Fluorolube provides advantages as the mulling agent, since it is transparent in the region 1400–4000 cm^{-1}, where absorptions due to hydrogen bonding are observed.

Registry No. R_2Y (R = diethylammonium; Y = fumarate), 6270-48-0; R_2Y (R = *tert*-butylammonium; Y = fumarate), 79722-95-5; R_2Y (R = *n*-butylammonium; Y = fumarate), 79722-96-6; R_2Y (R = *tert*-butylammonium; Y = adipate), 79722-97-7; RHY (R = piperidinium; HY = adipate), 29867-86-5; RHY (R = diethylammonium; HY = adipate), 72357-28-9; RHY (R = methylammonium; HY = adipate), 79722-98-8; RHY (R = dimethylammonium; HY = adipate), 79722-99-9; RHY (R = diisopropylammonium; HY = adipate), 79723-00-5; RHY (R = *N*-ethylpiperidinium; HY = adipate), 79723-01-6; RHY (R = tetramethylammonium; HY = phthalate), 79723-02-7; RHY (R = triethylammonium; HY = phthalate), 79723-03-8; RHY (R = *tert*-butylammonium; HY = phthalate), 79723-04-9; RHY (R = diisopropylammonium, HY = phthalate), 79723-05-0; RHY (R = piperidinium; HY = fumarate), 79723-06-1; RHY (R = *n*-butylammonium; HY = fumarate), 79723-07-2; RHY (R = tetraethylammonium; HY = fumarate), 79723-08-3; RHY (R = tri-*n*-propylammonium; HY = fumarate), 79723-09-4; RHY (R = piperidinium; HY = maleate), 31754-76-4; RHY (R = tetramethylammonium; HY = maleate), 67037-15-4; RHY (R = *tert*-butylammonium; HY = maleate), 79723-10-7; RH_3Y_2 (R = tetramethylammonium; H_3Y_2 = fumarate), 79723-11-8; RH_3Y_2 (R = tetramethylammonium; H_3Y_2 = maleate), 79723-12-9; RH_3Y_2 (R = tetramethylammonium; H_3Y_2 = phthalate), 79723-13-0; RH_3Y_2 (R = tetraethylammonium; H_3Y_2 = phthalate), 79723-14-1; RH_3Y_2 (R = tri-*n*-propylammonium; H_3Y_2 = glutarate), 79723-15-2; $R_2H_4Y_3$ (R = *tert*-butylammonium; H_4Y_3 = fumarate), 79723-16-3; $R_2H_4Y_3$ (R = tetraethylammonium; H_4Y_3 = fumarate), 79723-17-4; $R_2H_4Y_3$ (R = tri-*n*-propylammonium; H_4Y_3 = adipate), 79723-18-5; $R_2H_4Y_3$ (R = *N*-ethylpiperidinium; H_4Y_3 = succinate), 79723-19-6.

Stereoselective Control in the Alkylation and Annelation of Anions and Dianions Derived from 5-Norbornene-2,3-dicarboximides

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Received September 23, 1981

Lithiation of *endo*- (**1**) or *exo*-4-phenyl-4-azatricyclo[5.2.1.$0^{2,6}$]hex-8-ene (**2**) with 2 equiv of lithium diisopropylamide gives a common dilithiated species which methylates predominantly from the side of the one-carbon bridge. Lithiation of **1** and **2** with 1 equiv of *i*-Pr_2NLi gives different monolithiated species which methylate on opposite faces to give the products in which the cis stereochemistry of the ring function is retained. Sequential annelation of **1** and **2** with α,ω-dihalides involving formation of the monoanion, alkylation, formation of the alkylated monoanion, and intramolecular alkylation gives products in which the original stereochemistry of the product is retained. However, in the case of **2**, the isomer with opposite stereochemistry is also obtained, presumably because of the formation of the dianion. *endo*-10,10-Diethoxy-4-phenyl-4-azatricyclo[5.2.1.$0^{2,6}$]hex-8-ene (**14**) gives a dilithiated species which methylates predominantly from the two-carbon bridge face, presumably because of the steric protection afforded by the ethoxy groups. Annelation of this species with 1,3-dibromopropane gives the product derived from reaction on the two-carbon bridge face and annelation with 1,4-dichlorobut-2-ene also gives predominantly the product resulting from attack on that side.

Significant progress in the stereochemical control of organic reactions has been one of the major achievements in synthetic technology over the last three decades.[1] Such control depends on the adjustments of very small energy differences, usually no more than a few tens of kilojoules, and that such small differences in energy can be manipulated reflects both on the nature of organic reactions and the skill of organic chemists. We herein describe studies on the alkylation, including annelation, of anions and dianions derived from norbornene-2,3-dicarboximides which illustrates how ring strain and steric bulk can be employed to control the products obtained from these systems.

Methylation Studies

The *endo*- and *exo*-5-norbornene-2,3-dicarboximides (*endo*-**1**[2] and *exo*-**2**[3]) were prepared by known methods and each isomer was separately treated with 2 molar equiv of lithium diisopropylamide in THF below −100 °C.[4] After standing at this temperature for 30 min, the solutions were allowed to warm to the desired higher temperatures and were then treated with excess MeI. The reaction products were isolated, and the composition of the product mixtures is shown in Table I.

Table I

imide precursor	rctn temp,[a] °C	products (% yields)
1	−100	4 (30), 5 (2), 1 (13), 6 (15)
	−70	4 (50), 5 (8), 1 (10)
	−30	4 (50), 5 (8)
2	−100	4 (16), 5 (5), 2 (18), 7 (20)
	−70	4 (20), 5 (10), 2 (15)
	−30	4 (25), 5 (5)

[a] See Experimental Section for details of experimental conditions.

(1) See Woodward, R. B. In "Perspectives in Organic Chemistry"; Todd, A. R., Ed.; Interscience: New York, 1956; p 155. Izumi, Y.; Tai, T. "Stereodifferentiating Reactions"; Academic Press: New York, 1977; Ziegler, F. E. *Acc. Chem. Res.* **1977**, *10*, 227. Stevens, R. F. *Ibid.* **1977**, *10*, 193. Meyers, A. I. *Ibid.* **1978**, *11*, 375. Hanessian, S. *Ibid.* **1979**, *12*, 159. Oppolzer, W.; Snieckus, V. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 476. Heathcock, C. H.; Pirrung, M. C.; Buse, C. T.; Hagen, J. P.; Young, S. D.; Sohn, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 7077. Evans, D. A.; Nelson, J. V. *Ibid.* **1980**, *102*, 774.

(2) Wilder, P.; Culberson, C. F. *J. Am. Chem. Soc.* **1959**, *81*, 2021.

(3) Craig, D. *J. Am. Chem. Soc.* **1951**, *73*, 4889.

(4) For our earlier studies on dilithiated vicinal dianions, see Bilyard, K. G.; Garratt, P. J. *Tetrahedron Lett.* **1981**, *22*, 1755 and references therein. Our studies on lithiated cyclic imides will be reported elsewhere.

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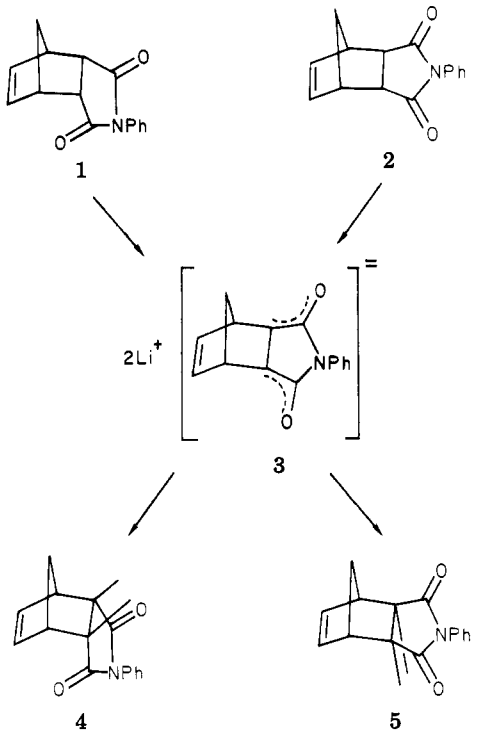
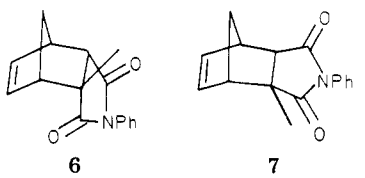
The structures of the products were assigned on the basis of the ^1H NMR spectra and by chemical correlation (vide infra).



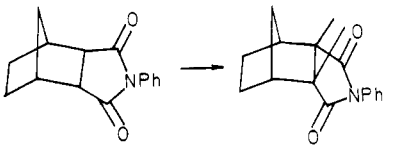
It can be seen from Table I that at all except the lowest temperature the products derived by methylation of the dianion produced from either 1 or 2 have approximately the same composition. Given the difficulty of exactly reproducing the reaction conditions, one can presume that the same dilithiated species (e.g., 3) is obtained from both 1 and 2. This dianion, as can be seen from the table, prefers to methylate from the side of the one-carbon bridge, although this preference is not large (4/5, ca. 5:1).

At −100 °C, besides the dimethylated products, monoethylated derivatives are also obtained. Significantly, the monomethylated product 6 obtained from the reaction of 1 is different from the monomethylated product 7 obtained from 2. It thus appeared probable that the stereochemistry of the product is related to the stereochemistry of the precursor and that these monomethylated compounds are derived from the corresponding monolithiated species. A variety of conditions were investigated in an attempt to generate the monoanion in high yield free from the dianion or precursor at a temperature at which methylation (and alkylation) would occur at a reasonable rate. The best procedure found for generation of the monolithiated species consisted of adding a solution of i-Pr_2NLi in THF to a solution of 2 in THF at between −30 and 0 °C and then allowing the solution to stand for 30 min at the selected temperature. Treatment of the solution formed under these conditions with MeI gave a monomethyl derivative identical with 7. Reaction of 7 with i-Pr_2NLi followed by MeI gave 5.



The structures of 4 and 7 were confirmed by direct correlation with the products derived from the Diels–Alder reactions of cyclopentadiene with dimethylmaleic and methylmaleic anhydride, respectively.[5] A comparison of the ^1H NMR spectra of 6 and 7 with those of 1 and 2 shows that the proton on the ring junction of the endo derivatives 1 and 6 resonate at δ 3.42 and 3.50, whereas these protons of the exo derivatives 2 and 7 resonate at δ 2.86 and 2.35. A similar comparison of the ^1H NMR spectra of 4 and 5 with those of 6 and 7 shows that the methyl group protons in the endo derivatives 5 and 7 resonate at δ 1.15 and 1.35, whereas these protons in the exo derivatives 4 and 6 resonate at δ 1.50 and 1.60.[6] Small differences in the chemical shifts of the olefinic and N-phenyl protons can also be observed between the two classes of derivative.

It has been assumed that the preference for methylation on the one-carbon bridge side in the dianion arises because of greater steric protection afforded by the two-carbon bridge. This concept receives substantiation from the finding that the dianion prepared from the saturated system 8, in which the steric protection of the two-carbon bridges is considerably enhanced, is methylated exclusively from the one-carbon bridge side to give 9. The structure of 9 was correlated with 4 by hydrogenation of the latter compound.



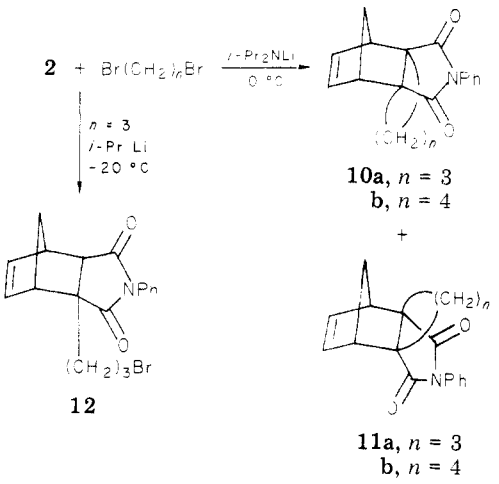
Annelation of 2. The absence of trans dimethylated products from the methylation of the dianion 3 suggests that ring strain in the monoethylated precursor is sufficient to direct the second methylation to the same side as the first. From the experiments in the formation and methylation of the monoanion derived from 2, described above, it appeared possible that the direction of annelation by α,ω-dihalides could be controlled if it was conducted in a stepwise manner.

The stepwise process requires the formation of the monoanion and its method of generation was described above. Unfortunately, with the bulkier alkylating agents the rate of reaction greatly decreased and under the conditions described for methylation little or no alkylated products were formed. After some considerable experimentation it was found that the most satisfactory results were obtained by treating a mixture of 2 and the dihalide in THF at 0 °C with a solution of i-Pr_2NLi at 0 °C when a mixture of the annelated products 10 and 11 were obtained in the ratio ca. 2:1.

The structures assigned to 10 and 11 are based on the ^1H NMR spectra and the major formation of 11a when the dianion is annelated (vide infra). Comparison of the ^1H NMR spectra of 10a and 11a shows the olefinic protons in 10a at lower field (δ 6.42) than those of 11a (δ 6.31) as are the bridgehead protons (δ, 3.23, cf. δ 3.12), and the phenyl region also shows the typical difference between endo and exo annelated systems. When the reaction with 1,3-dibromopropane was carried out at −20 °C, then the monoalkylated derivative 12 (together with some 2) was obtained but none of the annelated product.

(5) Diels, O.; Alder, K. *Chem. Ber.* **1929**, *62*, 554. Shenk, G. O.; Kuhler, J.; Krauch, C. H. *Ann. Chem.* **1966**, *693*, 20. Diels, O.; Alder, K. *Ann. Chem.* **1928**, *460*, 98.

(6) These chemical shift differences conform to the known differences in 4-methylnorbornenes: Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon: Oxford, 1969; p 84.



12

10a, n = 3
b, n = 4

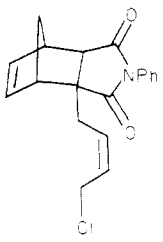
+

11a, n = 3
b, n = 4

We presume that **11** is obtained in these reactions because of the partial formation of the dianion due to the slowness of the alkylation reaction. Unfortunately, the balance between the rates of alkylation and deprotonation are fine, and although the monoanion can be formed exclusively at lower temperatures, the rate of alkylation is very slow and other unwanted reactions intrude. An attempt to carry out the reaction sequentially gave only a low yield of product (<5%). It may be possible to increase the ratio of **10**/**11** by adding the i-Pr_2NLi over a long period, but this has not been investigated.

In order to estimate the extent of the control of product being exerted by the stepwise process, we treated **2** with 2 equiv of i-Pr_2NLi and then with 1,3-dibromopropane. The two isomers **10a** and **11a** were obtained, and the ratio was estimated by a combination of preparative TLC and ^1H NMR spectroscopy to be ca. 1:15.

The annelation of **2** with *cis*-1,4-dichlorobut-2-ene was next examined. The conditions used for the α,ω-dibromoalkanes gave only low yields of products (<10%), and a two step sequence was therefore examined. The monoanion derived from **2** was treated with *cis*-1,4-dichlorobut-2-ene in THF when **13** was isolated in 49% yield, based on recovered starting material. However, all attempts to complete the ring closure failed, probably because of the acidity of the allylic protons which provided an alternative reaction pathway.



13

Although the effect of ring strain can be utilized to direct alkylation and annelation in these systems, its usefulness is clearly circumscribed. The increase in steric protection afforded on going from an unsaturated to a saturated two-carbon bridge (**2** to **8**) encouraged us to examine derivatives in which the steric bulk of the one-carbon bridge had been increased.

Annelation of 7,7-Diethoxynorborn-5-ene-2,3-dicarboximide (14). The endo adduct **14** was prepared by Diels–Alder addition of 5,5-diethoxycyclopentadiene[7] to *N*-phenylmaleimide. Treatment of **14** with 2 equiv of i-Pr_2NLi in THF gave a solution of the dianion **15** which, on quenching with excess MeI, gave a mixture (1:1) of the dimethylated derivatives **16** and **17** (Scheme I).

Clearly, the increased size of the substituents on the one-carbon bridge has a considerable influence on the direction of attack, removing the previous ca. 5:1 preference for exo addition. Methylation studies probably underestimate the effect since treatment of the dianion with 1,3-dibromopropane gives almost exclusively (>95%) the product **18** in which annelation has occurred from the two-carbon bridge face. The preferred direction of attack has thus been reversed as compared to the unsubstituted dianion.

Treatment of **15** with *cis*-1,4-dichlorobut-2-ene gave a 5:1 mixture (30%) of **19** and **20** from which **19** was readily isolated by crystallization. The ^1H NMR spectrum of **19** shows the expected nonequivalence of the cyclohexene ring methylene protons and the remainder of the spectrum is in accord with the assigned structure.

Discussion

Treatment of either **1** or **2** with 2 equiv of lithium diisopropylamide gives a species which has the properties of the dimetalated compound **3**. This is most likely to be in the dienolate form illustrated although the lithium atoms are almost certainly strongly covalently attached to the oxygen atoms, the molecule having much less ionic character than shown. ^{13}C NMR spectroscopic studies on related dilithiated cyclic imides are most readily interpreted by this type of structure.[8] Such a structure presumably gains some advantage both from the resulting pyrrole-type ring and from the localization of charge on the well-separated oxygen atoms. The preferred alkylation of this species from the one-carbon bridge side is indicated from models, the hydrogen on the one-carbon bridge being relatively remote from the sites of alkylation. In the saturated analogue **8**, the difference between the two bridges is accentuated since the protons on the two-carbon bridges are now positioned over the alkylating sites and the virtually exclusive attack from the one-carbon bridge side is readily explained. For the dimetalated diethoxy derivative **14**, one of the preferred conformations of the ethoxy groups appears to be that in which the methylene hydrogens of the ethyl group syn to the imide ring shield the potential sites of alkylation. Steric protection can thus again account for the preponderance of attack from the two-carbon bridge face.

No products were observed arising from O-alkylation or from alkylation at carbon bearing oxygen, the latter case having been observed by Flynn[9] for dilithiated *N*-methylphthalimide. Such alkylation in the *N*-methylphthalimide case restores the aromatic sextet of the benzene ring and may explain the occurrence of this mode of attack in that system. We have not observed such alkylation in any of the cyclic imides which we have dimetalated, but all of our experiments have been carried out in THF as solvent, with or without HMPA, rather than in liquid NH_3, which Flynn used.

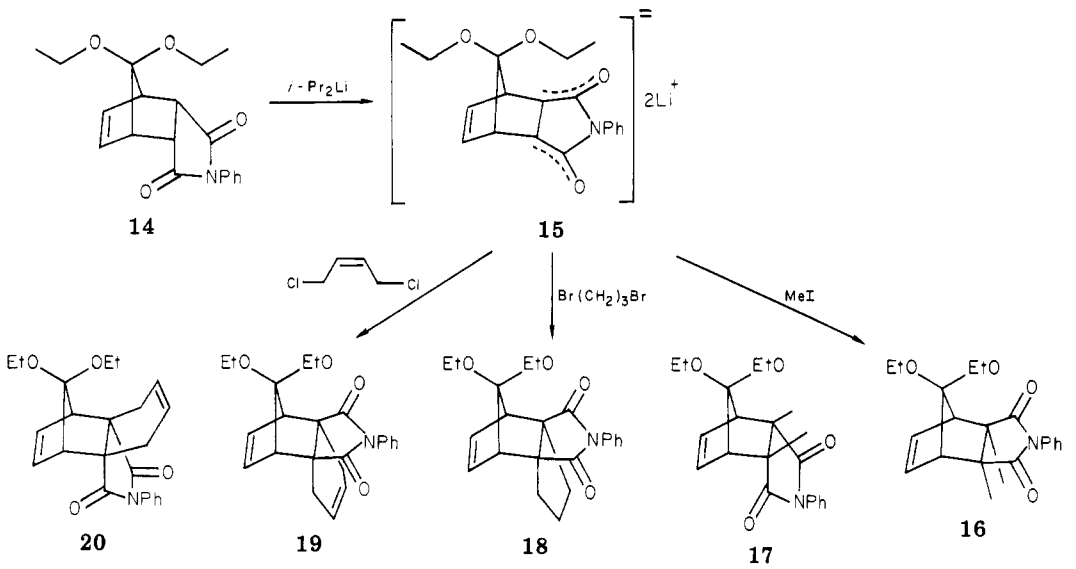
In the case of the monometalated derivatives of **1** and **2** alkylation is forced to occur on the same side as the proton remaining on the ring junction of the imide so that the cis ring junction is retained. Unfortunately with simple α,ω-dihaloalkanes the rate of reaction with these dianions is slow, and conditions were not found which gave only the desired annelated compound unaccompanied by its unwanted isomer. The latter presumably arises from the

(7) Eaton, P. E.; Hudson, R. A. *J. Am. Chem. Soc.* **1965**, *87*, 2769.

(8) Bilyard, K. G., unpublished experiments.

(9) Flynn, G. A. *J. Chem. Soc., Chem. Commun.* **1980**, 862.

Scheme I



generation of the dianion under the conditions used. With *cis*-1,4-dichlorobut-2-ene the first alkylation proceeds smoothly, but there appears to be a competitive process which subverts the second, intramolecular alkylation. This alternative reaction probably involves elimination from the allyl chloride introduced into **13** since *cis*-1,4-dichlorobut-2-ene readily eliminates HCl under basic conditions.

We continue to explore methods of using the monoanions to control the direction of annelation, but the superiority of steric control in the present examples has encouraged us to attempt to utilize this approach for the synthesis of more complex molecules. Ways of increasing the reaction yields, which have not been optimized in the examples described, are also being actively investigated.

Experimental Section

^{1}H NMR spectra were obtained on either a Varian T-60 or XL-200 spectrometer and are reported in δ units in $CDCl_3$ as solvent, using Me_4Si as internal standard. Mass spectra were obtained on a VG 7000-G spectrometer and IR spectra on a Perkin-Elmer 177 spectrometer. Melting points were taken on a Kofler hot-stage melting point apparatus and are uncorrected. Unless otherwise stated, reactions were worked up by addition to water and extraction with ether. The ethereal extract was washed with water and saturated $NaHCO_3$ and dried. After preliminary filtration through silica gel the reaction products were separated on a Harrison Chromatotron using SiO_2 (2 mm) coating on the disks.

Treatment of the Imides with Lithium Diisopropylamide. *n*-BuLi (6.6 cm^3, 5 mmol) was added to a stirred solution of diisopropylamine (0.75 cm^3, 6 mmol) and hexamethylphosphonamide (HMPA; 1.2 cm^3, 7 mmol) in THF (20 cm^3) at 0 °C under N_2. After being stirred for a further 30 min, the mixture was cooled to −115 °C and the imide (**1** or **2**, 1.20 g, 5 mmol) in THF (10 cm^3) was added over 10 min. The mixture was maintained at −115 °C for a further 30 min.

Reaction of the Lithiated Imide with MeI. The lithiated imide solution prepared as above was allowed to warm to the desired reaction temperature and then a solution of MeI (3.30 g, 2.3 mmol) in THF (2 cm^3) at the same temperature was added. The mixture was allowed to warm to room temperature and worked up. Elution from the Chromatotron used an ether/pentane gradient with initial composition of 1:10. Recovery of material was 50–60%, but the more polar components were not identified. The yields and product distribution is given in Table I.

***endo*-2,6-Dimethyl-4-phenyl-4-azatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (4):** colorless crystals, mp 107–109 °C; mass spectrum, *m/e* 267 (M$^+$, 12), 210 (M$^+$ − 66, 100), 66 (M$^+$ − 201, 56); ^{1}H NMR δ 7.47–7.34, 7.19–7.14 (m, 5 H), 6.28 (t, 2 H), 2.99 (m, 2 H), 1.92 (ddd, 1 H, J = 9.3 Hz), 1.74 (ddd, 1 H, J = 9.3, 1.7 Hz), 1.48 (s, 6 H); ^{13}C NMR δ 179.7, 135.7, 131.7, 128.7, 128.2, 126.3, 53.0, 52.6, 48.2, 18.1.

Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.30; H, 6.43; N, 5.19.

***exo*-2,6-Dimethyl-4-phenyl-4-azatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (5):** colorless crystals, mp 188–189 °C; mass spectrum, *m/e*, 267 (M$^+$, 41), 202 (M$^+$ − 65, 44), 201 (M$^+$ − 66, 100), 66 (M$^+$ − 201, 60); ^{1}H NMR δ 7.60–7.25 (m, 5 H), 6.50 (t, 2 H), 3.10 (m, 2 H), 1.55 (m, 2 H), 1.15 (s, 6 H); ^{13}C NMR δ 180.4, 136.6, 131.7, 128.7, 126.0, 53.5, 51.6, 44.4, 16.6.

Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 75.93; H, 6.31; N, 5.13.

***endo*-2-Methyl-4-phenyl-4-azatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (6):** colorless crystals, mp 108–110 °C; mass spectrum, *m/e*, 253 (M$^+$, 47), 66 (M$^+$ − 187, 100); ^{1}H NMR δ 7.55–7.10 (m, 5 H), 6.50–6.20 (m, 2 H), 3.50 (br s, 1 H), 3.10–2.90 (m, 2 H), 1.80 (m, 2 H), 1.60 (s, 3 H); ^{13}C NMR δ 179.5, 175.9, 136.4, 133.9, 131.7, 128.6, 128.0, 126.3, 52.5, 52.2, 51.0, 45.5, 21.1.

Anal. Calcd for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.37; H, 5.93; N, 5.44.

***exo*-2-Methyl-4-phenyl-4-azatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (7):** colorless crystals, mp 154–155 °C; mass spectrum, *m/e*, 253 (M$^+$, 18), 188 (M$^+$ − 65, 50), 187 (M$^+$ − 66, 100), 66 (M$^+$ − 187, 80); ^{1}H NMR δ 7.60–7.30 (m, 5 H), 6.50 (t, 2 H), 3.45 (m, 1 H), 3.20 (m, 1 H), 2.35 (br s, 1 H), 1.65 (br s, 2 H), 1.35 (s, 3 H).

Anal. Calcd for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N. 5.53. Found: C, 75.74; H, 5.85; N, 5.42.

Reaction of 8 with *i*-Pr$_2$NLi and MeI. A solution of *i*-Pr$_2$NLi (5 mmol) in THF (20 cm^3) was cooled to −80 °C and the imide **8** (0.45 g, 2.0 mmol) in THF (5 cm^3) was added over 10 min and the mixture stirred for a further 30 min. MeI (3.30 g, 23.0 mmol) in THF (2 cm^2) was then added and the mixture allowed to warm to room temperature. Workup gave **9**: colorless crystals, 0.27 g (55%), mp 115–117 °C; mass spectrum, *m/e*, 269 (M$^+$, 100), 203 (M$^+$ − 66, 71), 202 (M$^+$ − 67, 87), 94 (M$^+$ − 175, 89); ^{1}H NMR δ 7.55–7.20 (m, 5 H), 2.40 (m, 2 H), 2.20–1.30 (m, 4 H), 1.55 (br s, 4 H), 1.30 (s, 6 H).

Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11;, N, 5.20. Found: C, 75.48; H, 7.09; N, 5.11.

Hydrogenation of 4. Compound **4** (0.180 g, 0.67 mmol) was dissolved in a mixture of CH_3OH and $CHCl_3$ (4:1, 20 cm^3), Pd/C (10%, 0.100 g) was added, and the mixture was stirred under H_2 until no more gas was absorbed. The catalyst was removed by filtration and the filtrate evaporated to leave **9**, recrystallized from CH_3OH, white crystals, 0.100 g (56%), mp 115–117 °C, identical in all observed respects with the previous sample.

Reaction of 2 with *i*-Pr$_2$NLi and 1,3-Dibromopropane. a. By Formation of the Monoanion. A solution of *i*-Pr$_2$NLi (6 mmol) was added dropwise over 30 min to a solution of **2** (0.60 g, 2.5 mmol) and 1,3-dibromopropane (0.27 cm^3, 2.5 mmol) in THF

(40 cm^3) at 0 °C under N_2. The mixture was stirred for a further 30 min and then worked up to give **10a** and **11a**. **10a**: 0.22 g (33%), colorless crystals, mp 187–189 °C; mass spectrum, *m/e* 279 (M^+, 34), 214 (M^+ – 65, 44), 213 (M^+ – 66, 100), 184 (M^+ – 95, 15), 141 (M^+ – 138, 13), 77 (M^+ – 202, 17), 66 (M^+ – 213, 45); ^1H NMR δ 7.52–7.39, 7.32–7.27 (m, 5 H), 6.43–6.41 (t, 2 H), 3.24–3.22 (t, 2 H), 2.14 (dd, 2 H), 1.89 (br s, 2 H), 1.87–1.43 (m, 4 H).

Anal. Calcd for $C_{18}H_{17}NO_2$: C, 77.40; H, 6.13, N, 5.01. Found: C, 77.21; H, 6.24; N, 4.91.

11a: 0.090 g (14%), colorless crystals, mp 122–123 °C; mass spectrum, *m/e* 279 (M^+, 40), 214 (M^+ – 65, 17), 213 (M^+ – 66, 100), 184 (M^+ – 95, 19), 169 (M^+ – 110, 12), 141 (M^+ – 138, 14), 132 (M^+ – 147, 11), 77 (M^+ – 202, 12), 66 (M^+ – 213, 30); ^1H NMR δ 7.52–7.35, 7.22–7.14 (m, 5 H), 6.30 (t, 2 H), 3.11 (m, 2 H), 2.38 (ddd, 2 H), 2.18–1.54 (m, 4 H).

Anal. Calcd for $C_{18}H_{17}NO_2$: C, 77.40; H, 6.13; N, 5.01. Found: C, 77.14; H, 6.15; N, 5.01.

b. By Formation of the Dianion. A solution of *i*-Pr_2NLi (6 mmol) in THF (10 cm^3) was added over 10 min to a stirred solution of **2** (0.60 g, 2.5 mmol) in THF (40 cm^3) at –30 °C under N_2. The solution was allowed to warm to 0 °C and was stirred for a further 30 min. 1,3-Dibromopropane (0.27 cm^3, 2.5 mmol) was then added and stirring continued for 1 h. The reaction was worked up to give an oil (600 mg) which after separation on the Chromatotron gave **10a**/**11a** (ca. 1:15; 180 mg, 30%); early products contained **10a**, and later fractions were pure **11a** identical in all observed respects with **11a** above.

Reaction of 2 with *i*-Pr_2NLi and 1,4-Dibromobutane. A solution of *i*-Pr_2NLi (6 mmol) was added dropwise over 30 min to a solution of **2** (0.60 g, 2.5 mmol) and 1,4-dibromobutane (0.30 cm^3, 2.5 mmol) in THF (40 cm^3). The reaction was worked up to give **10b**: 0.18 g (28%), colorless crystals, mp 164–165 °C; mass spectrum, *m/e* 293 (M^+, 4), 227 (M^+ – 66, 100), 182 (M^+ – 111, 5), 66 (M^+ – 227, 18); ^1H NMR δ 7.54–7.34, 7.32–7.24, (m, 5 H), 6.37 (t, 2 H), 3.14 (t, 2 H), 2.16 (ddd, 2 H), 1.76–0.96 (m, 8 H).

Anal. Calcd for $C_{19}H_{19}NO_2$: C, 77.79; H, 6.53; N, 4.77. Found: C, 78.07; H, 6.61; N, 4.71.

Reaction of 2 with *i*-Pr_2NLi and 1,4-Dichlorobut-2-ene. A solution of *i*-Pr_2NLi (3 mmol) was added dropwise over 5 min to a stirred solution of **2** (0.60 g, 2.5 mmol) in THF (40 cm^3) at –60 °C. The mixture was allowed to warm to –30 °C and was stirred at this temperature for 2 h. The mixture was then cooled to –80 °C and *cis*-1,4-dichlorobut-2-ene (0.25 cm^3, 2.5 mmol) was added and the mixture allowed to warm to 0 °C and was maintained at this temperature for 1 h. The mixture was then worked up to give **13**, 0.18 g (49%, based on recovered **2**, 0.27 g), colorless crystals, mp 137–138 °C; mass spectrum, *m/e* 329, 327 (M^+, 1:3, 21), 292 (M^+ – 37, 52), 261 (M^+ – 68, 39), 226 (100), 66 (94); ^1H NMR δ 7.51–7.39, 7.26–7.20 (m, 5 H), 6.44 (ABXY, 2 H), 5.71 (ABXY, 2 H), 4.06 (ABXY, 2 H) 3.37 (m, 1 H), 3.21 (m, 1 H), 2.90 (ddd, 1 H), 2.47 (m, 1 H), 2.10 (ddd, 1 H), 1.64 (ABXY, 2 H).

Anal. Calcd for $C_{19}H_{18}NO_2Cl$: C, 69.62; H, 5.53; N. 4.27; Cl, 10.82. Found: C, 69.54; H, 5.68; N, 4.19; Cl, 10.88.

Reaction of 1,1-Diethoxycyclopentadiene with *N*-Phenylmaleimide. 1,1-Diethoxycyclopentadiene[7] [ca. 19 mmol, prepared from 4,4-diethoxycyclopentanone[7] (5.0 g, 32 mmol)] in petroleum ether (200 cm^3) was added to a solution of *N*-phenylmaleimide (3.6 g, 20 mmol) in ether (50 cm^3). The mixture was stirred for 2 h, the solvent removed by evaporation, and the residue triturated with Et_2O (40 cm^3) to give **14**: white solid, 3.35 g (54%), mp 179–180 °C; mass spectrum, *m/e* 327 (M^+, 2), 298 (M^+ – 29, 33), 252 (M^+ – 75, 56), 119 (M^+ – 209, 56), 79 (46), 78 (50), 77 (26), 29 (100); ^1H NMR δ 7.44–7.36, 7.17–7.12 (m, 5 H), 6.26 (t, 2 H), 3.58–3.38 (m, 8 H), 1.25–1.12 (m, 6 H).

Anal. Calcd for $C_{19}H_{21}O_4N$: C, 69.71; H, 6.47; N, 4.28. Found: C, 69.33; H, 6.43; N, 4.20.

Reaction of 14 with *i*-Pr_2NLi and MeI. A solution of *i*-Pr_2NLi (3 mmol) in THF (5 cm^3) was added to a solution of **14** (0.33 g, 1 mmol) in THF (20 cm^3) at –30 °C under N_2. The solution was stirred at –30 °C for 10 min and then allowed to warm to 0 °C and maintained at that temperature for 30 min. MeI (0.5 cm^3, 8 mmol) was then added and stirring was continued for a further 30 min. After workup, the brown oil was chromatographed on SiO_2, eluting with ether to give a pale yellow oil: 0.35 g; ^1H NMR δ 7.65–7.12 (m, 4.6 H), 6.50–6.23 (overlapping ddd, 1.64 H), 3.84–3.00 (m, 6.25 H), 1.62 (s, 2.38 H), 1.50–0.85 (m, 10.1 H).

Reaction of 14 with *i*-PrNLi and 1,3-Dibromopropane. A solution of *i*-PrNLi (3 mmol) in THF (5 cm^3) was added to a stirred solution of the imide **14** (0.33 g, 1 mmol) in THF (20 cm^3) at –30 °C under N_2. The mixture was stirred for 10 min and then allowed to warm to 0 °C and stirred for a further 1 h. The reaction mixture was worked up to give a red oil which was chromatographed on SiO_2, eluting with ether to give a solid (0.380 g), recrystallized from ether as **18**: colorless crystals, 0.090 g (25%), mp 183–186 °C; mass spectrum, *m/e*, 367 (M^+, 11), 265 (M^+ – 102, 16), 119 (M^+ – 248, 57), 118 (M^+ – 249, 100), 117 (M^+ – 250, 29), 91 (35), 29 (76); ^1H NMR δ 7.47–7.34 (m, 5 H), 6.35 (t, 2 H), 3.45–3.37 (m, 6 H), 2.17–2.14 (m, 2 H), 1.66–1.60 (m, 4 H), 1.12 (t, 3 H), 0.97 (t, 3 H).

Anal. Calcd for $C_{22}H_{25}O_4N$: C, 71.92; H, 6.86; N, 3.81. Found: C, 71.71; H, 6.91; N, 3.72.

Reaction of 14 with *i*-Pr_2NLi and 1,4-Dichlorobut-2-ene. A solution of *i*-Pr_2NLi (3 mmol) was added to a stirred solution of **14** (0.33 g, 1 mmol) in THF (20 cm^3) at –30 °C under N_2. The mixture was stirred for 10 min and then allowed to warm to 0 °C and stirred for a further 30 min. *cis*-1,4-Dichlorobut-2-ene (0.18 g, 1.5 mmol) was added and the mixture stirred for a further 2 h. The reaction mixture was worked up to give a red oil which was chromatographed on SiO_2 to give a solid which was separated on the Chromatotron to give a mixture of **19** and **20** (4:1), 0.115 g (30%). Crystallization from ether/petroleum ether (40–60 °C) gave **19**: colorless crystals, 0.045 g (12%), mp 147–149 °C; mass spectra, *m/e*, 379 (M^+, 27), 252 (M^+ – 127, 21), 224 (M^+ – 155, 90), 131 (36), 130 (100), 129 (38), 77 (26), 29 (99); ^1H NMR δ 7.49–7.30 (m, 5 H), 6.36 (t, 2 H), 5.75 (t, 2 H), 3.50–3.33 (m, 6 H), 2.70 (ddd, 2 H), 2.15 (dd, 2 H), 1.12 (t, 3 H), 0.98 (t, 3 H).

Anal. Calcd for $C_{23}H_{25}O_4N$: C, 72.80; H, 6.64; N, 3.69. Found: C, 72.76; H, 6.71; N, 3.59.

Acknowledgment. We thank the Science Research Council (U.K.) for support.

Registry No. 1, 29377-36-4; **2**, 29377-36-4; **4**, 79733-70-3; **5**, 79681-19-9; **6**, 71214-84-1; **7**, 71214-85-2; **8**, 29910-09-6; **9**, 79703-85-8; **10a**, 79681-20-2; **10b**, 79681-21-3; **11a**, 79732-87-9; **13**, 79681-22-4; **14**, 79681-23-5; **16**, 79703-86-9; **17**, 79733-71-4; **18**, 79681-24-6; **19**, 79681-25-7; **20**, 79732-88-0; iodomethane, 74-88-4; 1,3-dibromopropane, 109-64-8; 1,4-dibromobutane, 110-52-1; *cis*-1,4-dichlorobut-2-ene, 1476-11-5; 1,1-diethoxycyclopentadiene, 2931-32-0; *N*-phenylmaleimide, 941-69-5.