplet at 5.14 (J = 2 c.p.s.) (ring hydrogen at the benzoxy-substituted carbon), a broad singlet at 5.63 (ring hydrogen at the iodine substituted carbon), and a complex series of bands at 7.6–8.7 (remaining hydrogens). The relative peak intensities of these four sets of hydrogens were found to be 4.8:1.0:1.0:6.2, respectively. The evidence is consistent with that expected of the homoconjugate addition product (IV).

Our synthesis of II was carried out prior to the published account of Reusch, *et al.*,[3] and, while following the same general lines, differs sufficiently in detail and result to warrant inclusion in the Experimental section. These authors obtained a 10% yield of a 10:1 mixture of II and *p*-xylene as products of the pyrolysis of the *trans* diacetate (VI) at 350°. Upon increasing the temperature to 410°, *p*-xylene was obtained in 90% yield as the only identified product. In our hands, the pyrolysis of a 1:1 mixture of the *cis* and *trans* diacetates (VI) at 520 ± 5° resulted in the formation of II (25%), VII (23%), *p*-xylene (3%), and the recovery of 10% VI. Titration of the crude pyrolysis product indicated a 63% yield of acetic acid. The repyrolysis of VII under the same conditions resulted in a 41% yield of II.

The structure of II was confirmed by catalytic reduction to 1,1,4,4-tetramethylcyclohexane,[15] by formation of a tetrabromide (n.m.r.[16]: methyl hydrogens at τ 8.43 and ring hydrogens at 5.29 in the ratio 3.0:1.0, respectively), and from its n.m.r. spectrum[16] (methyl hydrogens at τ 8.96 and vinyl hydrogens at 4.60 in the ratio 3.0:1.0, respectively). The latter result confirms an earlier finding.[3]

The failure of I and several derivatives to react with maleic anhydride,[8,17] tetracyanoethylene,[18] and azodicarboxylic ester[19,20] in the Diels–Alder sense is paralleled in the lack of reactivity of the first two dienophiles and ethyl acetylene dicarboxylate with II under a wide variety of Diels–Alder conditions.

Experimental[21]

2,2,5,5-Tetramethylcyclohexane-1,3-diol (V).—This material was prepared by the lithium aluminum hydride reduction of 60.0 g. of dimethyldimedon.[22] The *cis* diol (13.6 g., 22%, m.p. 201–203°, lit.[22] 205–206°) and *trans* diol (29.3 g., 47%, m.p. 105–107°, lit.[22] 107–108°) were separated by fractional crystallization from chloroform.

2,2,5,5-Tetramethylcyclohexane 1,3-Diacetate (VI).—To a stirred solution of 20.2 g. of the *cis* diol in 250 ml. of dry ether containing 48 ml. of pyridine was added 20.0 g. of acetyl chloride dropwise. After refluxing for 3 hr. the cooled reaction mixture was poured into 1 l. of ice-water containing 48 ml. of acetic acid. The ether layer was separated, washed with 10% aqueous acetic acid, water, 1% aqueous sodium carbonate, and water and dried over sodium sulfate. Evaporation left a residue which was crystallized from ligroin (35–60°) to give 23.4 g. (78%) of the *cis* diacetate, m.p. 84–86°, lit.[22] 83.5–84.5°. Using an identical procedure, 38.9 g. of *trans* diol was converted to 41.0 g. (70%) of *trans* diacetate, m.p. 63–66°, lit.[22] 64–66°.

3,3,6,6-Tetramethyl-1,4-cyclohexadiene (II).—Approximately

---

[11] We are indebted to Professor E. H. White of the Johns Hopkins University for this spectrum and its interpretation.

[12] We have been unable to find a precedent for this unusually large coupling constant in a related environment.

[13] A general review of the Prevost and related reactions is given by C. V. Wilson, *Org. Reactions*, **9**, 339 (1957).

[14] G. V. D. Tiers, "N. M. R. Summary," Central Research Department, Minnesota Mining and Manufacturing Company, St. Paul, Minn.

[15] G. Chiurdoglu and A. Maquestiau, *Bull. soc. chim. Belges*, **63**, 357 (1954).

[16] We are indebted to Professor W. R. Moore of the Massachusetts Institute of Technology for this spectrum.

[17] R. Riemschneider, *Z. Naturforsch.*, **6b**, 48 (1951).

[18] D. T. Longone and G. L. Smith, *Tetrahedron Letters*, 205 (1962).

[19] B. Franzus and J. H. Surridge, *J. Org. Chem.*, **27**, 1951 (1962).

[20] B. Franzus, *ibid.*, **28**, 2954 (1963).

[21] All melting points and boiling points are uncorrected. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn., or C. F. Geiger, Ontario, Calif.

[22] A. Allen, R. Sneeden, and J. Colvin, *J. Chem. Soc.*, 557 (1958).

equal weights of the *cis* and *trans* diacetates (VI, 41 g.) were pyrolyzed at 520 ± 5° by the procedure of Bailey and King.[23] Premelted VI was added with dry nitrogen (4 ml./min.) at the rate of 0.2–0.3 g./min. to the reaction chamber which consisted of a 14 × 310 mm. Vycor tube packed with $^3/_{16}$-in. Pyrex helices. By titration of the crude pyrolysate with base, 0.20 mole (63%) of acetic acid was estimated. The pyrolysate was taken up in ether, washed repeatedly with 1% aqueous sodium carbonate, dried over sodium sulfate, and evaporated to a residue which was fractionally distilled to yield 6.0 g. (28%) of crude II, b.p. 130–134° (750 mm.). Fractional vacuum distillation of the residue resulting from the above distillation resulted in the recovery of 4.2 g. (10%) of VI, b.p. 130–138° (6–7 mm.), and 7.0 g. (23%) of a pale yellow liquid, b.p. 88.5–95.0° (6–7 mm.), which was unsaturated to bromine in carbon tetrachloride and had an infrared spectrum consistent with its formulation as 3,3,6,6-tetramethylcyclohexene 4-acetate (peaks at 1740 and 1030 cm.$^{-1}$). Repyrolysis of 5.3 g. of this acetate resulted in 1.5 g. (41%) of II. *p*-Xylene was detected as an impurity in crude II by gas–liquid chromatography and comparison of its infrared spectrum with that of an authentic sample. The gas chromatographic peak area ratio of II to *p*-xylene was found to be 10:1. An analytical sample of II was obtained by gas–liquid chromatography over a 7-ft. column of 30% silicone oil 550 on base-washed Chromosorb P, b.p. 132–133° (750 mm.), $n^{25}\text{D}$ 1.4367.

Anal. Calcd. for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.31; H, 11.68.

Bromination of II in carbon tetrachloride for 45 min. at 27° resulted in a tetrabromide which was crystallized from ethanol to m.p. 69.0–69.5°.

Anal. Calcd. for $C_{10}H_{16}Br_4$: C, 26.35; H, 3.54; Br, 70.12. Found: C, 26.41; H, 3.76; Br, 69.99.

Catalytic hydrogenation of II with Adams catalyst in glacial acetic acid resulted in the absorption of 99.2% of the theoretical volume of hydrogen. 1,1,4,4-Tetramethylcyclohexane was isolated and purified by fractional distillation, b.p. 146–148° (750 mm.), $n^{25}\text{D}$ 1.4237, d_{25} 0.7747; lit.[15] b.p. 152.6–153.3°, $n^{20}\text{D}$ 1.4258, d_{20} 0.7754.

4-Iodo-3,3,6,6-tetramethylcyclohexene 5-Benzoate (III).—A solution of 2.5 g. of iodine in 20 ml. of dry benzene was added in portions with shaking to 2.3 g. of freshly prepared dry powdered silver benzoate.[24] To this solution was added, all at once, 1.5 g. of II. After 1 hr. at reflux the solution was cooled and filtered; the filtrate was washed with water, 10% sodium bisulfite solution, 10% sodium carbonate solution, and water. After drying over sodium sulfate the solution was evaporated to a clear sirup which crystallized from methanol to yield 2.60 g. (68% based on iodine) of a white crystalline product, m.p. 78–81°. Repeated recrystallization from ligroin (35–60°) raised this to m.p. 80.5–81.5°.

Anal. Calcd. for $C_{17}H_{21}IO_2$: C, 53.17; H, 5.51; I, 33.03; mol. wt. (Rast), 384. Found: C, 53.14; H, 5.48; I, 33.16; mol. wt. (Rast), 374.

This substance failed to decolorize warm (50°) solutions of 3% bromine in carbon tetrachloride, bromine water, or 1% potassium permanganate in acetone over 5-min. periods relative to blank reagents. It also failed to react with a threefold excess of silver benzoate in refluxing dry benzene over an 85-hr. period.

3-Iodotricyclo[2.2.1.$0^{2,6}$]heptane 5-Benzoate (IV).—The reaction was carried out as described above using 3.0 g. of dry powdered silver benzoate, 3.3 g. of iodine, and 4.6 g. of freshly distilled bicyclo[2.2.1]heptadiene, b.p. 89° (753 mm.). Crystallization of the clear, sirupy product from methanol and then ligroin (35–60°) resulted in 1.25 g. (37% based on iodine) of a white crystalline product, m.p. 65–68°. Repeated recrystallization from ligroin raised the melting point to 67.5–69.0°.

Anal. Calcd. for $C_{14}H_{13}IO_2$: C, 49.45; H, 3.85; I, 37.33. Found: C, 49.54; H, 3.81; I, 37.11.

Attempted Diels–Alder Reactions of II.—Maleic anhydride tetracyanoethylene, and ethyl acetylene dicarboxylate were added to equal weights of II with and without solvent at temperatures from 37 to 150° and for periods of 1–24 hr. Thin layer chromatography and infrared analysis failed to indicate adduction.

Acknowledgment.—F. W. G. and C. H. B. gratefully acknowledge partial support from the Petroleum Research Fund of the American Chemical Society, Grant 528-B.

Alkylations of Ketone and Aldehyde Phenylhydrazones by Means of Alkali Amides in Liquid Ammonia to Form N-Alkyl Derivatives

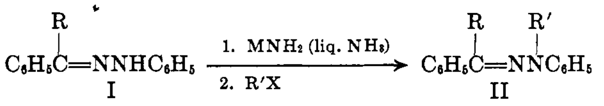
William G. Kenyon[1] and Charles R. Hauser

Department of Chemistry, Duke University,
Durham, North Carolina

Received August 20, 1964

Alkylations of benzaldehyde phenylhydrazone to form N-alkyl derivatives have previously been effected with alkyl halides by means of sodamide in benzene, but the details were not given.[2]

We have effected alkylations of this phenylhydrazone and of certain ketone phenylhydrazones (I) by means of sodamide or potassium amide in liquid ammonia to form the N-alkyl derivatives II (eq. 1, Table I).



$$\underset{\text{I}}{C_6H_5\overset{R}{\overset{|}{C}}{=}NNHC_6H_5} \xrightarrow[\text{2. R'X}]{\text{1. MNH}_2\text{ (liq. NH}_3)} \underset{\text{II}}{C_6H_5\overset{R}{\overset{|}{C}}{=}N\overset{R'}{\overset{|}{N}}C_6H_5} \quad (1)$$

Interestingly, the color of the intermediate anion of benzophenone phenylhydrazone was dark red, similar to that of the diphenylmethide ion. This suggests that resonance form IIIb makes some contribution to the structure of the anion, though the contribution of IIIa may be more important.

$$\underset{\text{IIIa}}{(C_6H_5)_2C{=}N{-}\bar{N}C_6H_5} \longleftrightarrow \underset{\text{IIIb}}{(C_6H_5)_2\bar{C}{-}N{=}NC_6H_5}$$

That the products were the N-alkyl derivatives, not the possible C-alkyl derivatives, was supported by the essential agreement of their melting points with the reported values, analysis in certain cases, and by independent syntheses of the N-benzyl derivatives of benzaldehyde and benzophenone phenylhydrazones (eq. 2).

$$C_6H_5\overset{R}{\overset{|}{C}}{=}O + H_2N\overset{CH_2C_6H_5}{\overset{|}{N}}C_6H_5 \longrightarrow \text{II} \quad (2)$$

$$R = H \text{ or } C_6H_5;\ R' = C_6H_5CH_2$$

Table I shows that the alkylations of the phenylhydrazones I to form the N-alkyl derivatives II (eq. 1) were realized in good to excellent yields (69–92%). This method appears more convenient than that represented by eq. 2, which has been reported difficult to effect.[2,3] Only the condensation of benzophenone with N-methylphenylhydrazine seems to have been realized previously in good yield (71%) and this required a

---

[23] W. J. Bailey and C. King, *J. Org. Chem.*, **21**, 858 (1956).

[24] B. I. Halperin, H. B. Donahoe, J. Kleinberg, and C. A. Vanderwerf, *J. Org. Chem.*, **17**, 623 (1952).

[1] Union Carbide and Carbon Chemicals Co. Fellow, 1961–1963.

[2] P. Grammaticakis, *Compt. rend.*, **209**, 994 (1939).

[3] F. Bovini, *Atti accad. naz. Lincei. Mem. Classe Sci. fis. mat. e nat., Sez II*, **22**, 460 (1913).