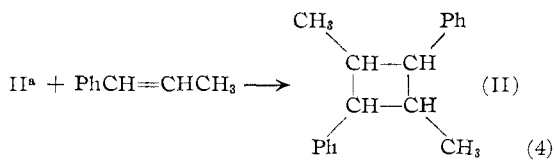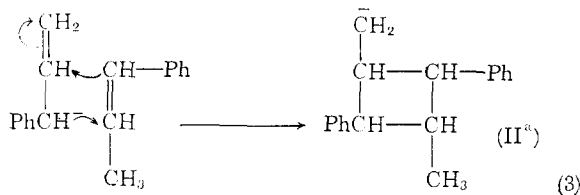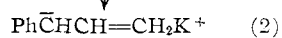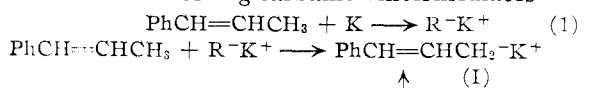The position of the B-band was practically identical with that observed in the spectra of a number of 1,3-diphenylalkanes (ca. 2600 Å.). The molecular extinction, however, was about twice that shown by the latter class of compounds.

Substantial support for the structure of a symmetrically substituted dimethyldiphenylcyclobutane assigned to the dimer was obtained by an examination of its nuclear magnetic resonance spectrum. The spectrum showed the presence of $CH_3CH<$ and the absence of CH_3CH_2- groupings in the molecule. The sharpness of the phenyl group signal was related to the equivalency of the two benzene rings. A third shift was attributed to the presence of tertiary hydrogen.

The conclusive proof for the structure of the dimer was obtained by a hydrogenolysis reaction using platinum–alumina as catalyst. The reaction was carried out in a flow system at 235° in the presence of a stream of hydrogen. The product was composed only of 1,3-diphenyl-2-methylpentane, which shows that compound (II) consisted of stereoisomers of 1,3-dimethyl-2,4-diphenylcyclobutane. 1,3 - Diphenyl - 2 - methylpentane, which was synthesized independently by Claisen–Schmidt condensation of propiophenone and hydrogenolysis of the resulting keto-olefin, distilled at 113–114° at 0.4 mm., $n^{20}D$ 1.5365.

Anal. Calcd. for $C_{18}H_{22}$: C, 90.67; H, 9.31. Found: C, 90.55; H, 9.30.

The formation of I can be explained by a chain mechanism involving carbanion intermediates

$$PhCH=CHCH_3 + K \longrightarrow R^-K^+ \quad (1)$$
$$PhCH=CHCH_3 + R^-K^+ \longrightarrow PhCH=CHCH_2^-K^+ \quad (I)$$

$$PhC\bar{H}CH=CH_2K^+ \quad (2)$$

$$(3)$$

$$II^a + PhCH=CHCH_3 \longrightarrow \quad (II)$$

$$(4)$$

The general steps in this mechanism are similar to those described previously.[2] Step 3 of the mechanism implies that a cyclobutane ring, because of a certain internal strain, has a stabilizing effect upon the primary carbanion II^a.

When the dimerization was carried out at 135° in ethylcyclohexane the initial product of the reaction was 1,5-diphenyl-4-methyl-1-pentene ($PhCH=CHCH_2C(CH_3)HCH_2Ph$), (III), which then through a depolymerization and resynthesis is converted to (II). The course of this reaction was followed by gas chromatography. Compound III distilled at 140–141° at 0.5 mm., $n^{20}D$ 1.5710. The structure was proved by a combination of

(2) M. Kolobielski and H. Pines, *J. Am. Chem. Soc.*, **79**, 5820 (1957).

ultraviolet spectroscopy, ozonization and comparison of the selectively hydrogenated dimer with a synthetic sample of 1,5-diphenyl-2-methylpentane.

1,1,3,3 - Tetramethyl - 2,4 - diphenylcyclobutane (IV) in over 90% yield was obtained on reaction of β,β-dimethylstyrene at 110° in the presence of potassium, using methylcyclohexane as a solvent. Compound IV melted at 133°. Its structure was confirmed by n.m.r. spectroscopy, which showed the presence of three sharp peaks, corresponding to the phenyl, CH_3^- and CH^- groupings, in the proper relative intensities.

Anal. Calcd. for $C_{20}H_{24}$: C, 90.84; H, 9.16. Found: C, 90.91; H, 9.50.

The outlined reaction, which represents a novel approach to the synthesis of cyclobutane derivatives, is presently applied to a study of related compounds having functional groups.

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THE DECOMPOSITION OF ACETYL PEROXIDE: THE EFFECT OF IODINE

Sir:

In an earlier publication[1] one of us proposed that the formation of cyclohexyl acetate from the decomposition of acetyl peroxide in cyclohexene solution is a result of acetoxy radical addition to cyclohexene. This proposal was quite contrary to the generally accepted behavior of acetoxy radicals, as was pointed out[1] at the time.

This general point of view is based to some extent on the undeniable fact that acetate groups are not widely found in the products of decomposition of acetyl peroxide. More substantial evidence as to the non-existence or very transient nature of acetoxy radicals has been provided by Szwarc[2,3] and by Walling.[4] That is, Szwarc has computed the heat of formation of the acetoxy radical, and its value is regarded as indicating that dissociation of the radical is the favored process. Walling[4] has reported that the decomposition of acetyl peroxide in moist carbon tetrachloride solution containing iodine gives carbon dioxide, methane and methyl iodide in contrast to benzoyl peroxide,[5] which gives benzoic acid almost quantitatively.

The two pieces of evidence[3,4] just referred to are used with increasing frequency in classifying the acetoxy radical as either non-existent or transient. Most recently, Martin and Drew[6] have pro-

(1) H. J. Shine and J. R. Slagle, *J. Am. Chem. Soc.*, **81**, 6309 (1959).

(2) A. Rembaum and M. Szwarc, *ibid.*, **77**, 3486 (1955).

(3) L. Jaffee, E. J. Prosen and M. Szwarc, *J. Chem. Phys.*, **27**, 416 (1957).

(4) C. Walling and R. B. Hodgdon, Jr., *J. Am. Chem. Soc.*, **80**, 228 (1958).

(5) G. S. Hammond and L. M. Soffer, *ibid.*, **72**, 4711 (1950).

(6) J. C. Martin and E. H. Drew, *ibid.*, **83**, 1234 (1961).

TABLE I

THE INFLUENCE OF IODINE ON THE YIELDS OF CARBON DIOXIDE

Solvent[a]	Ac_2O_2,[b] mole l.$^{-1}$	I_2, mole l.$^{-1}$	H_2O, ml.	CO_2,[c] %	Time,[d] hr.	Temp., °C.
Cyclohexene	0.056			57.7	45	80
Cyclohexene	.056			60.0	37	80
Cyclohexene	.050			65.4	40	80
Cyclohexene	.051	0.208	12	31.4	45	75
Cyclohexene	.056	.198	10	22.8	45	75
Cyclohexene	.056	.198	10	25.0	37	75
Cyclohexene	.050	.176	12	23.8	40	73
CCl_4	.051			100.0[f]	49	75
CCl_4	.040			80.8	51	75
CCl_4	.042			87.5	69	74
CCl_4	.039			84.3	54	73
CCl_4	.039			82.7	54	73
CCl_4	.043			79.9	53	74
CCl_4	.050	.190	10	25.3	43	67
CCl_4	.040	.160	10	33.2	61	68
CCl_4	.051	.143	12	28.4	49	69
CCl_4	.040	.142	12	37.7	51	69
CCl_4	.042	.042	7	54.4	69	70
CCl_4	.043	.045	10	52.9	53	70

[a] 300–400 ml. [b] Prepared as the solid, dissolved in the solvent and titrated by the method of Wagner, Smith and Peters.[7] [c] The carbon dioxide was swept out of the apparatus by a slow stream of carbon dioxide-free nitrogen, through an ice trap, a Dry Ice trap, concentrated sulfuric acid, magnesium perchlorate and absorbed on Ascarite. [d] The time during which the solution boiled gently and the time of last weighing of Ascarite tube; the Ascarite tube was weighed periodically and weighing was discontinued when the carbon dioxide evolution had appeared to cease. [e] Temperature of solution. [f] We cannot account for this result.

vided data from the decomposition of O^{18}-labeled acetyl peroxide in cyclohexene, which led them to rule out the possibility that the acetoxy radical is exclusively responsible for cyclohexyl acetate formation. Martin and Drew[3] prefer a molecular collision mechanism. They note, however, that their evidence does not rule out the possibility that the Shine and Slagle[1] mechanism may be operating simultaneously with their own, but they quote the earlier works[2,4] as making it seem unlikely that cyclohexene would trap acetoxy radicals before they decompose to methyl radicals and carbon dioxide.

While we are not able to comment at length at this stage on Martin and Drew's work it is necessary for us to point out that one of the corroborating pieces of evidence, the single experiment of Walling and Hodgdon, may lead to the wrong inference about the effect of iodine and water on the decomposition of acetyl peroxide.

For some time now we have been using Hammond's technique[5] with solutions of acetyl peroxide. Our results with cyclohexene were so consistently in accord with an acetoxy radical intermediate that we felt obliged to investigate carbon tetrachloride solutions, too. Our data, given in Table I, show that there is a very marked drop in carbon dioxide in the presence of iodine and water, in both the cyclohexene and carbon tetrachloride solutions. It is apparent that the amount of carbon dioxide liberated in the presence of iodine depends on the relative concentration of the iodine. The data point up the known difference between acetyl peroxide and benzoyl peroxide, since in the latter case an equimolar concentration of iodine will give a nearly quantitative yield of benzoic acid.[5]

(7) C. D. Wagner, R. H. Smith and E. D. Peters, Anal. Chem., 19, 976 (1947).

In spite of this difference, it is evident that iodine affects the acetyl peroxide decomposition markedly. In connection with the result of Walling and Hodgdon there is a small error in their calculations which, when corrected, shows that the yield of carbon dioxide obtained by them in the presence of approximately equimolar iodine was not almost quantitative but was 83%. Our data show that in carbon tetrachloride alone acetyl peroxide decomposes to give between 80–100% of the theoretical carbon dioxide. Induced decomposition in this system has been demonstrated by Edwards and Mayo[8] and by Ross and Fineman.[9] The former isolated 16% of methyl acetate from 0.1 M solutions at 76°.

Thus, it is faulty to use[6] the experiment of Walling and Hodgdon to show "completely negative results" in attempts at trapping acetoxy radicals, and the ruling out[6] of acetoxy radicals in solution reactions is, at this stage, precipitate.

At a later date we shall submit in full our work on this and similar systems, and also our kinetic data for decompositions in solution.

(8) F. G. Edwards and F. R. Mayo, J. Am. Chem. Soc., 72, 1265 (1950).

(9) S. D. Ross and M. A. Fineman, ibid., 73, 2176 (1951).

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LITHIUM–AMMONIA REDUCTION OF α,β-UNSATURATED KETONES. II. FORMATION AND ALKYLATION OF A β-CARBANION INTERMEDIATE

Sir:

In order to explain the stereochemical results obtained in the reduction of α,β-unsaturated ketones such as I with lithium in ammonia solution we suggested[1] recently that an intermediate β-carbanion (cf. II) is involved in which only those conformations are permitted which allow continual overlap of the developing p-orbital on carbon with the p-orbitals of the enol double bond. Of the three possible conformations for the protonation transition state this requirement is only met by IIa and IIb (the oxygen atom marked with a star is either ·O or M+ —O depending on whether β-protonation takes place after addition of one or two electrons) and the actual product obtained is that corresponding to that one of the two permitted conformations with the lowest energy (a trans decalone in this particular situation).

Implicit in this mechanistic picture are several assumptions: (a) the β carbon actually acquires carbanion character without the necessary concerted addition of a proton from ammonia; (b) the β-carbanion can be neutralized (for instance by a proton from ammonia) from either direction, i.e., transition states of conformation related to IIa and IIb must be in equilibrium.

We now have obtained evidence which strikingly confirms both assumptions: The unsaturated keto tosylate IV, R = H, was prepared by the reaction

(1) G. Stork and S. D. Darling, J. Am. Chem. Soc., 82, 1512 (1960).