Figure 1. First-order rate plots for *t*-butyl phenylperacetate decomposition in cumene (79.55°). The 2000- and 1-atm data are displaced upward by 0.2 and 0.4 unit, respectively, on the vertical axis.

pressure. No carbonyl absorption was detected in the infrared spectra of infinite time samples in cumene.

Table II. *t*-Butyl Phenylperacetate Product Data at 79.55°[a]

Product	% cumene at 1 atm	4000 atm	% chlorobenzene at 1 atm	4000 atm
t-Butyl alcohol	70	50	30	44
Acetone	Trace	Trace	50	28
Benzyl *t*-butyl ether	21.4	50.0	13	34
Total *t*-butoxy	91.4	100.0	92	106
Benzyl *t*-butyl ether	21.4	50.0	13	34
Bibenzyl	27.0	12.0	33	30
Toluene	6.4	12.0	Trace	Trace
Total benzyl[b]	>54.8	>74.0	>46	>64

[a] Determined by glpc. [b] In cumene, α,α-dimethyldibenzyl and bicumyl were formed in significant yields, but not quantitatively determined. In chlorobenzene, stilbene and benzaldehyde were detected, but not quantitatively determined.

Ether formation in cumene must occur by a cage recombination of the primary radical products since the *t*-butoxy radicals which have diffused from the primary cage should react exclusively with solvent.[19] Studies of the efficiency of radical production from *t*-butyl phenylperacetate have given variable results,[16] but approximately agree with the value 0.79 from our cumene data. The ether data thus offer another example of the effect of pressure on competition between cage reactions and diffusion[2,6,12] and give a value of $\Delta V^*_2 - \Delta V^*_{-1}$ in both solvents of about +10 cc/mole.

(19) (a) The lower ether yields in chlorobenzene may be due to secondary reactions with *t*-butoxy; the appearance of benzaldehyde (Table II) substantiates this view.[19b] Glpc analyses indicated no significant ether contamination of the unreacted perester. (b) See C. Walling and M. Mintz, *J. Am. Chem. Soc.*, **89**, 1515 (1967).

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2-Carbomethoxybenzocyclobutenone. Synthesis of a Photochemically Sensitive Small-Ring System by a Pyrolytic Wolff Rearrangement

Sir:

We wish to report a novel synthesis of 2-carbomethoxybenzocyclobutenone (I), the β-keto ester tautomer of a benzocyclobutadiene derivative (II) which might be expected to be stabilized not only by intramolecular hydrogen bonding but also by a "push–pull" resonance effect of the hydroxyl and carbomethoxy substituents.[1,2]

I   II
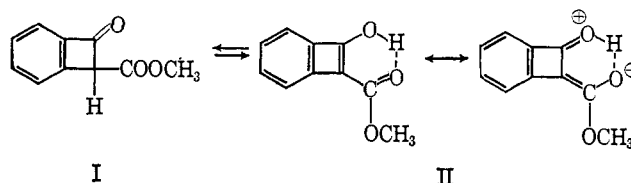
Since benzocyclobutenecarboxylic acid has been synthesized by the photochemical Wolff rearrangement of 2-diazoindan-1-one,[3] it was anticipated that photolysis of the known 2-diazoindan-1,3-dione (III)[4] in methanol solution would constitute a simple synthesis of I. Ultraviolet irradiation[5] of a 5×10^{-3} *M* solution of III in methanol afforded, however, dimethyl homophthalate (VI) as the major volatile product (30% yield). It seemed likely that the desired ring contraction was taking place, producing I as an intermediate which then underwent photochemical conversion to VI *via* the quinonoid ketene V. This postulate received indirect support by the smooth conversion of benzocyclobutenone (VII)[6] to methyl *o*-toluate (VIII) by irradiation in methanol solution under similar conditions.[7]

The mass spectral cracking pattern of diazo ketone III can best be rationalized as proceeding *via* the desired Wolff rearrangement path.[8] In view of the parallel behavior of certain other organic compounds on electron impact and on pyrolysis,[9] we were encouraged to inves-

(1) So-called "push–pull" stabilization of this type was initially proposed by J. D. Roberts, Special Publication No. 12, The Chemical Society, London, 1958, p 111.
(2) For the attempted synthesis of some "push–pull" stabilized cyclobutadiene derivatives, see R. Breslow, D. Kivelevich, M. J. Mitchell, W. Fabian, and K. Wendel, *J. Am. Chem. Soc.*, **87**, 5132 (1965); for the attempted synthesis of a "push–pull" stabilized benzocyclobutadiene, see A. T. Blomquist and C. G. Bottomley, *ibid.*, **87**, 86 (1965).
(3) M. P. Cava, R. L. Litle, and D. R. Napier, *ibid.*, **80**, 2257 (1958); L. Horner, W. Kirmse, and K. Muth, *Chem. Ber.*, **91**, 430 (1958).
(4) M. Regitz and G. Heck, *ibid.*, **97**, 1482 (1964).
(5) Melting points are uncorrected. Irradiations were carried out using a Model 679A36 Hanovia lamp and a Pyrex filter. Ultraviolet spectra were determined in dioxane; infrared spectra were determined in CHCl₃; nuclear magnetic resonance spectra were run in CDCl₃.
(6) M. P. Cava, D. Mangold, and K. Muth, *J. Org. Chem.*, **29**, 2947 (1964).
(7) A related photochemical cleavage of benzocyclobutenedione has been observed: H. A. Staab and J. Ipaktschi, *Tetrahedron Letters*, 583 (1966).
(8) R. Van Fossen, M.S. Thesis, Wayne State University, 1966.
(9) For example, see D. C. DeJongh, R. Y. Van Fossen, and C. F. Bourgeois, *Tetrahedron Letters*, 271 (1967), and references cited therein.
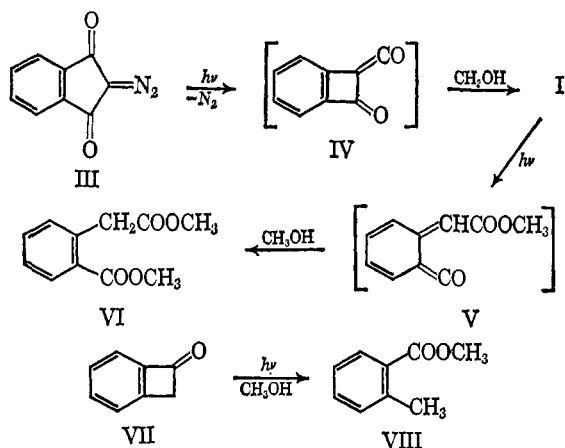
tigate the pyrolysis of III in the gas phase under conditions in which the keto ketene intermediate IV could be trapped by methanol. Indeed, pyrolysis of III vapor in a stream of nitrogen at 25 mm over a glowing Nichrome wire at *ca.* 750°, and introduction of a stream of methanol vapor directly above the Nichrome wire, gave I in 45–50% yield, mp 54–55° (*Anal.* Found: C, 68.10; H, 4.63); λ_{max} (dioxane) 215 mμ (log ϵ 3.98), 242 (3.78), 285 (3.13), and 295 (3.08); ν_{max} 1780 and 1735 cm^{-1}; δ 3.73 (singlet, 3 H), 5.07 (singlet, 1 H), and 7.50 ppm (multiplet, 4 H). The carbonyl absorption at 1780 cm^{-1} and the ultraviolet spectrum are fully consistent with the corresponding values for other benzocyclobutenones.[6] The mass spectrum of I included peaks with *m/e* 176 (molecular ion), 148, 133 (base peak), 105, 89, and 77, with metastable peaks for the transitions 176 → 148, 148 → 133, 133 → 105, and 105 → 77. Ultraviolet irradiation of I in methanol gave dimethyl homophthalate (VI). The spectroscopic data for I and its photochemical conversion to VI makes the structural assignment secure.

$$\text{III}_{\text{vapor}} \xrightarrow{750°} \text{[IV]} \xrightarrow{\text{CH}_3\text{OH}} \text{I}$$
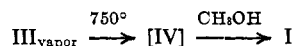
Attempted vpc of I on an SE-30 column at 160° gave an isomer, mp 56–61°; λ_{max} (dioxane) 231 mμ (log ϵ 4.40), 240 (4.31), 270 (4.04), 280 (4.03), and 346 (3.52); ν_{max} 1742 and 1645 cm^{-1}; δ 3.87 (singlet, 3 H), 5.53 (singlet, 1 H), 7.33 (multiplet, 3 H), and 8.10 ppm (multiplet, 1 H), considered to be 3-methoxyisocoumarin (IX), which probably arises *via* thermal cleavage of I to the *o*-quinodimethane (V). The mass spectrum of IX is identical with that of I, suggesting that I rearranges to IX in the mass spectrometer prior to fragmentation. Treatment of IX with dilute HCl gave, after preparative vpc,[10] homophthalic anhydride (X).

$$\text{I} \xrightarrow{\text{vpc, 160°}} \text{[V]} \longrightarrow$$
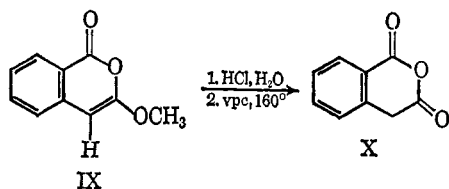
No evidence for the existence of the enol tautomer II of I has been obtained. The nmr spectrum of I con-

(10) Under these vpc conditions (a 6 ft × 0.25 in. column of 2.5% SE-30 on Chromosorb W at 160°) homophthalic acid is dehydrated to homophthalic anhydride.

tains no low-field signal typical of a hydrogen-bonded enolic proton, and the ratio of aromatic signals to methine signal to methyl ester signal is 4:1:3, as required by the keto tautomer I. Furthermore, solutions of I give a negative ferric chloride test.

The synthesis of I from III is the first example of the formation of a strained ring system by an uncatalyzed thermal Wolff rearrangement, in contrast to the now widely employed photochemical Wolff rearrangement.[11] In addition, the fact that I cannot be prepared from III by irradiation suggests that the pyrolysis of diazo ketones in the vapor phase may prove to be of use in the synthesis of other strained but photochemically unstable systems.

(11) W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, p 120.

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Total Synthesis of Δ^8-($\Delta^{1(6)}$)-Tetrahydrocannabinol, a Biologically Active Constituent of Hashish (Marijuana)

Sir:

Total syntheses[1-3] have been reported of ($\pm$)-Δ^8- and -Δ^9-tetrahydrocannabinols,[4] which occur in the corresponding enantiomorphic forms as psychotomimetically active constituents of hashish.[5] Recently, (−)-cannabidiol, which is convertible to the naturally occurring (−)-Δ^8- and -Δ^9-tetrahydrocannabinols,[6,7] has been synthesized from olivetol and (+)-*cis*- and -*trans*-*p*-mentha-2,8-dien-1-ols.[8] We now report a total synthesis of (−)-Δ^8-tetrahydrocannabinol which, since it involves the optical resolution of a racemic intermediate,
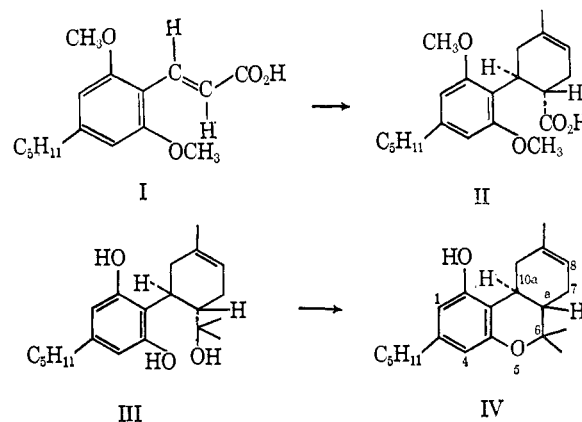
(1) R. Mechoulam and Y. Gaoni, *J. Am. Chem. Soc.*, **87**, 3273 (1965).
(2) E. C. Taylor, K. Lenard, and Y. Shvo, *ibid.*, **88**, 367 (1966).
(3) K. E. Fahrenholtz, M. Lurie, and R. W. Kierstead, *ibid.*, **88**, 2079 (1966).
(4) Fahrenholtz[3] has proposed, and we have adopted, the *Chemical Abstracts* nomenclature for these dibenzo[*b,d*]pyrans.
(5) U. Claussen and F. Korte, *Naturwissenschaften*, **53**, 541 (1966), have recently reviewed the chemistry and biological activity of hashish constituents.
(6) Y. Gaoni and R. Mechoulam, *J. Am. Chem. Soc.*, **86**, 1646 (1964).
(7) R. L. Hively, W. A. Mosher, and F. W. Hoffmann, *ibid.*, **88**, 1832 (1966).
(8) T. Petrzilka, W. Haefliger, C. Sikemeier, G. Ohloff, and A. Eschenmoser, *Helv. Chim. Acta*, **50**, 719 (1967).