43059-50-3; **5g**, 72903-62-9; **5h**, 72853-37-3; **5i**, 72853-38-4; **6a**, 39652-50-1; **6b**, 72853-39-5; **6f**, 72903-63-0; **7**, 78-84-2; **8**, 122-78-1; **9**, 70326-39-5; **10**, 432-25-7; **11**, 3917-41-7; **12**, 54226-17-4; **13**, 108-94-1; **14**, 79-77-6; **15**, 35217-21-1; **16**, 17298-18-9; **17**, 55848-91-4; **18**, 72853-40-8; **19**, 1658-21-5; **20a**, 30801-80-0; **20b**, 72853-41-9; **20b** acid, 72853-42-0; **20c**, 72853-43-1; **21a**, 72853-44-2; **21b**, 72853-45-3; **21c**, 72853-46-4; **22**, 72853-47-5; **23**, 72853-48-6; **24**, 72853-49-7; benzaldehyde, 100-52-7; methyl crotonate, 623-43-8.

Nitroethylene: A Stable, Clean, and Reactive Agent for Organic Synthesis

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Contrary to current belief, nitroethylene is a stable reagent and holds promise as a useful and reactive synthon. Nitroethylene can be prepared in 20–25-g lots, and standard, refrigerated solutions in common solvents provide a good and ready source of the reagent. The reagent purity can be easily monitored by titration against tetraphenylcyclopentadienone (tetracyclone) coupled with the isolation of the colorless crystalline adduct. With reactive substrates, nitroethylene reacts with greatest ease at low temperatures, leading to functionalized systems having potential for further elaboration. With systems that require heating, the limited stability of nitroethylene itself complicates the course of the reaction. Cyclopentadiene, 5-[(benzyloxy)methyl]cyclopentadiene, 5-(methoxymethyl)cyclopentadiene, 5-(1,3-dithianyl)cyclopentadiene, 5-(trimethylsilyl)cyclopentadiene, and spiroheptadiene readily gave (4 + 2) adducts with nitroethylene, each possessing attraction as a synthetic intermediate. Adducts from furan and acetoxyfulvene undergo rearrangement via σ cleavage. The (4 + 2) adduct from 9-diazofluorene spontaneously extrudes nitrogen, leading to spironitrocyclopropane. Indole readily undergoes Michael addition to give 80% 3-(nitroethyl)indole and 15% of novel bis adduct. The 2,6 Michael adduct arises with 1-morpholinocyclohexene, and β-pinene undergoes an ene reaction with nitroethylene. Novel 2-nitroethyl phosphonates, useful in Wittig–Horner reactions, arise from nitroethylene and phosphites in *tert*-butyl alcohol.

Nitroethylene figures only in a few (4 + 2) reactions[1] and a handful of Michael additions.[2] Having become familiar with handling quantities of nitroethylene in connection with our efforts in the prostaglandin area,[3] we thought that it would be worthwhile to possibly project this reagent as a useful synthon with the aim of making it more popular and acceptable.

In sharp contrast to reports that highlight its instability,[4] we have found that nitroethylene is stable as a standard solution in benzene for at least 6 months when stored in a refrigerator (~10 °C). Additionally, the highly characteristic NMR of nitroethylene (vide infra) is not changed at all under the above conditions, and the yield of isolated adducts with standards such as cyclopentadiene and tetracyclone is hardly affected during this period of storage.

Thus, 20–25-g batches of nitroethylene have been prepared in one lot and stored as a 10% solution in benzene at ~10 °C. Of the several methods that are available for the preparation of nitroethylene, in our hands, the phthalic

Table I. ^{1}H NMR Data for Nitroethylene[a] Adducts with Cyclopentadienes[b,c]

adduct	^{1}H NMR data[d]
1	6.4, 5.9 (2 q, olefinic), 5.0 (m, $HCNO_2$), 3.5, 3.0 (both br, bridgehead)[e]
2	6.32, 5.9 (2 q, olefinic), 5.1 (m, $HCNO_2$), 3.55, 2.92 (both br, bridgehead), 3.3 (d, J = 8 Hz, OCH_2CH), 3.3 (OCH_3)[f]
2a	6.45 (q), 5.75 (d) (olefinic), 5.13 (q, $HCNO_2$), 3.9 (dd, OCH_2C), 3.46 (OCH_3), 3.0 (br, bridgehead)[e]
3	7.28 (aromatic), 6.23, 5.8 (2 q, olefinic), 4.9 (m, $HCNO_2$), 4.4 (OCH_2Ph), 3.3 (d, J = 7 Hz, OCH_2CH), 3.42, 2.9 (both br, bridgehead)[e]
3a	7.25 (aromatic), 6.32 (q), 5.7 (d) (olefinic), 5.1 (q, $HCNO_2$), 4.6 (OCH_2Ph), 3.9 (dd, OCH_2C), 2.9 (br, bridgehead)[e]
4	6.3, 5.85 (2 q, olefinic), 4.97 (m, $HCNO_2$), 4.0 (d, J = 10.5 Hz, -H(S_2), 3.76, 3.15 (both br, bridgehead), 2.75 (m, S-CH_2)[f]
5	6.35, 5.9 (2 q, olefinic), 5.0 (m, $HCNO_2$), 3.6, 3.1 (both br, bridgehead), O($SiMe_3$)[e]
6	6.4, 5.95 (2 q, olefinic), 5.01 (m, $HCNO_2$), 0.52 (m, cyclopropane protons)[e]

[a] Nitroethylene: ^{1}H NMR δ 6.55 (dd, J = 7 and 15 Hz, $=C(NO_2)H$), 5.85 (dd, J = 15 and 2 Hz, syn H), 5.22 (br d, J = 7 Hz, anti H). [b] The adducts **1–6** exhibited IR (neat/KBr) ν_{max} 1534 ± 5 and 1368 ± 2 cm^{-1} for the nitro function. [c] For **7**, the tetraphenylcyclopentadienone–nitroethylene adduct: IR (KBr) ν_{max} 1786 (strained C=O), 1550, 1361 (nitro). [d] In δ with Me_4Si as internal standard. [e] CCl_4. [f] $CDCl_3$.

(1) M. M. Etienne, A. Spire, and E. Toromanoff, *Bull. Soc. Chim. Fr.*, 750 (1952); W. C. Wildman and C. H. Hemminger, *J. Org. Chem.*, **17**, 1641 (1952); K. Klager, *ibid.*, **20**, 650 (1955); W. E. Noland, H. I. Freeman, and M. S. Baker, *J. Am. Chem. Soc.*, **78**, 188 (1956); S. S. Novikov, G. A. Shvekgeimer, and A. A. Dudinskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 690 (1961); *Chem. Abstr.* **55**, 22166i (1961); N. L. Drake and C. M. Kraekel, *J. Org. Chem.*, **26**, 41 (1961); R. B. Kaplan and H. Shechter, *ibid.*, **26**, 982 (1961); J. Sims and K. N. Houk, *J. Am. Chem. Soc.*, **95**, 5798 (1973).

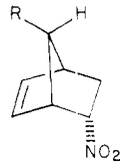
(2) M. Takabayashi, *Nippon Kagaku Kaishi*, **64**, 191 (1943); G. D. Buckley and C. W. Scaife, *J. Chem. Soc.*, 1471 (1947); A. Lambert, C. W. Scaife, and A. E. W. Smith, *ibid.*, 1474 (1947); R. L. Heath and A. Lambert, *ibid.*, 1477 (1947); R. L. Heath and H. A. Piggott, *ibid.*, 1481 (1947); R. L. Heath and J. D. Rose, *ibid.*, 1485, 1486 (1947); G. D. Buckley, *ibid.*, 1494 (1947); W. E. Noland and P. H. Hartman, *J. Am. Chem. Soc.*, **76**, 3227 (1954); H. Stetter and K. Hoehne, *Chem. Ber.*, **91**, 1344 (1958); R. M. Acheson and A. R. Hands, *J. Chem. Soc.*, 744 (1961); T. Yanami, M. Kato, and A. Yoshikoshi, *J. Chem. Soc., Chem. Commun.*, 726 (1975); D. Seebach, H. F. Leitz, and V. Ehrig, *Chem. Ber.*, **108**, 1924 (1975); D. Seebach, V. Ehrig, H. F. Leitz, and R. Henning, *ibid.*, **108**, 1946 (1975); P. N. Confolane, E. D. Lollar, G. Pizzolato, and M. R. Uskokovic, *J. Am. Chem. Soc.*, **100**, 6291 (1978).

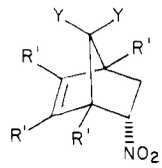
(3) S. Ranganathan, D. Ranganathan, and A. K. Mehrotra, *J. Am. Chem. Soc.*, **96**, 5261 (1974); *Tetrahedron Lett.*, 1215 (1975); S. Ranganathan, D. Ranganathan, and R. Iyengar, *Tetrahedron*, **32**, 961 (1976); S. Ranganathan, D. Ranganathan, and A. K. Mehrotra, *Synthesis*, 289 (1977).

(4) G. D. Buckley and C. W. Scaife, *J. Chem. Soc.*, 1471 (1947); K. Noma, T. Okumura, and T. Sone, *Kobunshi Kagaku*, **5**, 99 (1948).

0022-3263/80/1945-1185$01.00/0

Chart I[a]





1, R = H (100%)
2, R = CH_2OMe[b] (68%[c])
3, R = CH_2OCH_2Ph[b] (71%[c])

4, R = (35%[c])

5, R = $Si(Me)_3$ (44%[d])

6, R' = H; X, Y = CH_2CH_2 (89%)
7, R' = Ph; X, Y = O (91%)

[a] Spectral data (IR, ^1H NMR) for compounds 1–7 are presented in Table I. [b] In addition, the isomeric 1-(methoxymethyl)-2-*endo*-nitrobicycloheptene (2a, 6%) and 1-[(benzyloxy)methyl]-2-*endo*-nitrobicycloheptene (3a, 7%) were also isolated. [c] Yield based on a two-step sequence. The sensitive 5-substituted cyclopentadienes were not isolated. [d] Yield based on a three-step sequence from cyclopentadiene.

anhydride mediated dehydration of 2-nitroethanol gave consistently good results.[3,5] In all our studies the 2-nitroethanol was prepared conveniently from formaldehyde and nitromethane.[6]

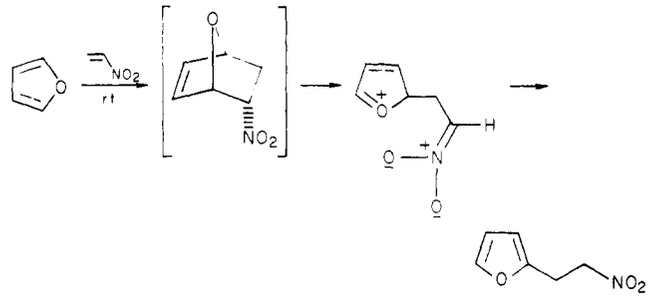
The recognition that (4 + 2) adducts involving 5-substituted cyclopentadienes are ideal starting points for further elaboration to prostaglandins led to a search for reactive 2 partners to obviate complications arising from isomerization of the sensitive 5-substituted cyclopentadienes.[7] Nitroethylene was indeed found to undergo (4 + 2) addition with cyclopentadiene even at −100 °C. For practical reasons, however, the additions involving sensitive 5-substituted cyclopentadienes were carried out at −15 °C and the others at around 0 °C. We believe that nitroethylene is an effective 2 component in cyclopentadiene cycloadditions, as illustrated with adducts 1–7 (Chart I). See Table I for spectral data on these adducts.

The further elaboration of **2** and **3** to prostanoids has been reported.[3] Of interest is the formation of crystalline adduct **4**, directly related to Corey aldehyde, from the novel 5-(1,3-dithianyl)cyclopentadiene. Parenthetically, the 1,3-dithiane unit in **4** will enable the preparation of diverse 7-substituted norbornenes.

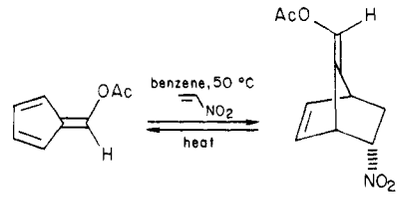
Among 5-substituted cyclopentadienes, the 5-trimethylsilyl derivative is unique in view of the extreme sluggishness with which it undergoes isomerization. This aspect coupled with an acid-induced regiospecific and stereospecific desilylation has recently led to a novel route to prostaglandins and loganin.[8] We have found that 5-(trimethylsilyl)cyclopentadiene readily undergoes (4 + 2) addition, leading to the novel 7-*syn*-(trimethylsilyl)-2-*endo*-nitrobicyclo[2.2.1]heptene (**5**). Compound **5** has potential for further elaboration to prostanoids[9] and 7-substituted 2-functionalized norbornenes.

The cyclopropane unit in the tricyclic spiro system **6** can, by either participation or rupture, lead to functionalized bicyclic systems possessing synthetic interest. The formation of **7** can be monitored by the disappearance of the pink color of the tetraphenylcyclopentadienone, and the isolation of the crystalline adduct serves as a reliable method to check standard refrigerated nitroethylene solutions.

The 2-*endo*-nitro group in adducts **1–7** inductively withdraws electronic charge from the allylic σ bond, and wherever the 1-bridgehead electron deficiency is further stabilized, either rearranged products are observed as illustrated with the formation of 2-(β-nitroethyl)furan (**8**) or there is clean thermal reversal, as exemplified with **9**.

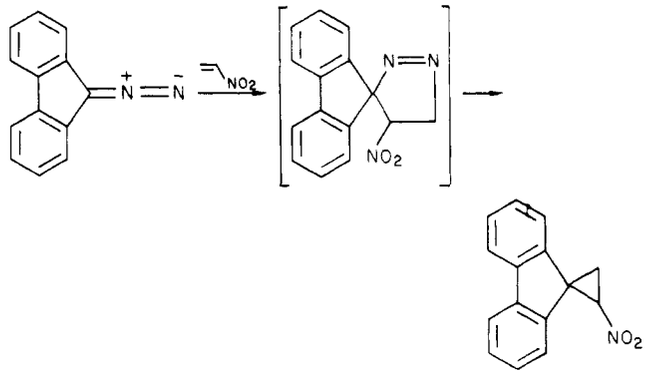


8



9

The inertness of thiophene under a variety of conditions toward nitroethylene supports the genesis of **8** via (4 + 2) addition rather than electrophilic substitution. After a short induction period, nitrogen is rapidly extruded on reaction of nitroethylene with 9-diazofluorene, leading to nitrocyclopropane **10** in 97% yields! Parenthetically, un-



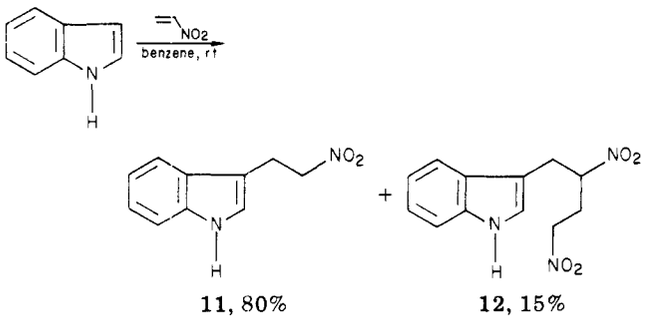
10

encumbered nitrocyclopropanes are rare, and the above reaction type should be general, leading to diverse nitrocyclopropanes.[10] As illustrative examples of enamines as nucleophiles in Michael addition, we chose to examine the reactions of indole and 1-morpholinocyclohexene. The reaction of indole with nitroethylene is of additional in-

(5) G. D. Buckley and C. W. Scaife, *J. Chem. Soc.*, 1471 (1947).
(6) W. E. Noland, *Org. Synth.*, 41, 67 (1961).
(7) For details see S. Ranganathan, D. Ranganathan, and A. K. Mehrotra, *Synthesis*, 289 (1977).
(8) D. W. A. Yeung and I. Fleming, *J. Chem. Soc., Chem. Commun.*, 79, 81 (1977).
(9) The transformation of **5** to prostanoids will be reported separately.

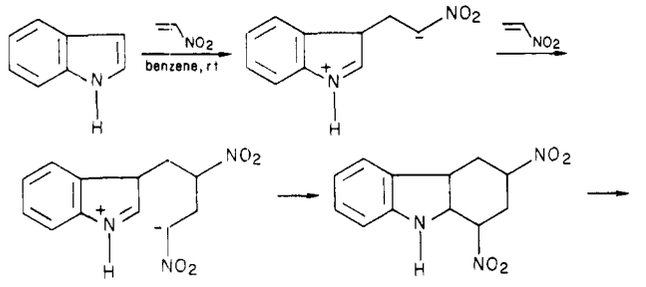
(10) 9-Diazafluorene has consistently shown a preference for spirocyclopropane formation with α,β-unsaturated systems. Its reaction with nitroethylene is noteworthy in the sense that at ambient temperatures, after a brief period, the evolution of nitrogen proceeds rapidly to produce the nitrocyclopropane **10**. 9-Diazofluorene reacts with PhCH=CHX (X = NO_2, COOEt, Ac, Bz) either in refluxing benzene or on prolonged standing at room temperature to yield spirocyclopropanes related to **10** (C. S. Panda, Ph.D. Thesis, Indian Institute of Technology 1972). However, diazomethane, diphenyldiazomethane, and diazoacetic ester form pyrazoles with substituted nitro olefins via group migration and HNO_2 loss [W. E. Parham and W. R. Hasek, *J. Am. Chem. Soc.*, **76**, 799 (1954); W. E. Parham and J. L. Bleasdale, *ibid.*, **73**, 4664 (1951); **72**, 3843 (1950)]. Diazomalonic ester did not react with nitroethylene even in refluxing benzene. A study relating to the possible generation of nitrosocyclopropanes and cyclopropylamines from **10** is in press.

terest as a route to tryptamines. Our results are in disagreement with those available concerning this reaction, which report a low yield (20%) of dimorphic adduct, mp 56.5–57 °C and 68–68.5 °C.[11] In our hands the desired tryptamine precursor **11**, mp 50–51 °C, was isolated in 80% yields along with 15% of the interesting bis adduct **12**, mp 100–101 °C. The spectral and analytical data leave little

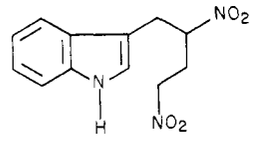


11, 80% **12**, 15%

doubt relating to the structure of the minor product. Its genesis, however, is intriguing, and the specific formation of **12** is rationalized on the basis of the initially formed

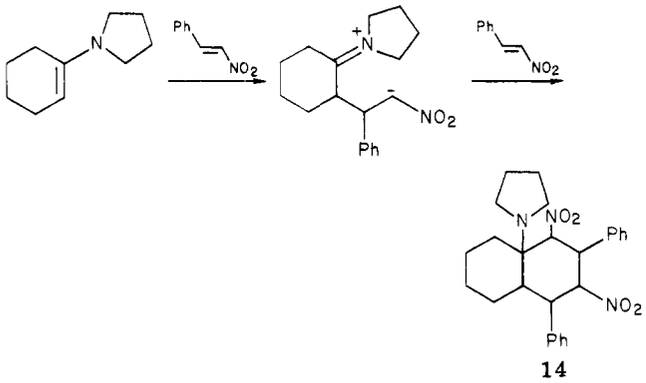


13



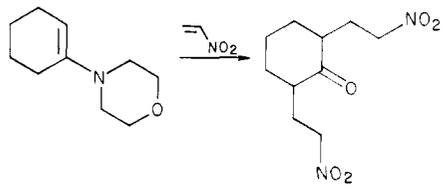
12

monoadduct accepting a second nitroethylene unit. The above pathway is similar to that involved in the reaction of 1-pyrrolidinocyclohexene with β-nitrostyrene[12] to give **14**. In the present case, however, the driving force for the



14

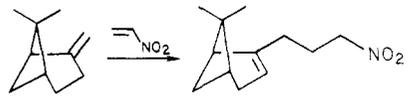
generation of the indole unit provides incentive for the further reactivity of **13**, which is analogous to **14**. A more direct possibility, namely, the addition of the second nitroethylene unit to **11**, is less attractive since attempts to effect the **12** → **11** change thermally and the **11** → **12** change with nitroethylene either thermally or in the presence of triethylamine led to unchanged starting material. 1-Morpholinocyclohexene, on the other hand, gave the novel crystalline 2,6 adduct **15**, which, in turn, could



15

provide ready access to a variety of useful systems by further elaboration. Cyclooctatetraene would be a logical substrate for cycloaddition with nitroethylene since the normal (4 + 2) adduct is suitable for further elaboration to systems such as basketene and Nenitzescu's hydrocarbon. In the event, however, the reaction was found to be complicated even at room temperature. Careful NMR analysis of the nitro-group-containing fraction showed that no (4 + 2) adduct was present.

We have explored the potential of nitroethylene in $_{\sigma}2_s + {}_{\pi}2_s + {}_{\pi}2_s$ processes. Thus β-pinene does undergo the ene reaction, leading to the desired product **16** in 90% yields.



16

A surprising discovery was made during the study of the action of nitroethylene with phosphites. In nonpolar solvents, the reactions were complicated, presumably due to extensive phosphite-initiated nitroethylene polymerization. In marked contrast, trimethyl phosphite gave a quantitative yield of 2-nitroethyl dimethyl phosphonate (**17**), a compound having application in Horner–Wittig

$$P(OMe)_3 + CH_2{=}CHNO_2 \xrightarrow{t\text{-BuOH}} (MeO)_2P(O)CH_2CH_2NO_2$$

17

reactions. Similar products are formed with triethyl, triisopropyl, and triphenyl phosphites.

On the debit side, no products could be isolated from nitroethylene and norbornadiene, α-pinene, camphene, Δ^3-carene, indene, and hexamethyl(Dewar benzene).

The real potential of nitroethylene would be in cases where the substrates are sufficiently reactive to undergo reaction under mild conditions. With recalcitrant substrates, where more forceful conditions might be required, the limited stability of the reagent would complicate the reactions.

We believe that the stability of nitroethylene in solution, coupled with its ability to undergo cycloadditions, Michael additions, and ene reactions, would kindle interest in this reagent. Additionally, the nitro group in the products could be used for a variety of transformations.

Experimental Section

General Methods. Melting points and boiling points are uncorrected. IR spectra were recorded on PE 137 and 580 instruments as neat liquids or KBr disks. NMR spectra were recorded on A-60 and HA-100 instruments, and chemical shifts are reported in δ units downfield from internal Me_4Si. Silica gel G (Stahl) was used for analytical and preparative TLC, and column chromatography was done on silica gel (BDH) columns prepared from its slurry in petroleum ether (60–66 °C). Reactions were monitored, wherever possible, by TLC.

Nitroethylene.[3,5] 2-Nitroethanol[6] (13.5 g, 0.15 mol) and resublimed phthalic anhydride (28 g, 0.225 mol) were mixed in a

(11) W. E. Noland and P. J. Hartman, *J. Am. Chem. Soc.*, **76**, 3227 (1954).

(12) S. K. Malhotra in "Enamines", A. G. Cook, Ed., Marcel Dekker, New York, 1969, p 19.

distillation unit equipped with a short fractionating column and an ice-cooled receiver. The apparatus was evacuated to 80 mm, and the bath temperature was maintained at 140–150 °C until the mixture was homogeneous and then increased and held at 175–180 °C until distillation ceased. The distillate was dried over $CaCl_2$ (anhydrous) to give 8.8 g (80%) of pale yellow nitroethylene which is suitable for further reactions. Nitroethylene as a solution in dry benzene was found to be stable (no change in NMR!) for at least 6 months when stored in a refrigerator.

2-*endo*-Nitronorbornene (1).[13] Under stirring and ice–salt cooling (−15 °C), a dry ether solution of nitroethylene (20 g, 0.273 mol) was added in drops to freshly cracked cyclopentadiene (60 g, 0.909 mol). The reaction mixture was allowed to stand overnight, the solvents were evaporated in vacuo, and the residue was distilled to give 39 g (99.6%) of 2-*endo*-nitronorbornene, bp 60–65 °C (1.8 mm).

7-*syn*-(Methoxymethyl)-2-*endo*-nitrobicyclo[2.2.1]heptene (2). 5-(Methoxymethyl)cyclopentadiene. Under N_2, chloromethyl methyl ether[14] (20 g, 0.25 mol) in dry ether (30 mL) was added dropwise to a well-stirred and ice–salt-cooled (−15 °C) suspension of freshly sublimed thallous cyclopentadienide[15] (45 g, 0.16 mol). The reaction mixture was stirred for an additional 6–8 h at −15 °C, filtered quickly into a precooled (−15 °C) flask, and concentrated in vacuo at −10 °C to half the volume, and this solution was directly used for the cycloaddition.

Cycloaddition with Nitroethylene. Under nitrogen, a dry ether solution of nitroethylene (14 g, 0.191 mol) was added over 0.5 h, in drops, to the above solution stirred at −15 °C. The reaction mixture was allowed to attain room temperature and left to stir overnight, the solvents were evaporated, and the residue was chromatographed over silica gel. Elution with benzene–ethylacetate (8:2) gave 2 g (6%) of 1-(methoxymethyl)-2-*endo*-nitrobicyclo[2.2.1]heptene (**2a**), bp 80 °C (0.1 mm).

Anal. Calcd for $C_9H_{13}O_3N$: C, 59.01; H, 7.1. Found: C, 59.44; H, 7.04.

Further elution with benzene–ethyl acetate (7:3) gave 20 g (68%) of 7-*syn*-(methoxymethyl)-2-*endo*-nitrobicyclo[2.2.1]-heptene (**2**), bp 90 °C (0.1 mm).

Anal. Calcd for $C_9H_{13}O_3N$: C, 59.01; H, 7.1. Found: C, 59.30; H, 6.8.

7-*syn*-[(Benzyloxy)methyl]-2-*endo*-nitrobicyclo[2.2.1]-heptene (3). A procedure similar to that described above for **2** and **2a**[16] gave, on chromatography of the crude adduct on silica gel and elution with benzene–ethyl acetate (90:10), 1.5 g (7%) of 1-[(benzyloxy)methyl]-2-*endo*-nitrobicyclo[2.2.1]heptene (**3a**), bp 120 °C (0.07 mm). Further elution with benzene–EtOAc (85:15) gave 7-*syn*-[(benzyloxy)methyl]-2-*endo*-nitrobicyclo[2.2.1]heptene (**3**): yield 15 g (71%); bp 122 °C (0.07 mm).

Anal. Calcd for $C_{15}H_{17}NO_3$: C, 69.48; H, 6.61. Found: C, 69.86; H, 6.90.

7-*syn*-(2′,6′-Dithianyl)-2-*endo*-nitrobicyclo[2.2.1]heptene (4). 5-(2′,6′-Dithiacyclohexyl)cyclopentadiene. Under N_2, a dry benzene solution of 1-chlorodithiane—prepared in situ from dithiane[17] (3.6 g, 0.03 mol) and *N*-chlorosuccinimide (4.6 g, 0.035 mol)[18] in dry benzene (10 mL) at room temperature—was added dropwise to a well-stirred and ice–salt-cooled (−15 °C) suspension of freshly sublimed thallous cyclopentadienide in dry ether (6 g, 0.022 mol; 60 mL of ether). The reaction mixture was stirred for a period of 6 h at −15 °C. The alkylated cyclopentadiene solution was filtered quickly into a precooled (−15 °C) flask, washed with ice-cold dry ether, and directly used for cycloaddition with nitroethylene.

Cycloaddition with Nitroethylene. Under nitrogen, nitroethylene (3 g, 0.041 mol) in dry ether (20 mL) was added in drops to the above alkylated cyclopentadiene at −15 °C, the mixture was stirred overnight, the solvents were evaporated under reduced pressure, and the residue was chromatographed on silica gel. Elution with benzene–EtOAc (90:10) gave compound **4** as colorless crystals: yield 2.0 g (35%); mp 138–140 °C.

Anal. Calcd for $C_{11}H_{15}S_2NO_2$: C, 51.36; H, 5.83. Found: C, 51.06; H, 5.53.

7-*syn*-(Trimethylsilyl)-2-*endo*-nitrobicyclo[2.2.1]heptene (5). 5-(Trimethylsilyl)cyclopentadiene.[19] Under nitrogen, a solution of freshly cracked cyclopentadiene (3.36 g, 0.0509 mol) in THF (10 mL) was added at room temperature, in drops, to a stirred suspension of sodium sand (1.22 g, 0.053 mol)[20] and THF (30 mL). The reaction was stirred for 4 h, the resulting red mixture was cooled to ~0 °C, and to this was added, under stirring, in drops, a solution of trimethylsilyl chloride (5.9 g, 0.054 mol) in THF (15 mL). After being stirred for 5 h at 0–5 °C, the reaction mixture was cautiously treated with cold water (50 mL) and extracted with ether (3 × 40 mL), and the organic extract was washed with cold water (2 × 40 mL), dried ($MgSO_4$), and directly used in the cycloaddition.

Cycloaddition with Nitroethylene. Under nitrogen, a solution of nitroethylene (5.8 g, 0.08 mol) in ether (60 mL) was added, in drops, to an ice-cooled and stirred ether solution of 5-(trimethylsilyl)cyclopentadiene, prepared as described above. The reaction mixture was stirred overnight, the solvents were evaporated, and the residue on fractionation gave 4.6 g (44% based on cyclopentadiene used) of product, bp 110 °C (2.0 mm), which on chromatography over silica and elution with benzene–petroleum ether (1:1) gave 3.0 g of pure adduct **5**.

Anal. Calcd for $C_{10}H_{17}SiNO_2$: C, 56.87; H, 8.05. Found: C, 57.2; H, 8.4.

7-*spiro*-Cyclopropyl-2-*endo*-nitrobicyclo[2.2.1]heptene (6). A stirred dry benzene solution of nitroethylene (4.55 g, 0.062 mol, 20 mL) at 0 °C was treated, in drops, with a benzene solution of spirocycloheptadiene[21] (5.75 g, 0.062 mol, 20 mL). The clear reaction mixture was stirred at room temperature for 12 h, the solvents were evaporated in vacuo, and the residue was distilled to give **6** as a pale yellow oil: bp 80 °C (1.4 mm); yield 9.2 g (89%).

Anal. Calcd for $C_9H_{11}NO_2$: C, 65.45; H, 6.66. Found: C, 65.30; H, 6.3.

7-Oxo-1,4,5,6-tetraphenyl-2-*endo*-nitrobicyclo[2.2.1]heptene (7). A stirred dry benzene solution of tetraphenylcyclopentadienone (0.384 g, 0.001 mol, 5 mL) at room temperature was treated with a benzene solution of nitroethylene (0.1 g, 0.0014 mol in 5 mL) and stirred for an additional 20 h. The colorless solution was evaporated under reduced pressure, and the residue was crystallized from hot benzene to give 0.424 g (91%) of **7**, mp 197–198 °C.

Anal. Calcd for $C_{31}H_{23}NO_3$: C, 81.10; H, 5.03; N, 3.06. Found: C, 80.90; H, 5.01; N, 2.95.

2-(β-Nitroethyl)furan (8). To stirred furan (0.5 g, 0.0073 mol) was added at room temperature, in drops, nitroethylene (0.5 g, 0.007 mol), and the reaction mixture was stirred for 40 h. Distillation of the crude reaction product gave **8** as pale yellow liquid: 0.73 g (71%); bp 120 °C (0.4 mm); IR (neat) ν_{max} 1555, 1370 cm^{-1} (NO_2); NMR ($CDCl_3$) δ 7.26 (m, α-furyl proton), 6.25, 6.1 (2 m, β-furyl protons), 4.6 (t, CH_2NO_2), 3.33 (t, aryl CH_2).

Anal. Calcd for $C_6H_7NO_3$: C, 51.06; H, 4.96. Found: C, 50.98; H, 5.35.

7-(Acetoxymethylene)-2-*endo*-nitrobicyclo[2.2.1]heptene (9). A solution of acetoxyfulvene[22] (1.2 g, 0.0088 mol) in dry benzene (2 mL) and nitroethylene (1 g, 0.0136 mol) was held at 50–52 °C for 10 h. Solvents were evaporated, and the residue was fractionated by preparative TLC (benzene as developer) to give 0.5 g (27%) of **9** as a pale yellow oil: IR (neat) ν_{max} 1718 (enol acetate), 1543, 1351 cm^{-1} (nitro); NMR ($CDCl_3$) δ 6.55 (enol acetate proton), 6.42, 6.04 (olefinic), 4.9 (m, $HCNO_2$), 2.05 ($COCH_3$).

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Attempted distillation of **9** led to clean reversal!

2-Nitrospiro[cyclopropane-1,9′-fluorene] (10). A solution of nitroethylene (2.85 g, 0.04 mol) in sodium-dried benzene (25 mL) was added over 0.75 h to a stirred solution of 9-diazofluorene[23] (7.5 g, 0.04 mol) in dry benzene (75 mL). After a 2-min induction period, nitrogen evolution started, and the expected volume of nitrogen was collected rapidly. Solvents were removed under reduced pressure at 45–50 °C, and the resulting cake powdered and was dried under vacuum. Crystallization from benzene gave 9.0 g (97%) of **10**: mp 110–111 °C; IR (KBr) ν_{max} 1531, 1351 cm^{-1} (nitro); NMR ($CDCl_3$) δ 7.3 (m, aromatic), 4.82 (dd, $HCNO_2$), 2.85 (dd, syn proton), 2.2 (t, anti proton).

Anal. Calcd for $C_{15}H_{11}NO_2$: C, 75.93; H, 4.67; N, 5.90. Found: C, 76.02; H, 4.65; N, 5.82.

3-(β-Nitroethyl)indole (11) and 3-(β,δ-Dinitrobutyl)indole (12). A stirred benzene solution of indole (1.2 g, 0.010 mol, 20 mL) at 0 °C was treated, in drops, with a dry benzene solution of nitroethylene (1.5 g, 0.02 mol, 10 mL). The reaction mixture was stirred for 20 h at room temperature, and the solvents were evaporated. The residue on preparative TLC (silica gel, 100% benzene) gave two pure compounds. The compound with higher R_f was **11**: yield 1.5 g (80%); mp 50–51 °C (recrystallized from benzene–hexane); IR (KBr) ν_{max} 1538, 1370 cm^{-1} (nitro); NMR ($CDCl_3$) δ 7.9 (br, NH), 7.2 (m, aromatic), 4.63 (t, CH_2NO_2), 3.43 (t, $CH_2CH_2NO_2$).

Anal. Calcd for $C_{10}H_{10}N_2O_2$: C, 63.15; H, 5.26. Found: C, 62.78; H, 5.56.

The compound with lower R_f was identified as **12**: yield 0.4 g (15%); mp 100–101 °C (crystallized from benzene–hexane); IR (KBr) ν_{max} 1563, 1370 (nitro), 1538, 1351 cm^{-1} (nitro); NMR ($CDCl_3$) δ 8.0 (br, NH), 7.2 (m, aromatic), 4.9 (m, $HCNO_2$), 4.4 (t, CH_2NO_2), 3.4 (dd, indolyl CH_2), 2.55 (q, $CH_2CH_2NO_2$).

Anal. Calcd for $C_{12}H_{13}O_4N_3$: C, 54.75; H, 4.94. Found: C, 54.44; H, 5.21.

2,6-Bis(β-nitroethyl)cyclohexanone (15). Under N_2, a stirred and cooled (~10 °C) solution of 1-morpholinocyclohexene[24] (2 g, 0.012 mol, in 20 mL of dry benzene) was treated dropwise with a solution of nitroethylene (1.83 g, 0.025 mol, in 10 mL of dry benzene) over a period of 0.5 h. The reaction mixture was stirred for an additional 20 h, treated with cold 2 N H_2SO_4 (50 mL) dropwise, and extracted with ether, and the organic layer was washed with bicarbonate and saturated sodium chloride and dried ($MgSO_4$). The residue on preparative TLC (silica gel, benzene–EtOAC, 80:20) gave pure product which on crystallization from benzene–petroleum ether gave colorless crystals of **15**: mp 64° C; yield 1.75 g (60%); IR (KBr) ν_{max} 1701 (carbonyl), 1536, 1370 cm^{-1} (nitro); NMR ($CDCl_3$) δ 4.45 (t, CH_2NO_2).

Anal. Calcd for $C_{10}H_{16}N_2O_5$: C, 49.18; H, 6.54; N, 11.4. Found: C, 48.95; H, 6.5; N, 11.3.

Reaction of Nitroethylene with β-Pinene: Isolation of Ene Product 16. A stirred dry benzene solution of β-pinene (1.36 g, 0.01 mol, 10 mL) was treated with nitroethylene (0.73 g, 0.01 mol, in 10 mL of benzene), the reaction mixture was refluxed for 16 h, the solvents were evaporated, and the residue on chromatography on silica gel gave on elution with a mixture of benzene–hexane (60:40) the ene product **16**: yield 0.33 g [90% based on recovered β-pinene (1.2 g)]; IR (neat) ν_{max} 1555, 1383 cm^{-1} (NO_2); NMR ($CDCl_3$) δ 5.18 (br, olefinic), 4.27 (t, CH_2NO_2), 0.76 (shielded methyl).

Anal. Calcd for $C_{12}H_{19}NO_2$: C, 68.89; H, 9.09. Found: C, 68.90; H, 8.51.

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Registry No. 1, 874-44-2; 2, 72776-94-4; 2a, 72726-24-0; 3, 60262-57-9; 3a, 60247-74-7; 4, 72726-25-1; 5, 72726-26-2; 6, 72726-27-3; 7, 72726-28-4; 8, 5462-90-8; 9, 72726-29-5; 10, 34163-56-9; 11, 31731-23-4; 12, 72726-30-8; 15, 72726-31-9; 16, 72726-32-0; nitroethylene, 3638-64-0; 5-(methoxymethyl)cyclopentadiene, 39872-54-3; 5-(2,6-dithiacyclohexyl)cyclopentadiene, 72726-33-1; 5-(trimethylsilyl)cyclopentadiene, 3559-74-8; spirocycloheptadiene, 765-46-8; tetraphenylcyclopentadienone, 479-33-4; furan, 110-00-9; acetoxyfulvene, 699-15-0; 9-diazofluorene, 832-80-4; indole, 120-72-9; 1-morpholinocyclohexene, 670-80-4; β-pinene, 127-91-3.

Supplementary Material Available: NMR spectra of nitroethylene and products described in this paper (14 pages). Ordering information is given on any current masthead page.

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One-Step Synthesis of Cyclic Compounds by Electrochemical Reduction of Unsaturated Compounds in the Presence of Dielectrophiles

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The one-step synthesis of cyclic compounds is achieved in a few cases by electroreduction of unsaturated compounds in DMF, at a mercury pool cathode, in the presence of a more difficultly reducible dielectrophile. Unsaturated compounds include activated olefins, aromatic Schiff bases, ketones, and azo, nitroso, and nitro compounds. Four dielectrophiles are used; they are tri- or tetramethylene bromide, succinyl chloride, and 4-bromobutyryl chloride. The electrochemical synthesis of derivatives of cyclohexane, piperidine, pyrrolidine, hexahydropyridazine, tetrahydropyridazinone, tetrahydropyridazinedione, tetrahydrooxazine, isoxazolidine, and spirolactone can be successfully performed. Their yields range from 8 to 78% depending on competitive reactions. Results of chemical reduction by alkali metals and electrochemical reduction are compared.

Electrochemical reductive alkylation of unsaturated compounds may occur if a stable radical anion is produced in the first reduction step. Nucleophilic attack of the radical anion on the alkyl halide is usually observed in a second step and a radical is formed (EC mechanism). Such an S_N2 reaction has been suggested or proved in the case

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