trans-4-*t*-butylcyclohexanecarbonyl peroxide[5d] in *non-polar* media is *via* rearrangement to the carboxy inversion product, *trans*-4-*t*-butylcyclohexyl *trans*-4-*t*-butyl-cyclohexanecarbonyl carbonate (eq. 1, R = R′ = *trans*-4-*t*-butylcyclohexyl), m.p. 102–103°, carbonyl absorption (CCl₄) 1800, 1750 cm.$^{-1}$, which has been isolated from the decomposition solution in carbon tetrachloride and found to be identical with an authentic sample prepared by an independent synthesis.[6,7] Extensive purification of the carbon tetrachloride or a change of solvent to benzene, hexane, or isooctane did not alter the course of the reaction; in all cases the rearrangement of peroxide to inversion product was the primary reaction. Upon further heating, the "inversion product" is converted in high yield to the *trans, trans* ester.[5d] In refluxing carbon tetrachloride substantially all of the peroxide (initial concentration 0.05 M) is consumed in the first 40 min. The resulting "inversion product" (approximately two-thirds of the product composition) is half destroyed (affording ester and carbon dioxide) after 1 day. Homolytic peroxide decomposition to alkyl radicals accounts for approximately one-third of the product composition in the form of a 2.7:1 ratio of *cis*- and *trans*-4-*t*-butylcyclohexyl chloride.[8] Decomposition of the peroxide is first-order (determined over a 13-fold difference in initial peroxide concentration by following the change of optical density at 1775 cm.$^{-1}$); the rate of rearrangement increases as the solvent is changed from isooctane to carbon tetrachloride to benzene.

Ethylmethylacetyl peroxide[4d,5a] (in addition to decomposition to alkyl radicals) is also observed (by nuclear magnetic resonance and infrared absorption) to undergo rearrangement to carboxy inversion product which in a subsequent, slower reaction is converted principally to ester.

The decomposition of peroxides *via* the intermediacy of an alkyl acyl carbonate provides an attractive explanation for the stereospecificity of ester formation observed in the past.[5] We suspect that rearrangement (eq. 1) may be a major route of decomposition for other secondary aliphatic diacyl peroxides.[9]

A third example further delineates mechanistic complexities in this area. Decomposition of *p*-bromobenzoyl phenylacetyl peroxide in benzene at 30° is first-order, yields only 2% of radicals scavengeable by galvinoxyl,[10] and affords benzyl *p*-bromobenzoate (45%), benzyl *p*-bromobenzoyl carbonate[11] (eq. 1, R = *p*-BrC₆H₄, R′ = CH₂C₆H₅, 30%), *p*-bromobenzoic acid (13%), and diphenylmethane (10%). Extensive control experiments indicate that *in this case* ester is not formed from the inversion product under the mild reaction conditions; thus, for this particular unsymmetrical peroxide, a path for ester formation must be operative which does not involve the carboxy inversion product. Oxygen-18 labeling in the carbonyl carbon of the *p*-

bromobenzoyl portion of the peroxide becomes divided 55–45 in the carbonyl and alkyl oxygens of the ester; this excludes formation of the ester solely by a six-center transition state but is consistent with cage recombination (or a combination of six- and four-center reactions). Of principal significance here also is the simultaneous operation of different modes of decomposition of a diacyl peroxide in a nonpolar medium.

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Isobenzofuran,* a Transient Intermediate

Sir:

We have found that 1,4-dihydronaphthalene-1,4-*endo*-oxide (1a), previously prepared by shaking a solution of *o*-fluorobromobenzene in furan with lithium amalgam (4 days),[1] is readily obtainable by aprotic diazotization of anthranilic acid[2] in the presence of furan. Use of 2,5-dimethylfuran as trapping agent affords 1b.[3] Having worked out improved procedures[4] for the preparation of hexaphenylbenzene and 1,2,3,4-tetraphenylnaphthalene from the purple reactive diene, tetraphenylcyclopentadienone (2), we were interested in the finding[3] that 1a is an effective Diels–Alder dienophile for simple dienes and decided to explore the reaction of 1a with 2. A solution of the reactants in diglyme was refluxed in the expectation that, at this temperature (165°), the adduct 3 would lose carbon monoxide and afford the tetrahydrotetraphenylanthracene *endo*-9,10-oxide 6. A vigorous reaction occurred with gas evolution and with discharge of the purple color in 2 min. Dilution with water precipitated a colorless, crystalline product, m.p. 190°, characterized by the n.m.r. spectrum as having only aromatic hydrogens and found by elemental analysis to be a hydrocarbon. Initial ideas about the nature of the product were dismissed by the finding that the 1,4-dimethyl *endo*-oxide 1b reacts with 2 to give the same aromatic hydrocarbon, and this eventually was identified as 1,2,3,4-tetraphenylbenzene (9).[5] Since this hydrocarbon must arise by thermal decomposition of an intermediate, the reaction of 1a with 2 was repeated in refluxing benzene. There resulted, in quantitative yield, a colorless product melting at 180–182° dec. and corresponding in analysis to the adduct 3. This structure is confirmed by infrared carbonyl absorption at 1775 cm.$^{-1}$ and by the n.m.r. spectrum: a multiplet at τ 2.6–2.9 (10 protons of the phenyl groups at C-2 and C-3 and 4 protons of the *ortho*-disubstituted benzene ring), a singlet at 3.17 (10 protons from the phenyl groups at C-1 and C-4), a singlet at 4.72 (C-9 and C-10 protons), and a singlet at 7.09 (C-9a and C-10a

(6) Prepared by the procedure of D. S. Tarbell and E. J. Longosz, *J. Org. Chem.*, **24**, 774 (1959).
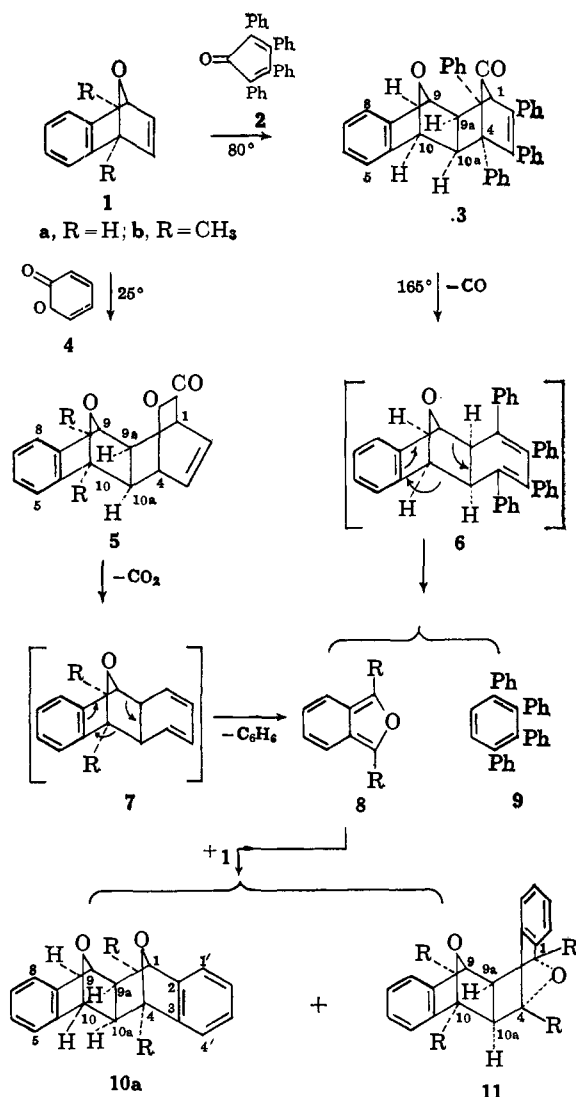
(7) Satisfactory combustion data and proof of structure have been obtained for all new compounds.

(8) F. D. Greene, C. C. Chu, and J. Walia, *J. Org. Chem.*, in press.

(9) Some data on bridgehead peroxides are also suggestive of the involvement of the carboxy inversion reaction [P. D. Bartlett and F. D. Greene, *J. Am. Chem. Soc.*, **76**, 1088 (1954)].

(10) P. D. Bartlett and T. Funahashi, *ibid.*, **84**, 3596 (1962); F. D. Greene, W. Adam, and J. E. Cantrill, *ibid.*, **83**, 3461 (1961).

(11) Melting point 67–67.5°, infrared absorption (CCl₄) in the carbonyl region: 1805, 1742 cm.$^{-1}$.

* For reasons set forth in L. F. Fieser and M. Fieser, "Style Guide for Chemists," Reinhold Publishing Co., New York, N. Y., 1960, L. F. F. strongly advocates the spelling isobenzofurane.

(1) G. Wittig and L. Pohmer, *Ber.*, **89**, 1334 (1956).

(2) L. Friedman and F. M. Logullo, *J. Am. Chem. Soc.*, **85**, 1549 (1963). See also M. Stiles and R. G. Miller, *ibid.*, **82**, 3802 (1960), and M. Stiles, R. G. Miller, and U. Burckhardt, *ibid.*, **85**, 1792 (1963).

(3) E. Wolthuis, *J. Org. Chem.*, **26**, 2215 (1961).

(4) Procedures submitted to *Org. Syn.* by L. F. Fieser, and by L. F. Fieser and M. J. Haddadin. See also L. F. Fieser, "Organic Experiments," D. C. Heath and Co., in press.

(5) W. Dilthey, W. Schomner, and O. Trösken, *Ber.*, **66**, 1627 (1933).
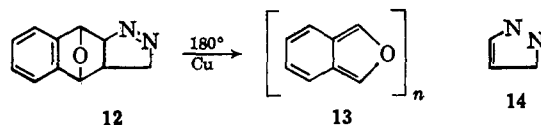
a, R = H; b, R = CH₃

2.9 and 3.05 (8 aromatic protons), unsymmetrical quartets at 4.85 and 7.35 (2 protons each, probably due to vicinal and long-range coupling),[7] singlet at 5.48 (2 protons adjacent to oxygen).

The structures assigned were further confirmed by an independent synthesis from 1 and α-pyrone[8] (4), a diene which is more reactive than 2 and which combines with 1 at room temperature to form the adduct 5a in 95% yield. This adduct, m.p. 105–107°, which decolorizes permanganate and bromine solutions, is characterized as follows: infrared: 1750 (carbonyl), 1635 cm.$^{-1}$ (C=C); n.m.r.: singlet at τ 3 (4 aromatic protons), triplet at 3.6 (2 olefinic protons), multiplet at 4.62–5.06 (3 allylic protons adjacent to oxygen), multiplet at 6.26–4.44 (1 proton adjacent to carbonyl group), unsymmetrical quartets at 6.26–6.44 and at 7.3–7.5 (probably due to the protons at C-10a and C-9a, respectively).

When adduct 5a was added to a hot solution of endo-1,4-oxide 1a in diglyme and the solution kept at 130° for 2 min., bis(oxides) 10a and 11a were isolated in total yield of 92% (ratio 11:9), with carbon dioxide and benzene as by-products. The same products resulted when reactants 1a and 4 were heated on a steam bath without solvent. The oxidelactone 5a on being heated decomposes with evolution of carbon dioxide and, presumably, the unstable intermediate 7, which rearranges to yield benzene and isobenzofuran (8). The fact that 10a and 11a result from two different reactions indicates a common intermediate, namely isobenzofuran (8).

Analogous reactions carried out with 1b and α-pyrone gave similar results. Reaction at room temperature for 3 days afforded adduct 5b (dec. 110–112°) in 95% yield. Addition of 5b to a solution of 1b in diglyme at 150° afforded the exo,endo-bis(oxide) 11b as the sole product; the absence of the exo,exo product 10b may be due to steric hindrance by the methyl groups. The analyses and spectroscopic properties of the compounds of the dimethyl series (b) are all consistent with the structures formulated and will be presented in a definitive paper.

This is the first report identifying isobenzofuran and 2,3-dimethylisobenzofuran as unisolated trapping agents. Wittig and Härle[6] report the formation of polymeric isobenzofuran on heating 12 at 180° with copper powder.

protons). The adduct 3 decomposed rapidly at the melting point with evolution of carbon monoxide and afforded tetraphenylbenzene (9) as the only isolated product. We believe that elimination of carbon monoxide affords tetrahydrotetraphenylanthracene endo-9,10-oxide (6), and that this suffers retrogressive Diels–Alder reaction[6] to isobenzofuran (8) and tetraphenylbenzene (9).

Isobenzofuran (8) is unknown, and all efforts to isolate it as a product of pyrolysis or to synthesize it thus far have been fruitless. Nevertheless, its transient existence was demonstrated by decomposing the adduct 3 in refluxing diglyme in the presence of the endo-1,4-oxide 1a as trapping agent and isolation of the exo,exo- and exo,endo-adducts 10a and 11, along with tetraphenylbenzene (9). This hydrocarbon and the exo, endo-adduct 11a are soluble in benzene, in which the exo,exo adduct 10a is practically insoluble; 9 and 11a are separated easily by chromatography on neutral alumina. The ratio of 10a to 11a is 9:11.

Product 10a was characterized as follows: m.p. 264–265°; n.m.r.: singlets at τ 2.92 and 2.98 (8 aromatic protons), singlet at 4.59 (4 allylic protons adjacent to oxygen), singlet at 8.02 (C-9a and C-10a protons). Product 11a had m.p. 175–176°; n.m.r.: singlets at τ

(6) Comparable reactions are described by K. Mackenzie, J. Chem. Soc., 473 (1960), and G. Wittig and H. Härle, Ann., 623, 17 (1959).

(7) J. Meinwald and Y. C. Meinwald, J. Am. Chem. Soc., 85, 2514 (1963), and references cited therein.

(8) Prepared by a procedure submitted to Org. Syn. by H. E. Zimmerman, G. L. Grunewald, and R. M. Paufler.

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