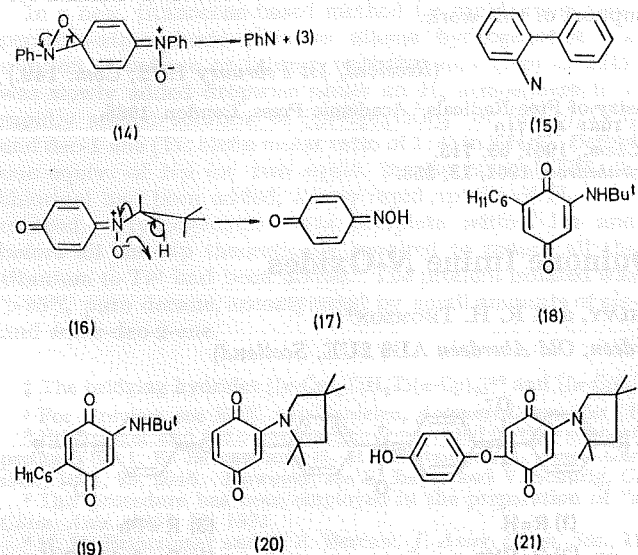


the nitrene (15), from (5), cyclises in the singlet state, and the relatively large amount of carbazole (9%) obtained was increased to 31% at the expense of the azo-compound (24%) when (5) was photolysed in the presence of oxygen (a triplet quencher³).



In parallel with the above results, irradiation of the *t*-butyl *N*-oxide (6) in benzene gave benzoquinone and the diaminoquinone (9); in cyclohexane the yield of (9) was increased, and the quinones (18) and (19) were isolated in low yield, being formed by addition of *t*-butylamine to cyclohexylbenzoquinone.⁵ Photolysis of the octyl analogue (16) gave the oxime (17) as major product† (possibly as indicated), the diaminoquinone (10), and, significantly, the pyrrolidinoquinone (20) in 1% yield. This compound is photo-labile⁶ and much of it was probably destroyed during the reaction. In cyclohexane solution only a trace of (20) was detected but (21) [formed by addition of quinol⁷ to (20)] was isolated. The isolation of (10), (20), and (21) establishes the formation of the triplet 1,1,3,3-tetramethylbutyl nitrene which abstracts hydrogen both inter- and intra-molecularly. The production of pyrrolidines⁸ by photolysis of alkyl azides has never been substantiated,⁹ and we found that irradiation of *n*-butyl azide⁸ and of 1,1,3,3-tetramethylbutyl azide, in benzene in the presence of benzoquinone, gave (11) and (10), respectively, but no pyrrolidinoquinone could be detected in either case. We expect that pyrrolidinoquinones can be obtained from quinone imine *N*-oxides in higher yields by selection of more appropriate starting materials and careful control of conditions.

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† Oxime and alkene were formed slowly but quantitatively even in the absence of light; (6) did not decompose in this way even in benzene under reflux.

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Reaction between Aldehydes and Isocyanates Catalysed by Metal Carbonyls

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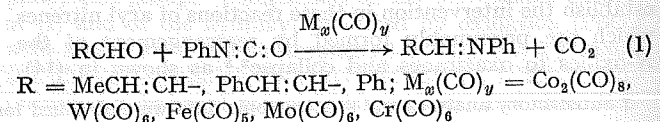
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Summary Metal carbonyls catalyse the condensation of isocyanates with aldehydes to give imines in high yields.

HETEROCUMULENES form complexes with metal carbonyls;^{2,1} with dodecacarbonyliron, some reduction of the isocyanate ligand to isocyanide occurred,² and phenyl isocyanate reacts with an oxo-complex of rhenium to yield a phenylimido-complex.³ The catalytic cyclotrimerisation of isocyanates,⁴ and the reaction of phenyl isocyanate with phenylacetylene,⁵ show that efficient catalytic processes may occur through activation of the isocyanate group.

We report the excellent catalytical efficiency of metal carbonyls at low concentration in the reaction between isocyanates and aldehydes (equation 1).

This reaction takes place smoothly with sulphonyl isocyanate,⁶ but with other derivatives like phenyl isocyanate it usually requires high temperatures and long reaction times and the yields are moderate.⁷



In the presence of various metal carbonyls, the reaction proceeds readily (100–150°, 0.5–3.5 h) and the yields are 90–100%. $\text{Co}_2(\text{CO})_8$ is the most efficient catalyst.

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Diazo-compounds in Heterocyclic Synthesis. Aziridine Ring Expansion in a Retro-Diels-Alder Reaction

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Summary Hydrolysis and decarboxylation of *exo*-diethyl 3-phenyl-3,6,7-triazatricyclo[3.2.1.0^{2,4}]octane-6,7-dicarboxylate followed by mild oxidation gives *N*-phenyl-1,4-dihydropyridine (50–70%), thus affording a simple route for the conversion of cyclopentadiene into 1,4-dihydropyridines.

THE remarkable rate enhancement of 10¹¹ for loss of molecular nitrogen from diazo-compound (I) compared with (II) has been attributed largely to relief of strain and steric interactions on opening the *exo*-cyclopropane ring and the near ideal geometry of the transition state for this ready retro-Diels-Alder reaction.¹ Synchronous loss of nitrogen and double-bond formation from (I) gave 1,4-cyclohexadiene quantitatively. The synthetic potential of this reaction has been developed in a synthesis of semi-bullvalene.²

We now report the conversion of cyclopentadiene into the dihydropyridine (III) (44–61% overall) via the analogous aziridine ring expansion. Bicyclic precursor (IV) was prepared from cyclopentadiene and diethyl azodicarboxylate (95%).³ Subsequent 1,3-dipolar addition of phenyl azide to (IV) gave exclusively the *exo*-adduct (V), m.p. 124–125° (92.5%). Photolysis of this triazoline in acetone (sun lamp; Pyrex filter)⁵ gave exclusively the *exo*-dicarboxylate (VI) (99%), m.p. 124–124.5°; M^+ 331; ν_{max} (Nujol) 1740 and 1720 cm^{-1} ; δ (CDCl_3) 1.12–1.45 (7H, t, J 7 Hz), 2.00–2.28 (1H, d, J 10 Hz), 2.81 (2H, s), 4.01–4.41 (4H, q, J 7 Hz), 4.85 (2H, s), and 6.72–7.36 (5H, m) p.p.m. Hydrolysis and decarboxylation of (VI) (hot KOH) gave the hydrazine (VII) as an unstable brown oil ν_{max} (neat) 3240 and 1600 cm^{-1} ; δ (CCl_4) 1.05–1.32 (1H, m), 1.91–2.19 (1H, d, J 10 Hz, further split), 2.33–2.42 (2H, s), 3.26 br (2H, s, disappears on addition of D_2O), 3.69 (2H, s), and 6.58–7.33 (5H, m) p.p.m., which was readily oxidized by oxygen in CH_2Cl_2 or better by yellow mercuric oxide to the dihydropyridine (III) [50–70% from (VI)], presumably by spontaneous decomposition of the diazo-compound (VIII). The product was identical in all respects with that published.⁶

