Nitroxide Radicals. Part XVII.[1] Transannular Interactions in [2.2]Paracyclophanyl Nitroxides

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N.m.r. measurements on four [2.2]paracyclophanyl t-butyl nitroxides indicate that there is substantial interaction of the unpaired electron with the proton which is pseudo-*gem* to the nitroxide group. Pseudo-*p*-[2.2]para-cyclophanylene bis-(t-butyl nitroxide) couples intramolecularly *O*-to-pseudo-*gem*-*C*. in solution to give mainly [2.2]paracyclophanequinone t-butylimine *N*-oxide.

THE unusual geometry of [2.2]paracyclophane, in which the slightly bent benzene rings are held face to face at most 3.1 Å apart, provides a convenient framework for the investigation of transannular electronic effects.[2]

However, consideration of charge distribution in mono-substituted [2.2]paracyclophanes, as indicated by canonical structures such as (1) ←→ (2), cannot be used to

[1] Part XVI, A. R. Forrester, S. P. Hepburn, and G. McConnachie, *J.C.S. Perkin I*, 1974, 2213.

[2] D. J. Cram and J. M. Cram, *Accounts Chem. Res.*, 1971, **4**, 204; D. J. Cram, R. B. Hornby, E. A. Truesdale, H. J. Reich, M. H. Delton, and J. M. Cram, *Tetrahedron*, 1974, **30**, 1757.

predict the principal product(s) of electrophilic substitution.[3] Usually, electrophilic substitution occurs predominantly at the position which is pseudo-*gem* to

(1)   (2)   (3)
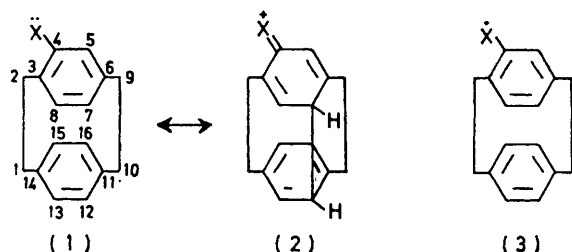
the most basic position or substituent in the already substituted ring since the product-determining step involves transannular proton transfer within the initial σ-complex. Hence, electrophilic substitution studies give no indication of the extent to which the electron

smoothly but repeated attempts to effect the same change with pseudo-*ortho*-dibromo[2.2]paracyclophane failed. Irrespective of the amount of butyl-lithium and the reaction conditions employed only a mixture of pseudo-*ortho*-dimethyl[2.2]paracyclophane and starting material was obtained. Presumably, the ease of solvation of the pseudo-*ortho*-dilithio[2.2]paracyclophane was the main reason for this failure.

Spectra.—The e.s.r. spectra of the four paracyclophanyl nitroxides showed three main lines (a_N ca. 14.6 G) with numerous ill-resolved subsplittings. The a_N values are much closer to that of di-t-butyl nitroxide [4] (15.2 G) than to that of t-butyl phenyl nitroxide [4] (12.3 G), and clearly steric interaction between the Bu^{t}NO• and the adjacent methylene group must cause the nitroxide group to be twisted out of conjugation with the ring to a large extent. Similar spectra have been recorded previously for *o*-alkylaryl t-butyl nitroxides [5]

Coupling constants * (G) of [2.2]paracyclophanyl t-butyl nitroxides

	a_N	Bu^t	$a_{o\text{-}H}$	$a_{m\text{-}H}$†	$a_{p\text{-}H}$	$a_{pseudo\text{-}gem}$†	$a_{o\text{-}CH_2}$	$a_{m\text{-}CH_2}$	Solvent
Unsubstituted	14.6	−0.25		+0.71 ‡	−0.61		+0.19	−0.10	CCl₄
		−0.24	−1.05	+0.72	−0.62	+0.77	+0.19		Bu$^t_2$NO•
Pseudo-*p*-methyl	14.6	−0.25					+0.20	−0.13	CCl₄
		−0.24	−1.06	+0.71	−0.62	+0.76	+0.20		Bu$^t_2$NO•
Pseudo-*p*-bromo	14.6	−0.24		+0.70 ‡			+0.18		CCl₄
		−0.24	−1.05	+0.69	−0.58	+0.73	+0.20		Bu$^t_2$NO•
Pseudo-*m*-methyl	14.6								CCl₄
		−0.25	−1.04	+0.60	−0.60	+0.71	+0.17		Bu$^t_2$NO•

* All values except a_N determined from n.m.r. measurements. † Values given in these columns could be reversed since it is not possible to distinguish between these protons. ‡ Evaluated only after measurements in Bu$^t_2$NO had been completed.

distribution in the unsubstituted ring is determined by that in the substituted ring. There is similar uncertainty regarding the extent and mode of transannular unpaired electron delocalisation in [2.2]paracyclophanyl radicals (3) but a more direct approach can be used in this case since unpaired spin densities can be readily obtained from measurements of the proton hyperfine coupling constants. Accordingly, we have prepared a number of stable [2.2]paracyclophanyl t-butyl nitroxides (3; X = ONBu^t) and measured their e.s.r. and n.m.r. spectra with a view to establishing a correlation between the unpaired spin densities on the carbon atoms of the ring bearing the nitroxide group and those on the corresponding (pseudo-*gem*) carbon atoms of the unsubstituted ring.

RESULTS AND DISCUSSION

The hydroxylamines from which the nitroxides listed in the Table were produced by oxidation with silver oxide were prepared by treatment of the corresponding mono- or di-bromo[2.2]paracyclophanes with butyl-lithium followed by 2-methyl-2-nitrosopropane. Conversion of the pseudo-*para*- and pseudo-*meta*-dibromo[2.2]paracyclophanes into the corresponding bromo-methyl-[2.2]paracyclophanes, by monolithiodebromination followed by treatment with dimethyl sulphate, proceeded

(a_N ca. 13.6 G), from which it was not possible to obtain proton coupling constants. However, proton coupling constants for these nitroxides were obtained from n.m.r. measurements on concentrated (ca. 2M) solutions of the radicals in carbon tetrachloride or chloroform. The four [2.2]paracyclophanyl nitroxides listed in the Table are even more stable than the *o*-alkylphenyl t-butyl nitroxides and we have now determined their proton coupling constants in a similar way.

The n.m.r. spectra of the mononitroxides measured in carbon tetrachloride solution (ca. 2M), initially at 100 MHz and subsequently at 220 MHz, showed only four signals [6] outside the δ 0—10 region, the most intense of which was that from the t-butyl protons. From a comparison of the width of the band envelope (>3 G) of one component of the nitrogen triplet of the e.s.r. spectrum with the sum of the coupling constants derived from the four n.m.r. signals (assuming that three arose from aromatic protons) it was clear that not all the n.m.r. signals had been detected, presumably because of their large linewidths. The likely dominant line broadening process [7] is the relaxation of the electron spin through electron spin exchange in which case h_1 (linewidth at half height) is given by $h_1 = T_1 a_i^2/8$, where T_1 is the spin-lattice relaxation time of the electron.

[3] H. J. Reich and D. J. Cram, *J. Amer. Chem. Soc.*, 1969, **91**, 3505.

[4] A. R. Forrester, J. M. Hay, and R. H. Thomson, ' The Organic Chemistry of Stable Free Radicals,' Academic Press, London, 1968.

[5] A. Calder, A. R. Forrester, J. W. Emsley, G. R. Luckhurst, and R. A. Storey, *Mol. Phys.*, 1970, **18**, 481.

[6] A. R. Forrester and R. Ramasseul, *Chem. Comm.*, 1970, 394.

[7] E. de Boer and H. van Willigen, *Progr. NMR Spectroscopy*, 1967, **2**, 111.

Because of the quadratic dependence of the linewidth on the coupling constant we have had difficulty previously[5] in detecting signals corresponding to coupling constants >1 G. When solutions of $<1.5M$ concentration are used, protons with even smaller coupling constants can give lines too broad to be detected. Kreilick[8] has overcome this difficulty by using a paramagnetic solvent, di-t-butyl nitroxide, for n.m.r. measurements on radicals, thus reducing T_1 and considerably narrowing the lines.

Repetition of our n.m.r. measurements using 0.3M-solutions of the nitroxides in di-t-butyl nitroxide resulted in the detection of three new peaks outside the δ 0—10 region, two at low and one at high field. By analogy with the known signs and magnitudes of the coupling constants of 2,5-dimethylphenyl t-butyl nitroxide and related ortho-substituted aryl nitroxides[5] (for which $a_{o-H} > a_{m-H} > a_{p-H}$) we derived and assigned six coupling constants from the seven n.m.r. peaks, viz. those of the t-butyl protons, those of the three protons of the ring bearing the nitroxide group, and those of the ortho- and meta-methylene groups (Table). The seventh signal cannot be due to the pseudo-meta- or pseudo-para-proton since the spectra of all four mononitroxides showed a peak in this region. It is unlikely to arise from a β-methylene proton of the ortho-alkyl group since models indicate that this proton is further from the oxygen atom than is the pseudo-gem-proton, especially in conformations in which non-bonding interactions between the t-butyl protons and the paracyclophane rings are at a minimum. Of the remaining two protons the pseudo-gem- would be expected to have the larger coupling constant since it is closer to the nitroxide group than is the pseudo-ortho-proton and in the n.m.r. spectra of diamagnetic [2.2]paracyclophane derivatives it is this proton which is most affected by substituent groups.[9] Hence, we envisage a direct interaction of the pseudo-gem-proton with the unpaired electron on oxygen analogous to that observed[10] for several aryl iminoxyls, e.g. (4), which exhibit relatively large ortho-proton coupling constants. Indeed, molecular models indicate
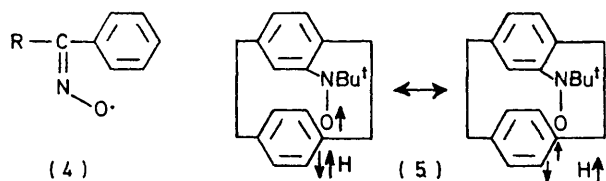
that the distance between the oxygen and the pseudo-gem-proton in (3; X = ONBu^t) is not much greater than between the oxygen and the ortho-protons (syn) in (4). Further, the interaction with the pseudo-gem-proton as envisaged in (5) should result in a positive proton coupling constant, which is in agreement with experiment.

[8] R. W. Kreilick, *J. Amer. Chem. Soc.*, 1968, **90**, 2711.

[9] H. J. Reich and D. J. Cram, *J. Amer. Chem. Soc.*, 1969, **91**, 3534.

[10] B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc. (B)*, 1966, 86.

We are reluctant to assign specifically the remaining signals which fall within the δ 0—10 region since this region is usually complicated by peaks due to diamagnetic impurities in the paramagnetic substrate or the solvent. However, the signals in this region which are due to protons in the paramagnetic substrate must correspond to very small coupling constants (in the range $+0.1$ to -0.09 G) and hence it is clear that transannular spin transmission is not efficient in these nitroxides. Para-cyclophanyl radicals (3) with higher unpaired spin densities on the carbon atoms of the substituted ring, e.g. the aryloxyl (3; X = O) would have been more appropriate for this work but it is not known whether such radicals would be sufficiently stable for the necessary n.m.r. measurements to be made.

The above results, which indicate a significant interaction between the unpaired electron on oxygen and the pseudo-gem-proton, are complemented by observations on the chemical behaviour of the [2.2]paracyclophanyl-ene bisnitroxide[11] (6). Although the four [2.2]para-cyclophanyl mononitroxides are stable indefinitely in solution the pseudo-para-diradical (6) is not. After 4 months at room temperature in chloroform solution it yielded several coloured products. The decomposition could be accelerated by heating under reflux but the product mixture then became even more complex. The principal product was a deep red solid, $C_{24}H_{32}N_2O_2$, whose u.v. ($\lambda_{max.}$ 382 nm) and i.r. ($\nu_{max.}$ 3400 and 1625 cm^{-1}) spectra indicated the quinone imine N-oxide structure (8). Its n.m.r. spectrum showed two t-butyl signals at δ 1.69 and 1.30 characteristic[12] of Bu^{t}N$^+$(O$^-$)= and Bu^{t}NH groups, respectively, and signals from two quinonoid protons at δ 5.58 and 6.79 (both sharp singlets) and three aromatic protons. Of the several minor products present in the decomposition mixture only three were identified. The first, $C_{24}H_{32}N_2O$, is a deoxy-derivative of the quinone t-butylimine N-oxide whose n.m.r. spectrum shows signals from Bu^{t}N= and Bu^{t}NH groups at δ 1.40 and 1.28, respectively,[12] and two quinonoid protons at δ 5.68 and 6.35, the latter being partly obscured by the signals of the three aromatic protons, and i.r. absorption at 3420 and 1650 cm^{-1}. These data are consistent with the quinone t-butylimine structure (9). The second, $C_{20}H_{24}N_2O_2$, is the quinone oxime (10); it shows only one t-butyl resonance, at δ 1.25, two quinonoid (δ 5.68 and 6.82) and three aromatic proton signals, and i.r. absorption at 3500—3300 and 1630 cm^{-1}. The third, $C_{23}H_{23}N_2O_4$, is partly derived from the ethanol in the chloroform solvent since its n.m.r. spectrum showed, in addition to signals from one t-butyl group and from two quinonoid and three aromatic protons, the presence of an ethyl group, the methylene resonating at δ 4.30. Carbonyl absorptions at 1780 cm^{-1} characteristic[13] of the $>$N·O·CO—

[11] A. R. Forrester and R. Ramasseul, *J. Chem. Soc. (B)*, 1971, 1638, 1645.

[12] A. Calder, A. R. Forrester, and S. P. Hepburn, *J.C.S. Perkin I*, 1973, 456.

[13] O. Exner and M. Horak, *Coll. Czech. Chem. Comm.*, 1959, **24**, 2992; J. D. Loudon and I. Wellings, *J. Chem. Soc.*, 1960, 3462.

group and at 1650 cm⁻¹ strongly suggest that this product is the carbonate (11). Its formation from the quinone oxime (10) can be easily accounted for if it is assumed that small quantities of phosgene are very slowly formed in the chloroform solution. Indeed, treatment of the

cess.[17] With the [2.2]paracyclophanequinone imine N-oxide (8) the reduction in molecular strain, when the non-bonding interactions between the t-butyl group and the [2.2]paracyclophane system are eliminated, could provide the driving force for the loss of the t-butyl
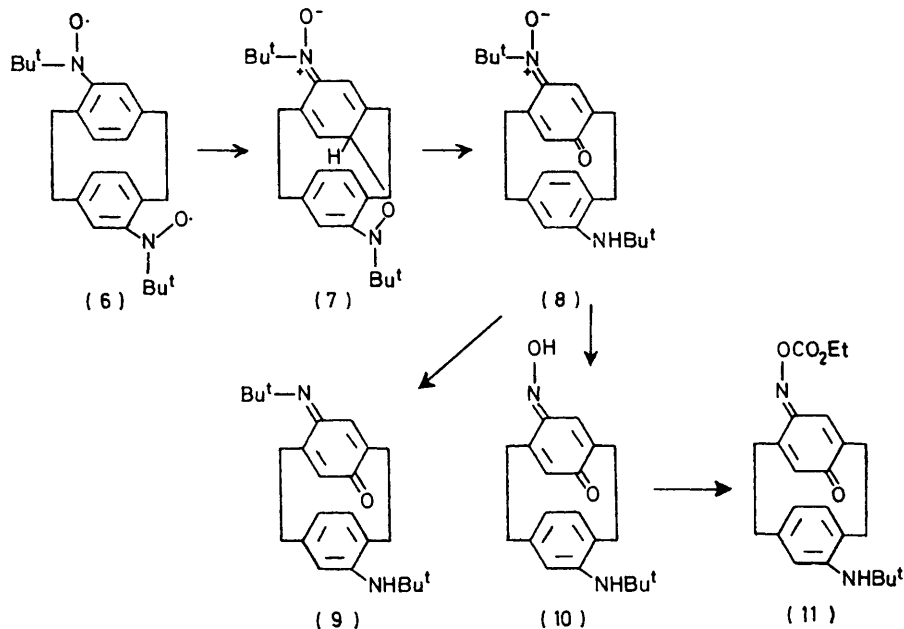
quinone oxime (10) in chloroform with ethyl chloroformate yielded the carbonate (11). Although mononitroxides are poor hydrogen abstractors, bisnitroxides, particularly those with $J > a$, such as (6), appear to be more reactive in this respect as evidenced by the increase in intensity of mononitroxide e.s.r. signals when solutions of such diradicals are left in good hydrogen-donating solvents.[14]

Formation of the principal product of the decomposition mixture is most satisfactorily accounted for by transannular O-to-pseudo-gem-C coupling of the bisnitroxide followed by fragmentation of the intermediate cyclo-hexadiene (7) as indicated. Intermolecular O-to-C coupling of aryl nitroxides is common [4,12] but this to our knowledge is the first intramolecular example of such a process. The coupling further exemplifies the favourable spatial disposition of the nitroxide group and the pseudo-gem-proton/carbon atom which had been indicated by the n.m.r. results for the monoradicals. Deoxygenation of quinone imine N-oxides [15] and nitrones [16] on irradiation has been noted previously and since we took no special precautions to mask the chloroform solution during the decomposition period we consider that the small quantity of quinone imine (9) isolated arises in this way. Spontaneous loss of the t-butyl group from benzoquinone t-butyl imine N-oxides has not been observed previously although bulkier alkyl groups such as t-octyl are eliminated (as 2,2,4-trimethylpentene) probably by an intramolecular pro-

[14] A. R. Forrester, G. R. Luckhurst, and R. H. Thomson, J. Chem. Soc. (B), 1968, 1311.

group. Significantly solutions of the quinone imine N-oxide (6) slowly gave the quinone oxime (10) and traces of the quinone imine (9).

EXPERIMENTAL

I.r. spectra were measured for Nujol mulls and n.m.r. spectra for solutions in CDCl₃ unless stated otherwise.

[2.2]Paracyclophan-4-yl t-butyl nitroxide, t-butyl pseudo-p-bromo[2.2]paracyclophanyl nitroxide, and pseudo-p-[2.2]-paracyclophanylene bis-(t-butyl nitroxide) were prepared as already described.[11]

Pseudo-p-*bromo(methyl)[2.2]paracyclophane.*— 4-Bromo-12-lithio[2.2]paracyclophane, prepared from pseudo-p-dibromo[2.2]paracyclophane (2.0 g, 5.5 mmol) in ether (200 ml) and ethereal butyl-lithium (ca. 0.62M; 22 ml, 13.6 mmol) under nitrogen, was treated with a solution of dimethyl sulphate (1.33 ml, 14 mmol) in ether (40 ml) at 0 °C. After 3 h the temperature was allowed to rise and aqueous ammonia (200 ml; s.g. 0.880) was added. The mixture was then extracted with methylene chloride and the extracts were washed with water and dried (MgSO₄). Removal of the solvent gave a colourless residue (1.64 g), crystallisation of which from chloroform–ether gave the product (940 mg), slightly contaminated with [2.2]paracyclophane (t.l.c.). Chromatography of a sample (40 mg) on silica with benzene–petroleum (1.5 : 8.5) gave *pseudo*-p-*bromo(methyl)[2.2]paracyclophane*, m.p. 216.5—217.5° (Found: C, 67.8; H, 5.4. C₁₇H₁₇Br requires C, 67.8; H, 5.65%), δ 2.1 (3 H, s, Me), 2.5—3.5 (8 H, m, 4 CH₂),

[15] A. R. Forrester, M. M. Ogilvy, and R. H. Thomson, J.C.S. Chem. Comm., 1972, 483.
[16] J. S. Splitter and M. Calvin, Tetrahedron Letters, 1970, 3995.
[17] M. M. Ogilvy, Ph.D. Thesis, University of Aberdeen, 1971.

6.06 (1 H, d, J 2 Hz, ArH, *ortho* to Me), 6.23—6.5 (3 H, m, ArH), 6.74 (1 H, q, J 8 and 2 Hz, ArH pseudo-*gem* to Me), and 7.0 (1 H, q, J 8 and 2 Hz, ArH pseudo-*gem* to Br).

Pseudo-p-(N-*hydroxy-t-butylamino*)*methyl*[2.2]*paracyclophane*.—To a solution of pseudo-*p*-bromo(methyl)[2.2]-paracyclophane (990 mg, 3.3 mmol; purity *ca.* 95%) in ether (75 ml) at 0 °C under nitrogen, a cold solution of n-butyl-lithium (14 ml, 7.9 mmol) was added dropwise with stirring. The mixture was allowed to warm to room temperature after which it was re-cooled at 0 °C. A solution of 2-methyl-2-nitrosopropane (1 g, 11.5 mmol) in ether (50 ml) was then added dropwise during 5 min and the temperature of the mixture was allowed to rise. Water was added and the green organic phase was separated; the aqueous phase was extracted with ether. The ethereal solutions were combined, washed with water, and dried. Evaporation gave a crude product, chromatography (column) of which on silica with ether–petroleum (5 : 95) as eluant gave *pseudo*-p-(N-*hydroxy-t-butylamino*)*methyl*-[2.2]*paracyclophane* (353 mg), m.p. 85—87° (from hexane) (Found: C, 81.3; H, 9.0; N, 4.2. $C_{21}H_{27}NO$ requires C, 81.5; H, 8.8; N, 4.5%), $\nu_{max.}$ 3 520 and 3 580 cm^{-1}, δ 1.0 (9 H, s, Bu^t), 2.16 (3 H, s, Me), 2.5—3.5 (8 H, m, 4 CH$_2$), 5.0br (1 H, s, OH), 6.20—6.70 (5 H, m, ArH), and 6.69 (1 H, d, J 2 Hz, ArH, pseudo-*gem* to Me).

Pseudo-p-*methyl*[2.2]*paracyclophanyl t-Butyl Nitroxide*.—The above hydroxylamine (300 mg) in benzene (15 ml) was shaken with silver oxide (0.15 g) for 1 h. The silver residues were collected and the solvent was removed at room temperature to give the *nitroxide* (290 mg) as red needles, m.p. 70—72° (from hexane) (Found: C, 81.5; H, 8.2; N, 4.2. $C_{21}H_{26}NO$ requires C, 81.8; H, 8.4; N, 4.5%).

Pseudo-m-*bromo*(methyl)[2.2]*paracyclophane*.—This was prepared from pseudo-*m*-dibromo[2.2]paracyclophane by treatment with butyl-lithium followed by dimethyl sulphate as described for the pseudo-*para*-isomer. The *product* (63%) had m.p. 102—104.5° (from petroleum) (Found: C, 67.5; H, 5.4. $C_{17}H_{17}Br$ requires C, 67.8; H, 5.65%), δ 2.05 (3 H, s, Me), 2.5—3.5 (8 H, m, 4 CH$_2$), 6.05br (1 H, s, ArH *ortho* to Me), 6.3 (2 H, m, ArH *para* to Me and *para* to Br), 6.5 (1 H, s, J 2 Hz, ArH *ortho* to Br), 6.69 (1 H, d, J 8 Hz, ArH pseudo-*gem* to Me), and 7.00 (1 H, d, J 8 Hz, ArH pseudo-*gem* to Br).

Pseudo-m-(N-*hydroxy-t-butylamino*)*methyl*[2.2]*paracyclophane*.—This was prepared from the above bromo(methyl)[2.2]paracyclophane (209 mg) as described for the pseudo-*para*-bromo(methyl) isomer. The *product* (70 mg) (Found M^+, 309.2096. $C_{21}H_{27}NO$ requires M, 309.2093) showed $\nu_{max.}$ 3 500 cm^{-1}, δ 1.0 (9 H, s, Bu^t), 2.1 (3 H, s, Me), 2.5—3.5 (8 H, m, 4 CH$_2$), and 6.2—6.3 (5 H, m, ArH). This hydroxylamine was oxidised with silver oxide to give *pseudo*-m-*methyl*[2.2]*paracyclophanyl t-butyl nitroxide*, m.p. 70—72° (from chloroform–petroleum) (Found: M, 308,2011. C_{21}-$H_{26}NO$ requires M, 308.2014).

Attempted Preparation of Pseudo-o-*bromo*(methyl)]2.2]-*paracyclophane*.—Treatment of pseudo-*o*-dibromo[2.2]paracyclophane (3 g, 8.2 mmol) with butyl-lithium (20 mmol) followed by dimethyl sulphate (1.9 ml, 20 mmol) gave *pseudo*-o-*dimethyl*[2.2]*paracyclophane* (1.36 g, 70%), m.p. 177—187° (from hexane) (Found: C, 91.3; H, 8.5. $C_{18}H_{20}$ requires C, 91.5; H, 8.5%), $\nu_{max.}$ 1 590 and 1 555 cm^{-1}, δ 2.01 (6 H, s, 2 Me), 2.5—3.5 (8 H, m, 4 CH$_2$), and 6.39 (6 H, s, ArH), and starting material (500 mg, 17%). Repe-

tition of the above reaction using a 1 : 1 molar ratio of pseudo-*o*-dibromo[2.2]paracyclophane to butyl-lithium gave the dimethyl[2.2]paracyclophane (31%) and starting material (46%).

Decomposition of Pseudo-p-[2.2]*paracyclophanylene Bis-*(t-butyl nitroxide)*.—The bisnitroxide (150 mg) in chloroform (5 ml) was left for 4 months at room temperature. Chromatography of the product mixture on silica with chloroform gave (a) 12-*t-butylamino*[2.2]*paracyclophane-4,7-quinone 4-t-butylimine N-oxide* (8) (72 mg) as red needles, m.p. 133—135° (from chloroform–petroleum) (Found: C, 75.4; H, 8.3; N, 7.1%; M^+, 380.2462. $C_{24}H_{32}N_2O_2$ requires C, 75.75; H, 8.5; N, 7.4%; M, 380.2464), $\lambda_{max.}$ 382 nm (log ϵ 4.04), $\nu_{max.}$ 3 400 and 1 625 cm^{-1}, δ 1.30 (9 H, s, NHBu^t), 1.69 [9 H, s, Bu^{t}N$^+$(O$^-$)], 2.5—3.5 (8 H, m, 4 CH$_2$), 3.80br (1 H, s, NH), 5.58 (1 H, s, quinone H), 6.28br (1 H, s, ArH), 6.36 (1 H, q, J 8 and 2 Hz, ArH), 6.47 (1 H, d, J 8 Hz, ArH), and 6.79 (1 H, s, quinone H), m/e 380(14%, M^+), 364(9), 363(9), 324(32), 307(56), 251(100), 235(10), 234(10), 205(8), 175(11), 119(28), 106(20), 91(14), and 77(11); (b) 12-*t-butylamino*[2.2]*paracyclophane-4,7-quinone 4-t-butylimine* (9) (12 mg), yellow needles, m.p. 157—159° (from chloroform–petroleum) (Found: M^+, 364.2515. $C_{24}H_{32}N_2O$ requires M, 364.2525), $\nu_{max.}$ 3 420 and 1 650 cm^{-1}, δ 1.28 (9 H, s, Bu^{t}NH), 1.40 (9 H, s, Bu^{t}N=), 2.5—3.5 (8 H, m, 4 CH$_2$), 5.63 (1 H, s, quinone H), 6.35 (1 H, s, quinone H), and 6.25—6.55 (3 H, m, 3 ArH), m/e 364(45%, M^+), 359(5), 308(25), 307(94), 252(25), 251(100), 223(13), 191(20), 189(3.5), 175(22), 149(40), 119(45), 98(40), and 83(50); (c) 12-*t-butylamino*[2.2]*paracyclophane-4,7-quinone 4-oxime* (10) (10 mg), brown needles, m.p. 102—105° (from chloroform–petroleum) (Found: M^+, 324.1837. $C_{20}H_{24}N_2O_2$ requires M, 324.1838), $\nu_{max.}$ 3 500—3 300 and 1 630 cm^{-1}, δ 1.25 (9 H, s, Bu^{t}NH), 2.5—3.5 (8 H, m, 4 CH$_2$), 5.68 (1 H, s, quinone H), 6.3—6.6 (3 H, m, 3 ArH), and 6.82 (1 H, s, quinone H), m/e 325(10%), 324(40) (M^+), 318(18), 317(32), 249(20), 251(100), 250(100), 249(13), 175(11), 144(11), 119(32), 107(22), and 91(13); (d) 12-*t-butylamino*[2.2]-*paracyclophane-4,7-quinone 4-(ethoxycarbonyloxy)imine* (11) (13 mg), red needles, m.p. 128—133° (from chloroform–petroleum) (Found: M^+, 396.2412. $C_{23}H_{28}N_2O_4$ requires M, 396.2413), $\nu_{max.}$ 3 420, 1 780, and 1 650 cm^{-1}, δ (CDCl$_3$) 1.30 (9 H, s, Bu^t), 1.42 (3 H, t, Me), 2.5—3.5 (8 H, m, 4 CH$_2$), 4.30 (2 H, q, CH$_2$), 5.60 (1 H, s, quinone H), 6.21 (1 H, d, J 2 Hz, ArH), 6.30 (1 H, q, J 8 and 2 Hz, ArH), 6.49 (1 H, d, J 8 Hz, ArH), and 6.65 (1 H, s, quinone H), m/e 396(7%, M^+), 380(5.5), 365(15), 309(35), 308(28), 253(25), 252(71), 251(40), 236(16), 223(16), 208(10), 175(35), 144(20), 130(18), 119(100), 106(35), 91(45), and 77(40).

Addition of ethyl chloroformate (one drop) to a small quantity of the quinone oxime (10) in chloroform at room temperature yielded after 20 min a product identical (t.l.c., mass spectrum) with the above carbonate.

Spectra.—E.s.r. spectra were measured with a Varian E3 spectrometer. N.m.r. spectra of the nitroxides were obtained with a Varian HR-220 spectrometer with a sweepwidth of 20 kHz upfield and downfield from Me$_4$Si.