resonance spectrum showed only a complex aromatic hydrogen multiplet in the region 450–520 c.p.s. (CDCl$_3$, external TMS); $\lambda_{max}^{95\% \ EtOH}$ mμ (ϵ): 213 (25,451), 217 (infl., 24,279), 248 (14,159), 257 (16,603), and 352 (15,350); ν_{max}^{KBr} cm.$^{-1}$: 1626 (s), 1542 (s), 1482 (s), 1055 (s), 930 (s), 810 (vs), 762, 733 (vs), 732, 738 (vs), 680 (vs), and 664 (s).

These data clearly indicated a highly conjugated aromatic structure quite unlike the benzophenone previously obtained. The following mechanistic consideration then led to the postulate that this product was 5-chloro-3-phenyl-2,1-benzisoxazole (III). An initially formed chlorosulfite ester was envisaged as cyclizing to the previously proposed intermediate ion A, which is resonance-stabilized by forms like B. In the absence of pyridine (see above), proton abstraction is suppressed and nucleophilic attack by chloride ion on the cyclic cation B supravenes, followed by rearomatization and dehydration to give III, as depicted in Scheme II.

SCHEME II
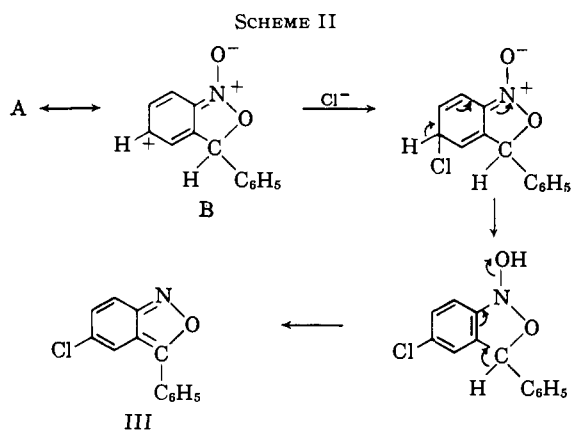
An authentic specimen of 5-chloro-3-phenyl-2,1-benzisoxazole was therefore prepared from p-chloronitrobenzene and phenylacetonitrile,[7] and unequivocally identified with that produced from the interaction of thionyl chloride and 2-nitrobenzhydrol by mixture melting point and infrared, ultraviolet, and n.m.r. spectral determinations.

In our opinion, the formation of 5-chloro-3-phenyl-2,1-benzisoxazole by the action of thionyl chloride on 2-nitrobenzhydrol under acidic conditions represents one of the most-facile displacements of a benzenoid hydrogen by a weak nucleophile that has yet been reported.

(7) R. B. Davis and L. C. Pizzini, J. Org. Chem., 25, 1884 (1960).

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Phenylation with Nitrosoacetanilides[1]

Sir:

Phenylation of aromatic hydrocarbons with nitrosoacetanilides has long aroused mechanistic interest because it leads to biaryls in good yields[2,3] and yet the

(1) Research was carried out in the Radiation Laboratory, operated under contract with the Atomic Energy Commission. This is AEC Document No. COO-38-359.

(2) E. C. Butterworth and D. H. Hey, J. Chem. Soc., 116 (1938).

"acetoxy radicals" which one might expect to be formed in the decomposition of the initially formed[4] diazonium acetate surprisingly do not lead to[5] carbon dioxide and methyl radicals. Instead, the acetoxy moiety ends up as acetic acid (possibly via acetate anions).

In a previous publication[3] we had, on the basis of circumstantial evidence, ascribed the apparent difference in behavior between benzoyl peroxide as an arylating agent on one hand and nitrosoacetanilide (NAA) and phenylazotriphenylmethane (PAT) on the other (particularly with respect to the absence of dihydrobiphenyl formation from the latter two reagents) to the operation of a cage effect in the case of NAA and PAT. In the meantime, however, it has been amply shown[6–8] that no cage effect is operative in the case of PAT but that the lack of dimerization and disproportionation of the phenylcyclohexadienyl radicals (from addition of phenyl radicals to benzene) in this case is due to the high stationary state concentration of triphenylmethyl radicals concomitantly formed in the primary act of decomposition; these radicals then abstract hydrogen from phenylcyclohexadienyl radicals or combine with them with great efficiency to give biphenyl and triphenylmethane or 3-phenyl-6-triphenylmethyl-1,4-cyclohexadiene.[6] Not enough phenylcyclohexadienyl radicals build up to disproportionate (to dihydrobiphenyl) or dimerize (to tetrahydroquaterphenyl) by reactions second-order in these radicals.

In view of recent indications[9,10] that the NAA reaction also does not involve a cage effect, we wish to record our own experimental observations, though incomplete, which strongly point in the same direction, i.e., militate against a cage effect with NAA.

The essential experimental data are shown in Table I. Nitrosoacetanilide was decomposed in aromatic solvents at room temperature in the presence of iodine in low concentrations (0.02–0.05 M). Under these conditions it is unlikely that iodine can compete efficiently with a reaction of NAA occurring in a benzene cage to give biphenyl, nitrogen, and acetic acid. Yet, Table I shows that 80–85% of the NAA was converted to iodobenzene.[11] In view of the fact[3,4] confirmed in the present study (see Table I) that the yield of biaryl from NAA is in the 80–90% region, one may calculate that 90–100% of the phenyl radicals from NAA are scavenged by iodine in low concentration. This almost certainly indicates that the phenyl radicals formed from NAA are free and not caged, although there is a possible complication in the hard-to-ascertain possibility that NAA complexes with iodine prior to decomposition.

Unfortunately, though our results are incompatible with the previously proposed[3,12] cage mechanism for

(3) E. L. Eliel, M. Eberhardt, O. Simamura, and S. Meyerson, Tetrahedron Letters, 749 (1962).

(4) R. Huisgen and L. Krause, Ann., 574, 157, 171 (1951).

(5) Such decomposition normally occurs rapidly [L. Jaffe, E. J. Prosen, and M. Szwarc, J. Chem. Phys., 27, 416 (1957)] and, in the decomposition of acetyl peroxide, may be concerted [M. J. Goldstein, Tetrahedron Letters, 1601 (1964)]. The pertinent studies refer to temperatures above 80° considerably higher than that (ca. 25°) in the present work.

(6) D. Hey, M. J. Perkins, and G. H. Williams, Tetrahedron Letters, 445 (1963).

(7) J. F. Garst and R. S. Cole, ibid., 679 (1963).

(8) G. A. Russell and R. F. Bridger, ibid., 737 (1963).

(9) D. B. Denney, N. E. Gershman, and A. Appelbaum, J. Am. Chem. Soc., 86, 3180 (1964).

(10) C. Dickermann, private communication.

(11) Excluding runs 3, 7, and 12 where an insufficient amount of iodine was employed; see below.

(12) R. Huisgen and G. Horeld, Ann., 562, 137 (1949).

TABLE I

PRODUCTS FORMED IN THE DECOMPOSITION OF NAA IN AROMATIC
SOLVENTS IN THE PRESENCE AND ABSENCE OF IODINE

		Concentration^a		Yield, %^{b}	
Run	Substrate	[NAA]	[I$_2$]	C$_6$H$_5$I	C$_6$H$_5$Ar
1	Toluene	2.15	5.06	81.5	None
2		2.06	2.36	79.1	c
3		2.07	1.18	70.7	c
4		2.10	0	None	86.0
5	Chlorobenzene	2.07	4.93	81.6	c
6		2.08	2.51	79.9	c
7		2.25	1.1	71.0	c
8		2.1	0	None	84.3
9		2.05	0	None	83.0
10	Benzene	2.28	5.05	85.4	c
11		2.21	2.52	79.2	c
12		2.2	1.2	69.8	c
13		1.21	2.5	83.6	c
14		2.07	0	None	87.9

^{a} In moles/l. $\times$ 10^2. Substrate was usually 100 ml. except in run 13 where it was 200 ml. ^{b} Based on NAA. Iodobenzene yield determined by gas chromatography on 20% Apiezon L on Chromosorb P at 200°, 10-ft. column, using 1-bromo-4-chlorobenzene as an internal standard. Biaryls were determined on a 10-ft. GE-SF-96 column at 165° using p-chloroaniline as the internal standard. ^{c} Not determined.

NAA arylation, they give no positive indication as to what the mechanism really is. Attempts to determine the fate of the acetoxy radical in the iodine-scavenged reactions were fruitless, the only product we were ever able to detect (by gas chromatography) being acetic acid. It is of interest, however, that in runs 3, 7, and 12 where the NAA:I$_2$ molar ratio was close to one-half and where, therefore, not enough iodine was present to combine with both the phenyl radical and whatever other radical (if any) is formed in the NAA decomposition, the phenyl radicals were still scavenged quite efficiently, iodobenzene being formed in about 70% yield (as compared to 83–85% in runs where iodine was in excess). These experiments suggest that whatever else is formed in the NAA decomposition combines with iodine either much less readily than phenyl radical does or else combines in such fashion as to regenerate iodine readily.

Regrettably our work leaves the mechanism of the NAA reaction still insufficiently understood. Speculations are possible but appear unwise at the present time.

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## Photochemical Cycloaddition as a Device for General Annelation

Sir:

Intermolecular photochemical cycloaddition to isolated ethylenic linkages, aside from the more venerable instance of dimerization, has recently attracted attention, and it has been demonstrated to be of synthetic utility.[1–8] With few exceptions,[1,4] however, the ini-

(1) P. de Mayo and H. Takeshita, *Can. J. Chem.*, **41**, 440 (1963).
(2) P. de Mayo, R. W. Yip, and S. T. Reid, *Proc. Chem. Soc.*, 54 (1963).
(3) E. J. Corey, R. B. Mitra, and H. Uda, *J. Am. Chem. Soc.*, **86**, 485 (1964).
(4) E. J. Corey and S. Nozoe, *ibid.*, **86**, 1652 (1964).
(5) J. A. Barltrop and R. Robson, *Tetrahedron Letters*, 597 (1963).
(6) G. O. Schenck, W. Hartmann, and R. Steinmetz, *Chem. Ber.*, **96**, 498 (1963).
(7) P. Eaton, *J. Am. Chem. Soc.*, **84**, 2454 (1962).

tially generated ring formed by such cycloaddition has remained intact, a feature apparently limiting the scope and versatility of the reaction.

We now wish to show that, in fact, photochemical cycloaddition provides an important means for the synthesis of a variety of ring systems both single and fused. A number of specific examples follow.

Irradiation[9] of dimedone in cyclohexene–ether (1:3) solution converted it to 1, m.p. 96–97.5°,[10] and 2, m.p. 79–81°. The dione 1, the initial product formed
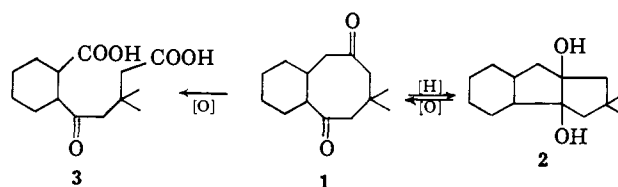
by the retroaldol opening of the cyclobutane adduct, was reduced to 2 by irradiation in cyclohexene or by zinc and acetic acid; sodium metaperiodate cleavage regenerated 1. The structure of 1 was established by oxidation (potassium permanganate–acetone) to 3, m.p. 154–156°, and further oxidation (nitric acid) to *trans*-cyclohexane-1,2-dicarboxylic acid and *as*-dimethylsuccinic acid. Dione 1 was also obtained by replacing dimedone, in the irradiation, by its enol acetate, and hydrolysing the resultant adduct, m.p. 103–105°.

Among other bicyclic ring systems to which a new route may be of utility is that of the perhydroazulenes common to many sesquiterpenoids. This was achieved by irradiation of the enol acetate[11] of cyclopentane-1,3-dione in cyclopentene–cyclohexane (2:3). The adduct (4) obtained was converted by mild alkali into 5, $\nu_{max}^{CCl_4}$ 1710 cm.$^{-1}$.

Cycloaddition is not restricted to cycloalkanes, and with other substrates may serve as a useful route to cyclooctane derivatives. Thus, irradiation of cyclohexane-1,3-dione in methyl acrylate gave 6a, m.p. 89–91°, and 6b, m.p. 104–105°. The former on standing in chloroform was slowly converted to the corresponding enol.

6a, R = COOMe, R' = H
6b, R = H, R' = COOMe
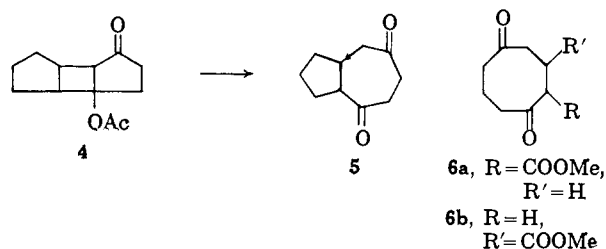
One evident feature of photochemical cycloaddition is that both substrate and addend may be modified to contain the number of potential units of unsaturation desired in the ultimate product, without the necessity of their subsequent and possibly difficult introduction. For instance, in tropolone syntheses, after construction of the ring the required aromaticity has been achieved,

(8) For other general references see G. S. Hammond and N. J. Turro, *Science*, **142**, 1541 (1963).
(9) Irradiations were conducted using a 450W source in a Hanovia water-cooled immersion unit with a pyrex filter. Concentrations varied from 0.3–0.5%.
(10) Adequate analyses have been obtained for all new compounds mentioned.
(11) Prepared by the action of ketene on the dione.