solution was discharged after 2 hr by rapid addition of alcohol. After evaporation of the ammonia and dilution with water, the product was obtained by filtration. It was taken up in acetone and filtered to remove a residue; the solvent was removed *in vacuo* to provide I (1.08 g, mp 111–112°).

**1,2,7,12-Tetrahydrobenz[*a*]anthracene (II).**—A similar procedure was followed for the reduction of I, except that ferric chloride was omitted. The oily yellow solid obtained was purified by chromatography on silica gel to give II as white flakes, mp 96–98°.

**1,4,7,8,11,12-Hexahydrobenz[*a*]anthracene (III)** was obtained both directly from II and from benz[*a*]anthracene, in both cases employing a method analogous to that employed for preparation of II. With benz[*a*]anthracene as the starting material, 7–10 equiv of lithium/mol of benz[*a*]anthracene provided optimum yield (Table I); greater excess led to increasing quantity of minor side products (detected on thin layers of trinitrobenzene on silica gel). These substances are suspected to arise from isomerization of double bonds into conjugation, followed by their reduction, rather than from hydrogenation of the B ring.

**1,2,3,4,7,8,11,12-Octahydrobenz[*a*]anthracene (V).**—To a solution of IV (1.17 g, 5 mmol) in 75 ml of THF and 150 ml of liquid ammonia was added lithium (694 mg, 100 g-atoms). The stirred solution was maintained at gentle reflux for 3 hr; then 20 ml of ethanol in 30 ml ether was added from a dropping funnel over a 45-min period. After evaporation of the ammonia, the solution was partitioned between ether and water. The ether phase was dried over magnesium sulfate and evaporated to dryness. Recrystallization of the resulting white solid from ethanol gave pure V (Table I).

**Reduction of IV with Lithium in Methylamine.**—IV (1.17 g, 5 mmol) was added to a solution of lithium (347 mg, 50 g-atoms) in 250 ml of liquid methylamine at reflux; 30 sec later 5 ml of *t*-butyl alcohol was added as rapidly as practicable. When the intense blue color of the solution disappeared (8 min), ethanol (5 ml) and water (10 ml) were added. Removal of the amine by evaporation, followed by partition of the product between ether and water, gave the crude product, recrystallization of which from ethanol furnished pure VII (Table I).

The mother liquors were evaporated to dryness and chromatographed on a column of silica gel prepared in petroleum ether (bp 30–60°). Elution with hexane gave the dodecahydro compound VI (42 mg) followed by an oily solid (445 mg), identified as the isomer VIII. Recrystallization from ethanol-methanol at 4° furnished pure VIII (Table I), a compound which appeared to be especially sensitive to autooxidation.

An analogous reaction in which the *t*-butyl alcohol was added 15 min after the lithium (243 mg, 7 g-atoms) over a 5-min period furnished VI as the major product. Recrystallization from ethanol gave the analytical sample of VI (mp 113.5–114.5°, white needles). Thin layer chromatography of the mother liquor showed a major spot of higher $R_f$ value (probably, therefore, a tetradecahydro derivative) which was not investigated further.

**Reduction of III with Lithium in Methylamine.**—Lithium (208 mg, 6 g-atoms) was added to a solution of 3 ml of *t*-butyl alcohol in 250 ml of methylamine at reflux. Then 2 min later III (1.17 g, 5 mmol) was added, followed by 15 ml THF in order to bring into solution the incompletely dissolved hydrocarbon. The blue color disappeared within 10 min. Work-up in the usual manner gave an oil (1.12 g), revealed by thin layer chromatography to contain two principal components. Chromatography on silica gel with elution by hexane furnished IX (716 mg) as a viscous oil.

**Registry No.**—I, 16434-59-6; II, 16434-60-9; III, 16434-61-0; IV, 16434-62-1; V, 16434-55-2; VI, 16452-37-2; VII, 16434-56-3; VIII, 16434-57-4; IX, 16434-58-5.

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# A Method for the Addition of the Elements of Ketene to Some Selected Dienes in Diels–Alder Fashion

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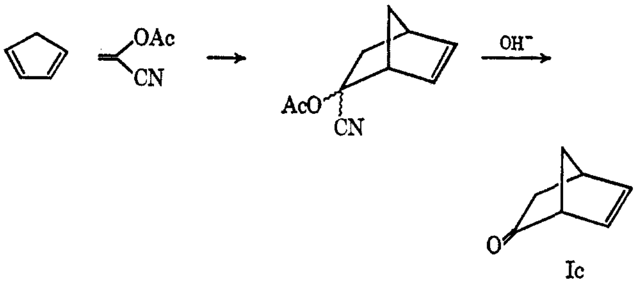
New and improved syntheses for dehydronorcamphor, bicyclo[2.2.2]oct-2-en-5-one, and tetracyclo[4.3.0.$0^{2,4}.0^{3,7}$]nonan-8-one and the syntheses of tricyclo[4.2.2.$0^{2,5}$]deca-3,7-dien-9-one and tricyclo[3.2.2.$0^{2,4}$]non-6-en-8-one are described. These syntheses consist of Diels–Alder or homo Diels–Alder addition of acrylonitrile, chlorination of the nitrile adduct with phosphorus pentachloride, followed by hydrolysis of the resulting α-chloronitrile with potassium hydroxide in aqueous dimethyl sulfoxide.

The addition of ketenes to dienes yields products in which a cyclobutanone moiety is produced by cycloaddition of the ketene to a single double bond.[1] This mode of reaction is distinguished from normal Diels–Alder addition in which a double bond adds 1,4 across a conjugated system. The alternative routes available for achieving the syntheses of addition products, which conceptually are the result of Diels–Alder addition of ketene, have been complicated by two factors. Dienophiles capable of forming adducts which are easily convertible to ketones, such as vinyl acetate, will not add easily to the less reactive dienes. On the other hand, dienophiles that do add easily to most dienes such as acrylonitrile or acrylate esters are not easily convertible to the corresponding ketone. Bartlett and Tate[2] suggested an elegant solution to this problem in their synthesis of dehydronorcamphor (Ic) from α-acetoxyacrylonitrile and cyclopentadiene (Scheme I). This method suffers principally from the commercial unavailability of α-acetoxyacrylonitrile.[3]

SCHEME I



In more recent studies Paasivirta and Krieger[4] prepared dehydronorcamphor (Ic) and bicyclo[2.2.2]oct-2-en-5-one (IIc) from chloronitriles, which were obtained by adding α-chloroacrylonitrile to cyclo-

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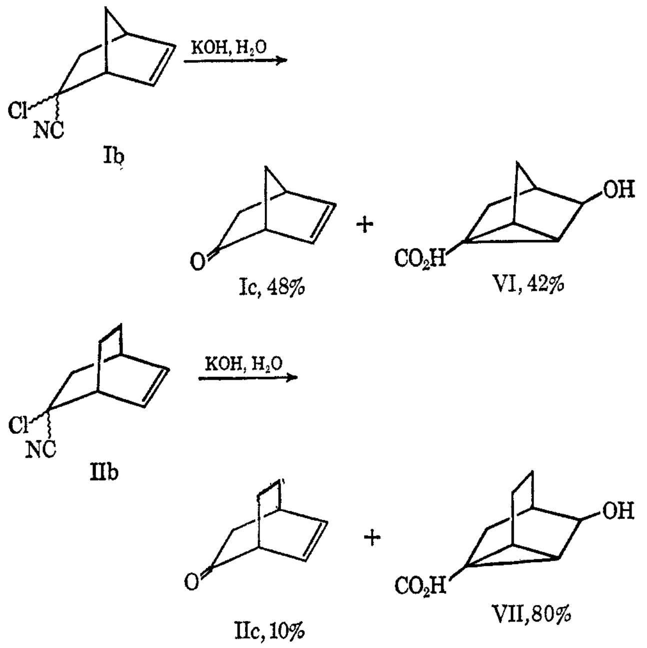
(1) J. D. Roberts and C. M. Sharts, *Org. Reactions*, **12**, 2 (1962).

(2) P. D. Bartlett and B. E. Tate, *J. Amer. Chem. Soc.*, **78**, 2473 (1956).

(3) R. M. Nowak, *J. Org. Chem.*, **28**, 1182 (1963).

(4) J. Paasivirta and H. Krieger, *Suomen Kemistilehti*, *B*, **38**, 182 (1965); J. Paasivirta, *Suomen Kemistilehti*, *A*, **39**, 120 (1966); see also H. Krieger and S. E. Masar, *ibid.*, **39**, 119 (1966).

SCHEME II

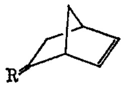
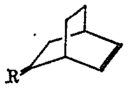
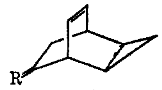
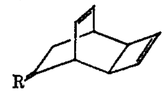
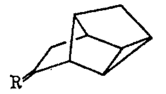


pentadiene and 1,3-cyclohexadiene (Scheme II). Although $\alpha$-chloroacrylonitrile is readily available, it has been our experience that it gives polymeric tars when heated with less reactive dienes at temperatures exceeding 140–160°.

We have developed a more generally applicable procedure for the syntheses of ketene Diels–Alder addition products, based on the conversion of readily obtainable Diels–Alder acrylonitrile adducts to $\alpha$-chloronitriles. Our chlorination method is adapted from a procedure reported by Stevens and Coffield[5] for halogenation of secondary nitriles with phosphorus pentachloride or phosphorus pentabromide. The chief differences are in the use of solvent to moderate the reaction and in the addition of pyridine in order that the chlorination can be performed in the presence of a double bond. In the second step of the procedure the $\alpha$-chloronitrile adducts are converted to ketones by treatment with potassium hydroxide in dimethyl sulfoxide (DMSO). As starting dienes cyclopentadiene and 1,3-cyclohexadiene were selected to illustrate completely standard reactions; cyclooctatetraene[6,7] and cycloheptatriene[8–16] were chosen as interesting examples of substrates which react and apparently react by way of their valence tautomers, 2,4,7-bicyclo[4.2.0]octatriene and norcaradiene; and norbornadiene was used to illustrate a synthesis *via* an initial homo Diels–Alder reaction. Table I lists the ring systems synthesized and the yields obtained. (Ring structure numerals are assigned letters to indicate substituents: a for R = H, CN; b for R = Cl, CN; and c for R = O.)

TABLE I

SUMMARY OF YIELD DATA

| | | Yield, %[a] | |
|---|---|---|---|
| | | Chloronitrile R = Cl, CN | Ketone R = O |
| I |  | 89 | 79 |
| II |  | 61 | 68 |
| III |  | 80 | 49 |
| IV |  | Not isolated | 50[b] |
| V |  | 76 | 73 |

[a] Yields are based on immediate precursor. [b] Yield is based on nitrile IVa.

This method gives an improvement in both yield and simplicity over previous methods for making ketones Ic,[2,4,17] IIc,[4,18] and Vc.[19] Structural confirmation for these three known ketones was provided by comparison of the spectral data obtained with an infrared spectrum of Ic,[17] nmr and infrared spectra of ketone Vc,[19] and with the reported infrared absorptions of ketone IIc.[18]

Ketones IIIc and IVc have not previously been reported and their structural assignments are based on infrared and nmr spectra (see Experimental Section) and on the known proclivity of these ring systems, synthesized *via* Diels–Alder reactions, to have the cyclopropyl or cyclobutenyl rings *syn* to the double bond.[7,11,12]

It is instructive to compare the results of Paasivirta and Krieger[4] with those presented here. The conditions used by these workers (aqueous potassium hydroxide) for the conversion of $\alpha$-chloronitrile to ketone would be expected to favor a larger SN1/SN2 ratio than under our conditions (DMSO–potassium hydroxide), which should favor a bimolecular displacement of chloride by hydroxide. This argument is based on the known ability of DMSO to enhance the nucleophilicity of anions, relative to reactions in protic solvents,[20] and is borne out by the isolation of hydroxy acids VI and VII by Paasivirta and Krieger and by the high yields obtained for ketones Ic and IIc in this work.

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(5) C. L. Stevens and T. H. Coffield, *J. Amer. Chem. Soc.*, **73**, 103 (1951).

(6) R. Huisgen and F. Mietzsch, *Angew. Chem. Intern. Ed. Engl.*, **3**, 83 (1964).

(7) R. C. Cookson, J. Hudec, and J. Marsden, *Chem. Ind.* (London), 21 (1961).

(8) E. Ciganek, *J. Amer. Chem. Soc.*, **89**, 1458 (1967).

(9) C. Ruchardt and H. Schwarzer, *Chem. Ber.*, **99**, 1861 (1966).

(10) H. Prinzbach, D. Seip, L. Knothe, and W. Faisst, *Ann. Chim.*, **698**, 34 (1966).

(11) M. J. Goldstein and A. H. Gervitz, *Tetrahedron Lett.*, 4417 (1965).

(12) M. J. Goldstein and A. H. Gervitz, *ibid.*, 4413 (1965).

(13) R. C. Cookson, S. S. Gilani, and I. D. R. Stevens, *ibid.*, 615 (1962).

(14) R. Huisgen and W. D. Wirth, unpublished results referred to in R. Huisgen, R. Grashey, and J. Sauer in S. Patai, "The Chemistry of Alkenes," Interscience Publishers, London, 1964, p 888.

(15) K. Alder and G. Jacobs, *Chem. Ber.*, **86**, 1528 (1953).

(16) E. P. Kohler, M. Tishler, H. Potter, and H. Thompson, *J. Amer. Chem. Soc.*, **61**, 1057 (1939).

(17) P. K. Freeman, Ph.D. Thesis, University of Colorado, 1957.

(18) The adduct of cyclohexadiene and nitroethylene was converted to IIc in 20.6% over-all yield by W. C. Wildman and D. R. Saunders [*J. Org. Chem.*, **19**, 381 (1954)] and in less than 20% yield by C. A. Grob, H. Kuy, and H. Gagneaux [*Helv. Chem. Acta*, **40**, 130 (1957)].

(19) (a) Synthesis of ketone Vc has been briefly described in a preliminary communication: P. K. Freeman and D. M. Balls, *Tetrahedron Lett.*, No. 5, 437 (1967). (b) H. K. Hall, Jr. [*J. Org. Chem.*, **25**, 42 (1960)], prepared this ketone in less than 1% yield from nitrile Va.

(20) A. J. Parker, *Advan. Org. Chem.*, **5**, 1 (1965).

## Experimental Section

Melting points are uncorrected. The nmr spectra were recorded with a Varian Associates A-60 nmr spectrometer, using tetramethylsilane as an internal standard. Infrared spectra were recorded with a Perkin-Elmer Model 137 infrared spectrophotometer (except as noted in Table II) and were calibrated with a polystyrene spike at 1601.4 cm$^{-1}$. Vapor phase chromatographic analyses were performed on an F & M Model 609 chromatograph equipped with a flame ionization detector. Two columns were used: column A, 14 ft × 0.25 in., 15% Carbowax 20M on 70–80 mesh Anakrom AS; column B, 18 ft × 0.25 in., 12% SE 30 on 110–120 mesh Anakrom AS. A Parr Instrument Co., Series 4500, pressure reaction apparatus was used for Diels–Alder reactions except as noted. Elemental analyses were performed by Max Bernhardt, Microanalytisches Laboratorium, Max-Planck Institute, Mülheim, Germany. The acrylonitrile, $\alpha$-chloroacrylonitrile, and olefins used were all practical grade and were distilled just before they were used. Dimethyl sulfoxide was practical grade (mp 18°). Chloroform was distilled from phosphorus pentachloride prior to using in chlorination of the nitriles.

TABLE II

A COMPARISON OF INFRARED STRETCHING FREQUENCIES OF RELATED NITRILES AND $\alpha$-CHLORONITRILES

| Ring system | Nitrile,[a] cm$^{-1}$ | Chloronitrile,[a] cm$^{-1}$ |
|---|---|---|
| I | 2238.8 | 2240.0 |
| II | 2238.8 | 2240.4 |
| III | 2238.2 | 2244.3 |
| IV | 2239.4 | |
| V | 2236.9 | 2242.4 |

[a] The absorption frequencies reported in this table were obtained by measurements with a Perkin-Elmer Model 621, equipped with a frequency marker, on dilute $CCl_4$ solutions, and are averages of two determinations. Indene was used for calibration and the values reported are believed to be accurate to better than 0.5 cm$^{-1}$.

**Synthesis of Dehydronorcamphor (Ic).**—5-Chloro-5-cyanobicyclo[2.2.1]hept-2-ene (Ib) was prepared by mixing cyclopentadiene and 2-chloroacrylonitrile at 70–80° according to the method of Krieger:[21] yield 89%; bp 54–56° (1.8 mm); mp 47–48° (lit. mp 45–47°). A 68.6-g (0.446 mol) sample of $\alpha$-chloronitrile Ib was dissolved in 400 ml of DMSO in a 1-l. flask fitted with mechanical stirrer and internal thermometer. A solution of 75 g of 85% potassium hydroxide (1.14 mol) in 25 g of water was prepared by mixing and heating until dissolved. The hot alkali was poured into the stirred DMSO–chloronitrile solution. After 24–36 hr the dark reaction mixture was subjected to steam distillation until the distillate no longer had a strong odor of product. The distillate was extracted three times with ether, and the combined ether extracts were dried. Distillation on an 18-in. semimicro spinning-band column gave 35.1 g (78.6%) of ketone Ic, bp 80–81° (45 mm), mp 22–23° (lit.[4] mp 22–23°). The infrared spectrum was identical with that of an authentic sample.[17]

**Preparation of 5-Chloro-5-cyanobicyclo[2.2.2]oct-2-ene (IIb).**—Using the Diels–Alder addition of 1,3-cyclohexadiene and $\alpha$-chloroacrylonitrile to prepare chloronitrile IIb[4] resulted in yields of only 17%. The following procedure gives a considerable improvement in over-all yield. 5-Cyanobicyclo[2.2.2]oct-2-ene (88.2 g, 0.65 mol) prepared in 88.7% yield as previously described[22] was added slowly, with stirring, to a solution of pyridine (106 g, 1.33 mol) and phosphorous pentachloride (207 g, 0.994 mol) in 1500 ml of dry chloroform. After refluxing for 16 hr, the mixture was poured onto 2 kg of ice. After the ice had melted, the layers were separated and the aqueous phase was washed twice with ether. The organic extracts were combined and washed once with saturated aqueous sodium chloride and once with 10% aqueous sodium carbonate. Removal of solvent and distillation gave 67.2 g (60.8%) of chloronitrile, mp 88–90°. The nmr and infrared spectra of the chloronitriles prepared by the two methods were essentially identical. Vapor phase chromatographic analyses of the chloronitriles prepared by the two methods on column B (180°) showed two peaks in the ratios 74:26 for the cyclohexadiene–$\alpha$-chloroacrylonitrile adduct and 70:30 for the product obtained from chlorination of IIb.

**Preparation of Bicyclo[2.2.2]oct-2-en-5-one (IIc).**—A hot solution of 106 g (1.61 mol) of 85% potassium hydroxide in 30 ml of water was added to a solution of 66.7 g (0.40 mol) of chloronitrile IIb in 600 ml of DMSO. There was a gradual darkening of color from yellow to black and a mild increase in temperature to 50–60°. After 12 hr, vpc analysis (column B, 170°) revealed that no more chloronitrile was present and that a new peak corresponding to ketone IIc had appeared. The reaction mixture was added to 1 kg of ice–water and extracted five times with petroleum ether (bp 30–60°). Drying over magnesium sulfate and distilling off the solvent left a semisolid mass which was sublimed to give 33.0 g (68%) of ketone, mp 84–86° (lit.[4] mp 84–86°).

**Preparation of 8-Cyanotricyclo[3.2.2.0$^{2,4}$]non-6-ene (IIIa).**—Cycloheptatriene (276 g, 3.00 mol), acrylonitrile (212 g, 4.00 mol), and 4-*t*-butylcatechol were placed in a Parr, Series 4500, pressure reaction apparatus. The vessel was heated, with stirring to 180–200° for 36–40 hr. Distillation of the contents after cooling on an 18-in. semimicro spinning-band column gave 302.0 g (70.2%) of nitrile, bp 70–76° (0.1–0.2 mm). The ir had $\nu_{max}$ at 3070 (cyclopropyl and vinyl C—H) and 2238 cm$^{-1}$ (—C≡N). The 1600–1700-cm$^{-1}$ region showed very weak absorptions. The nmr spectrum had complex patterns in the regions $\tau$ 4.1–4.45 (2 H), 6.8–9.3 (7 H), and 9.65–10.00 (2 H).

*Anal.* Calcd for $C_{10}H_{11}N$: C, 82.72; H, 7.64. Found: C, 82.58; H, 7.81.

**Preparation of 8-Chloro-8-cyanotricyclo[3.2.2.0$^{2,4}$]non-6-ene (IIIb).**—Nitrile IIIa (145 g, 1.00 mol) was added to a solution of phosphorus pentachloride (313.1 g, 1.50 mol), pyridine (160 g, 2.00 mol), and 1500 ml of dry chloroform. The mixture was refluxed with stirring for 72 hr under a nitrogen atmosphere. Work-up of the reaction mixture was similar to that described for chloronitrile IIb except that the product distilled at 84–92° (0.9–1.0 mm), 141 g (80%). The nmr spectrum exhibited absorptions at $\tau$ 3.9–4.6, complex multiplet (2 H); 6.50–6.88 and 6.88–7.22, broad multiplets (1 H each); 7.2–8.2 and 8.4–9.1, complex absorptions (2 H each); and 9.4–10.0, complex multiplet (2 H). The ir spectrum exhibited $\nu_{max}$ 2244 (C≡N stretch) and 3040 cm$^{-1}$ (vinyl C—H stretch). More accurate determination of the C≡N stretching frequencies in the infrared for each pair of nitriles, revealed, as in this case, that substitution of chlorine $\alpha$ to the nitrile group causes a shift to higher frequencies of 1.2–6.1 cm$^{-1}$ (Table II).

*Anal.* Calcd for $C_{10}H_{10}NCl$: C, 66.86; H, 5.61. Found: C, 67.03; H, 5.64.

**Preparation of Tricyclo[3.2.2.0$^{2,4}$]non-6-en-8-one (IIIc).**—Chloronitrile IIIb (122.4 g, 0.69 mol) and 800 ml of DMSO were heated to 50°. A hot solution of 120 g of 85% potassium hydroxide in 40 g of water was poured into the stirred reaction mixture. After 48 hr at this temperature, the black mixture was subjected to steam distillation. The distillate was extracted three times with ether; the ether extracts were dried over magnesium sulfate. Distillation of the ether extracts yielded 44.2 g (49%) of ketone IIIc, bp 72–74° (0.9–1.0 mm). In another experiment where the chloronitrile was not distilled a 52% yield was obtained based on nitrile IIIa. The nmr spectrum showed complex patterns in the following ranges: $\tau$ 3.90–4.55, 6.73–7.18, 7.20–8.08, 8.53–9.10, 9.38–9.75. The areas of each set of peaks were all equal and therefore correspond to two protons each. The ir showed $\nu_{max}$ 3040, 2990, 1710, 1430, 1410, 1360, 1285, 1160, 1145, 1100, 1040, 964, 888, 845, 812, 763, 728, and 705 cm$^{-1}$.

*Anal.* Calcd for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.61; H, 7.55.

**Preparation of Tricyclo[4.2.2.0$^{2,5}$]deca-3,7-diene-9-carbonitrile (IVa).**—Cyclooctatetraene (60 g, 0.576 mol), acrylonitrile (53 g, 1.00 mol), and 0.5 g of *t*-butylcatechol were heated in a sealed glass tube to 180° for 18 hr. Distillation of the reaction mixture under 0.01–0.05-mm pressure until an internal flask temperature of 250° was reached gave 78.8 g (88%) of nitrile whose vapor phase chromatogram (column B, 190°) showed two peaks of almost equal area. The ir spectrum showed $\nu_{max}$ at 2245 (—C≡N stretch) and 3060 (vinyl C—H stretch) cm$^{-1}$. The nmr spectrum had peaks at $\tau$ 3.95–4.4, complex multiplet (4 H); 6.93, triplet (1 H); 7.1–7.7, complex multiplet (4 H);

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[21] H. Krieger, *Suomen Kemistilehti*, **36**, B, 68 (1963).

[22] K. Alder, H. Krieger, and H. Weiss, *Chem. Ber.*, **88**, 144 (1955).

8.1–8.5, complex multiplet (2 H). Nitrile IVa gave $n^{25}$D 1.5240 (lit.[23] $n^{25}$D 1.5236).

**Preparation of Tricyclo[4.2.2.0$^{2,5}$]deca-3,7-dien-9-one (IVc).**—Pyridine (80 g, 1.0 mol) was slowly added to a solution of 121 g (0.58 mol) of phosphorus pentachloride in 700 ml of dry chloroform. To the resulting white suspension was added 64.8 g (0.388 mol) of nitrile IVa. Work-up after 36 hr of heating at reflux consisted of pouring onto ice, removing the aqueous layer, washing the aqueous phase twice with ether, washing the combined organic extracts with saturated sodium carbonate, and removing the solvent on a rotary evaporator. This treatment gives 88 g of dark liquid which was used without further purification. In a separate experiment, attempted distillation of the chloronitrile at 0.01 mm led to decomposition and loss of product. The 88 g of dark liquid described above was dissolved in 600 ml of DMSO, and to this was added a hot solution 66 g (1.0 mol) of 85% potassium hydroxide in 22 ml of water. After 24 hr the mixture was worked up as described for the purification of ketone IIc. After sublimation, 28.1 g (49.7% based on nitrile IVa) of ketone was obtained. The nmr spectrum exhibited bands at $\tau$ 3.80–4.42, complex multiplet (4 H); 6.9–7.5, broad absorption (4 H); 8.13 and 8.15, two doublets (1 H each). The ir showed absorptions at 1710 (C=O stretch) and 3060 cm$^{-1}$ (vinyl C—H stretch).

*Anal.* Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.90. Found: C, 82.07; H, 6.96.

**8-Cyanotetracyclo[4.3.0.0$^{2,4}$.0$^{3,7}$]nonane (Va).**—Nitrile Va was prepared from freshly dried and distilled norbornadiene [bp 86–87° (693 mm)] and acrylonitrile [bp 74–75° (693 mm)]. The method of Shrauzer and Glockner[24] or Shrauzer and Eichler[25] was scaled up to preparative proportions. The latter method is more convenient for large-scale preparations if the acrylonitrile is added slowly rather than all at once as described.[25] Yields were 85–93% using centigram quantities.

**8-Cyano-8-chlorotetracylo[4.3.0.0$^{2,4}$.0$^{3,7}$]nonane (Vb).**—A mixture of nitrile Va (494 g, 3.41 mol), 1000 ml of carbon tetrachloride, and phosphorus pentachloride (208 g, 1.00 mol) was heated at reflux in a vessel fitted with a stirrer, chlorine inlet, reflux condenser, and a gas bubbler. The chlorine inlet was placed between the flask and the condenser. There was a gradual evolution of hydrogen chloride, which after 24 hr becomes more sluggish. At this time chlorine gas was passed into the solution to convert phosphorus trichloride to the pentachloride. This process was continued until no more HCl was evolved (about 3 days). The completeness of reaction can be conveniently checked by vpc or nmr (by following the disappearance of the absorption corresponding to hydrogen $\alpha$ to nitrile). The cooled reaction mixture was poured onto 2.5 kg of ice and mixed until the ice melted. The two phases were allowed to separate (there may be an emulsion at this point which requires several hours to break up); the aqueous layer was extracted with carbon tetrachloride. The combined organic phases were washed once with water and then with 10% aqueous sodium carbonate until no more carbon dioxide was evolved. Simple distillation gives 463 g (76%) of oily chloronitrile: bp 89–94° (0.05–0.1 mm); ir, $\nu_{max}$ at 3060, 2245 cm$^{-1}$; nmr, multiplets at $\tau$ 7.65–7.82 (2 H), 7.82–8.0 (3 H), 8.27–8.44 (2 H), 8.44–8.62 (1 H), 8.68–8.87 (2 H).

*Anal.* Calcd for $C_{10}H_{10}ClN$: C, 66.85; H, 5.61; N, 7.80. Found: C, 66.92; H, 6.13; N, 8.16.

**Preparation of Tetracyclo[4.3.0.0$^{2,4}$.0$^{3,7}$]nonan-8-one (Vc).**—Chloronitrile Vb (463 g, 2.58 mol) was dissolved in 2 l. of DMSO and the solution heated to 50°. A hot solution of 400 g of 85% potassium hydroxide in 120 g of water was slowly added. After stirring for 3 days at 50–60°, the dark reaction mixture was subjected to steam distillation. The distillate was saturated with sodium chloride and extracted with ether. The ether extracts were dried over magnesium sulfate, concentrated, and distilled to give 252 g (73%) of ketone, bp 69–70° (4 mm). In another experiment where the chloronitrile was not isolated the yield was 69.7% based on nitrile. The nmr spectrum showed multiplets centered at $\tau$ 7.48 (3 H), 7.78 (2 H), 8.40 (2 H), and a broad multiplet from 8.50 to 8.88 (3 H); ir had $\nu_{max}$ at 3060 (cyclopropyl C—H stretch) and 1756] cm$^{-1}$ (carbonyl stretch). The ir and nmr spectra were identical with spectra of an authentic sample which were kindly supplied to us by Professor Alex Nickon.

**Registry No.**—Ic, 694-98-4; IIb, 6962-73-8; IIc, 2220-40-8; IIIa, 16282-02-3; IIIb, 16282-03-4; IIIc, 16282-04-5; IVc, 16282-05-6; Vb, 16282-06-7; Vc, 16282-07-8.

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# The Syntheses and Properties of Sterically Hindered Butadienes. A Modification of the Chugaev Reaction

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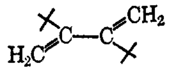
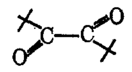
The synthesis of 4,5-dimethylene-3,3,6,6-tetramethyl-1-thiacycloheptane (IV) was accomplished *via* a double Wittig reaction with 3,3,6,6-tetramethyl-1-thiacycloheptane-4,5-dione (III). The synthesis of 2,3-diisopropyl-1,3-butadiene (VIII) from 2,3-diisopropyl-1,4-butanediol (XI) was accomplished *via* a modification of the Chugaev reaction. The chemical and spectroscopic properties of 2,3-di-*t*-butyl-1,3-butadiene (I), of dienes IV and VIII, and of diketone III and dipivaloyl (II) are discussed. The heavily substituted butadienes I and IV are shown to be unusually unreactive.

Our interest in crowded molecules led to several unsuccessful attempts to synthesize 3,4-di-*t*-butylthiophene.[1] Ring-closure reactions of 2,3-di-*t*-butyl-1,3-butadiene (I), 2,3-di-*t*-butylsuccinnic acid derivatives, or dipivaloyl (II) with suitable reagents were unsuccessful.[1] The lack of reactivity of these $\alpha,\beta$-di-*t*-butyl compounds in ring-closure reactions must be attributed to the bulky *t*-butyl groups. Spectroscopic evidence for an abnormal conformation in these $\alpha,\beta$-di-*t*-butyl compounds was found for 2,3-di-*t*-butyl-1,3-butadiene (I).[2]



I



II

The ultraviolet absorption spectrum of the vapor of the butadiene I, taken at room temperature under

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